1942

Organothallium compounds

Royal Kilburn Abbott Jr.
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UMI®
ORGANOTHALLIUM COMPOUNDS

by

Royal Kilburn Abbott, Jr.

A Thesis Submitted to the Graduate Faculty for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject Organic Chemistry

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Iowa State College

1942
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ACKNOWLEDGMENT

The author wishes to express his appreciation to Dr. Henry Gilman for his encouragement, criticism, and advice given throughout this research.
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Although the first organothallium compound, diethylthallium chloride, was prepared by Hansen in 1870, only nine years after the discovery of the element thallium by Crookes, there is to this date no complete survey of the organic chemistry of thallium or of organothallium chemistry, in a more restricted sense.

Metallic hydrides and carbides may in a sense be regarded as organometallic compounds: that is, they may be considered as first members of a series in which the hydrogen or carbon atoms may be replaced by methyl, ethyl, phenyl or other groups to produce what is more generally considered to be an organometallic compound. Thallium hydride has never been isolated, but its existence can be demonstrated spectrographically when an arc is caused to pass between thallium electrodes in an atmosphere of hydrogen. From the spectroscopic data the entropy of the gaseous diatomic hydride has been computed, and the thallium-hydrogen bond distance calculated to be 1.870 Å. Thallium in the molten state does not dissolve any appreciable amount of carbon, nor does it form a carbide.

There is no record in the literature of a thallium carbonyl, or of a thallium acetylide. An ammoniacal thallous salt solution does not yield a precipitate with acetylene, as do copper and silver. Thallium in this and in many other
respects resembles the alkali metals.

As a soft, low-melting, malleable metal, thallium in its elementary form probably most resembles lead. In spite of its place in the third group of the periodic table, its common valence is one, and in many of its properties it resembles the alkali metals, especially potassium. A long series of thallous and potassium salts crystallizes in isomorphous systems. Thallous hydroxide and carbonate are strong bases and readily soluble in water, in both of which respects they resemble the alkali metals. In the solubility of its fluoride, and insolubility of its chloride, bromide, iodide and sulfide it resembles silver. In the trivalent state thallium is a much weaker base, is subject to extensive hydrolysis, and resembles in this respect many other trivalent metals, such as bismuth. Thallic halides also have certain properties analogous to auric halides, especially with respect to solubility in water and the capacity to replace hydrogen by direct nuclear substitution (auration and thallation). Thallic halides, however, have much greater coordination powers, and tend to form acid salts. Indeed, a neutral thallic oxalate is not known, and thallium in this respect resembles other trivalent metals, such as aluminum, iron and chromium. The quantitative precipitation of thallic ion by an excess of oxalic acid relates thallium with scandium, yttrium and lanthanum; but the solubility of thallic acid oxalate in potassium chloride solution makes possible a separation from these three elements, and
from the other rare-earth elements.\textsuperscript{131} As would be expected, organothallium compounds show many properties similar to organogallium and organoindium compounds.\textsuperscript{37, 38, 39, 40} These relationships are discussed in detail in the section on R\textsubscript{2}Tl compounds. Finally, organothallium compounds are related to organomercury and organolead compounds. The series ethylmercury chloride, diethylthallium chloride, and triethyllead chloride has been the topic of rather acrimonious and polemical discussion.\textsuperscript{2, 26, 32, 122}

It will not be possible in this \textit{Review} to discuss the more general topic of the organic chemistry of thallium, as contrasted with the more restricted organothallium chemistry. But it should be pointed out that the applications and uses of thallium in organic chemistry are interesting and original. For example, thallous alkoxides and phenoxides have unique properties, and many have been studied\textsuperscript{28, 68, 83, 140} in great detail. Thallous hydroxide has many advantages as a titration agent\textsuperscript{105} in organic chemistry since it will replace not only carboxyl hydrogen, but hydroxyl hydrogen as well,\textsuperscript{17, 31, 100} as in sugars, tartaric acid, and related substances. For this reason it has been extensively used in cellulose chemistry as a means of estimating the internal surface of the polymer.\textsuperscript{57, 146, 147, 148, 149} Most acids form very well-defined thallous salts. Such salts have been used in the separation of isomers,\textsuperscript{80} in the isolation of acids from tannin,\textsuperscript{30} in the separation of saturated from unsaturated
fatty acids$^{11,65}$ and recently as a derivative for sulfonic acids.$^{33}$ Such thallous salts are readily esterified or alkylated by alkyl iodides.$^{27}$

A few other salts are known in which the thallium is not attached to oxygen, such as thallous ethylmercaptide,$^{18}$ thallous mercaptobenzothioazole and mercaptobenzimidazole,$^{81,141}$ and certain nitrogen-substituted thallous amides.$^{29}$

Thallous halides form very many complexes with pyridine, quinoline, and their derivatives, with alkaloids, and with aliphatic amines.$^{63,86,126}$ These are of such importance even in the organometallic chemistry of thallium that numerous references will be found throughout this Review.

Thallium is not a rare element and will prove to be a fruitful field for further research. At the present time Germany leads the world by a wide margin in the production of thallium followed by Belgium, Poland and the United States in that order. German production is already in tonnage quantities, as compared with a few hundred pounds produced yearly in this country. With Belgian and Polish production in German hands, Germany thus has practically a monopoly on thallium, and has developed many important industrial uses.$^3$
HISTORICAL

Compounds of the Type $R_xTl$

The search for trivalent thallium compounds in which all three valence bonds are attached to carbon was not successful until about a decade ago, although even the first paper on organothallium compounds indicated an awareness of the possibility or even probability of their existence. When eventually synthesized, an examination of the properties of this type of compound made evident the reason why Hansen, in 1870, and several others since him had had difficulties.

Hansen\(^5\) first tried four reactions unsuccessfully:

1. \((C_2H_5)_2Zn + TlCl\)
2. \(C_2H_5I + Tl\)
3. \((C_2H_5)_2Zn + Tl\)
4. \(C_2H_5I + Tl:Na\) alloy

where the alloy contained six parts of thallium to one of sodium by weight. In each case there was no reaction. Believing that the reason for the lack of reaction in the first equation was perhaps the insolubility of thallous chloride in diethylzinc, he tried the reaction of thallium trichloride on diethylzinc. In this case there was vigorous action, but he found it impossible to distill pure triethylthallium from the mixture, since the distillate always contained chlorine, derived from the
decomposition of chlorinated compounds formed in his unfortunate method of preparing thallium trichloride by the direct chlorination of a suspension of thallous chloride in ether. However, the fraction boiling between 110° and 170° gave positive tests for thallium and fumed strongly in the air. By shaking with dilute hydrochloric acid he easily obtained pure diethylthallium chloride.

Mendeleeff boldly predicted that triethylthallium would be discovered. A translation of this passage wherein he gives his reasons for such a prophecy reads as follows: "The members of the even rows do not form, as far as is known, volatile hydrides and organometallic compounds, as do the corresponding members of the uneven rows. Since the elements Zn, Cd, As, Sb, Se, Te, Br, I, Sn, Pb, Hg, Bi from the uneven rows can be changed by a common method into organometallic compounds, it is to be postulated with definiteness that the elements In and Tl, belonging to this group, will give organometallic compounds InAE and TlAE. No single one of the members of the even rows out of the higher groups has as yet given organometallic compounds. The experiments of Buckton, Cahours et al., wherein they attempted to prepare TiAE from TiCl4, were unsuccessful, regardless of the great similarity between TiCl4, SiCl4 and SnCl4. Should, therefore, organometallic compounds be obtained from elements of the even rows, they will be quite different in their behavior from the previously known organometallic bodies, just as the hydrides of Pd, Cu, Nb do not agree in their properties with the corresponding compounds from the uneven rows. Volatile hydrides and ethyl compounds will be obtained only with difficulty from Zr, Nb, Mo, W, U."

Hartwig, working under the direction of Carius, made further attempts at the synthesis of triethylthallium, as it was especially desired to supplement the determination of the specific heat of thallium made by Regnault with a molecular weight determination on a gaseous compound. He could not agree with Hansen that triethylthallium is formed
in the reaction between diethylzinc and thallium trichloride, but found instead that, if he used an ether solution of thallium trichloride which was free of chlorination products of the ether, and if such a solution was added to an ether solution of diethylzinc, diethylthallium chloride was formed directly in accordance with the equation:

\[ \text{TiCl}_3 + (\text{C}_2\text{H}_5)\text{Zn} \rightarrow (\text{C}_2\text{H}_5)\text{TiCl} + \text{ZnCl}_2 \]

Nevertheless, he proclaimed his belief that triethylthallium must exist. It is to be noted that he did not record that he had distilled the reaction mixture, as Hansen had done. Strong heating might have caused some decomposition and the distillation of the certainly more volatile triethylthallium. In two further experiments between diethylthallium chloride, diethylthallium iodide and diethylzinc, in an attempt to add the third ethyl group in place of the halogen, he found no triethylthallium, but instead metallic thallium, zinc chloride, and a gas which he assumed to be a mixture of ethane and ethylene.

Carius was not content with these negative results, and in a short time Carius and Frommuller\(^ {12} \) published two further experiments. Diethylthallium chloride and diethylmercury were heated for several hours at 150-160°, but the reaction was found to be:

\[ (\text{C}_2\text{H}_5)\text{TiCl} + (\text{C}_2\text{H}_5)\text{Hg} \rightarrow 2\text{C}_2\text{H}_6 + \text{TiCl} + \text{Hg}. \]

When diethylmercury was heated with metallic thallium no reaction was observed below 150° and at 170° decomposition of
the diethylmercury took place to give ethane, ethylene, and a thallium amalgam. They concluded: "The attempts at the preparation of triethylthallium here described probably exhaust all methods known for the preparation of analogous compounds. However, the negative results in all these experiments can not be considered as proof that triethylthallium does not exist, but rather that its preparation is attended with exceptional difficulties, which probably have their origin in the injurious effect of high temperatures. We believe that it will be possible to avoid these high temperatures by the application of other diethylthallium compounds."

It is evident that they were not yet aware of the different nature of the third valence of thallium. Trialkylthallium compounds were to be made, not by altering the dialkythallium salt to be used but rather by employing a more powerful organometallic reactant than diethylzinc or diethylmercury.

Nearly thirty years later Meyer and Bertheim attempted to alkylate thallous chloride up to a valence of three, but unlike their experience between lead chloride and the Grignard reagent where lead was found to have the higher valence state, they found that reduction to metallic thallium took place, and concluded that such a change in valence was not to be brought about by direct alkylation.

Basing his reasoning on the Bohr theory of atomic structure, v. Grosse stated that "those elements all of whose valence electrons possess the same major quantum number form typical alkylated organometallic compounds." By "typical" he meant completely alkylated, and since it was known that all three valence electrons of thallium possessed the same major quantum number, he predicted that completely alkylated
thallium compounds must be capable of existence.

Egerton and Gates\(^{24}\) examined the influence of various metallic vapors on the ignition temperature and anti-knock properties of gasoline. These vapors were carried by a stream of nitrogen from the surface of the molten metal into the explosion chamber. The most effective metal was found to be thallium, followed by potassium, lead and iron in that order. Triethylthallium was not then available for testing, but was later found\(^7\) to be only one-tenth as effective as tetraethyl-lead.

Hein and Segitz\(^6\) showed beyond all doubt that the electrolysis of ethylsodium in diethylzinc as a solvent liberated free ethyl radicals at the anode. Accidental observations led to the conclusion that these ethyl groups must possess a surprising chemical reactivity; for example the anodic solution of electrolytic zinc deposited on copper could only be explained by the reformation of diethylzinc, according to the equation:

\[
\text{Zn} + 2\text{C}_2\text{H}_5 \rightarrow (\text{C}_2\text{H}_5)_2\text{Zn}
\]

The transient existence and strong chemical activity of ethyl radicals was definitively proved by the formation of tetraethyl-lead when lead was used as the anode, which thereby experienced a loss in weight corresponding to 94% of the theoretical value.

It thus seemed appropriate to try other metals as anode in the same system and to examine their behavior and change.
in weight. The fact that thallium and gold were dissolved by the ethyl radicals in appreciable amounts appeared to be of especial interest in so far as this could only occur with the concomitant formation of compounds in which the said metals were exclusively united to organic groups; such thallium derivatives were, however, not known, for all organic compounds of thallium hitherto described contained halogen or some other acid group.

In the case of thallium as anode there was at the very beginning of the electrolysis not only a strong blackening of the electrode but also a simultaneous darkening of the liquid in the bath which hindered the observation of events at the anode, especially as to whether there was any gas evolution. It was conjectured that this phenomenon, which was certainly to be referred to the separation of finely divided metal, also caused the observed appreciable diminution in the resistance of the bath. After electrolysis lasting several hours the loss in weight amounted to approximately 13.3% of the theoretical value, based on univalent thallium. In the supposition of the formation of triethylthallium the decrease would amount to 43% of the theoretical amount. The probable course of the reaction was stated to be the primary reaction

$$3\text{Tl} + 3\text{C}_2\text{H}_5 \rightarrow 3\text{C}_2\text{H}_5\text{Tl}$$

followed by the secondary reaction

$$3\text{C}_2\text{H}_5\text{Tl} \rightarrow (\text{C}_2\text{H}_5)_2\text{Tl} + 2\text{Tl},$$
the nascent metal partially going into solution and thus causing the blackening, and partially being redeposited upon the anode.

A year later, in 1928, Berry and Lowry,⁶ apparently were brought by their studies of the third valence of thallium to a position where there was some doubt in their minds whether trialkylthallium compounds were capable of existence. They undertook to study the third valence of thallium by conductivity measurements on dialkythallium salts and bases. Although thallium formed many tervalent salts, the only alkyl derivatives which had been prepared up to the time were of the type $R_r^*TlX$; moreover, these dialkyl halides could not be condensed by the action of metallic sodium to molecules of the type $R_r^*Tl\cdot TlR_2^*$, comparable to the bimolecular lead compounds prepared by Krause and Smitz.⁷⁹ Since no convincing explanation had been given of the non-formation of trialkyl compounds of the type $R_r^*Tl$, it appeared desirable to investigate the dialky derivatives, in order to find out whether their ionization was "complete", as in the case of the quaternary ammonium bases and salts, or whether it was reversible and incomplete as in the case of ammonium hydroxide and mercuric chloride.

In their general conclusions the authors stated: "The chemistry of thallium presents certain peculiarities which await an explanation in terms of the electronic theory of valency. Thus, it is remarkable that thallium, although a third-group metal, forms a series of very stable univalent thallous salts, whilst gold, which might be expected (like
silver) to be most stable in the form of a univalent cation, gives rise generally to tervalent auric salts. Again, the alkyl derivatives, instead of being of the types EtAu and Et₂Tl, interleaving with Et₂Hg and Et₂Pb, are of the types Et₂AuBr₂, Et₂AuBr₃ and Me₂TlI₃. ... The univalent dialkyl ions of the type Me₂Tl⁺ correspond to the covalent molecules Ph₂Hg and HgCl₂ of the mercury series, with 82 electrons round the nucleus. In marked contrast to the univalent thallous salts, the dialkyl halides do not obey the formulas for strong electrolytes; the bases from which they are derived are also considerably weaker than thallous hydroxide, and can no longer be classed with the alkalis as examples of 'complete ionization'. There can therefore be little doubt that the dialkyl halides, and the bases from which they are derived, as well as the corresponding trihalides and their bases, are capable of yielding non-conducting molecules, such as Me₂Tl₁, Me₂TlOH and TlBr₂, which are of the same order of stability as their univalent ions. The spectroscopic evidence, however, indicates that the non-conducting forms of these salts may be ionic doublets, rather than covalent molecules. The existence of systems in which the thallium nucleus is surrounded by 84 electrons in molecules such as Me₂TlBr and TlBr₂ is therefore less well-established than in the case of mercury, where it is unlikely that the three halogens in the ion HgBr₂ are related unequally to the metal. The doubt which thus arises as to the real existence of the 84-electron system, with only two electrons less than the next inert gas, may furnish a clue to the reason why it has not been found possible to prepare the trialkyl derivatives of thallium, since these could not be expected to exist in a form corresponding with the ionized molecules of TlMe₂⁻¹, and could therefore only be produced if the 84-electron system were stable."

Goddard⁴⁶ came very near to the truth about the stability of thallium compounds of the type R₂Tl in an investigation which had for its object not only the synthesis of the R₂Tl type, but also of the mixed type R₂R₃Tl. He proposed to examine the stability of R₂TlX compounds toward various reagents, and tried first the action of a large excess of an alkyl Grignard reagent upon thallium trichloride. Whereas Meyer and Bertheim¹¹² by the action of four moles of methylmagnesium bromide on one mole of thallium trichloride obtained
dimethylthallium bromide in 62.5% yield, Goddard found that when five moles of the Grignard reagent was employed to one of thallium trichloride the yield always approximated to 50%. Since one half of the thallium trichloride was all that was thus accounted for, he speculated "it is possible that the other half goes to form a trialkyl compound, which may be either a gas, and is evolved during the reaction, or a liquid decomposed by water." Unfortunately, Goddard's observations were not as complete as would have been desired, for he does not mention how much thallium should be accounted for by reduction to thallous chloride, and certainly it would have been possible to definitely ascertain whether there was any gas evolution and if so what the gas was. He was, however, correct in his surmise that a trialkylthallium compound might be hydrolyzed by water. A further experiment by Goddard would seem to cast doubt on this alkylation by the Grignard reagent all the way up to the $R_3$Tl type: he first isolated his diethylthallium bromide and then subjected it to the action of phenylmagnesium bromide—there was no reaction either in the cold or on heating. Of course, there might be some difference in the activity of ethylmagnesium bromide as compared with phenylmagnesium bromide with respect to the power of setting up the third carbon-thallium linkage; at any rate the experiments were never pushed to the point of absolute certainty.

It was left to Groll in 1930 to see what was necessary for the successful synthesis of triethylthallium: the careful
experimental technique of working in a dry inert atmosphere and a more reactive alkylating organometallic. He employed the reaction

$$(C_2H_5)_2TlCl + C_4H_9Li \rightarrow (C_2H_5)_3Tl + LiCl$$

with complete success; the overall yield was 79%. The reaction was carried out in petroleum ether at room temperature; even a temperature of 50° was found to cause decomposition and a lower yield. At room temperature the reaction proceeded slowly and smoothly with little side reaction. When the ether had been removed with the aid of a slight vacuum, the triethylthallium distilled between 54.6° and 54.8° at a pressure of 1.50-1.55 mm. The specific gravity was sp. gr. 21.4 = 1.971. Although quite dense the liquid was described as mobile, with an odor similar to that of tetraethyllead. Interestingly enough the color was found to be distinctly yellow, although it paled when the temperature was lowered to -80°, at which temperature the triethylthallium was still liquid; at liquid-air temperature it had solidified to nearly colorless crystals. Groll did not mention molecular weight determinations on the compound, which is important in view of the known great tendency of thallium to undergo association. Certainly a disturbed electron state, or even a peculiar type of unsaturation is indicated by the color, which increases with increase in temperature, until finally, under atmospheric pressure, spontaneous decomposition takes place at 129°.

Soluble in the usual organic solvents, triethylthallium
is much more reactive than its neighbors in the periodic table, diethylmercury and tetraethyllead, reacting with water according to the equation:

\[(\text{C}_2\text{H}_5)_2\text{Hg} + \text{H}_2\text{O} \rightarrow (\text{C}_2\text{H}_5)_2\text{HgOH} + \text{C}_2\text{H}_5\]

The compound is stable toward dry oxygen, although it fumes in the air due to the presence of moisture.

Groll synthesized diethyltriphenylmethyllumthallium in an analogous reaction between diethylthallium chloride and triphenylmethyllumsodium in ether. The compound was not distilled, and no properties were recorded beyond the fact that it likewise was a yellow liquid which fumed in air and which reacted with water to give triphenylmethane and diethylthallium hydroxide.

It is interesting to note, in view of the negative results reported by Hansen\(^5\) that Groll found that triethylthallium could also be prepared by direct reaction between ethyl chloride and alloys of thallium with sodium. Finely divided alloys containing 7, 10, and 15\% of sodium were shaken for several hours with ethyl chloride. The reaction was very slow at room temperature. Small amounts of triethylthallium were formed in each experiment, but it was reported that no way had been found to increase the yield.

Groll used these discoveries as the basis of two patents\(^5\) wherein he described the preparation of trialkyl compounds of gallium, indium, thallium, and gold. An interesting point is amplified in the patent literature: "The maximum allowable
temperature is much below the decomposition temperature of either of the reaction components or of the finished product, for example, diethylthallium chloride and ethyllithium are each stable up to about 200°, and triethylthallium is stable up to about 150°; nevertheless, the reaction mixture consisting of diethylthallium chloride and ethyllithium under petroleum ether must not be heated above atmospheric temperature. Even heating to only 40° causes decomposition to gray spongy metallic thallium, vitiating the yield. Decomposition can easily be recognized and the most suitable temperature may be found from case to case by trial experiments."

Triethylthallium, as far as can be determined, was never put to the use which had been the announced reason for the first attempts to synthesize it—the classical determination of the molecular weight of a thallium compound in the vapor phase. This was because the atomic weight had long since been made secure before the triethylthallium ever became available. However, it was used by Aston to determine the isotopic constitution and physical atomic weight of thallium. A sample of triethylthallium especially prepared for the purpose by v. Grosse and Bergmann boiled at 64° under 3 mm. pressure, but showed some vapor pressure even at 0°. Lines were obtained on the plate which gave the constitution of thallium exactly as expected. Its mass numbers are 203 and 205, the heavier predominating. The presence of the lines of mercury in suitable strength made the determination of the relative abundance and the packing fraction unusually easy. The ratio worked out to be 2.40 and the packing fraction 1.8, which after the necessary corrections gave the atomic weight of thallium as 204.41 ± 0.03, in excellent agreement with Höngschmid's value 204.39 now in use.
An extension of Goddard's work, in which he had examined the question whether it was possible to perform the alkylation of the third valence of tervalent thallium by means of the Grignard reagent, was carried out by Menzies and Cope who examined the action of ethylmagnesium bromide on thallous chloride. Here oxidation as well as complete alkylation is required. They found that on heating one mole of thallous chloride with two moles of the Grignard reagent under reflux for three hours, quantitative reduction to metallic thallium took place; but without heating a 12.4% yield of diethylthallium bromide was obtained. It has thus been definitely established that the Grignard reagent is capable of oxidizing univalent thallium.

However, the reaction was slow, perhaps because of the insolubility of thallous chloride in organic solvents. Thallous ethoxide does not have this disadvantage, since is miscible with ether and benzene. In an experiment with two moles of ethylmagnesium bromide and one mole of thallous ethoxide, there was immediate alkylation of 22-24% of the metal contained in the ethoxide. Since the maximum possible would be 33% (two-thirds of the univalent thallium is necessarily reduced to the metal) that represents a theoretical yield of 72%. Even more important, however, especially with reference to Goddard's work previously discussed, was the observation that in all the cases where thallous chloride and thallous ethoxide were used, the alkylated thallium was found before addition of water.
almost entirely dissolved in the ethereal solution, and little, if any, in the dark gray precipitate formed on addition of the thallous compound to the Grignard solution. The order in which the addition was performed is to be noted—it is the reverse of that recommended by Meyer and Berthelot. With thallium trichloride, however, direct conversion into the dialkylthallium halide took place, the ethereal layer yielding only a negligible amount. Thus it is seen that the alkylation of the third valence in tervalent thallium by means of the Grignard was demonstrated conclusively. The observed facts and yields may be expressed in the equation:

$$3\text{TlCl} + 3\text{EtMgBr} \longrightarrow \text{Et}_2\text{Tl} + 2\text{Tl} + 3\text{MgBrCl}$$

The reaction is thus comparable to the one demonstrated previously for lead chloride and mercurous chloride. Menzies and Cope concluded that when thallous ethoxide was used, the first reaction was one of double decomposition with the Grignard reagent to give a precipitate of finely divided and highly active thallous bromide, which then underwent further reaction with more of the Grignard reagent. Low yields when only one equivalent of ethylmagnesium bromide was taken were regarded as confirmation of this interpretation.

Two years later, Birch doubled the number of known \( R_x\text{Tl} \) compounds when he published the synthesis of triisobutylthallium and triphenylthallium. In addition he improved the synthesis of triethylthallium by using the simplified methods of preparation for alkyl- and aryllithium compounds devised by Gilman,
Zoellner and Selby,\textsuperscript{45} which required an inert, dry atmosphere but no special apparatus. Phenyllithium, prepared in ether from bromobenzene and lithium, readily reacted with a suspension of diphenylthallium bromide in ether to give the expected triphenylthallium; the diphenylthallium bromide reacted and disappeared as fast as the phenyllithium was added. The triphenylthallium was obtained by removal of the ether, extraction with benzene and precipitation with petroleum ether (b.p. 60-80°) to give white needles, m.p. 188-189°, dec. 215-216°. The yield was 46%. When heated, the compound decomposed to metallic thallium and biphenyl. Moisture hydrolyzed the compound in much the same way as triethylthallium.

By similar means triisobutylthallium was prepared in 73% yield. The liquid distilled at 74-76° under 1.6 mm. pressure, with slight decomposition, to give a pale lemon-yellow liquid which tended to decompose and deposit metallic thallium on exposure to light. The compound was hydrolyzed to diisobutylthallium hydroxide and cleaved by glacial acetic acid to diisobutylthallium acetate.

The compounds could also be prepared, but less satisfactorily, in one operation by the action of the lithium compound upon thallous chloride suspended in pentane. The quantity of metallic thallium formed by reduction indicated that the reaction probably took place through the univalent RTl compound, in essential accordance with the equation:

\[
3RLi + 3T1Cl \rightarrow (3RTl + 3LiCl) \rightarrow R_2Tl + 2Tl + 3LiCl
\]
This is in agreement with the work of Menzies and Cope® discussed above. Another variant of the method was to suspend diethylthallium bromide in pentane, add lithium in very small pieces, and then slowly add ethyl bromide. The reaction began almost immediately, and was over in an hour. The crude diethylthallium acetate, formed by the cleavage of the filtered solvent layer by acetic acid, indicated that the reaction had taken place to the extent of 80% of the theoretical. Birch reported a boiling point of 50-51° at 1.5 mm. without decomposition for triethylthallium. As would be expected from analogy with other organometallic compounds, the compound with primary alkyl radicals proved to be more stable than the one with secondary alkyl groups. The yellow color and heavy nauseatingly sweet odor reported by Groll were confirmed.

The reaction of alkyl lithium compounds with dialkylthallium halides should provide a useful method for the preparation of mixed alkylthallium compounds. Birch made an attempt to prepare diethyl isobutylthallium by the action of isobutyllithium on diethylthallium bromide; fractionation of the product gave small quantities of yellow liquids lighter in color than triethylthallium and apparently less stable, but no analyses were obtained.

The original purpose of the investigation had been to test the suggestion advanced by Egerton and Gates that thallium, like lead, should possess marked anti-knock properties in an internal combustion engine. The compounds obtained were
soluble in gasoline, but their anti-knock rating was only about one-tenth that of tetraethyllead.

The only recorded attempt to synthesize a tervalent organothallium compound with three carbon-thallium bonds and containing thallium in a ring is that reported by Plätz,\textsuperscript{122} who unsuccessfully endeavored to prepare cyclopentamethylene-phenylthallium according to the equation:

\[ \text{C}_6\text{H}_5\text{ThCl}_3 + \text{BrMg(CH}_3)_2\text{MgBr} \rightarrow \]

He concluded, perhaps unwisely, that thallium is not capable of forming ring systems. The fanciful tables in which the methyl compounds of mercury, thallium, lead and antimony are neatly arranged in rows and columns do not add anything to the theory of \( R_n\text{Th} \) compounds which had not been already more adequately expressed in terms of the electronic theory by v. Grosse.\textsuperscript{54} The same may be said for similar papers, devoid of experimental results, by Erlenmeyer\textsuperscript{26} and by Garzuly-Janke.\textsuperscript{32} Their discussions concerning the radical \( R_n\text{Th}^- \), however, are of more interest and will be considered elsewhere in this Review.

A careful synthesis of triethylthallium was undertaken by Rochow and Dennis,\textsuperscript{136} who investigated the chemical and physical properties more thoroughly than had been previously reported. Three negative syntheses were tried for the preparation of trimethylthallium: (a) the interaction of dimethylmercury and metallic thallium at elevated temperatures, (b) methyl iodide and an alloy of sodium and thallium, and
(c) thallium-copper couple on methyl iodide. No appreciable yield of a volatile thallium compound could be obtained. The authors make no reference to the previous unsuccessful attempts along these lines by Hansen,\textsuperscript{56} which are somewhat contradicted by Groll,\textsuperscript{52} who did succeed in obtaining small yields of triethylthallium by the reaction of ethyl chloride on sodium-thallium alloys. Rochow and Dennis then turned to the only successful method then known for the synthesis of a trialkylthallium compound, namely the interaction of diethylthallium chloride and ethyllithium; they chose to repeat the work of Groll\textsuperscript{52} in order to gain experience in the method preparatory to undertaking the synthesis of trimethylthallium, which they had first begun by the three fruitless methods given above.

Some corrections and additions were supplied to those properties published by Groll: instead of "mobile", triethylthallium was described as an "oily", yellow liquid, which slowly decomposed on exposure to light, less rapidly when in evacuated containers in the dark. No explanation was given for the yellow color; a complete resonance picture of the electron system in trialkylthallium compounds would be interesting and valuable.

The density was found to be $d_{25}^{25} = 1.957$, the melting point $-63.0^\circ$. Near the melting point the compound was reported to become exceptionally viscous. From measurements made on the vapor pressure between 0 and $80^\circ$, the equation for the
vapor pressure curve was determined as

\[ \log P = -1.032 \times 10^{6} (1/T) + 2224 \]

The vapor pressure was found to be 1 mm. at 9\(^\circ\), and 25 mm. at 74\(^\circ\). Extrapolation of the vapor pressure curve gave 192.1\(^\circ\) as the normal boiling point, but this cannot be checked directly, as decomposition is rapid at this temperature.

No indication of an etherate could be found at room temperature, nor was there any apparent reaction with liquid ammonia or with carefully dried oxygen. The announced extension of the method to the synthesis of trimethylthallium was evidently never carried out.

Mel'nikov and Gracheva\(^{89}\) also recognized that R\(_2\)Tl compounds result from the action of RLi on TlCl\(_3\), they believed with the intermediate formation of R\(_2\)TlX. They investigated three lithium compounds: ethyl, phenyl, and \(\alpha\)-tolyl. In every case there was also partial reduction to TlCl and to metallic thallium. However, the R\(_2\)Tl compounds were not isolated as such, but hydrolyzed to give R\(_2\)TlX in each instance. Hence nothing is known of the properties of tri-\(\alpha\)-tolythallium itself, and it can not be regarded as a new compound of the type R\(_2\)Tl. The Russian scientists formulated the reaction as taking place in two stages:

\[ 2RLi + TlCl\(_3\) \rightarrow R_2TlCl + 2LiCl \]
\[ R_2TlCl + RLi \rightarrow R_2Tl + LiCl \]

They regarded it as probable that in the reaction investigated by Birch\(^7\) where R\(_2\)Tl compounds were produced by the
action of an organolithium compound on thallous chloride the reaction also proceeded in two stages:

\[
2RLi + 3TlCl \rightarrow R_2TlCl + 2LiCl + 2Tl \\
R_2TlCl + RLi \rightarrow R_3Tl + LiCl
\]

The most complete investigation of the chemical properties of \(R_3Tl\) compounds, and especially of triphenylthallium, was made by Gilman and Jones, who reported the action with several common functional groups and gave a general picture of the relative reactivity of this type of compound as compared with similar compounds of mercury, magnesium, aluminum, gallium, and indium. As might have been expected, one of the phenyl groups was found to be more reactive than in the symmetrically substituted diphenylmercury. Triphenylthallium was found to behave as a moderately reactive organometallic compound in reactions with compounds such as benzaldehyde, benzoyl chloride and phenyl isocyanate, whereas it was definitely less reactive than phenylmagnesium bromide toward ethyl benzoate, benzonitrile and benzophenone.

When the reactivities of organometallic compounds of Group III were compared it was found that aluminum was definitely more reactive, all three \(R\) groups being involved in reactions with functional groups. Then in Group III \(B\) the order of decreasing reactivity was found to be indium, gallium, thallium; two \(R\) groups were found to react in the case of \(R_2B\) compounds and again three \(R\) groups in \(R_3In\) compounds, hence it is more difficult to specify the exact order of
reactivity between boron\textsuperscript{43} and indium\textsuperscript{39}—the specific reactant used as a test reagent would have to be mentioned in every case if one had to be absolutely definite. It is to be noted that indium and gallium\textsuperscript{38} are given in the reverse order of their position in the periodic system. The ionization potentials of the metals are: In, 5.76; Ga, 5.97; Tl, 6.07 V. Only one R group reacted in experiments with triphenylthallium; with benzaldehyde a 76\% yield of benzohydrol was obtained by refluxing in benzene for two hours; with phenyl isocyanate a 40\% yield of benzanilide was obtained by refluxing in benzene for seven hours; with benzoyl chloride an 89\% yield of benzophenone was obtained by refluxing in benzene for two hours.

Optimum conditions for the color test\textsuperscript{44} were to heat a small sample of triphenylthallium for six or seven minutes at 80\(^\circ\) with a saturated solution of Michler's ketone in benzene. Very reactive organometallics, of course, react practically instantly at room temperature. A more exact measure of the relative reactivity of triphenylthallium was obtained from the reaction with benzalacetophenone; it had been previously shown\textsuperscript{36} that a very reactive organometallic compound would add exclusively 1,2; that less reactive compounds add exclusively 1,4; and that organometallic compounds of intermediate activity exist which add both 1,2 and 1,4. A 1,4-addition would be expected from an organometallic compound somewhat less reactive than a Grignard compound, and in the reaction between triphenylthallium and benzalacetophenone the reaction products to be
expected from such an addition were found, namely \( \beta, \beta \)-diphenylpropiophenone and \( \beta \)-phenyl-\( \gamma \)-benzoyl-\( \gamma \)-benzohydrylbutyrophenone.\(^{72}\)

Triphenylthallium and \( \eta \)-butylthallium\(^{40}\) were found to undergo prompt metal-metal interconversion in accordance with the equation:

\[
(C_6H_5)_3Tl + 3n-C_4H_9Li \rightarrow 3C_6H_5Li + (n-C_4H_9)_3Tl
\]

The reaction between triphenylthallium and \( \eta \)-butyllithium was allowed to take place for ten minutes in ether and then the reaction mixture was carbonated by pouring on crushed dry ice. The yield of pure benzoic acid was 66\%. Thus, the tri-\( \eta \)-butylthallium was not isolated as such, and no further knowledge is possessed of its properties.

Whereas Birch\(^7\) had found that dry air was without action on triphenylthallium, Gilman and Jones found that if the passage of dry oxygen were continued through a benzene solution for forty-eight hours, although the color test was still positive, an 11\% yield of phenol (as tribromophenol) could be isolated. There was also an odor of biphenyl. No chemiluminescence was observed during the oxidation. In agreement with Birch, they found that triphenylthallium was unaltered by a short exposure of the compound to the air. The odor of the compound was found to resemble that of tetraphenyllead.

With mercury, triphenylthallium gave diphenylmercury and thallium amalgam. Diphenylthallium bromide gave diphenylmercury and thallous bromide. Pure carbon dioxide was without action at room temperature on a benzene solution.
The synthesis of trimethylthallium, intended by Rochow and Dennis\textsuperscript{136} but never published by them, was accomplished by Gilman and Jones,\textsuperscript{41} employing the reaction between dimethylthallium chloride and methyllithium. They described the compound as a colorless mobile liquid which boiled as follows under the specified pressure:

<table>
<thead>
<tr>
<th>P (mm)</th>
<th>B. p.° C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>36</td>
<td>54.5</td>
</tr>
<tr>
<td>38</td>
<td>56</td>
</tr>
<tr>
<td>40</td>
<td>57</td>
</tr>
<tr>
<td>45</td>
<td>60</td>
</tr>
<tr>
<td>49</td>
<td>62</td>
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<td>63</td>
</tr>
<tr>
<td>55</td>
<td>65</td>
</tr>
<tr>
<td>60</td>
<td>66.5</td>
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<tr>
<td>65</td>
<td>69</td>
</tr>
<tr>
<td>70</td>
<td>71</td>
</tr>
<tr>
<td>73</td>
<td>71.5</td>
</tr>
<tr>
<td>75</td>
<td>72</td>
</tr>
<tr>
<td>85</td>
<td>76</td>
</tr>
</tbody>
</table>

From these data they derived the equation for the pressure-temperature curve.

$$\log P = -1980(1/T) + 7.603$$

which by extrapolation gave a normal boiling point of 147°.

The compound crystallizes in long colorless needles which show a melting point at 38.5°. It does not become viscous near its melting point as reported for triethylthallium.\textsuperscript{136} The ethyl compound would normally be expected to melt below the methyl compound, as is the case. It is interesting that the compound, both as a liquid and as a solid at ordinary temperatures is colorless. Measurement of the freezing-point
expression of benzene indicated that the compound is monomolecular. However, the compound becomes light yellow at higher temperatures. This would seem to indicate that the degree of "unsaturation" is less in the case of trimethylthallium than for triethylthallium.

Another method of synthesis of $R_3Tl$ compounds, of great potential importance, was discovered by Gilman and Jones when they reexamined the reaction between a thallous halide and an alkylthallium compound. Considering separately the three equations

\[
\begin{align*}
3\text{CH}_3\text{Li} + 3\text{TLX} &\longrightarrow (\text{CH}_3)_3\text{TL} + 2\text{TL} + 3\text{LiX} \\
2\text{CH}_3\text{I} + 2\text{TL} &\longrightarrow (\text{CH}_3)_2\text{TLI} + \text{TLI} \\
\text{CH}_3\text{Li} + (\text{CH}_3)_2\text{TLI} &\longrightarrow (\text{CH}_3)_3\text{TL} + \text{LiI}
\end{align*}
\]

the first equation has been amply demonstrated by Menzies and Cope and by Birch. The third is the well known method of synthesis employed by Groll, Rochow and Dennis, etc. The novelty lay in making the second reaction quantitative by combining all three equations into one operation represented by the equation:

\[
2\text{CH}_3\text{Li} + \text{CH}_3\text{I} + \text{TLX} \longrightarrow (\text{CH}_3)_3\text{TL} + \text{LiX} + \text{LiI}
\]

Actually when the proper amount of methyllithium was added to a solution of methyl iodide in ether containing a suspension of thallous iodide a quantitative yield of trimethylthallium was obtained. The order of addition was found to make no difference, although alkyl iodides were found to give a better yield than alkyl bromides, and alkyl chlorides a still poorer
yield. The Grignard reagent did not give as good yields as organolithium compounds. Triethylthallium also could be prepared in nearly quantitative yields by this reaction. A reaction between phenyllithium, thallous chloride and iodo-benzene gave a 79% yield of triphenylthallium; thus, the reaction is seen to give somewhat lower yields with aromatic derivatives than with alkyl.

It was also shown that the reaction was capable of extension to other metals. Thus, methyllithium and lead iodide reacted in the presence of methyl iodide to give a quantitative yield of tetramethyllead.

Several additional properties of trimethylthallium are recorded in this paper. Light causes decomposition with the separation of metallic thallium. Trimethylthallium is apparently perfectly stable, however, if kept in the dark. It is spontaneously inflammable and detonates when suddenly strongly heated. A weak positive color test was obtained after refluxing with Michler's ketone for twelve hours in benzene. With mercury, trimethylthallium reacted to give dimethylmercury and thallium amalgam.
### TABLE I

**COMPOUNDS OF THE TYPE R<sub>3</sub>TL**

<table>
<thead>
<tr>
<th>Compound</th>
<th>M.p., °C.</th>
<th>B.p., °C.</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diethylisobutyl- (?)</td>
<td>--</td>
<td>--</td>
<td>7</td>
</tr>
<tr>
<td>Diethyltriphenylmethyld- (?)</td>
<td>--</td>
<td>--</td>
<td>52, 53</td>
</tr>
<tr>
<td>Tri-&lt;i&gt;η&lt;/i&gt;-butyl- (?)</td>
<td>--</td>
<td>--</td>
<td>40</td>
</tr>
<tr>
<td>Triethyl-</td>
<td>-63.0</td>
<td>54.6-54.8/1.5 mm.</td>
<td>7, 42, 52, 53, 136</td>
</tr>
<tr>
<td>Triisobutyl-</td>
<td>--</td>
<td>74-76/1.6 mm.</td>
<td>7</td>
</tr>
<tr>
<td>Trimethyl-</td>
<td>38.5</td>
<td>60/45 mm.</td>
<td>41, 42</td>
</tr>
<tr>
<td>Triphenyl-</td>
<td>188-189</td>
<td>--</td>
<td>7, 37</td>
</tr>
</tbody>
</table>
Compounds of the Type $R\text{,}Tl$

No compound of this type has been isolated, but much information has been gained about the essential nature of organothallium compounds in attempts which were made to prepare these compounds, either as the $R\text{,}Tl$ type or as the dimer $R\text{,}Tl\text{-TlR}_2$. Moreover, their transient existence has been demonstrated and their decomposition products identified. Almost necessarily, then, it was found advisable to approach such problems through physico-chemical methods, such as conductivity measurements, dissociation constants, and oxidation-reduction potentials. An additional difficulty was presented by the insolubility of most $R\text{,}TlX$ compounds in water, which makes more difficult the examination of the dissociation according to the equation

$$R\text{,}TlX \rightarrow R\text{,}Tl^+ + X^-$$

in aqueous solution, which is desirable if the data obtained are to be comparable with the vast body of such knowledge in the literature. Shukoff$^{138}$ studied the conductivity of diethylthallium chloride and found it to be a strong electrolyte, but nevertheless appreciably hydrolyzed at high dilutions. His values for the molar conductance, $\kappa$, at 25° are as follows:

<table>
<thead>
<tr>
<th>$V$</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
<th>160</th>
<th>320</th>
<th>640</th>
<th>1280</th>
<th>2560</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\kappa$</td>
<td>84</td>
<td>93.5</td>
<td>100.4</td>
<td>105.9</td>
<td>111.9</td>
<td>120.3</td>
<td>131.3</td>
<td>149</td>
<td></td>
</tr>
</tbody>
</table>

It is to be noted that the conductance does not reach a
limiting value with increasing dilution.

When an aqueous solution of diethylthallium chloride was subjected to electrolysis between two platinum electrodes, crystalline metallic thallium and a gas separated at the cathode. Shukoff assumed that thallium ions were present in equilibrium with the organometallic cations and formed from them by dissociation. Accordingly, he measured the potential developed by the following half-cells at 25°:

\[
\begin{align*}
0.05 \text{ N } (\text{C}_2\text{H}_5)_2\text{TlCl} & \mid \text{ Normal Electrode } & 0.750 \text{ V.} \\
0.05 \text{ N } (\text{C}_2\text{H}_5)_2\text{TlCl} & \mid 0.005 \text{ N } (\text{C}_2\text{H}_5)_2\text{TlCl} & 0.029 \text{ V.} \\
0.005 \text{ N } (\text{C}_2\text{H}_5)_2\text{TlCl} & \mid 0.0005 \text{ N } (\text{C}_2\text{H}_5)_2\text{TlCl} & 0.001 \text{ V.} \\
0.05 \text{ N } (\text{C}_2\text{H}_5)_2\text{TlCl} & \mid 0.0005 \text{ N } (\text{C}_2\text{H}_5)_2\text{TlCl} & 0.030 \text{ V.}
\end{align*}
\]

The effect of dilution in these concentration cells does not follow the Nernst equation, which requires that the potential difference between solutions diluted in the ratio 1:10 be 0.059 volt. However, the measurements were constant and reproducible, and could not be attributed to anomalies that might be caused by the solution of the thallium metal deposited on the electrode with the resultant formation of a layer of thallium ions, for care was taken to have the electrode continually washed by fresh solvent.

Shukoff then made another series of measurements against a saturated thallous chloride solution, which he found to be 0.0161 N at 25°, with the following results:
0.0161 N (C₆H₅)_₂TlCl | 0.0161 N TlCl | 0.042 V.
0.0161 N (C₆H₅)_₂TlCl | Normal Electrode | 0.769 V.
0.0161 N TlCl | Normal Electrode | 0.727 V.

From these concordant values the thallium ion concentrations were determined by the Nernst equation, although its use without corrections for activities is certainly open to objection as shown by the data in the first experiment. For 0.0161 N aqueous thallous chloride solution the ionic concentration was found to be $10^{-2.07}$, and for the corresponding diethylthallium chloride solution, $10^{-2.78}$. Whence Shukoff concluded: "From these potentiometric determinations it can be stated only qualitatively that the univalent dialkylthallium cation functions as a complex ion from which thallous ions are dissociated to the extent of $10^{-2.5}$, i.e., to about 1/300 of its concentration. It is presupposed, naturally, that the potential of a thallium electrode is determined only by the concentration of thallous ions. In this sense it is at any rate worth noting that the ions of a dialkylthallium compound are capable of exerting definite potentials."

In an effort to establish whether an equilibrium existed in accordance with the equation

$$\text{(C}_6\text{H}_5\text{)}_2\text{Tl}^+ \rightleftharpoons \text{Tl}^+ + \text{C}_6\text{H}_5\cdot$$

he examined the gas collected at the cathode, but the amount was insufficient to enable any conclusion to be formed other than that the gas contained about 15% of unsaturated hydrocarbons.

Although working only with inorganic materials, Spencer examined several oxidation-reduction equilibria which are significant when considered in the light of Shukoff's findings. The potential for the general equation of reduction he found
Thalllic ions tend to go to thallous ions, and not the reverse. The tendency of the thallic ion to form complexes with anions he found to increase in the following order: chloride, tartrate, acetate, cyanate, oxalate, bromide, nitrite, iodide, thio-cyanate, sulfite, cyanide and thiosulfate. It is seen that Shukoff was fortunate to have chosen the chloride ion, thus avoiding further complication of his results. And finally Spencer determined that thallic and thallous salts are in equilibrium with metallic thallium when the ratio of concentrations is $\text{Tl}^{+++}/\text{Tl}^+ = 10^{-52.2}$. Thallic ion is thus seen to be completely reduced to thallous ion by metallic thallium. This is true even in solutions which, because of complex formation, contain only small concentrations of thallic ions. Thus, the value of the above ratio in solutions containing thiosulfate ion he found was still no larger than $10^{-36}$. The equation for the reduction of thallic ion to thallium metal he found to be

$$\text{Tl}^{+++} \rightarrow \text{Tl}^+ - 2\text{e}, 1.99 \text{ volts}$$

The work makes it at least understandable why in thallium chemistry, organic as well as inorganic, the tendency to find reduction to thallous salts and metallic thallium is always so great.

In a more direct chemical attack on the problem of preparing $R_4\text{Tl}$ compounds, Goddard found that copper bronze or
metallic sodium in anhydrous solvents had no action on dialkylthallium halides. In one experiment two grams of dimethylthallium iodide and one-half gram of copper bronze powder were refluxed in 15 ml. of dry acetone for seven hours. The solution was filtered and the dimethylthallium iodide recovered unchanged. By treating a like quantity of the iodide with metallic sodium in anhydrous benzene a similar result was obtained. No compound of the type \( R_2Tl-TlR \) was isolated in either case.

Hein and Markert attempted to isolate the dialkylthallium radical by the same general electrolytic procedure which they had used so successfully in the preparation of triphenylchromium and tetraphenylchromium. But parallel experiments designed to study the electrochemical behavior of diethylthallium were completely negative, as in the case of Shukoff. Invariably only metallic thallium separated, although the electrolyte was shown to contain not even a trace of a thallous or thallic salt. Both diethylthallium hydroxide and diethylthallium iodide were subjected to electrolysis, even at temperatures as low as \(-70^\circ\), in liquid ammonia and in methanol, with platinum and with mercury cathodes, but only metallic thallium was obtained. The diethylthallium radical must, therefore, even under these favorable conditions, decompose instantly in accordance with the equation:

\[
(C_2H_5)_2Tl \rightarrow Tl + C_2H_4 + C_2H_6 \quad \text{or} \quad C_4H_{10}
\]
The same reaction was observed by Shukoff to take place at ordinary temperatures. Hein and Markert decline the suggestion that the source of the metallic thallium is TlCl in equilibrium with undecomposed diethylthallium chloride, as advanced by Shukoff, for they point out that the reaction

\[(\text{C}_2\text{H}_5)_2\text{TlCl} \rightarrow \text{C}_2\text{H}_5 + \text{TlCl}\]

can only be irreversible. It is important to add that diethylthallium iodide is easily soluble in liquid ammonia to a colorless solution.

Berry and Lowry\(^6\) mention that dialkylthallium halides can not be condensed by the action of metallic sodium to molecules of the type \(\text{R}_2\text{Tl} - \text{TlR}_2\). This is presumably a reference to Goddard's work,\(^46\) but there is no exact citation and the reaction is not further discussed in the experimental part of their work. The ability of thallium to form compounds of the type \(\text{R}_2\text{Tl} - \text{TlR}_2\) is indirectly related to the tendency of thallium to form the thallium-thallium linkage. The equation

\[2\text{Tl}^+ \leftrightharpoons \text{Tl}_2^{++}\]

was advanced by Drucker,\(^23\) suggesting that thallium forms diatomic cations, like mercury, but by a reversible process. This hypothesis was advanced to explain freezing-point data, transference numbers and conductivities of dilute thallous nitrate solutions, but it is not supported by any independent evidence. Berry and Lowry, in particular, reject it on the ground that, whereas the presence of pairs of mercury atoms
can be inferred from the X-ray analysis of crystalline mercurous chloride, the same X-ray shows that the thallium in thallous halides is present exclusively in the form of single thallium atoms or ions. Also mercurous ions, by forming a diatomic molecule, maintain the duplet theory, with 80 electrons around each nucleus, just as in the monoatomic vapor, but thallium would have 81 electrons on the same basis.

Another connection between the inorganic chemistry of thallium and the possibility of the univalent dialkylthallium radical is considered by Berry and Lowry in an examination of the effect of progressively stripping electrons from the heavy metals: "The formation of the 78-electron group in Au⁺, Hg⁺⁺, Tl⁺⁺⁺, and Pb⁺⁺⁺ involves the removal of two electrons from the stable mercury configuration. This becomes progressively more difficult as the charge on the ion increases, so that we cannot be sure whether the relatively high conductivity of aqueous solutions of thallic chloride is due to the ability of the salt to behave as a quaternary electrolyte or merely to hydrolysis; on the other hand, the low conductivity of the salt in non-aqueous solutions shows that, under less favorable conditions, it behaves only as a binary electrolyte,

\[ \text{TlCl}_2 \leftrightarrow \text{TlCl}_2^+ + \text{Cl}^- \]
\[ \text{Me}_2\text{Thl} \leftrightarrow \text{Me}_2\text{Tl}^+ + \text{I}^- \]

The existence of thallic ions in infinitesimal quantities can, however, be inferred from potentiometric measurements."

Some careful experimental work by Perret and Perrot on compounds of the type RHgX led them to state some similarities these compounds have with the alkali salts; for instance, the lack of color and the solubility in alcohol of methyl-mercury sulfide can be duplicated in the alkali sulfides. Platz sided with Perret and Perrot in maintaining the
pseudometallic character of the radical \( R_n\text{TL}^- \), but claimed that, contrary to the opinion of Erlenmeyer\(^{26}\) and of Garzuly-Janke,\(^{32}\) and following the belief of Perret and Perrot, the salts of \( R_n\text{TL}^- \) do not resemble those of \( \text{Ag}^+ \), \( \text{Hg}^+ \), or \( \text{Hg}^{++} \) or of the alkali metals, but rather \( \text{Tl}^+ \). A lively polemical discussion ensued, without benefit of experimental work. Naturally, similarities can be found between thallium and all its near neighbors in the periodic system, and the debate did not contribute greatly to the advancement of thallium chemistry.

An important and interesting concept was advanced by Gilman and Jones,\(^{40}\) who suggested that diphenylthallium might be an intermediate in the transition of phenylthallium to triphenylthallium and thallium metal. They showed that when diphenylthallium bromide was treated with one equivalent of sodium in liquid ammonia, triphenylthallium and thallium metal were formed, for which they suggested the equations:

\[
(C_6H_5)_2\text{TLBr} + \text{Na} \longrightarrow (C_6H_5)_3\text{TL} + \text{NaBr}
\]

\[
3(C_6H_5)_2\text{TL} \longrightarrow 2(C_6H_5)_3\text{TL} + \text{TL}
\]

Although to date no \( R_n\text{TL} \) compound has been isolated, it is possible that under the proper experimental conditions and with the correct choice of the radical to be introduced such a compound might by synthesized. The cyclohexyl and naphthyl radicals would be preferable to the phenyl group. It must be acknowledged, however, that it is only to be expected that it would be more difficult to remove one group from a trivalent thallium than from a tetravalent lead.
Compounds of the Type RTl

The earliest paper by Hansen\textsuperscript{56} contains reactions which might have been expected to lead to the discovery of ethylthallium. These reactions were between diethylzinc and thallous chloride, diethylzinc and metallic thallium, ethyl iodide and metallic thallium, and ethyl iodide and thallium-sodium alloy. However, in no case was an organothallium compound obtained. Hansen himself did not definitely say that the expected compounds would have a valence of one; it remained for Hartwig\textsuperscript{58} to point out that Hansen's work contained that possibility. But in view of the negative success, Hartwig was led to seek more especially trivalent thallium compounds by starting directly from thallium trichloride. In a later publication that was essentially a more extended discussion of the work in his first paper, Hartwig\textsuperscript{59} declared that thallium, like lead, apparently could combine with "alcoholic radicals" only in its highest state. This argument is now obviated, of course, by the possession of lead compounds with an "apparent valence", as determined by quantitative analysis, less than four.

These first few tentative gropings in an obscure field remained the only knowledge on univalent organothallium compounds for fifty years. Then in 1927 Hein and Segitz\textsuperscript{62} published some brilliant experimental work in which they presented very good evidence for the transient existence of
ethylthallium. Their classical experiments on the electrolysis of ethylsodium in diethylzinc, using various metals as anodes, have been discussed in detail in the section on $R_Tl$ compounds. It should suffice here to emphasize those phases of the work which bear most directly on univalent thallium compounds. When thallium was used as the anode, an immediate darkening not only of the metal but also of the liquid in the bath took place. This was shown to be due to metallic thallium by measuring the loss in weight of the electrode and by quantitative analysis of the black precipitate. It was hard to imagine any other explanation than that the ethyl radicals, at the moment of their being set free, attacked the metallic thallium with the formation of ethylthallium. This in turn was very unstable and underwent oxidation-reduction to tri-ethylthallium and metallic thallium, which separated partly in the solution and partly was redeposited on the anode. It is to be regretted that there was no actual isolation of tri-ethylthallium from the electrolytic fluids—although admittedly this would involve a very difficult separation of three reactive organometallic compounds, all of which are altered by contact with moist air. Also the temperature of 50° employed in this experiment seems rather high for the isolation of unstable compounds. The current density was very modest, only 0.02 amperes.

The formation of a trivalent organothallium compound from an univalent salt almost necessarily demands the
postulation of an RT1 compound as intermediate. That this will then be transformed by a stepwise reaction through an R₂Tl compound as an intermediate is not so necessary, especially since thallium never has the valence of two. But the valence of one is the common inorganic valence, which makes the existence of RT1 compounds much more likely than R₂Tl. Meyer and Bertheim ¹¹² failed to alkylate thallous chloride by the action of alkylmagnesium halides, only metallic thallium being isolated. Groll, ⁵² however, did succeed in isolating triethylthallium in small yield by the direct action of ethyl chloride on sodium-thallium alloys. And Menzies and Cope ⁹⁹ found that if two moles of ethylmagnesium bromide were reacted with one mole of thallous chloride without heating, a 12.4% yield of diethylthallium bromide was obtained. Thallous ethoxide, being soluble in organic solvents gave even better yields, some as high as 24%. Birch ⁷ used ethyllithium to alkylate thallous chloride, which procedure gives somewhat better yields than the method employing the Grignard reagent. All these reactions must be presumed to pass through an RT1 compound as an intermediate, but there the matter was allowed to drop, and further work in these papers must be considered rather from the viewpoint of R₂Tl compounds and is so considered in that section.

Gilman and Jones, ⁴⁰ however, in the most extensive investigation to date on the chemical properties of an RT1 compound, were not content to present one bare sentence to
the effect that univalent organothallium compounds may exist as transitory forms—such as the above papers had chiefly done. Their choice of an aryl compound, phenylthallium, also favored greatly the examination, inasmuch as alkylmetallic radicals are less stable than arylmetallic radicals having the same metal. Pyrolysis of triphenylthallium was the source of the radical; earlier, triphenylthallium had been found to remain unaffected when carbon dioxide was passed for long periods through a solution in boiling benzene, and the same was true of solutions in boiling toluene. In other words, triphenylthallium must be sharply sensible to temperature, for when carbon dioxide was passed through a solution in boiling xylene a 70% yield of benzoic acid and a 73% yield of biphenyl was obtained. This suggests the following reactions:

\[
\begin{align*}
\text{(C}_6\text{H}_5\text{)}_3\text{Tl} & \rightarrow \text{C}_6\text{H}_4\text{Tl} + \text{C}_6\text{H}_5\text{C}_6\text{H}_5 \\
\text{C}_6\text{H}_5\text{Tl} + \text{CO}_2 & \rightarrow \text{C}_6\text{H}_4\text{COOTl}
\end{align*}
\]

However, another mechanism was examined which does not require the postulation of phenylthallium as an intermediate. One of the valence bonds in tervalent organothallium compounds is known to be distinctly more reactive than the other remaining two; it was considered possible that carbon dioxide might insert itself between the thallium atom and one phenyl group to give diphenylthallium benzoate, which would then break down to thallous benzoate and biphenyl, as in the following scheme:
But when an authentic sample of diphenylthallium benzoate was refluxed in xylene in a stream of carbon dioxide, no benzoic acid was obtained, and the diphenylthallium benzoate was recovered almost quantitatively. Hence the first reaction mechanism is greatly to be preferred, and finds support in other chemical reactions of triphenylthallium. For instance, triphenylthallium was found to react with benzophenone in boiling xylene to give triphenylcarbinol and biphenyl, as if the intermediate reaction had been the formation of biphenyl and phenylthallium. Again, no reaction was observed in benzene, and the sensitivity of trivalent thallium compounds to temperature must be stressed. Somewhat similar situations can be found among the inorganic trivalent thallium compounds, for instance the decomposition of thallium trichloride to the sesquichloride and chlorine, and the impossibility of completely precipitating all the chlorine from thallium trichloride by silver nitrate.

In analogous fashion triphenylthallium was found to react with benzonitrile to give benzophenone. But, whereas in the Entemann-Johnson series of the relative reactivities of various functional groups toward phenylmagnesium bromide ethyl benzoate is placed above benzonitrile in reactivity, triphenylthallium was shown not to react with ethyl benzoate.
under conditions comparable to those used with benzonitrile, one of the several illustrations that a series of relative reactivities established with one organometallic compound may not have exactly the same order when determined by another organometallic compound.

Since it had been found that phenylthallium was moderately reactive and, more especially, thermally unstable, attempts were made to prepare the compound at lower temperatures by the reaction between thallous chloride and phenyllithium, but even at -70° there was an immediate deposition of metallic thallium, which seems to indicate that the phenylthallium first formed has a very short life, and that disproportionation to thallium and triphenylthallium takes place in accordance with the equations:

\[
\text{C}_6\text{H}_5\text{Li} + \text{TlCl} \rightarrow \text{C}_6\text{H}_5\text{Tl} + \text{LiCl}
\]

\[
3\text{C}_6\text{H}_5\text{Tl} \rightarrow (\text{C}_6\text{H}_5)_3\text{Tl} + 2\text{Tl}
\]

Since the amount of biphenyl isolated from the reaction was larger than that which normally is encountered as resulting from the Wurtz reaction incidental to the preparation of phenyllithium from bromobenzene and lithium, it was suggested that part of the thallium may have resulted from reactions such as

\[
2\text{C}_6\text{H}_5\text{Tl} \rightarrow \text{C}_6\text{H}_5\text{C}_6\text{H}_5 + 2\text{Tl}
\]

and the coupling reaction

\[
2\text{C}_6\text{H}_5\text{Li} + 2\text{TlCl} \rightarrow \text{C}_6\text{H}_5\text{C}_6\text{H}_5 + 2\text{LiCl} + 2\text{Tl}
\]

To complete the picture of the chemical properties of
phenylthallium, Gilman and Jones stated the decreasing order of reactivity of some RM compounds to be:

\[ \text{RMgX, RTl, } R_2\text{In, } R_3\text{Ga, } R_3\text{Tl.} \]
Compounds of the Type $R_xTl^Y_x$  

Trivalent organothallium compounds of this type, where thallium has a covalence of four, were first prepared by Menzies and coworkers$^102$ in 1928. It was already known that the many dialkylthallium compounds of the type $R_xTlX$ were salts of a strong univalent base, $R_xTlOH$. They accordingly prepared a series of derivatives of dimethylthallium hydroxide and diethylthallium hydroxide with the two $\beta$-diketones, acetylacetone and benzoylacetone, with ethyl acetoacetate, and with salicyaldehyde, in order to determine whether the products were chelate compounds or salts. Simple salts would have the general properties of $R_xTlX$ compounds (q.v.), for instance, very high melting points (or more often no melting points at all), great insolubility, lack of volatility, etc. But the presence of the two alkyl groups would give the thallium in a monochelate derivative a stable covalence of four, hence it seemed more than likely that derivatives of this covalent type should be formed—much more readily than in the case of the alkali metals, for instance, where the valence of the free base is also one.

Actually, it was found that covalent compounds were readily formed by three reactions: (1) by double decomposition of the dialkylthallium halides with thallous acetylacetone and similar compounds, (2) by the action of crude dialkylthallium ethoxide (from the iodide or bromide and thallous ethoxide) on the diketone, and (3) from the dialkylthallium carbonate.
and the diketone. It was found that the products have unusual properties, quite different from those met with in compounds of the type \( R_2TZ \). They are crystalline solids, which can be sublimed with ease under reduced pressure and are readily soluble in benzene and even in hexane. This indicates that they are not ionized. It seemed reasonable, then, to assign structures of the type:

![Structure I](image1)

![Structure II](image2)

Surprisingly enough, however, the compounds (with the exception of the benzoylacetone derivatives) are extremely soluble in water, which this structure would not lead us to expect, and they are clearly ionized, since the solutions have a strong alkaline reaction (containing the salt of a strong base and a weak acid) and can be titrated quantitatively, using methyl red as an indicator. Also, potassium iodide gives a precipitate of the sparingly soluble dialkylthallium iodide from aqueous solutions. Thus in water they pass, like hydrogen chloride and stannic chloride, from the covalent to the ionized state. Dimethylthallium benzoylacetone and diethylthallium benzoylacetone dissolve in water very slowly, even on boiling; their alcoholic solutions, however, remain clear on mixing with much water, and can be titrated quantitatively.
By reference to Table II at the end of this section it will be seen that in every case the ethyl compound melts lower than the corresponding methyl derivative. The lowest melting compound of all in this particular group is dibutylthallium dipropionylmethane, which melts at 41°. It also is the most soluble in organic solvents.

Advantage was taken of the low melting points of this class of compounds to determine the parachor value for the element thallium. Sugden\textsuperscript{145} determined the density and surface tension on a sample of dimethylthallium benzoylacetonate supplied by Menzies. The sample melted at 128-129° corr. and was stable up to 170°. Values were obtained as follows:

<table>
<thead>
<tr>
<th>t</th>
<th>133°</th>
<th>142.5°</th>
<th>149°</th>
<th>157°</th>
</tr>
</thead>
<tbody>
<tr>
<td>\gamma</td>
<td>32.08</td>
<td>31.1</td>
<td>30.52</td>
<td>29.85</td>
</tr>
<tr>
<td>d</td>
<td>1.795</td>
<td>1.783</td>
<td>1.773</td>
<td>1.763</td>
</tr>
<tr>
<td>p</td>
<td>524.0</td>
<td>523.4</td>
<td>523.7</td>
<td>523.8</td>
</tr>
</tbody>
</table>

Values for the other elements and for a six-membered ring and a singlet linkage were deducted from the above values of \( P \) to give a parachor value for the element thallium itself, \( P = 64.6 \). Other measurements were made on thallous ethyl acetoacetate, ethoxide, formate, and acetate. As a mean value Sugden assigned \( P = 64 \) for the element thallium. It is interesting to compare this value with \( P_{\text{Hg}} = 69 \) and \( P_{\text{Pb}} = 76 \); thus there is a minimum at thallium between mercury and lead.

Sidgwick and Brewer\textsuperscript{139} pointed out that compounds of the
alkali metals with \( \beta \)-diketones and related substances might be divided into three classes: (1) salts, insoluble in organic solvents, and charring without melting on being heated; (2) intermediate compounds, soluble in organic solvents immediately on formation, but reverting on isolation to class (1); (3) chelate compounds, soluble in organic solvents and having definite melting points. It is readily seen that the dimethylthallium and diethylthallium chelate derivatives described above, where acetylacetone and benzoylacetone are the chelating agents, belong to class (3). Menzies and Wiltshire\(^{106}\) showed further that it is possible to prepare non-alkylated thallous chelates which belong to class (3), and even dialkylthallium chelates which belong to class (1). For instance, the thallous derivative of tetraacetylethane belongs quite definitely to class (1). The corresponding dimethyl compound also belongs in this category, as does the diethyl compound, although less closely; on the other hand, the thallous and dimethylthallium derivatives of tetraacetylpropane, although very unstable, behave as chelate compounds belonging to class (3). It is understandable that this regular gradation in properties should exist. If the chelating group is sufficiently "organic" in its nature, then even a thallous derivative may be moved from class (1) to class (3). Tetraacetylthane is not sufficiently "organic", but the larger tetraacetylpropane is. On the other hand, a dialkylthallium derivative requires much less help from the chelating group to enter class (3). This gradual and predictable
shift in properties may be seen from an examination of the following summary of the solubilities of the tetraacetylene derivatives:

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Tl-</th>
<th>(CH₃)₄Tl-</th>
<th>(C₂H₅)₄Tl-</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>Soluble</td>
<td>Soluble</td>
<td>Soluble (on heating)</td>
</tr>
<tr>
<td>Benzene</td>
<td>Insoluble</td>
<td>Insoluble</td>
<td>Slightly soluble</td>
</tr>
<tr>
<td>Toluene</td>
<td>Insoluble</td>
<td>Soluble (on heating)</td>
<td>Soluble</td>
</tr>
</tbody>
</table>

Following the same line of reasoning, one is not surprised to find that by the time dimethylthallium tetraacetylpropane is reached, the "organic nature" and membership in class (3) is completely established: dimethylthallium tetraacetylpropane melts at 98°.

Also, the dialkylthallium derivatives are much more stable than the thallous chelates; e.g., thallous ethyl acetoacetate and acetylacetone darken on standing, but the corresponding dialkylthallium compounds appear to keep indefinitely. Moreover, chelate thallous compounds are very easily hydrolyzed in solution, and require much more care in their preparation and recrystallization than the chelate dialkyl compounds; aqueous solutions of the latter can often be boiled almost to dryness.

Another interesting gradation in properties in this series of compounds is observed in the decrease in color. Whereas the thallous compounds are a distinct yellow, the dimethyl compounds are much paler, and the diethyl compounds are almost white. This is a general effect, observed in most colored
thallous and dialkylthallium derivatives. It thus appears that the decrease in color is associated with the attachment to the thallium atom of inert radicals.

Further generalizations can be made from an extension of work on these compounds which was carried out by Menzies and Wiltshire. The more stable chelate compounds, the derivatives of polyvalent metals with acetylacetone and similar substances, contain two or more rings attached to each metallic atom. Compounds containing only one chelate ring are, as a rule, unstable, the ring structure easily reverting to the open enolic form. Importance should be ascribed, therefore, to the chelate derivatives of dialkylthallium, all of which are stable crystalline solids containing only one chelate ring attached to each metallic atom. The molecules are unsymmetrical, but they are frequently volatile. The following compilation will serve to make clear certain additional generalized relationships:
The first series with acetylacetone presents a graduated scale in which the thallous compound approaches, but does not reach, the instability of sodium or potassium acetylacetone, whereas dibutylthallium acetylacetone in its greater stability and insolubility in water resembles copper or beryllium acetylacetone. Inspection of the melting points shows that in passing from the thallous to the dimethylthallium compounds there is a considerable rise in melting point, followed by a gradual fall on passing to the higher dialkylthallium derivatives. It would be interesting to extend the series to still higher dialkyl derivatives, for at some point the melting points should reach a minimum and then rise again slightly. Also, the

<table>
<thead>
<tr>
<th>Compound</th>
<th>M.p.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thallous acetylacetone</td>
<td>161°</td>
</tr>
<tr>
<td>Dimethylthallium acetylacetone</td>
<td>215°</td>
</tr>
<tr>
<td>Diethylthallium acetylacetone</td>
<td>200°</td>
</tr>
<tr>
<td>Di-n-propylthallium acetylacetone</td>
<td>181°</td>
</tr>
<tr>
<td>Di-n-butylthallium acetylacetone</td>
<td>139°</td>
</tr>
<tr>
<td>Thallous dipropionylmethane</td>
<td>70°</td>
</tr>
<tr>
<td>Dimethylthallium dipropionylmethane</td>
<td>121°</td>
</tr>
<tr>
<td>Diethylthallium dipropionylmethane</td>
<td>116°</td>
</tr>
<tr>
<td>Di-n-propylthallium dipropionylmethane</td>
<td>89°</td>
</tr>
<tr>
<td>Di-n-butylthallium dipropionylmethane</td>
<td>41°</td>
</tr>
<tr>
<td>Dimethylthallium propionylacetone</td>
<td>162°</td>
</tr>
<tr>
<td>Diethylthallium propionylacetone</td>
<td>147°</td>
</tr>
</tbody>
</table>
replacement of methyl by ethyl groups attached to carbon has a greater effect on the melting point than the replacement of ethyl by methyl groups attached to thallium, for dimethyl-, diethyl-, and dipropylthallium dipropionylmethane have each, in turn, lower melting points than the respectively isomeric diethyl-, dipropyl-, and dibutylthallium acetylacetone.

All the alkylated thallium compounds listed above can be sublimed in air by careful heating in a test tube. It is to be regretted that no determination of the vapor pressures of dialkylthallium chelates has ever been made, for it does not necessarily follow that the vapor pressure will obey the same generalizations as the melting points. A compound may be a liquid, such as hexyl sebacate, and have no measurable vapor pressure; it may be a solid, such as camphor, and have a considerable vapor pressure.

Further insight into the essential nature of chelated dialkylthallium compounds was afforded by an investigation conducted by Wiltshire and Menzies\(^{151}\) on their degree of association and apparent molecular weights, as determined by cryoscopic measurements on their benzene solutions. For the purposes of the following discussion it will be convenient to regard the dialkylthallium derivatives of \(\beta\)-diketones and \(\beta\)-ketonic esters as having the general structure

\[
\begin{align*}
R_1 - C & \xrightarrow{\text{CH}} C - R_2 \\
\text{O} & \xrightarrow{Tl} \text{O} \\
\text{Alk_2} &
\end{align*}
\]
Differentiation in position between the organic radicals $R_1$ and $R_2$ is immaterial, as the ring structure is probably symmetrical.

It was found that the compounds are associated in benzene solution, and that the degree of association depends to a marked extent both on the nature of the groups $R_1$ and $R_2$ and, to a smaller extent, on the alkyl groups attached to the thallium atom. The compounds show a degree of association from slightly more than one to slightly less than two. The association at first increases slightly with concentration, but in most cases an approximately constant value is reached below a molecular concentration of 0.01 g.-mole/100 g. of benzene. The following representative data will serve as a basis for comparison and generalization.

<table>
<thead>
<tr>
<th>Dimethylthallium-</th>
<th>Diethylthallium-</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mol. conc.</td>
<td>Association</td>
</tr>
<tr>
<td>Ethyl acetoacetate</td>
<td>0.00932</td>
</tr>
<tr>
<td>Methyl acetoacetate</td>
<td>0.00715</td>
</tr>
<tr>
<td>Propionylacetone</td>
<td>Too sparingly soluble</td>
</tr>
<tr>
<td>Ethyl benzoylacetate</td>
<td>0.00974</td>
</tr>
<tr>
<td>Benzoylacetone</td>
<td>0.0103</td>
</tr>
<tr>
<td>Dipropionylmethane</td>
<td>0.0111</td>
</tr>
<tr>
<td>Dibenzoylmethane</td>
<td>0.00621</td>
</tr>
</tbody>
</table>

Wiltshire and Menzies summarize the influence of the groups $R_1$ and $R_2$ attached to the chelate ring as follows: "In
both the dimethyl- and the diethylthallium series of derivatives the association is very small when \( R_i \) and \( R_j \) are the same hydrocarbon radical, as in the compounds of dipropionylmethane \((R_i = R_j = \text{C}_6\text{H}_{13})\) and dibenzoylmethane \((R_i = R_j = \text{C}_6\text{H}_{13})\). When \( R_i \) is changed to \( \text{CH}_3 \), as in the propionylacetone \((R_i = \text{CH}_3; R_j = \text{C}_6\text{H}_{13})\) and benzoylacetonc \((R_i = \text{CH}_3; R_j = \text{C}_6\text{H}_{13})\) derivatives, the association is increased. Another increase in association resulting from a similar change is seen by comparing the derivatives of ethyl benzoylacetate \((R_i = \text{C}_6\text{H}_{13}; R_j = \text{CH}_3)\) and ethyl acetocacacetate \((R_i = \text{CH}_3; R_j = \text{OC}_3\text{H}_7)\), the latter being more associated.

"An increase in association is also observed when an oxygen atom is introduced into \( R_i \) or \( R_j \), diethylthallium ethyl acetooacetate \((R_i = \text{C}_6\text{H}_{13}; R_j = \text{OC}_3\text{H}_7)\) being considerably more associated than diethylthallium propionylacetone \((R_i = \text{CH}_3; R_j = \text{C}_6\text{H}_{13})\). Moreover, the derivatives of ethyl and methyl acetooacetate, in which \( R_i \) is a methyl group and \( R_j \) an alkoxy group, are the most highly associated of all the compounds studied. The methyl ester, however, is slightly less associated than the ethyl, indicating that substituting a methyl for an ethyl group in this position has not the same effect.

"Summarizing, it can be said that the dimethylthallium derivatives investigated form a well-defined series in which the association decreases in the order given above. In the diethylthallium derivatives the association decreases in the same order, but the separation between the curves representing successive members is in several instances much smaller. Moreover, preliminary experiments with several dipropyl- and dibutylthallium derivatives indicate that in these cases the order is slightly different, probably owing to the effect of the groups \( R_i \) and \( R_j \) being modified as the size of the alkyl groups attached to thallium is increased."

In every case investigated, the dimethylthallium derivative exhibits a slightly greater association than the corresponding diethylthallium derivative at the specified molecular concentration. Thus, again, the effect of substituting methyl for ethyl groups in the molecule is to cause an increase in association.

Sidgwick and Sutton\(^{140}\) found that thallous ethyl acetooacetate has a double molecular weight in boiling benzene, and accounted for the association by assuming that the octet of
electrons around the thallium atom is thereby completed, either by a double bond between two thallium atoms (which now seems less likely) or by coordinate links between the thallium of one molecule and an oxygen of another. But in the dialkyl-thallium compounds now under consideration, the thallium has, in the unimolecular formula, an effective atomic number of 86, and its electronic octet is thus complete. Hence it is rather surprising to find association in these compounds. The thallium atom, however, is certainly concerned in this association, for ethyl acetoacetate itself, for instance, is unassociated in freezing benzene. It must be assumed, therefore, that, although the unimolecular form of chelate dialkyl-thallium compounds, containing an electronic group of 8 is very stable, yet there is a less strong tendency for the number to be increased above 8. Examples are definitely known in the inorganic chemistry of thallium where the effective atomic number is greater than 86. Compounds of all three types, $\text{MT}_1\text{X}_2$, $\text{M}_2\text{T}_1\text{X}_2$, and $\text{M}_2\text{T}_1\text{X}_4$ have been described\textsuperscript{109, 110, 133} where the thallium atom possesses a covalence of 4, 5, and 6 and an effective atomic number of 86, 88, and 90. The substitution of the smaller methyl for the ethyl or phenyl group, either in the positions $\text{R}_1$ and $\text{R}_2$ or on the thallium atom, may increase the probability of coordination by allowing the atoms taking part to approach closer together. In addition, the molecules are asymmetric, and if they have a dipole moment, the association may also be due to electrostatic attraction.
between similar molecules oriented in opposite directions.

Menzies and Wiltshire also found that trimethyl-
platinum chelate compounds are more highly associated than
dimethylthallium derivatives. Usually the platinum compounds
decompose without melting on heating, and are less soluble in
water, although they resemble the corresponding dimethylthallium
compounds in being soluble in organic solvents and in being
quite volatile. But platinum has an effective atomic number
of 84 in these compounds, or two less than the next inert gas.
Hence it is not surprising that the molecular weight comes
out nearly double, thus increasing the effective atomic number
to 86 and the coordination number of the metal to six.

Some observations by Menzies and Overton on chelate
compounds of several heavy metals can be correlated in the
following fashion:

<table>
<thead>
<tr>
<th></th>
<th>Me₄Pt⁺</th>
<th>Et₂Au⁺</th>
<th>MeHg⁺</th>
<th>(Alk)₂Tl⁺</th>
<th>Et₄Pb⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Valence</td>
<td>4</td>
<td>3</td>
<td>2</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>Effective coordination number</td>
<td>6</td>
<td>4</td>
<td>2</td>
<td>4-6</td>
<td>4</td>
</tr>
<tr>
<td>Chelate compounds</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Molecular association of halides</td>
<td>2.3-4.5</td>
<td>2</td>
<td>1</td>
<td>Up to 8</td>
<td>1</td>
</tr>
</tbody>
</table>

It will be noticed that the compounds with diketones have been
made only in those cases where the effective coordination
number is greater than the valence, and where the organometallic
halides are associated. Methylmercury iodide and triethyllead
chloride have the simple molecular weight in benzene. Thallium displays an unusually high degree of coordination.

It was later pointed out by Menzies that not only does the stability of a number of compounds of the heavier metals depend on the tendency for the central atom to attain a rare-gas structure, but also on the preference for an even rather than an odd covalence. Triethyllead acetylacetonate, for example, requires a coordination number of five and an effective atomic number of 88, and thus fulfills neither of the above conditions, and attempts to prepare it failed.

The hypothetical ethylthallium would also have in its coordinated form an effective atomic number of 82 with a coordination number of unity. It has been shown that under conditions where its formation might be expected (see the section on RTl Compounds) triethylthallium and metallic thallium are obtained instead. Both the stable diethylthallium ion and ethylthallium have the same effective atomic number; hence the difference in stability is apparently connected with the even and odd coordination numbers of two and one.

Compounds with an effective atomic number of 84 are also unstable when they have an odd covalence. Such compounds include the reactive triethylthallium and the monomeric undissociated dialkylthallium halides, which have been shown to be highly associated in the few cases in which their solubility in benzene allows their molecular weights to be determined.

Essentially the same arguments were advanced by Menzies.
in a summary designed to repel some attacks made by others on the theory of coordinate linkages. This summary contains no new material that need be considered here.

Two distinct dialkythallium compounds from a single chelating agent have never been obtained. In all the compounds of the type under discussion there are two equally probable positions of the bonding electrons:

\[
\begin{align*}
R_1 - &\quad \text{H} \\
\text{C} &\quad \text{C} - R_2 \\
\text{O} &\quad \text{O} \\
\text{Ti} &\quad R_3 \\
R_3 &\quad R_4
\end{align*}
\]

Stability is thus associated with the possibility of resonance. No mixed dialkythallium compounds are known, as is indicated by both alkyl groups attached to thallium being denoted by \( R_4 \). Menzies and Walker\textsuperscript{104} attempted unsuccessfully to prepare derivatives in which the median hydrogen atom is substituted. Methylacetylacetone and ethyl methylacetoacetate both gave very unstable dialkythallium derivatives.

These same workers did provide a striking demonstration of the greater stability toward hydrolysis of the higher dialkythallium compounds, and showed at the same time that it is not conditioned merely by their greater insolubility in water, by examining the volatility with steam of a series of dialkythallium compounds from 0.2 N alkaline solution. Their results
may be summarized as follows:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Tl-Me₂Tl</th>
<th>Tl-Et₂Tl</th>
<th>Tl-Pr₂Tl</th>
<th>Tl-Bu₂Tl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetylacetone</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Propionylacetone</td>
<td>-</td>
<td>-</td>
<td>m. p.</td>
<td>m. p.</td>
</tr>
<tr>
<td>Dipropionylmethane</td>
<td>-</td>
<td>+</td>
<td>m. p.</td>
<td>m. p.</td>
</tr>
</tbody>
</table>

A minus sign indicates that the distillate contained no thallium; a plus sign, that the distillate gave a precipitate with potassium iodide; the designation m. p., that the compound distilled with steam so readily that a sample could be collected and its melting point determined. It is evident that an increase in the size of the alkyl groups leads to increased protection.

They also put the familiar increase in solubility in organic solvents, as solubility in water and reactivity with aqueous solutions diminish, on a quantitative basis by measuring the solubility in n-hexane at 27° of the above series of compounds in terms of grams of substance in 100 grams of solution:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Tl-Me₂Tl</th>
<th>Tl-Et₂Tl</th>
<th>Tl-Pr₂Tl</th>
<th>Tl-Bu₂Tl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetylacetone</td>
<td>0.012</td>
<td>0.12</td>
<td>0.20</td>
<td>0.15</td>
</tr>
<tr>
<td>Propionylacetone</td>
<td>1.52</td>
<td>0.77</td>
<td>4.65</td>
<td>12.4</td>
</tr>
<tr>
<td>Dipropionylmethane</td>
<td>41.1</td>
<td>14.5</td>
<td>17.0</td>
<td>21.7</td>
</tr>
</tbody>
</table>

Cox, Shorter and Wardlaw examined the stereochemistry of both univalent quadricovalent and trivalent quadricovalent...
thallium in the light of their generalization: "so far, no exception has been found to the rule that a tetrahedral valency distribution is shown by a metal atom whenever its effective atomic number in the complex is that of an inert gas, but the converse is not true, and no simple rule appears to be applicable to those cases in which the four metal valencies lie in a plane." They found it difficult to get very precise results from thallium, partly because few compounds suitable for investigation were known, and partly because of the high atomic number of the element, 81. But in general their results indicated that the thallous compounds have a planar distribution of the four valences, whereas the thallic compounds seem to follow the above generalization and have a tetrahedral structure. The only thallous compounds found suitable for investigation were the thiourea derivatives Tl 4CS(NH₃)ₓ, first prepared by Rosenheim and Löwenstamm. A complete investigation was not possible on account of the small size of the crystals, but the general results indicated that the four valences have a planar distribution (or very nearly so).

Dimethylthallium acetylacetone was examined as a typical trivalent quadricovalent compound, which was known to have the rare-gas structure, and which should, therefore, be tetrahedral in obedience to the above general rule. The molecule in the crystalline state was found to have a two-fold axis of symmetry, which is possible with either a tetrahedral or planar configuration if it is assumed that the acetylacetone group has a symmetrical resonance structure. Considerations of the probable method of packing in the unit cell suggested
that of the two possibilities the tetrahedral configuration was to be regarded as most likely. A dimeric formulation, either planar or tetrahedral, was definitely excluded. It was thought that by replacing the methyl groups by the larger phenyl groups a subject more favorable for crystallographic analysis might be obtained. Diphenylthallium acetylacetone was accordingly synthesized, but it proved to be less symmetrical than the methyl derivative. It remains the only diarylthallium chelate compound.

The optical resolution of an organothallium compound has never been reported. From the above work it would seem that there should be at least a good chance that the type of organothallium compound discussed in this section actually has a tetrahedral structure, and that an optical resolution should be possible. The reaction between methylthallium dichloride and p-aminophenyllithium might well be the first step in such a synthesis.
<table>
<thead>
<tr>
<th>Compound</th>
<th>M. p., °C.</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Di-(n)-butyl- acetylacetone</td>
<td>139</td>
<td>104, 107</td>
</tr>
<tr>
<td>Di-(n)-butyl- dipropionylmethane</td>
<td>41</td>
<td>104</td>
</tr>
<tr>
<td>Di-(n)-butyl- propionylacetone</td>
<td>72</td>
<td>104</td>
</tr>
<tr>
<td>Diethyl- acetylacetone</td>
<td>200</td>
<td>102, 106, 107, 151</td>
</tr>
<tr>
<td>Diethyl- benzoylacetone</td>
<td>118</td>
<td>102, 151</td>
</tr>
<tr>
<td>Diethyl- dibenzoylmethane</td>
<td>112</td>
<td>151</td>
</tr>
<tr>
<td>Diethyl- dipropionylmethane</td>
<td>116</td>
<td>104, 107, 151</td>
</tr>
<tr>
<td>Diethyl- ethyl acetoacetate</td>
<td>90</td>
<td>102, 107</td>
</tr>
<tr>
<td>Diethyl- ethyl benzoylacetate</td>
<td>95</td>
<td>107</td>
</tr>
<tr>
<td>Diethyl- methyl acetoacetate</td>
<td>127</td>
<td>107</td>
</tr>
<tr>
<td>Diethyl- propionylacetate</td>
<td>147</td>
<td>104, 107, 151</td>
</tr>
<tr>
<td>Diethyl- tetraacetylethylene</td>
<td>dec.</td>
<td>106</td>
</tr>
<tr>
<td>Dimethyl- acetylacetone</td>
<td>215</td>
<td>20, 102, 104, 106</td>
</tr>
<tr>
<td>Dimethyl- benzoylacetone</td>
<td>129</td>
<td>102, 107, 145</td>
</tr>
<tr>
<td>Dimethyl- dibenzoylmethane</td>
<td>175</td>
<td>107</td>
</tr>
<tr>
<td>Dimethyl- dipropionylmethane</td>
<td>121</td>
<td>104, 107, 108, 151</td>
</tr>
<tr>
<td>Dimethyl- ethyl acetoacetate</td>
<td>130</td>
<td>102, 107, 108</td>
</tr>
<tr>
<td>Dimethyl- ethyl benzoylacetate</td>
<td>133</td>
<td>107</td>
</tr>
<tr>
<td>Dimethyl- methyl acetoacetate</td>
<td>184</td>
<td>107</td>
</tr>
<tr>
<td>Dimethyl- propionylacetone</td>
<td>162</td>
<td>104, 107, 151</td>
</tr>
<tr>
<td>Dimethyl- salicylaldehyde</td>
<td>dec. 200</td>
<td>102</td>
</tr>
<tr>
<td>Compounds</td>
<td>M. p., °C.</td>
<td>References</td>
</tr>
<tr>
<td>---------------------------------</td>
<td>------------</td>
<td>------------</td>
</tr>
<tr>
<td>Dimethyl- tetraacetylene</td>
<td>dec.</td>
<td>106</td>
</tr>
<tr>
<td>Dimethyl- tetraacetylpropane</td>
<td>98</td>
<td>106</td>
</tr>
<tr>
<td>Diphenyl- acetylacetone</td>
<td>---</td>
<td>20</td>
</tr>
<tr>
<td>Di-\text{\textit{n}}-propyl- acetylacetone</td>
<td>181</td>
<td>104, 151</td>
</tr>
<tr>
<td>Di-\text{\textit{n}}-propyl- dipropionylmethane</td>
<td>89</td>
<td>104, 151</td>
</tr>
<tr>
<td>Di-\text{\textit{n}}-propyl- propionylacetone</td>
<td>108</td>
<td>151</td>
</tr>
</tbody>
</table>
Compounds of the Type RTlX₃

An unsuccessful attempt was made in 1926 by Krause and von Grosse to synthesize compounds of the type RTlX₃. They started from compounds of the type R₂TlX, and made use of their method of controlled bromination in pyridine. This method had been used by Krause and coworkers with great success in the moderated cleavage of alkyl and aryl radicals from organolead and organotin compounds. However, no compound of the type RTlX₃ was obtained, but instead complex compounds with the empirical analysis TlX₃, RX, C₆H₅N. Several possible structural formulas were considered for these unusual compounds. The supposition that there is present such a grouping as RTlX₃, C₆H₅NX, with the alkyl group directly attached to thallium and thus representing an addition product of an alkylthallium dihalide to an addition product of halogen and pyridine, is not justified by the facts available on the chemical behavior of the compounds. For example, alkali very readily causes decomposition, with the separation of thallic hydroxide, which would be unusual in the case of an organometallic compound. Rather Krause believed that the complex TlBr₄ is present. They can be formulated as addition products of alkylpyridinium halide with thallic halide; that is, as an alkylpyridinium tetrabromothallate (C₆H₅NR)(TlBr₄). This would correspond to the inorganic compounds of the type TlCl₃, C₆H₅N, HCl, of which a great many have been prepared by
Meyer.\textsuperscript{109} Or a formulation more in keeping with Werner's conception of complex compounds, \(\left[\text{Tl}^\text{Br}_\text{C}_\text{H}_\text{N}\right]\), with thallium having a coordination valence of six, might be borrowed from the inorganic chemistry of thallium trichloride tripyridine, as elucidated by Meyer.\textsuperscript{110} In general, however, the compounds of \(\text{TlX}_n\) with \(\text{C}_\text{H}_\text{N}\), \(\text{HX}\) have been shown by Renz\textsuperscript{135} to have a much more complicated structure.

This somewhat extended discussion of structure would not be justified if it were not for the unusual nature and properties of these compounds. These complex compounds are crystalline and characterized by sharp melting points. In general, they are almost insoluble in water, slightly soluble in benzene and ether, readily soluble in hot alcohol, and very soluble in cold pyridine. By double decomposition with alcoholic potassium iodide the magnificently red tetraiodo compounds may be obtained. The tetrabromo compounds vary from colorless to straw yellow. The iodides also have a red color in solution. Several instances have already been pointed out in this Review of the color change of organothallium compounds with temperature, i. e., triethylothallium and trimethylthallium in the section on compounds of the type \(\text{R}_n\text{Tl}\) (q. v.). Instances are even known in thallous compounds. But all other thallium compounds are surpassed by the remarkable thermochromatic properties of the tetraiodo complexes here under discussion.

The following description will serve as an example:
Even more remarkable is the stability of the compounds. They can be heated above 200° without decomposition. They are completely stable toward hydrolysis. n-Butylpyridinium tetrabromo-thallate can even be recrystallized from hot 20% hydrobromic acid! Hot concentrated sulfuric acid or fuming nitric acid do cause decomposition.

This stability led to a simple method of preparation which gives much better yields than the method of cleavage of R₂TLX compounds by an excess of bromine in pyridine solution: it is by the action of a halogen on a thallous halide in pyridine in the presence of an alkyl halide, in accordance with the equation:

\[ \text{TIX} + X_2 + RX + \text{C}_8\text{H}_5\text{N} \rightarrow (\text{C}_8\text{H}_5\text{N} \cdot \text{R})(\text{TIX}_4) \]

This synthesis also sheds further light on the essential composition and structure of the compounds. The great variety of the melting points obtained from the different alkyl halides makes it a possible means for the ready identification of this class of compounds.

Even more interesting are the mixed melting points. The melting-point depressions are so large that it is possible to obtain liquid mixtures from two low-melting solid compounds.
In an attempt to prepare \( n \)-octylpyridinium tetraiodothallate from a sample of Kahlbaum \( n \)-octyl iodide, no solid product could be obtained even with the strongest cooling. Krause and von Grosse attribute this to impurities in the alkyl iodide—although it was purchased from one of the finest sources of pure chemicals. But it must not be forgotten that this method of eutectic mixtures as a means of obtaining liquid thallium compounds can be reenforced by the known tendency of longer alkyl groups to lower the melting point of thallium compounds. This generalization has been discussed at some length in the section on dialkylthallium chelate compounds (\( \text{g. } \text{v.} \)). It should be pointed out now that Menzies prepared, as the lowest-melting representative of the dialkylthallium chelate compounds, di-\( n \)-butylthallium dipropionylmethane, which melts at 41°. He did not go beyond butyl groups, and it is quite possible that the liquidity of Krause's \( n \)-octylpyridinium tetraiodothallate may be, in part, due to the longer alkyl group as well as to the eutectic properties of mixtures.

It is possible, therefore, by combining the generalization on the length of alkyl groups with the generalization on eutectic properties to produce liquid thallium compounds which resist hydrolysis. No information, however, is available on the vapor pressures of this class of compounds. Two more interesting generalizations can be introduced in this connection, however: it is known that a great variety of nitrogen
bases can be substituted for pyridine in the purely inorganic complexes of trivalent thallium, among them such compounds as diethylamine. The possibility of varying the nitrogen base in the alkyl-nitrogen base tetrahalomethallates most certainly will exist also, and here is a method for increasing the volatility of this class of compounds by the proper choice of base. Secondly, it is obvious that the halogen can be varied also. Fluorine is the natural choice here, both for its known great lowering of the boiling points of many organic compounds and for its known effect of promoting stability.

Finally, it is not at all unlikely that two or more of the halogens might be replaced by sulfur and other negative elements. This would permit further wide variations in the properties of these compounds. There is great latitude in the replacement within the complex in thallium chemistry.

The first true \( \text{RTlX}_2 \) compounds were synthesized by Challenger and Parker, who employed the reaction between an arylboric acid and a thallic halide. They reasoned correctly that since Michaelis and Becker had shown that phenylboric acid and mercuric chloride react in hot aqueous solution to give insoluble phenylmercury chloride, by analogy the same reaction might work with phenylboric acid and thallic halides. Actually, it was found that two reactions can take place, depending on the relative amounts of reactants used:

\[
\text{ArB(OH)}_2 + \text{TLX}_2 + \text{H}_2\text{O} \rightarrow \text{ArTlX}_2 + \text{HX} + \text{H}_2\text{BO}_3
\]

and

\[
2\text{ArB(OH)}_2 + \text{TLX}_2 + 2\text{H}_2\text{O} \rightarrow \text{Ar}_2\text{TlX} + 2\text{HX} + 2\text{H}_2\text{BO}_3
\]
Thallium chloride and bromide reacted at once in hot aqueous solution with phenylboronic acid, giving, according to the proportion of phenylboronic acid employed, either \( R_TlX \) or \( R_TlX_2 \) compounds, or a mixture. The mixed chlorides could be easily separated by taking advantage of the much greater solubility in water of the \( R_TlX_2 \) type. The mixed bromides are not so easily separated, since the decomposition reaction

\[
2ArTlX_2 \longrightarrow Ar_TlX + TlX_2
\]

takes place rapidly with the dibromide. Phenylthallium dichloride or dibromide gave an immediate yellow precipitate with potassium iodide which quickly turned black, eliminating iodobenzene. Hence it appears that the diiodides are spontaneously unstable and decompose according to the equations:

\[
2ArTlI_2 \longrightarrow TlI_2 + Ar_TlI
\]

\[
5ArTlI_2 \longrightarrow 3TlI + 3ArI
\]

Phenylthallium dibromide undergoes a similar decomposition on heating, thallous bromide and bromobenzene being formed, whereas diphenylthallium bromide gives biphenyl.

Challenger and Parker also demonstrated that \( R_TlX_2 \) compounds can be synthesized by the usual Grignard reaction:

\[
RMgX + TlX_2 \longrightarrow RTlX_2 + MgX_2
\]

This is the reaction that is ordinarily used for the preparation of \( R_TlX \) compounds. However, when the insoluble precipitate obtained in these reactions is recrystallized from pyridine, small amounts of \( R_TlX_2 \) compounds can be thrown out of the mother-liquor by the addition of water. There is no
report in the literature that this reaction has been put on a preparative basis, but that is not surprising, since a large excess of Grignard reagent has always been used. It would be significant to try the reaction with only one equivalent of Grignard reagent, as demanded by the above equation, and add the Grignard reagent to the ether solution of thallium trichloride. Also, a great variety of organolithium compounds with functional groups might be employed. To date, however, this is not a practical method for the synthesis of RTlX₃ compounds.

These same workers also showed that RTlX₃ compounds form addition compounds with pyridine. This is to be expected. Phenylthallium dibromide tripyridine and phenylthallium dibromide tetrapyridine were both obtained with sharp melting points. Apparently the valence bonds approach in indefiniteness those encountered in solvent of crystallization. The complexity and extent of the coordination valences of thallium have already been discussed at length in this Review. The relationship with the alkylpyridinium tetrahalothallates investigated by Krause and discussed above should, however, be commented on at this point. It will be recalled that Krause arrived at one and the same compound whether he proceeded from the cleavage of R₄TlX compounds in pyridine by an excess of bromine or whether he started from a thallous halide, alkyl halide and pyridinium dihalide. In the former case the alkyl group was known to be attached to thallium;
in the latter, to a halogen atom. The experiment should now be tried with the pyridine addition compounds of Challenger and Parker to see whether the addition of \( X \) to \( \text{RTLX}_2 \cdot \text{C}_6\text{H}_5\text{N} \) would not also give the same compound as obtained by Krause and von Grosse, in accordance with the equation:

\[
\text{RTLX}_2 \cdot \text{C}_6\text{H}_5\text{N} + X \rightarrow (\text{C}_6\text{H}_5\text{N}\cdot \text{R})(\text{TLX}_4)
\]

This should be the case if the compounds are to be formulated as entirely within the radical in the complex \([\text{Br}_2 \text{TLR}_2 \text{C}_6\text{H}_5\text{N}]\). If this is not the case, the possibility of structural isomers is presented, with the same empirical formula but different melting points, colors, etc. accordingly as different parts are within or without the complex. Also the possibility of obtaining optically active stereoisomers from this class of compounds should not be entirely neglected. It should be possible to prepare compounds with mixed halogens—perhaps with varying combinations within and without the complex, as in the case of chromium and other well-known examples in inorganic chemistry.

Essentially the same material was presented by Challenger and Parker in a paper read before the Chemical Society.\(^{14}\) Several years later, Challenger and Richards\(^{15}\) published additional information on \( \text{RTLX}_2 \) compounds. They found that double decomposition reactions are possible according to the equation:

\[
\text{ArTLX}_2 + 2\text{KY} \rightarrow \text{ArTLY}_2 + 2\text{KX}
\]

From phenylthallium dichloride they prepared the dihydroxide, diazide, dicyanide and dithiocyanate. The last two compounds
were found to lose benzonitrile and phenylthiocyanate at 228° and 120°, respectively. Phenyllithium dichloride is more stable than the dibromide, which rather easily loses bromobenzene. The corresponding diiodide is unknown, iodo-benzene being immediately liberated. With an excess of potassium cyanide, phenyllithium dicyanide was found to form a complex, which on boiling in water breaks down thus:

$$2K\left(CH_2CN\right)_2 \rightarrow 2KC + (C_6H_5)_2 TlCN + Tl(CN)_2$$

A striking difference was found when the reaction between alkylboric acids and thallium trichloride was attempted. n-Propylboric acid was found to remain unaffected by thallium trichloride at 140°. Hence alkylthallium dihalides must be prepared by reversing the reaction previously discussed:

$$2RTlX \rightarrow R_2TlX + TlX_2.$$

This may be done by boiling the dialkylthallium halide, prepared by the Grignard reaction or other reactions discussed in the section on $R_2TlX$ compounds, with a large excess of thallium trichloride:

$$R_2TlX + TlX_2 \rightarrow 2RTlX.$$  

This extension to the synthesis of alkylthallium dihalides was first carried out by Mel'nikov and Gracheva. They did state that the boric acid synthesis might be made to give small yields in the case of alkyl compounds if high molecular weight alkylboric acids were used, but they gave no compounds thus prepared as examples.

Challenger and Richards found that phenyl- and p-bromo-phenyllithium dichlorides react with mercuric chloride by
transferring their aryl group, giving phenyl- and \( \rho \)-bromo-
phenylmercury chlorides, and eliminating thallium trichloride:

\[
\text{ArTlCl}_3 + \text{HgCl}_2 \rightarrow \text{ArHgCl} + \text{TlCl}_3
\]

It might be imagined possible to synthesize mixed organo-
thallium compounds of the type \( \text{R}_1\text{R}_2\text{TlX} \) by subjecting an \( \text{RTlX} \)
compound to the further reaction of a Grignard reagent:

\[
\text{R}_1\text{TlX}_2 + \text{R}_2\text{MgX} \rightarrow \text{R}_1\text{R}_2\text{TlX} + \text{MgX}_2
\]

This reaction was tried by Challenger and Richards,\textsuperscript{15} who
reacted phenylthallium dichloride with ethyl- and cyclohexyl-
magnesium bromides, but a mixed halide could not be isolated.
Instead, diethylthallium bromide, dicyclohexylthallium bromide
and diphenylthallium bromide were obtained, the latter naturally
from both reactions. This recalls the behavior in certain
circumstances of aryl- and alkylmercury chlorides.\textsuperscript{64, 69}

Another possible reaction for the synthesis of \( \text{R}_1\text{R}_2\text{TlX} \)
compounds is represented by the equation:

\[
\text{R}_1\text{TlX}_2 + \text{R}_2\text{B(OH)}_2 + \text{H}_2\text{O} \rightarrow \text{R}_1\text{R}_2\text{TlX} + \text{H}_2\text{BO}_2 + \text{HX}
\]

Actually Challenger and Richards synthesized phenyl-\( \rho \)-tolyl-
thallium chloride by this reaction. Moreover, it could be
obtained as well by starting from phenylthallium dichloride
and \( \rho \)-tolylboric acid as by starting from \( \rho \)-tolylthallium
dichloride and phenylboric acid. This compound still stands
as the only organothallium compound of the type \( \text{R}_1\text{R}_2\text{TlX} \) yet
synthesized.

The orientation phenomena encountered in the nitration
of organometallic compounds containing the phenyl group were
studied by Challenger and Rothstein, who examined the phenyl derivatives of Hg, Tl, Pb, Bi, Sn, I. In every case, nitration is found to take place predominately in the meta-position, with small amounts of the para isomer, and still smaller amounts of the ortho. The compounds investigated and their results may be presented as follows:

<table>
<thead>
<tr>
<th>Compound</th>
<th>% m-Nitration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenylmercury nitrate</td>
<td>50</td>
</tr>
<tr>
<td>Diphenylthallium oxide</td>
<td>74</td>
</tr>
<tr>
<td>Diphenylthallium nitrate</td>
<td>75</td>
</tr>
<tr>
<td>Phenylthallium hydroxynitrate</td>
<td>86</td>
</tr>
<tr>
<td>Diphenyllead dinitrate</td>
<td>94</td>
</tr>
<tr>
<td>Triphenylbismuth dinitrate</td>
<td>86</td>
</tr>
<tr>
<td>Diphenyltin oxide</td>
<td>79</td>
</tr>
<tr>
<td>Diphenyliodonium nitrate</td>
<td>82.5</td>
</tr>
</tbody>
</table>

It is readily seen that m-orientation is stronger with an RTlX₃ compound than with an R₂TLX compound. Also m-orientation is stronger toward the middle of the periodic table, reaching a maximum with lead. No theoretical explanation has ever been presented why this is so.

Namestkin, Mel’nikov and Gracheva, although they developed no new method of synthesis for RTlX₃ compounds, did extend the general methods of Challenger, which are presented above, to the creation of a large number of compounds, and in so doing recorded various interesting details. For example, not
all arylboric acids gave good yields with thallium trichloride. Ortho-substitution seems to cause some steric hindrance. And anisylboric acids also give low yields, apparently due to complex formation with the ether linkage. Benzylboric acid was found to undergo oxidation in accordance with the equation:

\[ \text{C}_6\text{H}_5\text{CH}_2\text{B(OH)}_2 + 3\text{H}_2\text{O} + 2\text{TLBr} \rightarrow 2\text{TLBr} + 4\text{HBr} + \text{H}_2\text{BO}_2 + \text{C}_6\text{H}_5\text{COOH} \]

These authors also pointed out that, whereas \( R_\text{TlX} \) compounds are colorless, most \( R\text{TlX}_3 \) compounds are colored yellow or orange. Molecular weight determinations are unfortunately still lacking for this class of compounds but it is probable that they will be found to be associated.

Mel'nikov and Gracheva prepared \( R_\text{TlX} \) compounds by cleaving \( R_\text{Tl} \) compounds with \( \text{TlX}_3 \). This they found to be a very violent reaction, for which they advanced three possible equations:

\[
\begin{align*}
2R_\text{Tl} + \text{TlX}_3 \rightarrow 3R_\text{TlX} \\
R_\text{Tl} + \text{TlX}_3 \rightarrow R_\text{TlX} + \text{TlX} + RX \\
2R_\text{Tl} + \text{TlX}_3 \rightarrow 2R_\text{TlX} + \text{TlX} + R-R
\end{align*}
\]

They also found that alkylthallium dihalides, as well as the arylthallium dihalides reported by Challenger, form complex compounds with pyridine, but they did not investigate the properties of such compounds in detail. It is to be noted that the solubility of \( R_\text{TlX} \) compounds in pyridine is also probably due to complex formation, but the isolation of definite compounds has not been reported.

Another example of the failure of the reaction

\[ R_\text{TlX} + \text{TlX}_3 \rightarrow 2R\text{TlX}_3 \]
to take place was discovered by Mel'nikov and Rokitskaya when they boiled dibiphenylthallium chloride with an excess of thallium trichloride. However, they found that the corresponding bromides, in the presence of traces of copper salts, react easily to give biphenylylthallium dibromide. This is perhaps an example of catalysis in the preparation of organothallium compounds.

These same workers also provided the solitary example recorded in the literature of still another method of preparing RTlX₃ compounds: the controlled cleavage of one radical from an RT₂lX₃ compound. Whereas Krause had started with the avowed purpose of doing just this, and had obtained instead complex compounds with his method of controlled bromination in pyridine, Mel'nikov and Rokitskaya started with the intention of nitrating diphenylthallium chloride in acetic anhydride at -20°C. They obtained no nitrophenylthallium compounds, but instead phenylthallium diacetate. The only other compound reported isolated from this reaction was nitrobenzene.

The most recent paper in the literature on compounds of the type RTlX₃ is also by Mel'nikov and Rokitskaya. Interestingly enough, it is from the Soviet Laboratory of Insecticides and Fungicides, a section of the Institute of Fertilizers and Insecticides. This suggests that thallium compounds were examined as a possible alternative for mercury compounds in seed treatment. It is quite within reason to imagine that thallium compounds could be developed which would not have
some of the objectional features of mercury compounds, such as high toxicity to workers, etc. This would not exclude even more general use as insecticides and fungicides.
### TABLE III
COMPOUNDS OF THE TYPE RTLX₃

<table>
<thead>
<tr>
<th>Compound</th>
<th>M. p., °C.</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzylthallium dibromide</td>
<td>205</td>
<td>118</td>
</tr>
<tr>
<td>Biphenylthallium dibromide</td>
<td>185 dec.</td>
<td>91</td>
</tr>
<tr>
<td>2,4-Bromomethylphenylthallium dibromide</td>
<td>180</td>
<td>92</td>
</tr>
<tr>
<td>2,4-Bromomethylphenylthallium dichloride</td>
<td>177</td>
<td>92</td>
</tr>
<tr>
<td>p-Bromophenylthallium dibromide</td>
<td>dec. 200</td>
<td>118</td>
</tr>
<tr>
<td>p-Bromophenylthallium dichloride</td>
<td>263</td>
<td>15,88,118</td>
</tr>
<tr>
<td>n-Butylpyridinium tetrabromothallate</td>
<td>119</td>
<td>77</td>
</tr>
<tr>
<td>n-Butylpyridinium tetrachlorothallate (?)</td>
<td>---</td>
<td>77</td>
</tr>
<tr>
<td>n-Butylpyridinium tetraiodothallate</td>
<td>193.5</td>
<td>77</td>
</tr>
<tr>
<td>p-Chlorophenylthallium dibromide</td>
<td>not at 250</td>
<td>118</td>
</tr>
<tr>
<td>p-Chlorophenylthallium dichloride</td>
<td>not at 250</td>
<td>88,118</td>
</tr>
<tr>
<td>2,4,5-Dimethylbromophenylthallium dibromide</td>
<td>192</td>
<td>92</td>
</tr>
<tr>
<td>2,4,5-Dimethylchlorophenylthallium dibromide</td>
<td>190</td>
<td>92</td>
</tr>
<tr>
<td>?, ?, Dimethylphenylthallium dibromide</td>
<td>215</td>
<td>92</td>
</tr>
<tr>
<td>p-Ethylphenylthallium dibromide</td>
<td>170</td>
<td>92</td>
</tr>
<tr>
<td>p-Ethylphenylthallium dichloride</td>
<td>dec. 155</td>
<td>92</td>
</tr>
<tr>
<td>Ethylpyridinium tetrabromothallate</td>
<td>119</td>
<td>77</td>
</tr>
<tr>
<td>Ethylpyridinium tetraiodothallate</td>
<td>130</td>
<td>77</td>
</tr>
<tr>
<td>Ethylthallium dibromide</td>
<td>dec. 160</td>
<td>88</td>
</tr>
<tr>
<td>Ethylthallium dibromide pyridine (?)</td>
<td>---</td>
<td>88</td>
</tr>
<tr>
<td>Compound</td>
<td>M. p., °C</td>
<td>References</td>
</tr>
<tr>
<td>----------------------------------------------------</td>
<td>-----------</td>
<td>------------</td>
</tr>
<tr>
<td>Ethylthallium dichloride</td>
<td>dec. 180</td>
<td>88</td>
</tr>
<tr>
<td>Isoamylthallium dibromide</td>
<td>dec. 110</td>
<td>88</td>
</tr>
<tr>
<td>Isoamylthallium dichloride</td>
<td>dec. 210</td>
<td>88</td>
</tr>
<tr>
<td>2,5-Methylchlorophenylthallium dibromide</td>
<td>182</td>
<td>92</td>
</tr>
<tr>
<td>4,5-Methylchlorophenylthallium dibromide</td>
<td>188</td>
<td>92</td>
</tr>
<tr>
<td>Methylpyridinium tetrabromothallate</td>
<td>171.5</td>
<td>77</td>
</tr>
<tr>
<td>Methylpyridinium tetraiodothallate</td>
<td>132</td>
<td>77</td>
</tr>
<tr>
<td>Methylthallium dibromide</td>
<td>dec. 160</td>
<td>88</td>
</tr>
<tr>
<td>α-Naphthylthallium dibromide</td>
<td>185</td>
<td>92</td>
</tr>
<tr>
<td>α-Naphthylthallium dichloride</td>
<td>144</td>
<td>92</td>
</tr>
<tr>
<td>m-Nitrophenylthallium dibromide</td>
<td>178 dec. 91</td>
<td>91</td>
</tr>
<tr>
<td>m-Nitrophenylthallium dichloride</td>
<td>217 dec. 91</td>
<td>91</td>
</tr>
<tr>
<td>m-Octylpyridinium tetraiodothallate (?)</td>
<td>---</td>
<td>77</td>
</tr>
<tr>
<td>Phenylthallium diacetate (?)</td>
<td>---</td>
<td>91</td>
</tr>
<tr>
<td>Phenylthallium diazide</td>
<td>--- stable to 200</td>
<td>15</td>
</tr>
<tr>
<td>Phenylthallium dibromide</td>
<td>153</td>
<td>13, 88</td>
</tr>
<tr>
<td>Phenylthallium dibromide pyridine</td>
<td>85</td>
<td>13, 15</td>
</tr>
<tr>
<td>Phenylthallium dibromide tripyridine</td>
<td>92</td>
<td>13, 15</td>
</tr>
<tr>
<td>Phenylthallium dibromide tetrapyridine</td>
<td>90</td>
<td>13, 15</td>
</tr>
<tr>
<td>Phenylthallium dichloride</td>
<td>234 dec. 13, 88</td>
<td>88</td>
</tr>
<tr>
<td>Phenylthallium dichloride pyridine</td>
<td>172 dec. 13, 15</td>
<td>15</td>
</tr>
</tbody>
</table>
TABLE III (Continued)

<table>
<thead>
<tr>
<th>Compound</th>
<th>M.p., °C.</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenylthallium dicyanide</td>
<td>228 dec.</td>
<td>15</td>
</tr>
<tr>
<td>Phenylthallium dicyanide potassium cyanide</td>
<td>265.5 dec.</td>
<td>15</td>
</tr>
<tr>
<td>Phenylthallium dihydroxide</td>
<td>dec. 285</td>
<td>15</td>
</tr>
<tr>
<td>Phenylthallium dinitrate (?)</td>
<td>---</td>
<td>91</td>
</tr>
<tr>
<td>Phenylthallium dithiocyanate</td>
<td>dec. 120</td>
<td>15</td>
</tr>
<tr>
<td>Phenylthallium hydroxynitrate</td>
<td>expl. 268</td>
<td>16</td>
</tr>
<tr>
<td>n-Propylpyridinium tetrabromothallate</td>
<td>118</td>
<td>77</td>
</tr>
<tr>
<td>n-Propylpyridinium tetraiodothallate</td>
<td>127.5</td>
<td>77</td>
</tr>
<tr>
<td>p-Tolythallium dibromide</td>
<td>165</td>
<td>13</td>
</tr>
<tr>
<td>p-Tolythallium dibromide pyridine (?)</td>
<td>---</td>
<td>13</td>
</tr>
<tr>
<td>p-Tolythallium dichloride</td>
<td>224</td>
<td>15,88</td>
</tr>
</tbody>
</table>
Compounds of the Type $R_xTl_x$

Methods of Synthesis and Chemical Properties

By far the greater number of the known organothallium compounds belongs in this section now to be considered. $R_xTl_x$ compounds are the most stable organothallium representatives. But whereas they have hitherto been considered in connection with other compounds and types, they will now be considered with special emphasis on their own methods of synthesis, chemical and physical properties. The equations representing a distinct method of synthesis are numbered consecutively in the following section.

Hansen,\(^56\) in an attempt to synthesize triethylthallium, actually obtained diethylthallium chloride. This work has been discussed in detail in the section on compounds of the type $R_xTl$. It will be sufficient here to recall that he obtained his organothallium compound by the action of diethylzinc on a solution of thallium trichloride in anhydrous ether, in essential accordance with the equation:

$$(C_2H_5)_2Zn + TlCl_3 \rightarrow (C_2H_5)_2TlCl + ZnCl_2 \quad (1)$$

It must not be overlooked in this and following methods of synthesis that alkylation of the third valence may partially take place, and that a method of synthesis of $R_xTl$ compounds may be represented by the equation for hydrolysis of $R_xTl$ in acid solution:
Gilman and Jones\textsuperscript{40} have actually shown that this is a method of choice for the synthesis of diphenylthallium benzoate. It is to be recommended in cases where the organic acid is not too stable: the diethylthallium salt of cysteine, for instance, might be made by this method of cleavage of triethylthallium, itself very easily prepared by the unpublished method of Gilman and Jones.\textsuperscript{42}

The diethylthallium chloride Hansen obtained directly in his synthesis was converted to the sulfate and nitrate by double decomposition between the diethylthallium chloride and the soluble silver sulfate and silver nitrate, respectively. This represents another general method of synthesis of $\text{R}_n\text{Tl}_m\text{X}_p$ compounds from $\text{R}_n\text{Tl}_m\text{Y}_q$ compounds:

\[
\text{R}_n\text{Tl}_m\text{Y}_q + \text{AgX} \longrightarrow \text{R}_n\text{Tl}_m\text{X}_p + \text{AgY}
\]

Many variations of this equation have been used since the time of Hansen, but they are too obvious to be listed as separate methods of synthesis. Perhaps the commonest method of preparing long series of salts from a given organothallium compound has been to synthesize first the organothallium hydroxide or carbonate, and then neutralize this with a variety of acids.

Hartwig\textsuperscript{58} employed the same reaction between diethylzinc and thallium trichloride in ether to synthesize diethylthallium chloride, and then used the method of double decomposition with silver salts to extend somewhat the list of diethylthallium
salts then known. The only compound of particular interest here is diethylthallium acetate, which he reported could be distilled. It is certain that the thioacetate would be even more volatile. This compound has never been reported, however, so an exact comparison can not be made at this time.

The efforts of Carius and Frommuller\textsuperscript{12} to synthesize triethylthallium from diethylthallium chloride and diethylmercury have been discussed in the section on $R_Tl$ compounds. Their only direct contribution to the chemistry of $R_TlX$ compounds was the observation that diethylthallium bromide and diethylthallium iodide reacted rather slowly with moist silver oxide. They did, however, prepare diethylthallium hydroxide by this method, but the reaction was very sluggish.

Hartwig\textsuperscript{59} later published a more detailed account of his preparation of several diethylthallium salts, and gave the following data on the solubility of these compounds:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Sol./100 g. water</th>
<th>Sol./100 g. alcohol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloride</td>
<td>3.3792$^\circ$ 2.7820$^\circ$</td>
<td>0.3378$^\circ$ 0.1220$^\circ$</td>
</tr>
<tr>
<td>Iodide</td>
<td>0.3496$^\circ$ 0.1020$^\circ$</td>
<td>0.0878$^\circ$ 0.0720$^\circ$</td>
</tr>
<tr>
<td>Sulfate</td>
<td>Very soluble</td>
<td>Very soluble</td>
</tr>
<tr>
<td>Phosphate</td>
<td>20.7075$^\circ$ 23.6620$^\circ$</td>
<td>Quite soluble</td>
</tr>
<tr>
<td>Nitrate</td>
<td>5.6770$^\circ$ 3.1920$^\circ$</td>
<td>Difficultly soluble</td>
</tr>
<tr>
<td>Acetate</td>
<td>Quite soluble</td>
<td>Quite soluble</td>
</tr>
</tbody>
</table>

A dialkylthallium bromide is less soluble than the chloride, and the iodide less soluble than the bromide. The salts of
oxygen acids are much more soluble in water than the salts of halogen acids. It is rather surprising to find that diethylthallium chloride has a moderate solubility in water but such a small solubility in alcohol. The decrease in solubility of the phosphate in hot water is probably due to hydrolysis.

Hartwig also prepared diethylthallium hydroxide, but was puzzled when it would not react with carbon dioxide, although it formed the correct salts with all mineral acids. Meyer\textsuperscript{112} showed twenty-five years later that Hartwig had had the carbonate and not the hydroxide. Hartwig had exposed his preparation of diethylthallium hydroxide to the air, and it had very rapidly taken up carbon dioxide. Other examples of similar behavior are known among organometallic hydroxides; for example, triethyllead hydroxide rapidly turns to the carbonate on exposure to air. All the diethylthallium salts prepared by Hartwig decompose with a small puff or explosion in the neighborhood of 200°.

No new organothallium compound was reported until Meyer\textsuperscript{112} and his pupil Bertheim employed the Grignard reagent in the synthesis of \( R_{n} \text{TlX} \) compounds and enormously added to the small stock of knowledge then available on these compounds. The reaction may be formulated as follows:

\[
2\text{RMgX} + \text{TlCl}_{2} \rightarrow \text{R}_{n}\text{TlX} + 2\text{MgXCl}
\]

From the date of this publication there is no further record of organozinc compounds ever having been used in the synthesis
of organothallium compounds. The only thallium halide that can practicably be used in this synthesis is the trichloride. The tribromide undergoes too much reduction to thallous bromide, and the triiodide is of very doubtful existence. Alkyl Grignard reagents are preferably prepared from alkyl chlorides for use in this reaction, for then the reduction caused by the Grignard reagent—and there is always some—is at a minimum, and the product is quite pure. In the aryl series convenience requires the use of the aryl bromide, but in this case the product is always a mixture of $R,TlCl$ and $R,TlBr$. Grignard reagents prepared from iodides cause much reduction. Meyer and Bertheim recommended that four moles of the Grignard reagent—twice the amount calculated for the above equation—be added to the ether solution of thallium trichloride.

By this method they prepared dimethylthallium, diethylthallium, dipropylthallium, and diphenylthallium salts. Although the effect of varying the $X$ group in $R,TlX$ compounds had been studied on the diethylthallium salts, it was now possible for the first time to study the effect of varying the $R$ groups. The solubility of the dialkylthallium salts was found to increase with respect to organic solvents as the length of the alkyl chain was increased, but the alkyl groups were still too short to have more than a bare solubility in alcohol, ether, and like solvents. Pyridine proved to be an excellent solvent for the $R,TlX$ compounds. Diphenylthallium
bromide could be very readily recrystallized from this solvent, but the dialkylthallium halides were almost too soluble. They could be better recrystallized from concentrated aqueous ammonia, or from strong potassium hydroxide solution, neither of which strangely enough attacks the halogen atom. Solubility in these solvents must in every case be attributed to complex formation.

Goddard\(^4\) made a large number of dimethyl- and diethyl-thallium salts of nitrophenols. They were prepared by neutralizing the dialkylthallium hydroxide with the calculated amount of the nitrophenol. Goddard announced his interest in the great resemblance between dialkylthallium hydroxides and thallous hydroxide, and between alkali salts of nitrophenols and dialkylthallium salts of nitrophenols. Although he did not say so, he may also have been interested in the explosive properties of such compounds. Diethylthallium chloride tends to "puff" when heated, and a diethylthallium nitrophenoxide much more so. Langhans\(^2\) has found that the thallous salts of nitrophenols resemble in their detonation and explosive properties the alkali metal nitrophenoxides rather than the salts of the heavy metals, such as lead, with nitrophenols.

Goddard also found that all dimethylthallium nitrophenoxides have a more intense color than the diethylthallium nitrophenoxides. This is the reverse of the situation with trimethyl- and triethylthallium. This "electron unsaturation" so often encountered in thallium chemistry is further
strengthened by the evidence for residual affinity in dimethyl-
thallium m-nitrophenoxide, which was obtained both as the simple
salt and also crystallized with one mole of m-nitrophenol.
The color of the latter complex salt was deep red, whereas
the color of the simple salt was light orange. The conclusion
that Goddard immediately jumped to—that thallium requires an
acid group for coordination—is patently not true; many
examples of coordination with amines have been presented in
this Review, and complex formation between amines and these
dialkylthallium nitrophenoxides could undoubtedly easily be
demonstrated. Some further observations by Goddard on the
color changes occasioned by shifting the position of the nitro
group around in the ring are of too small general interest to
be considered here.

By means of the well-known reaction with silver salts,
Goddard prepared further diethylthallium derivatives, such
as the thiocyanate, chromate, and trichloroacetate. Something
better than this somewhat random production of compounds was
Goddard's synthesis of the series of diethylthallium salts
of the normal fatty acids, from formate to n-octoate. The
predictions that are now obvious after the generalizations
which have already been discussed in this Review were completely
verified: salts of these organic acids have a good melting
point, unlike salts of inorganic acids; the melting point
falls as the length of the alkyl chain in the fatty acid is
increased; and the solubility in water decreases and the
solubility in organic solvents increases markedly as the length of the chain is increased.

Goddard demonstrated the stability of diethylthallium chloride when he found that concentrated hydrochloric acid, thionyl chloride, ammonia gas, and mercuric chloride were without action. Iodine trichloride, however, even in the cold, violently attacked the corresponding diethylthallium bromide, with the production of thallous iodide. In reality this probably amounts to cleavage by chlorine, the iodine acting as a carrier, since iodine added to a boiling aqueous solution of diethylthallium bromide had practically no action.

Two further reactions by which \( R_3\text{TLX} \) compounds could be synthesized have never reached any great preparative importance. They may be illustrated by the equations:

\[
2(C_4H_9)_2\text{Bi} + \text{TlCl}_3 \rightarrow 2(C_4H_9)_2\text{BiCl} + (C_4H_9)_2\text{TlCl} \quad (5)
\]
\[
2(C_4H_9)_2\text{Hg} + \text{TlCl}_3 \rightarrow 2C_4H_9\text{HgCl} + (C_4H_9)_2\text{TlCl} \quad (6)
\]

Synthetic possibilities from organomercury compounds should be more completely investigated, as a variety of organomercurials with interesting substituents is available.

Triphenylstibine and thallium trichloride, however, were found to react quantitatively and immediately in the cold in accordance with the equation:

\[
(C_6H_5)_3\text{Sb} + \text{TlCl}_3 \rightarrow (C_6H_5)_3\text{SbCl}_3 + \text{TlCl}
\]

Thallium trichloride here acts as a chlorinating agent and is itself reduced to thallous chloride. There are other examples of this chlorinating action and reduction to thallous chloride.
in the chemistry of thallium.

In the reaction between triphenylarsine and thallium trichloride, a precipitate of yellow scales was obtained after some time, but the product was not further identified.

Further similar reactions were investigated by Goddard and Goddard.\textsuperscript{50} They may be represented by the equations:

\begin{equation}
(C_6H_5)_3Sn + TlCl_3 \rightarrow (C_6H_5)_2TlCl + (C_6H_5)_2SnCl_2
\end{equation}

\begin{equation}
(C_6H_5)_4Pb + TlCl_3 \rightarrow (C_6H_5)_3TlCl + (C_6H_5)_4PbCl_2
\end{equation}

Tetraphenyltin and tetraethyllead also were found to give the corresponding reactions.

Goddard and Goddard\textsuperscript{51} also studied the cleavage of some unsymmetrical organolead compounds by thallium trichloride. Triethylmethyllead gave triethyllead chloride, thallous chloride and methyl chloride; diethyldiphenyllead gave diethyllead dichloride and diphenylthallium chloride; and diphenyldi-\(\alpha\)-naphthyllead gave diphenyllead dichloride and di-\(\alpha\)-naphthylthallium chloride. These results agree with the general order of cleavage of groups from organolead compounds by halogen. The general equation is:

\begin{equation}
R'_3PbR'' + TlCl_3 \rightarrow R'_3PbCl_2 + R''_2TlCl
\end{equation}

Triphenylphosphine was found to react with thallium trichloride after the manner of triphenylstibine: thallous chloride and triphenylphosphine dichloride were produced, the latter being unstable and breaking down to triphenylphosphine and chlorine.

In another publication Goddard\textsuperscript{49} recorded the preparation
of the series of the diphenylthallium salts of the normal fatty acids up to the octoate. As in the corresponding series of diethylthallium salts, the melting point was observed to fall as the length of the acid chain increased. The solubility in organic solvents, however, decreased. The diphenylthallium salts also were reported to crystallize with a second molecule of fatty acid, which was not removed by recrystallization from some solvents. This is a rather unexpected property, the known great power of the thallium atom for complex formation notwithstanding.

A very important contribution to the knowledge of organothallium compounds of the type $R\text{,}Tlx$ was made by Krause and v. Grosse,\textsuperscript{75} who prepared the first dialkyl- and diarylthallium fluorides. Chlorides, bromides, and iodides in both series were known, and their general properties, especially solubility, have been discussed above. Silver fluoride, in great contrast to the other silver halides, was known to be readily soluble in water; thallous fluoride was known to occupy a similar position with respect to the other thallous halides. It is not altogether surprising, therefore, that dialkylthallium fluorides were found to be extremely soluble in water. Dimethyl- and diethylthallium fluorides even crystallize from water as the dodecahydrate. Even diphenylthallium fluoride was found to be much more soluble in water than the other diphenylthallium halides, although understandably less soluble than the dialkylthallium fluorides. All the organothallium fluorides
were reported as insoluble in ether and benzene. A polar solvent and the possibility of dissociation seem necessary for these fluorides to go into solution.

These compounds could be readily prepared by the general double decomposition reaction between an organothallium halide and a silver salt previously mentioned. In this case silver fluoride was naturally used. The fluorides were found to be markedly more volatile than the other dialkylthallium halides, which was apparent even by their strong odor at room temperature. Dimethyl- and diethylthallium fluorides could be sublimed without decomposition.

A one per cent solution of nitrate, nitrite, chlorate, carbonate, oxalate, chromate, chloride, bromide, or iodide ion gave a precipitate with a diphenylthallium fluoride solution. A five per cent solution of sulfate, phosphate, perchlorate, or acetate ion failed to do so. The insolubility of the nitrate is very striking: a precipitate could even be obtained from a solution diluted 1:10,000 in two minutes. Krause suggested the possibility of finding diarylthallium compounds whose nitrate would be even more insoluble, so that the corresponding fluoride could be used as a reagent for the qualitative detection and quantitative determination of the nitrate ion.

Later the dialkylthallium fluoride series was extended to include di-n-butylthallium fluoride and diisoamylthallium fluoride. Also, other halides were prepared of diisopropylthallium, di-sec.-butylthallium, and dicyclohexylthallium.
The organothallium compounds with branched chains were found to be less stable than those with normal radicals. No tertiary organothallium compound of the type $R_3\text{TLX}$ has ever been reported.

Di-$\alpha$-thienylthallium bromide, the only heterocyclic thallium compound of the type now under discussion, whose analysis has been reported, was prepared by Krause and Renwanz by the usual Grignard reaction. The compound, as might be expected, was found to be insoluble in water and the usual organic solvents, but soluble in pyridine. A dilute solution in alcohol gave a precipitate with the following ions: nitrate, nitrite, chloride, carbonate, and oxalate. There was no precipitate with the following ions: phosphate, arsenate, iodide, chromate, sulfate, perchlorate, and acetate. The presence of the iodide ion in this latter group is somewhat disconcerting, and might well be an error. The other acids are all found in their expected group.

A different type of dialkylthallium salt was prepared by Menzies, who obtained a dialkylthallium alkoxide by the action of thallous ethoxide on a dialkylthallium halide, in essential accordance with the equation:

$$R_3\text{TLX} + \text{TLOR}' \longrightarrow R_3\text{TLOR}' + \text{TLX}$$

The first compound prepared was dimethylthallium ethoxide, which Menzies found to be a yellow oil boiling at 110-120° under 15 mm. pressure. The freshly distilled liquid is, however, water-white and very mobile, but soon turns yellow and becomes
cloudy on exposure to air. A glass rod dipped in the liquid fumes in air. This is due to the rapid hydrolysis, to which the compound is very sensitive. Later, Menzies and Walker synthesized dimethylthallium methoxide, which they found to be a crystalline solid, melting at 177-181°. On attempted distillation in vacuum, it decomposed at about 120-130° with some violence. The differences between dimethylthallium ethoxide and methoxide thus resemble those between thallous ethoxide and methoxide, and between aluminum ethoxide and methoxide. All three pairs constitute examples of the familiar high melting points of many methyl as contrasted with the corresponding ethyl compounds.

All these dialkylthallium alkoxides are so completely hydrolyzed that their thallium content may readily be determined simply by dissolving the compound in water and titrating the thus liberated dialkylthallium hydroxide with standard acid.

Diethylthallium ethoxide has also been studied to determine the effect of altering the alkyl groups attached to the thallium atom. This compound was found to boil at 101-102° under 0.1 mm. pressure, the pale yellow liquid solidifying on cooling to a nearly colorless crystalline mass which melted at 43-45°.

Volatility may be readily obtained in this class of compounds, but resistance to hydrolysis is a more difficult matter. This is primarily due to the weakly acidic nature of the alkoxy group. Hence to attain greater stability towards
hydrolysis, it is necessary to employ groups whose acid nature is more pronounced. Two good possibilities are mercaptans and fluorinated alcohols. For example, dimethylthallium \( \text{Me}_2 \text{SnH} \) should be a distillable liquid with fair resistance to hydrolysis.

Also, these compounds hitherto have always been made through a thallous alkoxide, which is convenient, but expensive. It should be possible to develop a method using the ordinary sodium salt.

Another closely related type of compound about which very little is known should be mentioned here, although it is not an organometallic type. Criegee, Kraft and Rank\(^{21}\) mention compounds of the type ethoxythallium diacetate, stating merely that they are crystalline solids. Many interesting variations in both the alkoxide group and in the acid could be imagined which might increase the volatility of such compounds.

The reaction between an arylboric acid and thallium trichloride or tribromide, which was first investigated by Challenger and Parker,\(^{13}\) has been discussed in great detail in the section on \( \text{R}_2 \text{TLX}_3 \) compounds, primarily because when first discovered the main direction given to the early investigations was toward \( \text{R}_2 \text{TLX}_3 \) compounds. It should not be overlooked, however, that \( \text{R}_2 \text{TLX}_3 \) compounds can also be made by this reaction, either directly, in essential accordance with the equation:

\[
2\text{ArB(OH)}_2 + \text{TLX}_3 + 2\text{H}_2\text{O} \rightarrow (\text{Ar})_2\text{TLX} + 2\text{HX} + 2\text{H}_3\text{BO}_3 \quad (10)
\]
or by first using the arylboric acid synthesis to prepare an
RT\textsubscript{1}X\textsubscript{2} compound and then decomposing this by heating in water:

\[ 2\text{ArTlX} \rightarrow \text{Ar}_{2}\text{TlX} + \text{TlX}, \]  

(11)

Another variant\textsuperscript{15} is represented in the following equation:

\[ \text{ArTlX}, + \text{Ar}^{'}\text{B(OH)}_{2} + \text{H}_{2}\text{O} \rightarrow \text{Ar}^{'}\text{ArTlX} + \text{H}_{2}\text{BO}_{2} + \text{HX} \]  

(12)

Challenger and Richards actually found it possible to obtain phenyl-\textit{p}-tolylthallium chloride either by the reaction between phenylboric acid and \textit{p}-tolylthallium dichloride, or by the reaction between \textit{p}-tolyboric acid and phenylthallium dichloride. This is the only RR'TlX compound recorded in the literature. They found that an RR'TlX compound could not be made by the Grignard reaction as suggested by the equation:

\[ \text{RTlX}, + \text{R}^{'}\text{MgX} \rightarrow \text{RR'TlX} + \text{MgX}, \]  

A full discussion of this negative reaction may be found in the section on RTlX\textsubscript{2} compounds.

By far the most extensive use of the arylboric acid synthesis in the preparation of RR'TlX compounds was made by Mel'nikov and coworkers,\textsuperscript{91, 92, 118} who reported a long series of compounds which will be found in Table IV at the end of this section. By this means they found it possible to prepare compounds which could not be made directly by the customary Grignard reaction, for example, di-\textit{m}-nitrophenylthallium chloride. In general, however, these three papers represent routine production work, with little in the way of essentially new chemistry involved. One interesting bit of information reported by these workers is the poor yields when some heavily substituted arylboric acids are employed in this synthesis.
This seems to be a case of steric hindrance in organothallium chemistry.

Whereas Meyer and Bertheim\textsuperscript{112} failed in their attempt to alkylation of thallous chloride by means of the Grignard reagent, Menzies and Cope\textsuperscript{99} showed that if only two equivalents of the Grignard reagent were taken and the refluxing omitted, alkylation with oxidation to the trivalent state found in $RJT_{1}X$ could be shown to take place. The great drawback to this method is that necessarily two-thirds of the total thallium must appear as metal, in accordance with the equation:

$$2RMgCl + 3TlCl \longrightarrow RJT_{1}Cl + 2MgCl_{2} + 2Tl \quad (13)$$

Even better yields were obtained when thallous ethoxide was substituted for thallous chloride. Still better yields were obtained by Birch\textsuperscript{7} when he alkylated thallous chloride with ethyllithium, instead of with the Grignard reagent, as shown in the reaction:

$$2RLi + 3TlCl \longrightarrow RJT_{1}Cl + 2LiCl + 2Tl \quad (14)$$

This reaction also was used by Mel'nikov and Gracheva\textsuperscript{89} to prepare several simple $RJT_{1}X$ compounds. A more extended discussion of this reaction can be found in the section on R\textsubscript{T}1 compounds, through which intermediate the reaction is assumed to proceed. An interesting application is the preparation of di-$p$-dimethylaminophenylthallium chloride from $p$-dimethylaminophenyllithium and thallous chloride. If thallium trichloride is used, it acts as a chlorinating and oxidizing agent on the amine, a violet dye is produced, and no $RJT_{1}X$ compound.\textsuperscript{35}
This ability of thallium trichloride to act as a chlorinating and oxidizing agent has been known for some time. A brief consideration of a few examples is not out of place here because of the connection with the direct thallation of an organic molecule, as that term is understood for the well-known reactions with derivatives of mercury and arsenic. Renz\textsuperscript{133} prepared many complex compounds of thallium trichloride with derivatives of pyridine and quinoline, and with many alkaloids. These are stable, crystalline compounds, usually possessing a sharp melting point. $\beta$-Naphthylamine hydrochloride readily forms such a compound. But, in sharp contrast, $\alpha$-naphthylamine formed no such crystalline compound with thallium trichloride. When alcoholic solutions of $\alpha$-naphthylamine and thallium trichloride were mixed, the solution turned deep violet, and after standing several days deposited a violet precipitate. Aniline and its homologs also underwent radical change. Renz\textsuperscript{134} also discovered that an alcoholic solution of dimethylaniline and thallium trichloride immediately turned green, and after standing a week deposited dark violet crystals, together with much thallous chloride. The organic dye could be recrystallized, and was shown to have the same analytical composition as crystal violet. Dimethyl-\textsuperscript{2}-toluidine and methyldiphenylamine gave similar dyes.

Marino\textsuperscript{87} found that $\alpha$-naphthol underwent a similar reaction with thallium trichloride, and that if a very small quantity of dimethyl-\textsuperscript{p}-phenylenediamine then be added, the
characteristic blue color of the indophenols was produced. The reaction was much more sensitive than the detection of thallous ion with potassium iodide, and allowed thallic ion to be demonstrated even in the presence of thallous ion. The sensitivity was found to be about one part in 30,000.

Mel'nikov and Gracheva investigated the very similar reactions of thallium trichloride and thallium tribromide with a variety of phenols. \( \alpha \) - and \( \beta \)-Naphthols were transformed to the corresponding naphthoxides, for which they gave the equation:

\[
3C_6H_5OH + TlX_3 \rightarrow (C_6H_5O)_3Tl + 3HX
\]

It would be interesting to confirm this unusual reaction. Hydroquinone they found was oxidized to quinone; this is the expected reaction. Other more complex phenols formed coordination compounds. This was the case with pyrocatechol, pyrogallol, and phloroglucinol. The latter complex was mentioned as "very toxic", but details were not given.

Thus it is seen that the problem of direct thallation is made difficult by several factors not encountered in the chemistry of mercury and arsenic: (1) \( \text{TlX}_3 \) can act as a chlorinating agent; (2) it can act as an oxidizing agent, itself being reduced; and (3) it can form complex compounds. The tendency for anhydrous thallium trichloride to lose chlorine even at 25° is especially vexatious. However, the direct thallation of an organic molecule has been accomplished by selecting a compound which is not readily oxidized,
dibenzoconuran, and by making use of thallium trichloride
tetrahydrate, which is stable at 100°. Reaction takes place
to give an \( \text{R}_2\text{TlX} \) compound, di-4-dibenzofuranylthallium chloride.

Mercury, the close neighbor of thallium in the periodic
table, readily undergoes another reaction which has not as
yet been successfully carried out with thallium: the decompo-
sition of the double salt formed between an aryldiazonium
halide and the heavy metal salt. Thallium trichloride and
thallium tribromide very readily form such complex salts,
which have sharp decomposition points, but no organothallium
compound was reported formed by the decomposition.\(^{71,116,117,119}\)

In a similar experiment by Waters,\(^{150}\) an aryldiazonium chlo-
ride was warmed under acetone containing chalk and a metal.
Arsenic and gold were attacked, but thallium was not. It is
probable, however, that means will be found to so conduct the
decomposition that \( \text{R}_2\text{TlX} \) compounds may be obtained.

It would also seem likely from considerations of the
great stability, resistance to acid cleavage, and high melting
point of \( \text{R}_2\text{TlX} \) compounds, that new and important organothallium
compounds might be made by direct nuclear substitution.
Challenger and Rothstein\(^{16}\) studied the nitration of diphenyl-
thallium nitrate and phenylthallium hydroxynitrate, but
immediately cleaved their nitration products by bromine and
determined the amount of \( m \)-bromonitrobenzene. Mel'nikov and
Rokitskaya\(^{91}\) attempted to nitrate diphenylthallium chloride,
but obtained only nitrobenzene and phenylthallium dinitrate.
However, it has recently been found possible to carry out successfully both the nitration and sulfonation of diphenyl-thallium bromide. Monosubstitution in the m-position takes place in both nuclei:

\[
2(C_6H_5)_2\text{TLBr} + 5\text{H}_2\text{SO}_4 \rightarrow (3-\text{HOSO}_2\text{C}_6\text{H}_5)_2\text{TL} + 4\text{H}_2\text{O} + 2\text{HBr}
\]  

(15)
Physical Properties

Some of the more common physical properties of $R_2TlX$ compounds have already been mentioned in the above discussion of methods of synthesis. In general these compounds are colorless, crystalline, high-melting solids. They are salts, formed from the base $R_2TlOH$ and an acid, and thus have most of the customary properties of salts. The dialkylthallium bases resemble thallous hydroxide, being soluble in water and alcohol; the diarylthallium bases are much less soluble. $R_2TlOH$ compounds are strong enough bases to rapidly take up carbon dioxide from the air and form carbonates. When neutralized by inorganic acids, these bases form salts which in general do not melt, but rather decompose more or less rapidly at 200-300°. The compounds with secondary alkyl groups are appreciably less stable, and it is to be expected that the (still unknown) compounds with tertiary alkyl groups will scarcely be capable of existence above 100°. The solubility of the salts in organic solvents, such as alcohol and pyridine, is slight in the case of the lower members, but increases greatly with increasing length of the alkyl groups. It also increases greatly when the "X group" is an organic acid. The halide salts are quite insoluble in water, with the notable exception of the fluorides. Salts of oxygen-containing acids are in general fairly soluble in water, with the surprising exception of the nitrates. $R_2TlX$ compounds that are salts of
organic acids generally have a good melting point.

The first extensive physico-chemical measurements on R₄TlX compounds were made by Shukoff in 1905, who studied the conductivity of diethylthallium chloride and found it to be a strong electrolyte, but nevertheless appreciably hydrolyzed at high dilutions. Complete details and an extended discussion of their significance may be found in the section on R₄Tl compounds (q.v.).

Hein and Meininger twenty years later measured the basic strength of several dialkyl- and diarylthallium hydroxides, both in aqueous and in methyl alcoholic solution, and compared their strength as bases both with thallous hydroxide and with other organometallic bases. They found that organothallium hydroxides must be numbered among the strong bases, although they were not found to be so strong as thallous hydroxide itself, which resembles in basic strength the univalent alkali metals. In the following list the compounds are arranged from top to bottom in decreasing order of basic strength:

1. Thallous hydroxide
2. Dimethylthallium hydroxide
3. Diethylthallium hydroxide
4. Diphenylthallium hydroxide
5. Ammonium hydroxide

The increase in length of the alkyl chain is seen to make diethylthallium hydroxide a slightly weaker base than dimethylthallium hydroxide. This may in part be due to the
lessening of mobility of the ion under migration as the alkyl chain becomes longer. As would be expected, the introduction of the negative phenyl group causes a further decrease in the basic strength, but all these compounds are still much stronger bases than ammonium hydroxide.

The comparison by Hein and Meininger of the strength of several organometallic bases of different metals is even more interesting. The examples in the following list are arranged from top to bottom in the order of their increasing basic strength:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molecular conductivity of 0.0156 molar solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Triethyltin hydroxide</td>
<td>0.45</td>
</tr>
<tr>
<td>2. Ethylmercury hydroxide</td>
<td>1.20</td>
</tr>
<tr>
<td>3. Triethyllead hydroxide</td>
<td>8.10</td>
</tr>
<tr>
<td>4. Diethylthallium hydroxide</td>
<td>140.00</td>
</tr>
<tr>
<td>5. Triphenylchromium hydroxide</td>
<td>212.0</td>
</tr>
</tbody>
</table>

Tin is seen to be strongly non-polar, triethyltin hydroxide approaching in character triethyl carbinol. Thus, it would seem reasonable to suppose that even very complicated tin compounds might be distilled in a high vacuum. And at the other extreme of the list, if triethylchromium hydroxide had been available for comparison, it naturally would have been found an even stronger base than triphenylchromium hydroxide.

Berry and Lowry measured the conductivity of dipropylthallium and dibutylthallium hydroxides, and found them to be
slightly weaker bases than dimethyl- and diethylthallium hydroxides. This is in conformity with the generalization on the effect of increasing the length of the alkyl groups. Some further details of a theoretical nature discussed in this paper by Berry and Lowry are considered in the section on $R_x$Tl compounds.

When Menzies\textsuperscript{94} examined the action of thallous hydroxide and dimethylthallium hydroxide on tartaric acid he found that thallous hydroxide neutralized four hydrogen atoms, but dimethylthallium hydroxide only three. In the first instance, there can be no great doubt about the structure, since there are only two carboxyl groups and two hydroxyl groups. In the second instance it would seem reasonable to suppose that both the carboxyl groups are neutralized by dimethylthallium hydroxide, and one of the hydroxyl groups, steric considerations not allowing the possibility of another dimethylthallium group, but this has never been demonstrated experimentally.

The striking insolubility of $R_x$TlX compounds in general, and more especially of the chlorides, bromides, and iodides, led Krause and Dittmar\textsuperscript{74} to examine the reason for this anomalous behavior. That $R_x$Tl compounds were then still unknown seemed to them to be a closely related phenomenon exhibited by this unusual element. It seemed likely to them that secondary valence forces, such as Krause had already observed in boron and aluminum, might well be found in thallium to explain at least a part of the obvious peculiarities.
It was apparent to all that molecular weight determinations were needed on $R_nTlX$ compounds, but the general insolubility of this class of compounds made the matter difficult. Krause and Dittmar solved the problem by selecting the dialkylthallium fluorides for examination, and when the known dimethyl- and diethylthallium fluorides proved to be too insoluble in benzene, they increased the solubility by synthesizing diisobutyl-, diisooamyl-, and di-$n$-hexylthallium fluorides. These compounds were all found to be strongly associated, the molecular weight varying from two to five times the simple calculated value. They carefully proved that their method was valid by examining the molecular weight of triisooamyltin fluoride, which also has a somewhat limited solubility. It was shown to be monomolecular, as were triphenyltin chloride and triphenyllead chloride.

The more exact nature of this polymolecular structure of $R_nTlX$ compounds was elucidated by Powell and Crowfoot, who found that the observed crystallographic and x-ray properties could best be explained by assuming a layer-chain (Schichtkette) structure:

$$\begin{align*}
\text{R} & \quad \text{R} & \quad \text{R} & \quad \text{R} \\
\text{R} & \quad \text{R} & \quad \text{R} & \quad \text{R}
\end{align*}$$

In this structure the chains do not rotate, nor are they zig-zag. The two alkyl groups on a single thallium atom are
at an angle of 180°. Thallium and halogen atoms alternate along an axis, and the coordinate valence is in this direction. Dimethylthallium halides crystallize in the tetragonal system, diethyl- and dipropylthallium halides are orthorhombic and pseudo-tetragonal. All exhibit the face-centered cubic structure found in sodium chloride. The crystals are double-refracting, with the following sign:

<table>
<thead>
<tr>
<th></th>
<th>Me₂Tl⁻</th>
<th>Et₂Tl⁻</th>
<th>n-Pr₂Tl⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Br</td>
<td>-</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Cl</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

In another article, Powell and Crowfoot examined more fully the crystallographic properties of dimethylthallium chloride, bromide, and iodide. The length of the thallium-halogen bond was found for the chloride to be 4.29 Å; for the bromide, 4.47 Å; and for the iodide, 4.78 Å. The length of the thallium-carbon bond was found for the chloride to be 14.02 Å; for the bromide, 13.78 Å; and for the iodide, 13.48 Å. Thus it is seen that as the length of the thallium-halogen bond must be increased as the molecular weight of the halogen atom is increased, the carbon atom is pulled in to the thallium atom somewhat.

Powell and Crowfoot then concluded that if the halogen ion radius were still further reduced by the substitution of fluorine, the thallium-halogen dimension would be reduced to about 3.5 Å. But two carbon atoms on adjacent dimethylthallium
ions could not approach so close together, hence dimethylthallium fluoride must have a different structure. They promised "an account will be given later of investigations which have confirmed this supposition." It is to be regretted that long search has not turned up this promised article, for it would probably afford a clue to the solubility of dialkylthallium fluorides in water, to their ability to coordinate with water to form a dodecahydrate, and to their much greater volatility as compared with other dialkylthallium halides.

A small observation by Menzies on the crystal structure of dimethylthallium iodide might be mentioned in conclusion, although it is more of the nature of a laboratory curiosity than a scientifically important observation. He found that a solution of dimethylthallium iodide on cooling formed a crystal pattern on the surface of the liquid, rather than through its interior, and described this phenomenon as a "two-dimensional space lattice."
<table>
<thead>
<tr>
<th>Compound</th>
<th>M. p., °C.</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Di-p-acetoxyphenylthallium bromide</td>
<td>---</td>
<td>91</td>
</tr>
<tr>
<td>Dibiphenylylthallium bromide</td>
<td>not at 305</td>
<td>91</td>
</tr>
<tr>
<td>Dibiphenylylthallium chloride</td>
<td>245</td>
<td>91</td>
</tr>
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TABLE IV (Continued)

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<th>Compound</th>
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<td>Di-(2,4,5-dimethylbromophenyl)thallium bromide</td>
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<td>Diethylthallium (p)-benzoquinone oxime, quinhydrone</td>
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<td>Diethylthallium (m)-bromobenzoate</td>
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TABLE IV (Continued)

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<td>Diethylthallium 4,6-dinitro-2-aminophenoxide</td>
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<tr>
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<tr>
<td>Diethylthallium 2,4-dinitronaphthoxide-7-sulfonate</td>
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<tr>
<td>Diethylthallium 2,4-dinitrophenoxide</td>
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<td>Diethylthallium 2,2'-dinitro-o-tolyloxide</td>
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<td>Diethylthallium ethoxide</td>
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<td>Diethylthallium ferricyanide (?)</td>
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<tr>
<td>Diethylthallium ferrocyanide (?)</td>
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<td>Diethylthallium fluoride</td>
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<td>Diethylthallium 2,4-dinitronaphthoxide-7-sulfonate</td>
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<td>Diethylthallium 2,4-dinitrophenoxide</td>
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<td>Diethylthallium 2,2'-dinitro-o-tolyloxide</td>
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### TABLE IV (Continued)

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<th>Compounds</th>
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<td>Diethylthallium $p$-nitrosophenoxide (?)</td>
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<td>Diphenylthallium p-octoate</td>
<td>195</td>
</tr>
<tr>
<td>Diphenylthallium oleate (?)</td>
<td>---</td>
</tr>
<tr>
<td>Diphenylthallium oxalate</td>
<td>---</td>
</tr>
<tr>
<td>Diphenylthallium oxide</td>
<td>not at 300</td>
</tr>
<tr>
<td>Diphenylthallium (acid) propionate</td>
<td>164</td>
</tr>
<tr>
<td>Substance</td>
<td>Formula</td>
</tr>
<tr>
<td>--------------------------------------------------------------------------</td>
<td>----------------------------------------------</td>
</tr>
<tr>
<td>Diphenylthallium pyrophosphate</td>
<td>---</td>
</tr>
<tr>
<td>Diphenylthallium saccharide</td>
<td>320</td>
</tr>
<tr>
<td>Diphenylthallium sulfanilate</td>
<td>345</td>
</tr>
<tr>
<td>Diphenylthallium ?,?,?-trinitro-1-naphthoxide</td>
<td>232</td>
</tr>
<tr>
<td>Diphenylthallium ?,?,?-trinitro-m-tolypoxide</td>
<td>231</td>
</tr>
<tr>
<td>Diphenylthallium (acid) valerate</td>
<td>176</td>
</tr>
<tr>
<td>Di-n-propylthallium bromide</td>
<td>---</td>
</tr>
<tr>
<td>Di-n-propylthallium chloroform</td>
<td>dec. 202</td>
</tr>
<tr>
<td>Di-n-propylthallium ethoxide (?)</td>
<td>---</td>
</tr>
<tr>
<td>Di-n-propylthallium hydroxide</td>
<td>---</td>
</tr>
<tr>
<td>Di-n-propylthallium iodide</td>
<td>---</td>
</tr>
<tr>
<td>Di-n-propylthallium nitrate</td>
<td>---</td>
</tr>
<tr>
<td>Di-n-propylthallium propionate (?)</td>
<td>---</td>
</tr>
<tr>
<td>Di-x-pyridylthallium chloride</td>
<td>---</td>
</tr>
<tr>
<td>Di-x-pyridylthallium lactate</td>
<td>205</td>
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<tr>
<td>Di-sec.-butylthallium chloride</td>
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</tr>
<tr>
<td>Di-sec.-butylthallium nitrate</td>
<td>---</td>
</tr>
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<td>Di-2-(4-sulfotoluene)thallium sulfate</td>
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<tr>
<td>Di-x-thiénylthallium bromide</td>
<td>dec. 270</td>
</tr>
<tr>
<td>Di-x-thiénylthallium chloride</td>
<td>---</td>
</tr>
<tr>
<td>Di-o-tolylthallium bromide</td>
<td>---</td>
</tr>
<tr>
<td>Di-m-tolylthallium bromide</td>
<td>242</td>
</tr>
<tr>
<td>Compound</td>
<td>Temperature</td>
</tr>
<tr>
<td>--------------------------------------</td>
<td>-------------</td>
</tr>
<tr>
<td>Di-p-tolylthallium bromide</td>
<td>---</td>
</tr>
<tr>
<td>Di-o-tolylthallium chloride</td>
<td>not at 290</td>
</tr>
<tr>
<td>Di-m-tolylthallium chloride</td>
<td>235</td>
</tr>
<tr>
<td>Di-p-tolylthallium chloride</td>
<td>not at 296</td>
</tr>
<tr>
<td>Di-p-tolylthallium fluoride</td>
<td>---</td>
</tr>
<tr>
<td>Di-p-tolylthallium nitrate</td>
<td>---</td>
</tr>
<tr>
<td>Phenyl-p-tolylthallium chloride</td>
<td>---</td>
</tr>
</tbody>
</table>
Physiological Properties of Organothallium Compounds

A great deal has been written about the physiological, toxicological and therapeutic properties of inorganic thallium compounds, but very little is known about the corresponding properties of organothallium compounds. Only brief mention can be made here of inorganic thallium compounds. The wide-spread use of thallous salts in rodent poisons, and the ready availability of these preparations and of thallous salts in general are the reason why the forensic medicine of thallium is so well developed. Cases of industrial thallium poisoning, resembling industrial lead poisoning, are not unknown. One of the most marked physiological properties of thallium—whether thallous, thallic or organothallium compound—is its depilatory action. Pharmaceutical preparations containing thallium and intended for use as depilatants at one time were actually widely available in the drug market. Thallous salts, for example sulfate or acetate, are very poisonous. In the strength of their toxicity they exceed lead and approach mercury in their physiological action. An oral administration of one-half gram of thallous acetate rapidly causes death in a rabbit. Much smaller doses (forty to sixty milligrams) can be fatal when injected subcutaneously. The therapeutic oral dose of a rabbit (one-tenth gram) is sufficient to cause the characteristic depilatory action. In serious cases of thallium poisoning the symptoms become
much more diverse: atrophy of the peripheral nerves, including the optic nerve (which leads to blindness), stunting of the growth and of the sexual development, rachitic disturbances of the skeletal system, neuralgia, and not infrequently psychoses are common. When administered in larger doses, irritation of the mucous membranes, vomiting, pains in the body, increased reflex sensibility, tonic cramps, motor and sensory paralysis of the legs, bleeding from the lungs and cardiac hemorrhage lead to death. The development of a tolerance for thallium (as is possible, for instance, with arsenic) does not take place. Thallium belongs to the cumulative poisons. The review article by Steidle on the physiology and toxicology of thallium is representative of the many to be found in the literature.

There is no specific therapy for thallium poisoning. Brumm states that sodium sulfite and vitamin B<sub>1</sub> have been found to be of some aid. Buschke and Konheim reported that dihydrotachysterol had been found to remove some of the growth-disturbances caused by thallium poisoning in rats, but it did not reduce the strong depilatory action of the thallium.

A preliminary testing of organothallium compounds was reported by Avetisyan, who administered to Angora rabbits diisoamylthallium bromide, diethylthallium bromide, and dimethylthallium bromide, whose depilatory and toxic action he found to decrease in that order. This work was all in-
cluded in a later publication which, as far as can be ascertained, contains all the information that has ever been published on the pharmacology of organothallium compounds. In this work it appears that Il'in and coworkers studied around fifty thallium compounds, both thallous salts and organothallium compounds, although data for all the compounds tested, or even their names, were not presented in the article.

Wool-bearing and fur-bearing animals have an important position in the animal husbandry of Russia, and the extent and completeness of the work under the direction of Il'in, director of the Institute of Medicine of Moscow, attest the importance and significance attached to the search for a pharmacon which will produce a rapid and synchronous wool-shedding, without harm to the animal. Very large resources were evidently available, for the work included large numbers of animals, including Angora rabbits, fine-wooled sheep, sheep with mixed wool, goats, reindeer, and others. Unfortunately, all thallium compounds used up to this time have had certain toxic effects, and research work on thallium detoxication was carried out in the following principal directions: (1) the determination of the least toxic method of introducing thallium into the organism; (2) the determination of external conditions (keeping, feeding, etc.) optimal for the least toxic and highest depilatory effect of the drug upon the experimental animals; (3) the introduction of different
substances into the thallium-treated animals in order to prevent or reduce the symptoms of thallium poisoning (sodium thiosulfate, etc.); and (4) the change of the chemical structure of both univalent and trivalent thallium compounds.

It was conclusively shown that the depilatory and toxic effects of thallium could be completely dissociated by the use of certain trivalent organothallium compounds: it was possible to obtain a distinct moult without toxic after-effects. The Angora wool rabbit was found to be the most suitable test animal, for its long fur responded readily to thallium depilation, and a single dose of compound would permit the wool to be completely removed by hand as a mass of more or less interwoven hairs, leaving the animal entirely denuded.

It was established that all thallous salts, irrespective of the acid radical, function in exactly the same manner, and have the same moult dose and toxic dose when the amount employed is calculated in terms of actual thallium content. Such thallous salts as the aminoacetate, arsanilate, anthranilate, m-aminobenzoate, p-aminobenzoate, albuminate, acetate, etc. all had the same moult dose of from eight to ten milligrams of actual thallium per kilo of body weight in the Angora rabbit; and the minimum lethal dose was also the same in terms of actual thallium content, being sixteen to eighteen milligrams per kilo of body weight. In every case the thallium functioned as the thallous ion, which was shown to be converted
to thallous chloride in the body of the animal. The toxicity of univalent thallium compounds depends solely on the absolute quantity of thallium contained in doses of these compounds, and does not depend on the structure of the compound.

In sharp contrast, the effects produced by trivalent thallium compounds were found to be extremely varied, and the greatest variations were encountered in the trivalent organothallium compounds. The depilatory dose and toxic dose are summarized for the compounds reported in Table V, where in every case the figure refers to the number of milligrams of actual thallium content per kilo of body weight in the Angora rabbit.


<table>
<thead>
<tr>
<th>Compound</th>
<th>Depilatory* dose</th>
<th>Lethal* dose</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thallium tribromide-phloroglucinol complex</td>
<td>above lethal</td>
<td>less than 10</td>
</tr>
<tr>
<td>Thallium tribromide-pyridine complex</td>
<td>above lethal</td>
<td>over 20</td>
</tr>
<tr>
<td>Ethylthallium dibromide</td>
<td>15-20</td>
<td>40</td>
</tr>
<tr>
<td>Di-β-bromophenylthallium bromide</td>
<td>30</td>
<td>40</td>
</tr>
<tr>
<td>Di-α-naphthylthallium bromide</td>
<td>15-30</td>
<td>15-30</td>
</tr>
<tr>
<td>Dimethylthallium bromide</td>
<td>400</td>
<td>600</td>
</tr>
<tr>
<td>Diethylthallium phenylacetate</td>
<td>60</td>
<td>90</td>
</tr>
<tr>
<td>Diethylthallium chloride</td>
<td>40</td>
<td>60</td>
</tr>
<tr>
<td>Diethylthallium bromide</td>
<td>40</td>
<td>60</td>
</tr>
<tr>
<td>Di-p-tolylthallium bromide</td>
<td>20</td>
<td>over 30</td>
</tr>
<tr>
<td>Thallium acetate</td>
<td>10-15</td>
<td>20</td>
</tr>
<tr>
<td>Phenylthallium dibromide</td>
<td>15</td>
<td>30</td>
</tr>
<tr>
<td>Di-m-tolylthallium bromide</td>
<td>15</td>
<td>30</td>
</tr>
<tr>
<td>Diphenylthallium bromide</td>
<td>less than 30</td>
<td>60</td>
</tr>
<tr>
<td>Di-p-carboxyphenylthallium bromide</td>
<td>15-20</td>
<td>30-60</td>
</tr>
<tr>
<td>Diisooctylthallium bromide</td>
<td>above lethal</td>
<td>less than 30</td>
</tr>
<tr>
<td>Diethylthallium isovalerate</td>
<td>above lethal</td>
<td>40</td>
</tr>
</tbody>
</table>

*Milligrams of actual thallium content per kilo of body weight in the Angora rabbit*
The number and variety of compounds in Table V permit some interesting generalizations to be made as to the effect of structure on depilation and toxicity. The complexes with thallium tribromide are seen to be extremely toxic, and the rabbits died before any depilatory action was observed. Thus it is concluded that the depilatory dose lies above the lethal dose in the case of these compounds.

Dimethylthallium bromide is seen to have a strikingly low toxicity. A similar low toxicity has been observed with trimethyllead derivatives. However, the amount necessary for depilation also had to be increased, hence the therapeutic index—the quotient obtained by dividing the lethal dose by the depilatory dose—was only 1.5. It is naturally desired to have as wide a margin as possible between the depilatory dose and the lethal dose. Diethylthallium chloride and diethylthallium bromide were much more effective depilatants, but they were also more toxic, and the therapeutic index remained at 1.5. It is to be noted that apparently there is no choice between an organothallium bromide and an organothallium chloride. No mention was made of testing organothallium fluorides or iodides. When, however, the halide group was changed for the isovalerate group in diethylthallium isovalerate, there was a decrease in depilatory action and an increase in toxicity, hence this direction of investigation was abandoned. The unfavorable effect of lengthening the hydrocarbon chain can be
seen from the data on diisoamylthallium bromide, which is quite toxic and has no depilatory action.

The most satisfactory compound is seen to be diphenylthallium bromide, with a therapeutic index of two. Nothing essential was gained by substituting in the phenyl group, as can be seen by comparing the data for di-p-bromophenylthallium bromide, di-p-tolylthallium bromide, di-m-tolylthallium bromide, and di-p-carboxyphenylthallium bromide. And effectiveness was distinctly lost by going to a heavier radical, as can be seen from the data on di-α-naphthylthallium bromide. Also, the R₅TLX type is more desirable than the RTLX₅ type, as can be seen by comparing the data on diethylthallium bromide and ethylthallium dibromide.

From the data presented in Table V, Il'in stated two broad generalizations: (1) "certain structural groups in the molecule of thallium compounds increase preferentially, selectively, the toxic while other groups increase preferentially the depilatory effect of these compounds; and (2) the depilatory action is not a direct result of the toxic action of thallium."

This leaves the possibility of a further dissociation of these two effects in the future preparation of organothallium compounds. Thallium is actually used in several European countries as a depilatant in human therapy, especially in the treatment of certain mycotic diseases of the hairy part of the head, and Kahlbaum markets tablets containing thallium which are used in dermatological practice in the cure of
certain skin diseases in children. The synthesis of organothallium compounds promises the discovery of further variation in the properties of these compounds, so that it is likely that more extended application can be made to other ills, both human and animal.
Analytical Procedures

Qualitative Analysis

Probably the simplest and surest qualitative detection of the element thallium is by means of the strong and characteristic green color produced in the ordinary flame test. Potassium iodide is another excellent means of detection: when added to a solution of a thallous salt it gives the lemon-yellow precipitate of thallous iodide, whose color and structure the analyst soon learns to distinguish at a glance from the insoluble iodides of mercury, lead and silver, the only other elements whose insoluble halides are likely to be found with thallium. With the thallic ion potassium iodide gives a dark purple-black precipitate. If this is collected on a filter and dried at 110°, two atoms of iodine are driven off and yellow thallous iodide remains. The delicate qualitative test for thallic ions developed by Marino has been discussed in the section on $R_2\text{TLX}$ compounds. He found that when a solution containing thallic ions was treated with $\alpha$-naphthol and then with dimethyl-$p$-phenylenediamine a light blue color was produced. Behrens has developed micro-methods for the detection of thallium.
Although a good volumetric method has been worked out for the determination\textsuperscript{115} of thallium in organothallium compounds, we have in general found it more expedient to determine thallium gravimetrically as the iodide. A thallous salt, for example thallous p-toluenesulfonate, need not be treated with nitric acid or other agents to destroy the organic material, but instead is merely dissolved in hot water and the thallium is precipitated with slightly more than the calculated quantity of 10\% potassium iodide solution. In an organothallium compound the destruction of the organic material must first be completed before precipitation. If possible this should be done with nitric acid alone, the excess acid removed by gentle heating, the solution taken up in water before it quite reaches dryness, and after reduction with sodium arsenite precipitated with potassium iodide. Alkyl organothallium compounds can readily be brought into solution with nitric acid, but aryl compounds are more resistant. In the latter case, hydrogen peroxide has been found a very satisfactory oxidizing agent. The customary oxidation with hot sulfuric and nitric acids is to be avoided, because of the difficulty of removing the sulfuric acid, and an excess of sulfuric acid leads to low results, because of the solubility of thallous sulfate. After the complete destruction of the organic matter has been accomplished, the trivalent thallium must be reduced to the thallous state. We have found
sodium arsenite the most convenient reagent for this purpose. A drop of the solution can be tested from time to time with potassium iodide solution to determine when complete reduction has been reached. However, the experienced analyst soon learns to tell by the way the powdered sodium arsenite behaves when it strikes the solution whether reduction is complete or not. As long as trivalent thallium ion is present, a faint yellow color passes through the solution for two or three seconds as each small portion of sodium arsenite is added.

Most of the men who have done extensive work on organothallium compounds have published their method of analysis. Hartwig\(^59\) destroyed the organic material in his compounds with nitric acid in a sealed tube—"a very excellent method"—and weighed as thallous iodide. Meyer and Berthiem\(^112\) added a few improvements, and their method is substantially the one we have used, except they performed the reduction with an aqueous solution of sulfur dioxide, which we have found to be much less convenient than sodium arsenite. Further valuable details have been given by Meyer.\(^109\) We have also found suggestions by Goddard and Goddard,\(^51\) by Mach and Lepper,\(^85\) and by Proszt\(^127\) to be helpful to the organic chemist.
Summary

An attempt has been made in the present Review to survey the literature on organothallium compounds up to November, 1942. The position of thallium in the periodic table and some of the general chemistry of thallium of interest to the organic chemist have been briefly mentioned. The history, preparation, chemical and physical properties of the six known types of organothallium compounds have been discussed at length. What little is known on the physiological properties of organothallium compounds has been presented as completely as possible. It has been the constant aim in writing this Review to stress completeness, and it is hoped that the organization of the many details of the organic chemistry of thallium, with the inclusion of all known references, will provide in one place by far the larger part of the essential knowledge available on organothallium chemistry.
References


(10) A. Buschke and W. Konheim, Schweiz med. Wochenschr., 69, 702 (1939); C. A., 34, 170 (1940); Chem. Zentr., 111 I, 1228 (1940).


(12) L. Carius and G. Fronmüller, Ber., 7, 302 (1874).


(41) H. Gilman and R. G. Jones, Unpublished Paper I: "Trimethylthallium".

(42) H. Gilman and R. G. Jones, Unpublished Paper II: "A New Method of Preparing Organothallium and Organolead Compounds".


(53) H. P. A. Groll, U. S. patents 1,938,179 and 1,938,180; \[ 134 \].
(56) C. Hansen, Ber., 5, 9 (1870).
(57) C. A. Harris and C. B. Purves, Paper Trade J., 110 No. 6, 29 (1940); C. A., 34, 2587 (1940).
(58) F. C. Hartwig, Ber., 7, 298 (1874).
(59) F. C. Hartwig, Ann., 176, 257 (1875).
(60) F. Hein and E. Markert, Ber., 61, 2255 (1928).
(63) W. Hieber and P. Sonnekalb, Ber., 61, 555 (1928).
(64) S. Hilpert and G. Grüttnier, Ber., 48, 906 (1915).
(65) D. Holde and M. Selim, Ber., 58, 523 (1925).
(66) N. A. Il'in, Arch. intern. pharmacodynamie, 60, 377 (1938); C. A., 35, 4316 (1939).
(67) N. A. Il'in, P. Hofman, N. N. Mel'nikov and A. M. Avetisian, Arch. intern. pharmacodynamie, 58, 371 (1938); C. A., 32, 5911 (1938).
(70) H. Kluge, Z. Untersuch. Lebensm., 76, 156 (1938).
(71) (continued from page 135) (U.S.S.R.), 8, 144 (1936);  
2148 (1937). 

(72) E. P. Kohler and W. P. Peterson, J. Am. Chem. Soc., 55,  
1073 (1933). 

(73) E. Krause, Ber., 51, 912 (1918). 


(75) E. Krause and A. von Grosse, Ber., 58, 272 (1925). 

(76) E. Krause and A. von Grosse, Ber., 58, 1933 (1925). 

(77) E. Krause and A. von Grosse, Ber., 59, 1712 (1926). 


(81) M. Kuras, Chem. Obzor, 14, 145 (1939); \[ C. A., 35, 9200 \]  
(1939). 

(82) E. Kurowski, Ber., 43, 1076 (1910). 

(83) C. A. Lamy, Compt. rend., 59, 782 (1864). 

(84) Langhans, Z. ges. Schieß-Sprengstoffw., 31, 359, 402  
(1936); \[ C. A., 31, 2008 \] (1937). 


(86) C. Mahr and H. Ohle, Ann., 542, 44 (1939). 

(87) L. Marino, Gazz. chim. Ital., 37, 55 (1907). 

5, 1786 (1935); \[ C. A., 30, 3403 \] (1936); \[ Chem. Zentr., \]  
107, 4554 (1936).
(89) N. N. Mel'nikov and G. P. Gracheva, J. Gen. Chem. (U.S.S.R.), 6, 634 (1936); \( \text{C. A.}, 30, 5557 \) (1936);
   \( \text{Chem. Zentr.}, 107 \text{ II}, 1150 \) (1936).

(90) N. N. Mel'nikov and G. P. Gracheva, J. Gen. Chem. (U.S.S.R.),
   7, 467 (1937); \( \text{C. A.}, 31, 4310 \) (1937); \( \text{Chem. Zentr.}, 108 \text{ II}, 1563 \) (1937).

(91) N. N. Mel'nikov and M. S. Rokitskaya, J. Gen. Chem. (U.S.S.R.),
   7, 1472 (1937); \( \text{C. A.}, 32, 127 \) (1938); \( \text{Chem. Zentr.}, 109 \text{ I}, 581 \) (1938).

(92) N. N. Mel'nikov and M. S. Rokitskaya, J. Gen. Chem. (U.S.S.R.),
   8, 1768 (1938); \( \text{C. A.}, 33, 4969 \) (1939); \( \text{Chem. Zentr.}, 110 \text{ I}, 4933 \) (1939).

(93) D. Mendeleéeff, Ann. Supplement Vol. 9, 133 (1872).


(102) R. C. Menzies, N. V. Sidgwick, E. F. Cutcliffe and J. M. C.

     (1934).
(112) R. J. Meyer and A. Bertheim, *Ber.*, 37, 2051 (1904).
(114) H. Moissan, "Traité de chimie minérale", Masson et Cie.,


(121) P. Pfeiffer and P. Truskier, Ber., 37, 1125 (1904).


(125) H. M. Powell and D. Crowfoot, Z. Krist., 87, 370 (1934).


(128) F. de la Provostaye, Compt. rend., 55, 610 (1862).


(133) C. Renz, Ber., 35, 1110 (1902).

(134) C. Renz, Ber., 35, 2768 (1902).

(135) C. Renz, Z. anorg. Chem., 36, 100 (1903).


(138) I. Shukoff, Ber., 38, 2691 (1905).


(143) H. Steidle, Med. Welt, 15, 1557 (1939); Z. B., 34, 4157 (1940).


(146) W. Traube and A. Funk, Ber., 69, 1476 (1936).

(147) W. Traube and F. Kuhbier, Ber., 69, 2655 (1936).

(148) W. Traube and F. Kuhbier, Ber., 69, 2664 (1936).


EXPERIMENTAL

The chief emphasis in the preparation of the organothallium compounds described in the following section has been upon the introduction of new groups into the molecule. In general, the introduction of water-solubilizing groups has received more attention in this work than the synthesis of compounds which are substituted by non-functional groups, such as methyl or p-bromophenyl. Thus, it has been found possible to effect the direct nitration and the direct sulfonation of an organothallium compound. In these cases substitution is found to follow the general rule observed with most organic derivatives of elements in the lower portion of the periodic table: nitration and sulfonation are found to take place in the meta-position.

In many cases detailed directions are given before a preparation for the synthesis of certain starting materials, such as thallium trichloride or thallous ethoxide, although these compounds are known. In these cases certain improvements have been discovered which simplify the preparation of large quantities of the materials.

Certain other organic compounds of thallium are also mentioned. For instance, thallium trichloride tripyridine and thallium tribromide tripyridine are described; these compounds were prepared in order to eliminate by their melting points any
chance of confusion with such compounds as di-α-pyridylthallium bromide.

**The Preparation of an Anhydrous Ether Solution of Thallium Trichloride.** A weighed amount of pure thallous chloride was placed in an Erlenmeyer flask, covered with the amount of water calculated for the formation of thallium trichloride tetrahydrate plus ten percent, and heated by an oil bath at 60° while a slow stream of chlorine was bubbled through the thick paste. The time required for everything to go into solution depended on the amount of thallous chloride taken, and varied from two or three hours to several days. When everything was in solution, the heating was discontinued, and the chlorine passed into the solution for three or four hours as it cooled to room temperature. Then the excess chlorine was removed by passing a stream of pure dry nitrogen through the heavy colorless liquid until the emerging gas no longer smelled of chlorine, whereupon the flask was cooled at 0° until crystallization took place. A tendency to supersaturation was often noticed, and crystallization was accordingly induced by the addition of a crystal of thallium trichloride tetrahydrate from a previous run. The hard white crystals which separated were filtered from the mother-liquor through sintered glass, pressed very dry and washed into a glass-stoppered bottle with anhydrous ether. Anhydrous calcium sulfate was added as a

drying agent, and after being allowed to stand for several
days with occasional shaking, the solution's titer was
determined by the analysis of an aliquot portion.

The Preparation of Di-o-tolylthallium Bromide. The
Grignard reagent prepared from 85 g. (0.5 mole) of o-bromotoluene
and 12.2 g. (0.5 g. atom) of magnesium in a total volume of 400
ml. of anhydrous ether was added over a period of one hour to
a solution of 50 g. (0.16 mole) of thallium trichloride in 500
ml. of ether cooled to -15°. The reaction was allowed to warm
up to room temperature, and was then stirred for one hour.
The color test was negative at the end of this time, and may
have been negative earlier. The solution was hydrolyzed by
the addition of 300 ml. of 10% hydrobromic acid, and the
precipitate which separated was filtered, washed with methanol
and dried. The crude product weighed 30 g., which represented
a 40% yield. Purification was readily carried out by re-
crystallization from pyridine. The pure compound formed color-
less crystals, which did not melt at 340°.


The Attempted Preparation of Di-o-tolylthallium Sulfamate.
Two grams (0.01 mole) of silver sulfamate, prepared by the double
decomposition between equimolecular quantities of sodium sulfamate
and silver nitrate, was suspended in pyridine (it appeared to
be absolutely insoluble even in boiling pyridine) and 4.7 g.
(0.01 mole) of di-o-tolylthallium bromide was added. The reaction
was boiled over a small flame for one-half hour. The organothallium
compound went into solution, but the silver sulfamate did not, and there was apparently no reaction, for no silver bromide was formed, and filtration of the reaction left behind the water-soluble silver sulfamate. The compound could, of course, readily be prepared by the direct titration of di-o-tolylthallium hydroxide with sulfanilic acid, if it were so desired.

The Preparation of Di-2-(4-sulfotoluene)thallium Sulfate. Nine and two-tenths grams (0.02 mole) of di-o-tolylthallium bromide ground to a very fine powder was added over a period of fifteen minutes to 25 ml. of fuming sulfuric acid cooled to -20°. The reaction was stirred for 45 minutes, and then poured on ice. When all the ice had melted, the mixture was warmed until nearly everything had gone into solution, filtered, and then cooled strongly. Fine white crystals separated, which after drying weighed 5.6 g., which represented a 50% yield of di-2-(4-sulfotoluene)thallium sulfate.

The compound was somewhat soluble in water, especially on warming. It was immediately soluble in 10% potassium hydroxide solution.

Anal. Caled. for C₈H₇O₁₈S₂Tl₁₁: Tl, 36.4; neut. equiv., 281.5. Found: Tl, 36.0; neut. equiv., 292.

The Preparation of Thallous 2-Bromotoluene-4-sulfonate. The position of sulfonylation in the above compound was established by cleaving 5.6 g. (0.01 mole) suspended in 50 ml. of chloroform by the gradual addition of 3.2 g. (0.02 mole) of bromine in
25 ml. of chloroform. The stirring was continued until complete disappearance of the bromine color was noticed. The chloroform was then removed on the steam-bath, the residue taken up in water, neutralized with thallous hydroxide, and extracted with hot water to remove the thallous 2-bromotoluene-4-sulfonate from the thallous bromide. The yield was 5.8 g. or 64% of thallous 2-bromotoluene-4-sulfonate, melting sharply at 220-222° after recrystallization from alcohol.


The Preparation of Thallous 2-Bromotoluene-4-sulfonate by an Authentic Reaction. Fifty grams (0.268 mole) of 2-aminotoluene-4-sulfonic acid was dissolved in 125 ml. of 2 N sodium hydroxide solution (from 10 g. of sodium hydroxide), and to that solution was added 19 g. (0.275 mole) of sodium nitrite dissolved in 250 ml. of water. This combined solution was cooled to 0° and added dropwise to 200 ml. of 48% hydrobromic acid cooled to and maintained at 0°. Vigorous stirring was maintained throughout the addition. The reaction was allowed to stand for one-half hour at 5°, and then decomposition of the diazonium complex was carried out by the gradual addition of very small portions of copper bronze powder, care being taken that the escaping nitrogen did not at any time become so vigorous as to project the contents from the flask. The reaction was completed by warming to 35°, and the absence
of any diazonium salt was demonstrated by the usual test with β-naphthol. The solution was then neutralized with sodium hydroxide solution and evaporated to dryness in a vacuum desiccator over sulfuric acid. The thoroughly dried residue was extracted with 95% alcohol until the extracted solution on cooling overnight at 0° deposited no more crystals. Five or six extractions were necessary. The combined crystalline material was recrystallized once from 95% alcohol to effect a further separation from sodium bromide, the chief contaminant. The yield was 53 g. or 72% of sodium 2-bromotoluene-4-sulfonate.²

Two and seven-tenths grams (0.01 mole) of this sodium 2-bromotoluene-4-sulfonate was dissolved in the minimum amount of hot water and added to a similar solution of 2.5 g. (0.01 mole) of thallous formate. A small precipitate of inorganic thallium salt was filtered from the hot solution, and the solution was then allowed to cool. The yield was 3.8 g. or 84% of white crystals which melted at 220-222° and which gave no depression in a mixed melting point with the thallous 2-bromotoluene-4-sulfonate prepared from the di-2-(4-sulfotoluene)-thallium sulfate by bromine cleavage.

The Preparation of Di-β-nitrophenylthallium Nitrate by Direct Nitration. A mixture of 10 ml. of fuming nitric acid and 8 ml. of fuming sulfuric acid was placed in a small

(²) Hayduck, Ann., 172, 205 (1874).
round-bottomed flask equipped with a stirrer and cooled by means of ice-hydrochloric acid to -20°. To this solution was added over the period of one-half hour 4.2 g. (0.01 mole) of diphenylthallium nitrate, prepared in essential accordance with the directions of Goddard and Goddard by the double decomposition between diphenylthallium bromide and silver nitrate in hot pyridine. The solution was stirred for 15 minutes after the addition was completed and then poured on ice. The precipitate was filtered, washed twice with water and dried. The material proved to be very soluble in pyridine—too soluble to permit recrystallization from that solvent. Hence purification was achieved by solution in pyridine, filtration from a small amount of undissolved material, and reprecipitation by the addition of water. Finally, the slightly yellow crystalline powder was boiled with absolute alcohol to remove traces of pyridine and water and dried thoroughly in a vacuum.

Qualitative analysis demonstrated the presence of nitrogen and thallium and the absence of sulfur. When heated on a spatula the compound flashed with a sharp puff.

(4) Meyer and Bertheim, Ber., 37, 2051 (1904).
Challenger and Rothstein\textsuperscript{5} have shown that the nitration takes place in the meta-position, but they did not actually isolate their compound, but instead cleaved the crude nitration product with bromine and determined the amount of m-nitrobromobenzene.

**Anal.** Calcd. for $C_{12}H_8O_2N_2Tl$: Tl, 40.0 Found: Tl, 39.8.

The Preparation of Di-m-nitrophenylthallium Nitrate from m-Nitrophenylboric Acid and Thallium Trichloride.

Di-m-nitrophenylthallium chloride was prepared from m-nitrophenylboric acid\textsuperscript{6} and aqueous thallium trichloride solution in essential accordance with the directions of Mel'nikov and Rokitskaya.\textsuperscript{7} Their melting point of 245° with decomposition was confirmed. This compound was converted to the corresponding nitrate by warming 4.8 g. (0.01 mole) in pyridine with 1.7 g. (0.01 mole) of silver nitrate, which is also very soluble in hot pyridine. The hot solution was filtered from silver bromide. The di-m-nitrophenylthallium nitrate was precipitated from the pyridine solution by the addition of water, washed once with water, and then boiled with absolute alcohol, filtered, and carefully dried in a vacuum. Above 300° the compound shows gradual decomposition, which takes place with

\textsuperscript{(6)} Bean and Johnson, J. Am. Chem. Soc., 54, 4415 (1932).
\textsuperscript{(7)} Mel’nikov and Rokitskaya, J. Gen. Chem. (U.S.S.R.), 7, 1472 (1937).
a sharp flash if the compound is rapidly heated above this
temperature. The absence of a definite melting point un-
fortunately precluded the possibility of a satisfactory test
of the identity of the compound as compared with the product
obtained by direct nitration of diphenylthallium nitrate, but
in appearance, crystal structure under the microscope,
behavior on heating and solubility the two compounds were
identical.


The Preparation of Thallous Hydroxide. Thallous
hydroxide has been prepared in a variety of ways, including
from thallous sulfate by double decomposition with barium
hydroxide. This is the method used in the following prepara-
tion, since thallous sulfate is the most readily available
commercial form of thallium at the present time. A weighed
amount of thallous sulfate, usually 100 g., was placed in a
two-liter flask, and just brought into solution with the mini-
mum amount of water at the boiling point. While waiting for
complete solution, a large excess of barium hydroxide solution
saturated at room temperature was prepared by placing several
inches of C. P. barium hydroxide octahydrate in a liter bottle
and filling with distilled water, shaking vigorously, and
allowing to settle. Precipitation of barium sulfate was carried
out in hot solution by adding barium hydroxide solution to the

thallous sulfate solution until addition of barium hydroxide solution to a small, filtered, clear test-portion from the main solution barely produced an opalescence, indicating that sulfate ion, and therefore thallium, was still in very slight excess. It is absolutely necessary to have thallous sulfate in very slight excess, since otherwise barium hydroxide is present, which will contaminate all thallous salts prepared from the solution with barium salts. It is not possible to obtain barium hydroxide pure enough and containing sufficiently constant water of hydration to permit simple double decomposition with the weighed amount of barium hydroxide octahydrate as demanded by the stoichiometric equation, and resort must be had to the tedious but very accurate method of testing small filtered portions of the solution with sulfate and barium ions. Naturally, in case too much barium hydroxide has been added, it is possible to back-titrate with thallous sulfate solution. All unnecessary exposure to the air should be avoided, as both barium and thallium very readily form insoluble carbonates from the carbon dioxide in the air. When the proper end-point had been reached, the barium sulfate was allowed to digest on the steam-bath for two or three hours to improve its filtering qualities. Filtration was carried out using a 20 cm. funnel in order to perform the operation as rapidly as possible. The clear filtrate was concentrated under 15 mm. pressure until a yellow precipitate started to form. At this point the concentration was discontinued and a small amount of water added to get
rid of the yellow color (solid thallous hydroxide is yellow, but dissolves in water to a colorless solution), and then the solution was filtered from small amounts of white precipitate (mostly barium sulfate). If an aqueous thallous hydroxide solution was desired, this very nearly saturated solution was bottled and standardized by titration against standard acid. If the solid thallous hydroxide was desired, the evaporation under reduced pressure was continued in a clean flask to the point of dryness. Dry, solid thallous hydroxide will keep indefinitely, but the aqueous solution slowly undergoes oxidation, with the deposition in the bottle of brown thallium hydroxide. The yield in this preparation was about 80%. The filter papers, washings, precipitates, etc. contained the rest of the thallium, and were added to "thallium recovery".

The Preparation of Thallous Ethoxide. Thallous ethoxide has been generally prepared either by the action of ethanol on metallic thallium in the presence of oxygen or by the action of alcohol on thallous hydroxide. It has been found more convenient to employ the latter method, especially since thallous hydroxide may be readily prepared from the commercially available sulfate. Advantage is taken of the equilibrium reaction:

\[
\text{TlOH} + \text{C}_2\text{H}_5\text{OH} \rightleftharpoons \text{TlOC}_2\text{H}_5 + \text{H}_2\text{O}
\]

which in the presence of an excess of alcohol is displaced far to the right. In a separatory funnel was placed 100 g. of thoroughly dried thallous hydroxide, which was then just covered with absolute alcohol which had been prepared from the "commercial absolute alcohol" by distillation from magnesium ethoxide. After thorough shaking, the solid appeared to crumble somewhat. The material was allowed to settle, and the clear alcohol was poured off. Two more extractions with alcohol were sufficient to remove all the water, and the thallous ethoxide remained as a heavy oily layer below the alcohol. It was tapped off from the bottom of the funnel, and filtered through sintered glass directly into seal-off vials, which were immediately sealed to protect the compound from hydrolysis by the moisture in the air. The yield was 90 g. or 80%

The Preparation of Diethylthallium Ethoxide.

(I) From Thallous Ethoxide. Fifteen grams (0.05 mole) of diethylthallium chloride was suspended in 100 ml. of ether and 12.5 g. (0.05 mole) of thallous ethoxide added. The mixture was refluxed for four hours, but apparently there was no reaction, since a test-portion of the clear ether solution when evaporated left practically no residue. Accordingly most of the ether was distilled off and replaced by 100 ml. of pyridine, and the reaction was heated on the steam-bath for one hour. At the end of this time almost all the material had gone into solution, except for a small amount of thallous chloride. The
solution was filtered and the solvents removed under 15 mm.
pressure. The liquid residue was then distilled under greatly
reduced pressure: b. p. 101-102° / 0.1 mm. The pale yellow
liquid, which had an odor somewhat resembling tetraethyllead,
solidified on cooling to a nearly colorless crystalline mass,
which melted at 43-45°. The yield was 10.2 g. or 66.7%. The
compound was immediately soluble in water because of complete
hydrolysis.

Anal. Calcd. for C₉H₁₅OTl: Tl, 66.5. Found: Tl, 66.3.

(II) From Sodium Ethoxide. One and two-tenths grams
(0.05 g. atom) of sodium was dissolved in 100 ml. of absolute
alcohol, and then 15.0 g. (0.05 mole) of solid diethylthallium
chloride was added, and the reaction was warmed on the steam-
bath and stirred for two hours. Nearly everything went into
solution, and the reaction was filtered, and the solvent was
removed from the clear solution under reduced pressure. The
compound was then distilled as above. The same physical con-
stants were observed. The yield was 10.8 g. or 70%.

The Preparation of Di-o'-hydroxyphenylthallium Bromide.
To 23.5 g. (0.156 mole) of o'-bromophenol in 200 ml. of ether
cooled to 0° was added 0.272 mole of butyllithium (as determined
by the "double titration" method of Haubein)¹⁰ in 425 ml. of
ether. After the addition was completed,¹¹ the cooling bath

was removed, and the reaction was allowed to stir for one-half hour at room temperature, then cooled to -15°. A 60% yield on the halogen-metal interconversion was assumed. Accordingly, 12.7 g. (0.041 mole) of thallium trichloride in 200 ml. of anhydrous ether was added slowly to the solution of the lithium compound. A white precipitate formed, the solution gradually turning first green, and then blue. After five minutes a color test was negative, and may have been negative sooner. The reaction was hydrolyzed by the addition of 200 ml. of 5% hydrobromic acid. The precipitate which was insoluble in both water and ether was filtered off, dried, and extracted with pyridine, which dissolved the organothallium compound away from a large amount of thallous halides. The organothallium compound was then obtained from the pyridine solution by adding water. The compound could be quite readily recrystallized from dioxane. The yield of di-o-hydroxyphenylthallium bromide, which did not melt at 340°, was 3.1 g. or 15.6% based on thallium trichloride. The compound was slightly soluble in hot 10% potassium hydroxide solution, from which it was reprecipitated by acidification.

**Anal. Caled. for C₁₂H₁₀O₂BrTl: Tl, 43.4. Found: Tl, 43.1.**

The Preparation of Dimethylthallium Saccharide.
Two and seven-tenths grams (0.01 mole) of dimethylthallium chloride, prepared in the usual manner from methylmagnesium
chloride and an anhydrous ether solution of thallium trichloride,\textsuperscript{12} and 2.9 g. (0.01 mole) of silver saccharide were each dissolved in the minimum amount of hot pyridine, and the two solutions were poured together. There was an immediate precipitate of silver chloride. The dimethylthallium saccharide was very soluble in pyridine, and did not precipitate on cooling the solution. Accordingly, the pyridine was removed under 15 mm. pressure, with slight warming, and the white crystals were washed with alcohol, dried, and weighed: the yield was 4.0 g. or 95\%. After recrystallization from alcohol, the compound melted at 231-233°. The compound was obviously much more than one percent soluble in water, hence the exact solubility was not determined. The material was recovered unchanged after solution in water, hence there was no hydrolysis. Qualitative analysis demonstrated the presence of thallium, nitrogen, and sulfur.

\textbf{Anal. Caled. for C}_7\text{H}_{10}\text{O}_5\text{Tl}: \ Tl, 49.2. \ Found: 
Tl, 49.0.

The Preparation of Diethylthallium Saccharide. Three grams (0.01 mole) of diethylthallium chloride, prepared in the usual manner from ethylmagnesium chloride and an anhydrous ether solution of thallium trichloride,\textsuperscript{12} and 2.9 g. (0.01 mole) of silver saccharide were each dissolved in the minimum amount of hot pyridine, and the two solutions were poured together.

\textsuperscript{(12)} Meyer and Bertheim, \textit{Ber.}, \textbf{37}, 2051 (1904).
There was an immediate precipitate of silver chloride. The diethylthallium saccharide was very soluble in pyridine, and did not precipitate on cooling. Accordingly, the pyridine was removed under 15 mm. pressure, with slight warming, and the white crystals were washed with alcohol, dried, and weighed: the yield was 4.1 g. or 92%. After recrystallization from alcohol, the compound melted at 220-221°, and was 1.55% soluble in water at 25°. The material obtained by the evaporation of the solvent from the clear filtrate in the solubility determination melted at 220° and showed no depression with material which had not been dissolved in water, hence there was no hydrolysis.

Qualitative analysis showed the presence of thallium, sulfur, and nitrogen. This compound, as well as the other organothallium saccharides prepared, had a sweet taste, although it did not seem as strong as that experienced with pure saccharine.

Anal. Calcd. for $C_{12}H_{14}O_2NSTl$: Tl, 45.8 Found: Tl, 45.7.

The Preparation of Diphenylthallium Saccharide. Two and nine-tenths grams (0.01 mole) of silver saccharide (prepared by the double decomposition between equimolecular quantities of sodium saccharide and silver nitrate in aqueous solution, filtration of the precipitate, and careful drying) and 4.4 g. (0.01 mole) of diphenylthallium bromide were mixed in a small flask, covered with 40 ml. of pyridine, and warmed on the steam-bath for one-half hour. Most of the material went into solution, leaving a small amount of yellow precipitated
silver bromide on the bottom of the flask. The clear solution was filtered hot, and the filtrate cooled in ice for several hours, during which time long white needles separated. These were filtered off and dried over sulfuric acid at less than one mm. pressure. Very thorough drying was found to be necessary to prevent the crystals from powdering (apparently due to the loss of pyridine of crystallization still contained in them after insufficient drying) on the melting point block as the temperature range 70-100° was passed through in the course of the melting point determination. The total yield of crude material was 4.6 g. or 85% melting at 315-320° with slight decomposition. The compound was recrystallized from pyridine, when it melted at 322-324°, still with slight decomposition. Qualitative analysis demonstrated the presence of nitrogen, sulfur, and thallium. The compound was 0.17% soluble in water at 25°. The material recovered by the evaporation of the clear filtrate in the solubility determination started to melt at 225° and continued melting in very indefinite fashion on up to 300°, indicating that hydrolysis had taken place.

This same reaction could not be made to take place using chloroform instead of pyridine as a solvent.


The Preparation of Diphenylthallium Sulfanilate. One and four-tenths grams (0.005 mole) of silver sulfanilate (prepared by the double decomposition reaction between
equimolecular quantities of sodium sulfanilate and silver nitrate, filtration and drying of the precipitate in the dark) and 2.2 g. (0.005 mole) of diphenylthallium bromide were each dissolved in the minimum amount of hot pyridine. The solutions were poured together, boiled three minutes, filtered from silver bromide and cooled. Beautiful white crystals deposited, which melted at approximately 345° with decomposition. The compound was only 0.06% soluble in water at 25°. Qualitative analysis demonstrated the presence of sulfur, nitrogen, and thallium.

Anal. Calcd. for C₁₆H₁₄O₄N₃S₂Tl₂: Tl, 38.5.
Found: Tl, 38.3.

The Preparation of Di-2-pyridylthallium Chloride.
The 2-bromopyridine used in this preparation was first purified by careful distillation through a modified Vigreux column under reduced pressure. The compound boiled at 76°/13 mm. (bath at 97°) and showed these physical constants: 
$$d^2₅ = 1.5682,$$
$$d_{20} = 1.6110.$$ To 190 ml. of ether containing 0.127 mole of

Note on the Solubilities of Some Compounds in Pyridine. Glycine was found to be insoluble in boiling pyridine, while its silver salt was considerably reduced to metallic silver by boiling in pyridine. Potassium chloride was insoluble in boiling pyridine, and the whole solution took on somewhat of a "colloidal gel" look. Silver chloride was insoluble in pyridine, silver bromide was very slightly soluble, and silver iodide was definitely more soluble. Silver nitrate was very soluble in hot pyridine, and separated readily from the solution in large crystals on cooling. Potassium gluconate was insoluble in hot pyridine, and would not react with diphenylthallium bromide dissolved in pyridine.
butyllithium and cooled to -25° was added over a period of
five minutes 20 g. (0.127 mole) of 2-bromopyridine in 75 ml.
of ether. The reaction was stirred for ten minutes at -25°
and the temperature was then lowered to -75°. During one hour
200 ml. of ether containing 21.1 g. (0.0676 mole) of thallium
trichloride was added dropwise. The characteristic red color
of 2-pyridyllithium disappeared and a creamy precipitate
separated. The reaction was stirred for three hours, during
which time it was allowed to warm up to room temperature.
The reaction mixture was hydrolyzed by the addition of 100 ml.
of water and the precipitate was collected on a filter, boiled
out first with water and then with methanol. After thorough
drying it weighed 22.4 g., which represented an 83.5% yield
of di-2-pyridylthallium chloride, which melted at 288-291°
and was insoluble in water, chloroform, alcohol, and dioxane.

*Anal. Caled. for C_{16}H_{14}N_{4}ClTl: Tl, 54.2 Found: Tl, 54.0.*

**The Preparation of Di-2-pyridylthallium Lactate.**

When the pyridine solutions prepared separately from 4.0 g.
(0.01 mole) of di-2-pyridylthallium chloride and 2.0 g.
(0.01 mole) of silver lactate (which was very readily soluble
in warm pyridine) were mixed, a precipitate of silver chloride
separated almost immediately. The reaction mixture was filtered,
and the clear solution cooled to -20°. Long white crystals

(13) Gilman and Spatz, Unpublished data.
deposited, which after filtration, drying with methanol, and strong drying over sulfuric acid in a vacuum desiccator melted with decomposition at 205-208°. The yield was 3.4 g. or 75%. The compound was fairly soluble in water.


The Attempted Rearrangement of the Pyridine Complex of Thallium Trichloride to an Organothallium Compound. Thallium trichloride tripyridine has been described by Meyer¹ and by Renz,² but neither worker mentioned the melting point, which we have found to be 149-150° without decomposition. To 300 ml. of an ether solution containing 31.1 g. (0.1 mole) of thallium trichloride was slowly added 100 ml. of an ether solution containing 26.1 g. (0.3 mole plus 10%) of pyridine. The precipitation of thallium trichloride tripyridine was immediate and complete. The compound is very insoluble in ether, but may readily be recrystallized from absolute alcohol. The quantitative yield (54 g.) of the crude product was added without further purification to 200 ml. of pyridine, and the entire reaction was heated at 180° for 10 hours. At the end of this time, the cooled solution was concentrated under reduced pressure, and the crystalline material which deposited was washed with methanol and then recrystallized from absolute alcohol. It was shown by its melting point and mixed point with an authentic specimen to be the starting material. The recovery was 82%.

(14) Renz, Ber., 35, 1110 (1902); Z. anorg. Chem., 36, 100 (1905).
The Preparation of the Thallium Tribromide Complex of Pyridine. Although mention has been made of thallium tribromide tripyridine in the literature, no analyses were presented, and the melting point of the compound was not recorded. Since the melting point was desired in connection with other work, its preparation was accordingly carried out. At the same time a new method of preparation was tried. The previous method of making the thallium tribromide complex of pyridine and related amines was to mix an ether solution of thallium tribromide with an ether solution of pyridine. The following method oxidizes a suspension of thallous bromide in pyridine in the presence of pyridinium bromide.

Two and eight-tenths grams (0.01 mole) of thallous bromide was covered with 10 ml. of pyridine and mechanically stirred while a solution of 1.6 g. (0.01 mole) of bromine in 10 ml. of pyridine was added dropwise. When the addition was complete, the reaction was heated gently on the steam-bath until a clear solution was obtained (five minutes). The flask was then strongly cooled in an ice-hydrochloric acid bath. Fine needles separated, which "felted" together when filtered. Under the microscope they appeared as slim rods with blunt ends.

(16) Il'in, Hofman, Mel'nikov and Avestisian, Arch. intern. pharmacodynamie, 58, 371 (1938); C. A., 32, 5911 (1938).
The yield was 5.2 g. or 76%. The compound was readily re-
crystallized from absolute alcohol, and then melted at 113-115°
without decomposition.

Anal. Calcd. for C₁₅H₁₅N₅Br₂Tl: Tl, 30.0 Found:
Tl, 29.8.

The Preparation of the Thallium Trichloride Complex
of 2-Bromopyridine. The solutions prepared by dissolving
4.8 g. (0.03 mole) of 2-bromopyridine in 10 ml. of ether and
3.1 g. (0.01 mole) of thallium trichloride in 35 ml. of ether
were mixed and allowed to stand overnight at 0°. The shining
white crystals, when filtered and dried, weighed 5.4 g., which
represented a 79% yield of thallium trichloride tri-(2-bromo-
pyridine). The compound melted sharply at 145-146° and was
decomposed by water. It was insoluble in gasoline; very
slightly soluble in ether, benzene, and chloroform; and some-
what more soluble in pyridine.

Found: Tl, 29.4.

The Preparation of the Thallium Trichloride Complex of
2-Aminopyridine. The solutions prepared by dissolving 2.85 g.
(0.03 mole) of 2-aminopyridine in 10 ml. of ether and 3.1 g.
(0.01 mole) of thallium trichloride in 35 ml. of ether were
mixed and allowed to stand overnight. The crystals were gummy,
even when allowed to stand for a considerable time at 0°.
Accordingly, dry hydrogen chloride gas was passed into the
mixture in order to form the hydrochloride of the complex.
Upon standing, 4.8 g. of slightly yellow crystals deposited, which represented a 68% yield of thallium trichloride tri-(2-aminopyridine hydrochloride). The compound melted not too sharply and with some decomposition at 121-125°. No attempt was made to recrystallize the compound, as preliminary experiments showed the stability to be unsatisfactory.

**Anal. Calcd. for C_{16}H_{12}N_{6}Cl_{6}Tl:**  Tl, 29.1

**Found:**  Tl, 28.1

**The Preparation of the Thallium Trichloride Complex of Cysteine Hydrochloride.** One and six-tenths grams (0.01 mole) of cysteine hydrochloride was dissolved in the minimum amount of water at room temperature, and a saturated solution of thallium trichloride tetrahydrate was added dropwise until precipitation was complete. The shining yellow platelets were filtered and dried. The yield was 3.8 g. or 81% of thallium trichloride cysteine hydrochloride, melting at approximately 350°. The compound was 0.29% soluble in water at 25°. Qualitative analysis demonstrated the presence of sulfur, nitrogen, chlorine, and thallium.

**Anal. Calcd. for C_{16}H_{12}N_{6}Cl_{6}STl:**  Tl, 43.5.

**Found:**  Tl, 43.2.

**The Preparation of o-Bromodimethylaniline.** This compound was prepared in essential accordance with the directions of Gilman and Banner\(^{17}\) by the action of methyl sulfate on

o-bromoaniline. The yield, however, has been raised from 70% to a nearly quantitative figure by the use of more methyl sulfate. The purity of the product is chiefly dependent on the purity of the o-bromoaniline used as starting material. The o-bromoaniline used in this preparation was the Eastman Kodak Co. C. P. grade, but was liquid at 25° and slightly colored (the melting point of very pure o-bromoaniline is recorded as 31-32° in Beilstein). Its index of refraction was n D 1.6145, and its picrate melted at 127-128°. Holleman and Rinkes\(^{18}\) reported the purification of o-bromoaniline over the picrate, but did not give the melting point of the picrate. Contrary to their statement, the picrate is not "extremely insoluble" in 95% alcohol, and is not nearly so insoluble as the picrate of o-bromodimethylaniline.

In a three-necked flask equipped with stirrer, dropping funnel and air condenser were placed 100 ml. of water and 100 g. (0.582 mole) of o-bromoaniline. Then 70 ml. of methyl sulfate which had been carefully purified by vacuum distillation was added dropwise at room temperature over a period of two hours. At the end of this time the solution had become clear and homogeneous; it was made alkaline with saturated sodium carbonate solution, whereupon two layers were again formed. A second and then a third 70 ml. portion of methyl sulfate were added, all heating being avoided, and the neutralization with

\(^{18}\) Holleman and Rinkes, *Reg. trav. chim.*, 30, 49 (1911).
sodium carbonate being repeated after each addition was com-
pleted. Care was taken at the end of the reaction to destroy
any unused methyl sulfate with an excess of sodium carbonate.
After extraction with ether, drying over sodium sulfate, and
removal of the ether on the steam-bath, the compound was dis-
tilled under reduced pressure in the usual manner: b. p.
101-102° / 12 mm. The colorless oily liquid, which was a
glass both at 0° and at -75°, weighed 111 g., which represented
a 95.7% yield. The following physical constants were obtained:
\[ \text{n}^D_{25} 1.5748, \text{d}^2_{25} 1.3880. \] The picrate melted sharply at
150-151°.

The Preparation of Di-o-dimethylaminophenylthallium
Bromide. The Grignard reagent was prepared in 62.5% yield,
as determined by titration of a 5 ml. aliquot portion with
0.1 N sulfuric acid, from 40 g. (0.2 mole) of o-bromodimethyl-
aniline and 4.8 g. (0.2 g. atom) of magnesium in a total volume
of 250 ml. of anhydrous ether. The Grignard solution was
cooled to -75° and 150 ml. of ether containing approximately
15.5 g. (0.05 mole) of thallium trichloride was added dropwise.
The reaction was allowed to warm up to room temperature and was
then stirred for one hour. It was hydrolyzed by the addition of
150 ml. of 10% ammonium chloride solution. Recrystallized from
pyridine in the usual manner, the compound formed colorless,
very hard crystals, which contained nitrogen and thallium.
The yield was 15 g. or 60%.
Anal. Caled. for C\textsubscript{16}H\textsubscript{20}N\textsubscript{3}BrTl: Tl, 39.0.

Found: Tl, 39.0.

The Reaction between \(p\)-Dimethylaminophenyllithium and Thallium Trichloride. The solution of \(p\)-dimethylaminophenyllithium prepared from 60 g. (0.3 mole) of \(p\)-bromodimethylaniline and 4.5 g. (0.65 g. atom) of lithium in a total volume of 400 ml. of ether was allowed to settle and the clear, pale yellow, supernatant liquid was decanted into a dropping funnel. The lithium compound was then added dropwise to a solution of 31.0 g. (0.1 mole) of thallium trichloride in 250 ml. of anhydrous ether cooled to -20°. A brownish precipitate formed around every drop as it hit the solution, which soon turned dark blue-green. The reaction was stirred for 15 minutes at 0° after the addition was completed and then hydrolyzed by the addition of 5% aqueous hydrobromic acid until the aqueous layer showed a faint acid reaction. An excess of acid was thus carefully avoided. The ether layer contained all the color, the aqueous layer being colorless. The deep blue ether layer was separated and washed several times thoroughly with water to remove any thallium trichloride which might have been present, but tests on the washings with potassium iodide showed that there was no thallium trichloride present. Nevertheless, the ether layer was shown to contain thallium, presumably either as an organothallium compound or as a complex which could not be broken up by water and which was not soluble in water. The original water layer contained 8.1 g. of an inorganic material
which was identified as thallous chloride; this represented 33.7% of the thallium in the reaction. The ether layer was dried over anhydrous sodium sulfate and the ether was removed. The sticky violet tar which remained could not be made to crystallize by any of the usual methods, which were continued over a period of eight weeks. It does not seem likely that an \( R_3TLX \) compound, which is the type expected from this reaction would be soluble in ether. The similar chlorinating and oxidizing action of thallium trichloride on many amines with the resultant production of dyes has been discussed in detail on p. 98 of this Thesis.

The Preparation of \( p \)-Dimethylaminophenylboric Acid.
The solution of \( p \)-dimethylaminophenyllithium prepared from 20.0 g. (0.1 mole) of \( p \)-bromodimethylaniline and 2.1 g. (0.3 g. atom) of lithium in a total volume of 150 ml. of anhydrous ether was allowed to settle until clear and then carefully decanted into a dropping funnel. The lithium solution was then added dropwise to 23 g. (0.1 mole) of \( n \)-butyl borate in 100 ml. of ether cooled to -75°. No precipitate was formed, although the solution turned very slightly darker. The addition required one-half hour, and the solution was then allowed to warm up to room temperature, which required about two hours. It was then cooled to 0° and hydrolyzed by 60 ml. of 10% sulfuric acid. The ether layer was separated and the aqueous layer extracted twice with 50 ml. of ether. The combined ether extracts were warmed on the steam-bath to remove the ether,
25 ml. of 10% potassium hydroxide solution were added, and the  
\( \text{p} \)-butanol removed under reduced pressure. A slight precipitate  
separated, which was filtered off. Then the clear solution  
was exactly neutralized with 10% sulfuric acid. A white pre-  
cipitate separated, which when filtered off and carefully  
dried weighed 10.2 g. which represented a 62.5% yield of  
\( \text{p} \)-dimethylaminophenylboric acid. The compound was found to  
contain both nitrogen and boron, to be soluble in both acid and  
base, to be very soluble in alcohol, and not very soluble in  
water. It melted at 243-245° with decomposition.  

**Anal.** Caled. for \( \text{C}_8\text{H}_8\text{O}_2\text{NB} \): N, 8.49; B, 6.56.  
Found: N, 8.34; B, 6.21.

**The Preparation of \( \text{p} \)-Dimethylaminophenylmercury Chloride.** When the solutions prepared from 1.65 g. (0.01 mole)  
of \( \text{p} \)-dimethylaminophenylboric acid and 2.72 g. (0.01 mole) of  
mercuric chloride, each dissolved at 50° in the minimum amount  
of 50% ethanol, were poured together an immediate white  
crystalline precipitate formed, which was allowed to stand at  
0° for two hours and then filtered. The shimmering white crystals  
were recrystallized from alcohol, when they showed the melting  
point 224-225° with decomposition, (the value 225° with decomposi-  
tion is found in the literature).\(^ {19} \) The yield was 2.6 g. or 73%.  

**Anal.** Caled. for \( \text{C}_8\text{H}_8\text{NClHg} \): Hg, 56.3. Found: Hg, 56.0.

**The Reaction Between \( \text{p} \)-Dimethylaminophenylboric Acid**

and Thallium Trichloride. When the solutions prepared from 1.65 g. (0.01 mole) of p-dimethylaminophenylboric acid and 1.91 g. (0.005 mole) of thallium trichloride tetrahydrate, each dissolved at 40° in the minimum amount of 70% ethanol, were poured together an immediate purple color resulted. The reaction was allowed to stand overnight and then was filtered. The precipitate was washed free of the purple color and then was found to consist of shimmering white crystals, containing only thallium and chlorine, which would not melt or burn. The precipitate weighed 1.1 g., which indicated a quantitative reduction to thallous chloride. The aqueous purple solution was not further examined.


The Preparation of Bi-p-dimethylaminophenylthallium Bromide. A solution of p-dimethylaminophenyllithium, prepared from 40 g. (0.2 mole) of p-bromodimethylaniline and 3.5 g. (0.5 g. atom) of lithium in a total volume of 250 ml. of ether, was added dropwise to a suspension of 24 g. (0.1 mole) of thallous chloride in 250 ml. of ether. Metallic thallium rapidly separated. The reaction was allowed to stand overnight, poured on 200 g. of ice, and acidified by the addition of 100 ml. of 10% hydrobromic acid. After thorough stirring, the precipitate was filtered off, washed with a small quantity of methanol, and dried. The organothallium compound was dissolved away from the metallic thallium and thallous halides by boiling
pyridine, from which it was reprecipitated by the addition of water. After washing with methanol to remove pyridine and water, the compound was carefully dried, and weighed 11.8 g. which represented a 68% yield based on one-third of the thallium available in the reaction—two-thirds of the thallium in this reaction was necessarily reduced to the free metal. The compound could be recrystallized from a small amount of pyridine, in which it was found to be very soluble. It did not melt at 350°. Qualitative analysis demonstrated the presence of thallium, bromine, and nitrogen.

A trace of blue color was produced in this reaction, but nothing like the amount produced when thallium trichloride was used, and what little there was could be completely removed by the treatment with boiling pyridine. The compound would not undergo salt-formation with moderately concentrated aqueous acids.

Anal. Calcd. for C_{14}H_{14}N_{2}BrTl: Tl, 39.0. Found:
Tl, 38.6.

The Preparation of Di-p-anisylthallium Bromide. The Grignard reagent prepared from 2.4 g. (0.1 g. atom) of magnesium and 19.0 g. (0.1 mole) of p-bromoanisole in a total volume of 250 ml. of anhydrous ether separated into two layers during the course of its preparation, similar to the phenomenon observed with the Grignard reagent prepared from p-dibromobenzene. The Grignard solution was cooled to -75° and 200 ml. of ether containing 13.1 g. (0.042 mole) of thallium trichloride was
added dropwise over a period of one hour. The reaction was allowed to warm up to room temperature, and was then stirred for one hour. The white precipitate formed when the reaction was hydrolyzed by the addition of 100 ml. of 10% hydrobromic acid, when filtered, washed and dried, weighed 10.2 g., which represented a 48.7% yield of di-p-anisylthallium bromide. Recrystallized from pyridine, the compound formed glistening white needles which did not melt at 330°. The qualitative presence of thallium and bromine was demonstrated.

Anal. Caled. for C_{14}H_{14}O_{4}BrTl: Tl, 41.0.
Found: Tl, 40.8.

The Preparation of Di-o-anisylthallium Bromide. The Grignard reagent prepared from 2.4 g. (0.1 g. atom) of magnesium and 19.0 g. (0.1 mole) of o-bromoanisole in a total volume of 250 ml. of anhydrous ether was cooled to -75° and 125 ml. of ether containing 13.1 g. (0.042 mole) of thallium trichloride was added dropwise over the period of one hour. The reaction was allowed to warm to room temperature and stand overnight. The precipitate formed when the reaction was hydrolyzed by the addition of 100 ml. of 10% hydrobromic acid, when filtered, washed with methanol and dried, weighed 10.0 g., which represented a 47.7% yield of di-o-anisylthallium bromide. Recrystallized from pyridine, the compound formed long white needles which did not melt at 330°. Qualitative analysis showed the presence of thallium and bromine.
Anal. Calcd. for C_{14}H_{10}O_{4}BrTl: Tl, 41.0.
Found: Tl, 40.9.

The Attempted Coupling of p-Nitrobenzenediazonium
Chloride with Di-p-dimethylaminophenylthallium Bromide.

To prepare the diazonium solution 1.4 g. (0.01 mole) of p-nitroaniline was dissolved in 10 ml. of water and 4 ml. of conc. hydrochloric acid, cooled to 0°, and then 16 ml. of a sodium nitrite solution prepared from 1.0 g. of sodium nitrite and 20 ml. of water was added all at once. After ten minutes the solution was clear, and the starch-iodide test slightly positive. The excess nitrous acid was removed by the addition of traces of sulfamic acid until the starch-iodide test was negative. This diazonium salt solution was added all at once to the solution of 4.8 g. (0.005 mole) of di-p-dimethylamino-phenylthallium bromide in 100 ml. of glacial acetic acid. A faint red color appeared almost immediately, and increased considerably when the solution was buffered with 20 g. of sodium acetate. The reaction was stirred for two hours, during which time a heavy precipitate formed as the solution was allowed to warm up to room temperature. At the end of this time it appeared that no more precipitate was forming, hence the reaction was filtered, the precipitate stirred into 75 ml. of water, filtered again and washed with water, and dried over potassium hydroxide in a vacuum. The precipitate melted at 227-230°, weighed 2.1 g., and contained no thallium. Apparently cleavage with coupling into the para-position had taken place,
with the formation of 4'-nitro-4-dimethylaminoazobenzene, which has been reported melting at 229-230°. The aqueous filtrate from the precipitate contained large amounts of thallium in solution.

A blank experiment in which di-p-dimethylaminophenylthallium bromide was treated with glacial acetic acid, hydrochloric acid, sulfamic acid and sodium acetate in exactly the above quantities, manner and times yielded the organothallium compound unchanged. This is the normal behavior of \( R_2TLX \) compounds, which are not usually cleaved even by strong mineral acids.

The Attempted Coupling of \( p \)-Nitrobenzenediazonium Chloride with Di-p-anisylthallium Bromide. A diazonium salt solution was prepared from 1.4 g. (0.01 mole) of \( p \)-nitroaniline, 10 ml. of water, 4 ml. of cone. hydrochloric acid, and 16 ml. of a sodium nitrite solution prepared from 1.0 g. of sodium nitrite and 20 ml. of water. The temperature was carefully maintained at 0°, and the solution of sodium nitrite was added all at once to the suspension of \( p \)-nitroaniline hydrochloride. The usual precautions mentioned in the preceding experiment to insure complete diazotization and the absence of an excess of nitrous acid were taken. To this diazonium salt solution was added 2.5 g. (0.005 mole) of di-p-anisylthallium bromide and 10 g. of sodium acetate. The reaction was stirred at 5°.

for ten hours, but there was no evidence of reaction, and when the mixture was warmed at the end of this time, there was a vigorous evolution of nitrogen and the unchanged di-p-anisylthallium bromide was recovered in practically quantitative amounts. The great insolubility of the R₂TIX compound and the known difficulty of coupling phenol ethers in general probably account for the absence of reaction.

The Attempted Coupling of p-Nitrobenzenediazoniium Chloride with Di-o-anisylthallium Bromide. Exactly the same quantities, temperature and time were employed as in the preceding experiment, except di-o-anisylthallium bromide was added instead of di-p-anisylthallium bromide to the diazonium salt solution. The reaction was stirred for ten hours, but there was no evidence of reaction, and unchanged di-o-anisylthallium bromide was recovered from the reaction. The reasons for lack of reaction are the same as in the preceding experiment: insolubility and general low reactivity toward the coupling reaction.

The Attempted Coupling of p-Nitrobenzenediazoniium Chloride with Di-p-anisylthallium Bromide in the Presence of Ethyl Acetate. A diazonium salt solution was prepared from 1.4 g. (0.01 mole) of p-nitroaniline, 10 ml. of water, 4 ml. of conc. hydrochloric acid, and 16 ml. of a sodium nitrite solution prepared from 1.0 g. of sodium nitrite and 20 ml. of water. The temperature was carefully maintained at 0°, and
the solution of sodium nitrite was added all at once to the suspension of \( p \)-nitroaniline hydrochloride. The usual precautions were taken to insure complete diazotization and the absence of an excess of nitrous acid. To this diazonium salt solution was added 2.5 g. (0.005 mole) of di-\( p \)-anisylthallium bromide and 10 g. of sodium acetate suspended in 100 ml. of ethyl acetate. The reaction was stirred at 5° for ten hours, but there was no evidence of reaction, and when the mixture was warmed at the end of this time, there was a vigorous evolution of nitrogen, and the unchanged di-\( p \)-anisylthallium bromide was recovered practically quantitatively.

**The Attempted Coupling of \( p \)-Nitrobenzenediazonium Chloride with Di-\( o \)-anisylthallium Bromide in the Presence of Ethyl Acetate.** The same materials, quantities, temperature, and time were employed as in the preceding experiment, with the sole exception that di-\( o \)-anisylthallium bromide was substituted for di-\( p \)-anisylthallium bromide. There was no evidence of reaction, and when the mixture was warmed at the end of ten hours, there was a vigorous evolution of nitrogen, and the unchanged di-\( o \)-anisylthallium bromide was recovered practically quantitatively.

**The Attempted Coupling of \( p \)-Nitrobenzenediazonium Chloride with Di-\( p \)-anisylthallium Bromide in the Presence of Pyridine.** A diazonium salt solution was prepared from 2.8 g. (0.02 mole) of \( p \)-nitroaniline, 20 ml. of water, 8 ml. of conc.
hydrochloric acid, and 32 ml. of a sodium nitrite solution prepared from 2.0 g. of sodium nitrite and 40 ml. of water. The temperature was carefully maintained at 0°, and the solution of sodium nitrite was added all at once to the suspension of p-nitroaniline hydrochloride. The usual precautions were taken to insure complete diazotization and the absence of an excess of nitrous acid. After the diazotium salt solution had been stirred for 15 minutes, 5.0 g. (0.01 mole) of di-p-anisylthallium bromide was added as a suspension in 50 ml. of 70% pyridine-30% water mixture. The reaction was allowed to stand for 48 hours, but there was no evidence of reaction with the di-p-anisylthallium bromide, which was recovered in practically quantitative amounts. There was some tar formation, probably due to the slow reaction of the diazonium salt with the pyridine.21, 22, 23

The Reaction between Methylmagnesium Chloride and Thallous Sulfate. As determined by titration, the yield in the preparation of the Grignard reagent from 9.7 g. (0.4 g. atom) of magnesium and an excess of methyl chloride (the methyl chloride gas was passed through the solution until all the magnesium had disappeared) in 500 ml. of ether was practically quantitative. The solution was cooled to -75°, and 25 g.

(21) Möhlau and Berger, Ber., 26, 1994 (1893).
(22) Kühling, Ber., 26, 523, (1895); ibid., 26, 165 (1896).
(0.05 mole, 0.1 g. equiv.) of very finely powdered thallous sulfate was added. There was no sign of reaction, and the solution was allowed to warm up to room temperature, and then was stirred overnight. In the morning there was no sign of reaction, such as the deposition of metallic thallium, and an aliquot portion of the solution was titrated: there was no change in titer. The solution was refluxed for four days, and then another aliquot portion was titrated: again there was no significant change in titer.

The Reaction between $\alpha$-Naphthyllithium and Thallous Sulfate. As determined by titration, $\alpha$-naphthyllithium was prepared from 40 g. (0.2 mole) of $\alpha$-bromonaphthalene and 3.5 g. (0.5 g. atom) of lithium in 75% yield. This solution was added dropwise to a suspension of 12.5 g. (0.025 mole, 0.05 g. equiv.) in 100 ml. of ether cooled to -75°. There was no evidence of reaction, and the mixture was allowed to warm up to room temperature, and was stirred overnight. An aliquot portion of the solution then showed no significant change in titer. The reaction was cooled to 0° and hydrolyzed by the gradual addition of 100 ml. of 10% hydrobromic acid. The ether layer was steam distilled, and 17.6 g. or 91.7% of naphthalene melting at 78-80° was obtained.

The Action of Diazomethane on Thallium Trichloride. Three and one-tenth grams (0.01 mole) of thallium trichloride in 40 ml. of anhydrous ether was treated by a constant stream of bubbles of diazomethane gas for a period of ten hours. At
no time was there any evidence of chemical reaction, such as evolution of nitrogen bubbles. At the end of this time, the ether was removed under reduced pressure, and the residue was examined by the conventional procedures for carbon and nitrogen, neither of which was found. Analysis showed the residue to be nearly pure thallium trichloride, with a trace of insoluble thallous chloride, evidently formed by a slow loss of chlorine from the trichloride.

Anal. Caled. for TlCl₃: Tl, 64.3. Found: Tl, 65.0.

The Preparation of Thallous 2,4,6-trinitrobenzoate.

Two and six-tenths grams (0.01 mole) of 2,4,6-trinitrobenzoic acid was dissolved in 100 ml. of 70% alcohol at 50° and slowly titrated with a 0.4 N solution of thallous hydroxide. A blood-red precipitate formed as each drop of thallous hydroxide solution hit the 2,4,6-trinitrobenzoic acid solution, evidently due to the momentary excess of thallous hydroxide forming a salt not only with the carboxyl group, but also with a nitro group. However, each drop of red precipitate redissolved as it sank to the bottom of the flask and thus came under the influence of an excess of 2,4,6-trinitrobenzoic acid. Accordingly, no indicator was necessary in the titration, for the instant there was an excess of thallous hydroxide above the one equivalent necessary for the titration of the carboxyl group, the whole solution turned blood-red. A few tiny crystals of the free acid were then added to decolorize the solution, and nearly
colorless needles precipitated rapidly as the solution cooled. The yield was 4.3 g. or 93% of thallous 2,4,6-trinitrobenzoate melting at 160-163° with decomposition and gas evolution. The compound flashed with a loud report when heated on a spatula.

Anal. Calcd. for C₃H₆O₅N₅Tl:  Tl, 44.3.

Found:  Tl, 44.1.

The Reaction between 2,4,6-Trinitrobenzoic Acid and Two Equivalents of Thallous Hydroxide. In order to demonstrate that the red precipitate transitorily encountered in the preparation of thallous 2,4,6-trinitrobenzoate actually contains more than one equivalent of thallium, 2.6 g. (0.01 mole) of 2,4,6-trinitrobenzoic acid was dissolved in 75 ml. of warm methanol and titrated with 9.6 ml. (0.01 mole) of 1.04 N thallous hydroxide solution. The same momentary formation of a red precipitate was observed as in the preparation of thallous 2,4,6-trinitrobenzoate. Then a second equivalent, 9.6 ml. (0.01 mole), of 1.04 N thallous hydroxide solution was added, and a heavy red precipitate formed rapidly. The flask was stoppered and shaken for one hour in a shaking machine and then allowed to stand at 0° for ten hours. The chocolate-red precipitate was filtered and dried, and then weighed 5.6 g. It was very explosive when heated on a spatula by an open flame. Analysis showed that a large additional amount of thallium had been taken up from the second
equivalent of thallous hydroxide, but did not give good agreement for any definite compound.

**Anal. Calcd. for C₆H₄O₃N₂Tl₂:** Tl, 61.7.

**Found:** Tl, 59.4.

**The Action of Thallous Hydroxide on 1,3,5-Trinitrobenzene.** Two and one-tenth grams (0.01 mole) of 1,3,5-trinitrobenzene was dissolved in hot methanol and 9.6 ml. (0.01 mole) of 1.04 N thallous hydroxide solution was added. The red precipitate which formed was allowed to stand at 0° overnight, and was then filtered and dried. The yield was 3.3 g. The compound did not melt, and was not especially explosive when heated on a spatula by an open flame. Analysis showed the compound to have nearly the thallium content demanded for the complex addition product of thallous hydroxide with 1,3,5-trinitrobenzene.

**Anal. Calcd. for C₆H₄O₃N₂Tl₂:** Tl, 46.9.

**Found:** Tl, 41.1.

When in a similar experiment 0.01 mole of 1,3,5-trinitrobenzene was titrated with 0.02 mole of thallous hydroxide solution, the precipitate obtained weighed 5.5 g. Analysis showed greater departure from the thallium content demanded by the complex addition product of 1,3,5-trinitrobenzene with two moles of thallous hydroxide.

**Anal. Calcd. for C₆H₄O₃N₂Tl₂:** Tl, 62.5.

**Found:** Tl, 56.8%.
Similarly, when 0.01 mole of 1,3,5-trinitrobenzene was titrated with 0.3 mole of thallous hydroxide solution, the precipitate obtained weighed 6.7 g. Analysis showed still greater departure from the thallium content demanded by the complex addition product of 1,3,5-trinitrobenzene with three moles of thallous hydroxide.

**Anal. Calcd. for C₉H₆O₃N₃Tl₃: Tl, 70.0.**

**Found: Tl, 62.5.**

**The Decarboxylation of Thallous 2,4,6-Trinitrobenzoate in Pyridine.**

Four and six-tenths grams (0.01 mole) of thallous 2,4,6-trinitrobenzoate was covered with 25 ml. of pyridine and slowly heated to boiling. At first the solution was clear, and the light yellow-brown crystals of thallous 2,4,6-trinitrobenzoate could be seen on the bottom of the flask. They appeared to be quite insoluble in pyridine. As the reaction was slowly warmed, solution took place, but apparently not without chemical reaction: for a short time the solution had an intense green color and all material appeared dissolved. Gradually, however, the color faded to a light brown that was almost transparent, and a very fine microcrystalline precipitate began to separate. The pyridine was refluxed gently for fifteen minutes after the first appearance of this precipitate, and then the reaction was allowed to stand overnight at 0°. The reaction mixture was then filtered, and water was added to the clear filtrate. A light yellow crystalline precipitate
gradually separated, and after the crystals had been allowed to grow overnight at 0° they were filtered off and dried.

The yield was 1.4 g. (67%) of material melting at 120-122° and showing no depression in a mixed melting point with an authentic sample of trinitrobenzene (m. p. 120-122°). The entire thallium content in the filtrate from this 1,3,5-trinitrobenzene was determined as thallous iodide, of which only 0.413 g. was obtained, showing that all but an insignificant amount of the original thallium was present in the microcrystalline precipitate which separated during the course of the reaction.

This precipitate was crystalline under the microscope and weighed 2.1 g. (84%). It melted in the neighborhood of 320° with decomposition and gas evolution. When heated in a test tube, no charring took place; instead, there was a strong gas evolution (the gas was identified with barium hydroxide water as carbon dioxide) and a droplet of molten thallium metal remained in the bottom of the test tube. The material was fairly readily soluble in hot water, and contained all its thallium in the univalent condition and none in the trivalent state. The compound contained no nitrogen, and was practically insoluble in boiling pyridine. The results in the quantitative determination of thallium gave reason to believe that the compound was thallous oxalate. This belief was strengthened by the comparison of the properties of an authentic sample of thallous oxalate as recorded below.
The Preparation of Thallous Oxalate. Although this compound is fairly well known, no record could be found of its melting point. This information was desired in connection with the identification of the thallous salt obtained in the pyridine decarboxylation of thallous 2,4,6-trinitrobenzoate. Nine-tenth gram (0.01 mole) of oxalic acid was covered with 50 ml. of water and brought to a vigorous boil while 26 ml. (0.02 mole) of 0.77 N thallous hydroxide solution was slowly added dropwise. During the titration the monothallous salt started to separate, but it went into solution as the remainder of the thallous hydroxide was added. The boiling solution was filtered from turbidity and allowed to cool. Glistening platelets separated rapidly, and the salt was quite insoluble in cold water. The solution was allowed to stand overnight at 0°, and was then filtered. The yield was 4.7 g. or 94%. The compound melted at 315-320° with decomposition and gas evolution. When heated in a test tube, there was no charring, but instead gas evolution and the formation of a droplet of molten thallium metal in the bottom of

the tube. Thallous oxalate was found to be practically insoluble in boiling pyridine.

**Anal. Calcd. for C₈O₄Tl₂: Tl, 82.5. Found: Tl, 82.3.**

**The Preparation of p-Iodophenylmagnesium Iodide.**
The reaction of magnesium on p-diodobenzene has been studied by several workers. Hydrolysis has been used to determine the yield of Grignard reagent, but this is not a satisfactory method, and carbonation by means of dry ice was used in the present studies, which were made to investigate the possibilities of this method for introducing the p-iodophenyl group into organometallic compounds. In a three-necked flask were placed 16.5 g. (0.05 mole) of p-diodobenzene, 1.2 g. (0.05 g. atom) of magnesium, and 100 ml. of n-butyl ether. It had been found in a preliminary experiment that neither ethyl ether nor toluene could be used as a solvent because of the extreme insolubility of the p-iodophenylmagnesium iodide (or its etherate); the reaction would begin in these solvents, but when a small amount of gummy material had coated over the magnesium, the reaction would stop. The reaction was heated with stirring on the steam-bath overnight and everything went into solution. Titration of an aliquot

(30) Mihăilescu and Caragea, *Bull. sect. sci. acad. roumaine*, 12, No. 4-5, 7 (1929); *C. A.*, 24, 2116 (1930).
portion by the usual method employing an excess of dilute acid as the hydrolyzing agent and back titration with standard base indicated a 54% yield. The remainder of the solution, when carbonated by pouring on dry ice and worked up by the usual procedures for the isolation of an acid, gave 6.2 g. or a 50% yield of crude p-iodobenzoic acid, m. p. 254-265°, from which the pure acid melting at 268-270° was readily obtained by sublimation. This yield by carbonation is in substantial agreement with the value found by titration.

The Halogen-Metal Interconversion of p-Iodophenol.
To 11.0 g. (0.05 mole) of p-iodophenol in 100 ml. of ether at room temperature was added slowly 0.1 mole of butyllithium in 150 ml. of ether. There was vigorous refluxing during the addition of the first equivalent (active hydrogen) and somewhat less vigorous refluxing during the addition of the second equivalent of butyllithium. The reaction was stirred for twenty minutes, and then carbonated by pouring on dry ice. The tube projecting into the flask containing the dry ice was nearly choked by the dilithium salt of the p-hydroxybenzoic acid formed by the gaseous carbon dioxide rushing out of the mouth of the flask. The rapidity of formation and great insolubility of this precipitate was very striking. At the same time a very characteristic red color was formed. Water was added, and then hydrochloric acid to acid reaction. The ether layer was separated and extracted three times with 10% potassium hydroxide solution. The alkaline layer was warmed and air
passed through to remove the small amount of ether it con-
tained, and then a small amount of phenols was removed by
passing carbon dioxide through the solution, until there
was no further precipitate. The phenols were then extracted
with ether, and the aqueous alkaline layer thus purified was
acidified with conc. hydrochloric acid. The p-hydroxybenzoic
acid was allowed to crystallize overnight at 0°, and the
weight of acid obtained was corrected for the known solubility
of p-hydroxybenzoic acid in water at 0°, viz., 0.17%. The
corrected weight was 3.3 g., which represented a 47.8% yield.
The crude acid melted at 211-215°, and after one recrystalliza-
tion from 70% methanol, melted at 215-216°.

**The Preparation of Thallous Naphthalene-β-sulfonate.**
Two and three-tenths grams (0.01 mole) of naphthalene-β-sul-
fonic acid monohydrate was dissolved in a very small amount of
warm water and titrated in the usual manner with thallous
hydroxide solution, using phenolphthalein as an indicator.
The precipitate which formed was dissolved by heating the
solution to boiling, and a small amount of turbidity, perhaps
due to traces of inorganic thallous salts, was removed by
filtration. The solution on cooling deposited beautifully
defined shining white crystals, which melted at 234-236°. The
yield was 3.8 g. or 92%.

**Anal. Calcd. for C_{10}H_{7}O_{3}STl: Tl, 49.7. Found, Tl, 49.5.**

**The Preparation of Thallous Benzenesulfonate.** Three
and two-tenths grams (0.02 mole) of benzenesulfonic acid was titrated with thallous hydroxide solution in the usual manner. The salt proved to be very soluble in water, and the volume of water had to be reduced by 80% in order to obtain a proper yield: 3.4 g. or 94% of thallous benzenesulfonate was thus obtained melting at 185-187°.

**Anal. Calcd. for C₈H₅O₂STl: Tl, 56.5. Found: Tl, 56.3.**

**The Preparation of Thallous Laurylsulfonate.** Two and seven-tenths grams (0.01 mole) of sodium laurylsulfonate and 2.5 g. (0.01 mole) of thallous formate were each dissolved in a small amount of water with warming, and the two solutions were poured together. There was no immediate precipitate. On cooling a soapy precipitate separated, and its crystalline structure was considerably improved by allowing it to stand overnight at 0°. The precipitate was filtered, twice recrystallized from water and once from 95% alcohol, and then thoroughly dried. The yield was 2.4 g. or 53%. The crystals sintered at 120° and showed a peculiar half-transparency, although the outlines of the crystal form were maintained. The compound remained in this condition until it melted fairly sharply at 143-145° to a clear melt.

**Anal. Calcd. for C₁₈H₃₆O₄STl: Tl, 45.1. Found: Tl, 44.6.**

**The Preparation of Thallous p-Toluenesulfinate.**

One and eight-tenths grams (0.01 mole) of sodium p-toluenesulfonate and 2.5 g. (0.01 mole) of thallous formate were each
dissolved in the minimum amount of hot water, and the solutions were poured together. There was an immediate white precipitate, which when filtered and dried weighed 3.2 g., which represented an 89% yield. The compound melted sharply at 154-156° without decomposition.


The Preparation of Lead o-Toluenesulfonate. Four and two-tenths grams (0.02 mole) of o-toluenesulfonic acid dihydrate was dissolved in a small amount of warm water, and to this solution was added 3.3 g. (0.01 mole) of lead acetate dissolved in a small amount of warm water. For nearly a minute after mixing the solutions there was no precipitate, then hard, well-defined crystals rapidly separated. They were filtered and dried, and then weighed 5.0 g., which represented a 90% yield. The compound could be very satisfactorily re-crystallized from hot water, but it showed no melting point up to 360°. The salt, but no melting point, has been widely described.


The Preparation of Monothallous Phenylphosphonate. One and six-tenths grams (0.01 mole) of phenylphosphonic acid was dissolved in 20 ml. of water at room temperature and 23 ml. (0.01 mole) of 0.436 N thallous hydroxide solution was added.
A slight turbidity was filtered off, and the clear filtrate was evaporated to dryness in a vacuum desiccator over calcium chloride. The residue was recrystallized from 70% alcohol (the salt was found to be very soluble in water and practically insoluble in boiling absolute alcohol). On cooling, glistening white platelets deposited from the solution. After filtration and thorough drying, they weighed 3.1 g., which represented an 86% yield of monothallous phenylphosphonate, melting very sharply at 200-201° without decomposition.

Anal. Calcd. for C₅H₅O₂PTl: Tl, 56.5. Found: Tl, 56.3.

The Preparation of Dithallous Phenylphosphonate.

Three and two-tenths grams (0.08 mole) of phenylphosphonic acid was dissolved in 30 ml. of water at room temperature and 52 ml. (0.04 mole) of 0.77 N thallous hydroxide solution was added. There was no true precipitate, but a slight amount of turbidity, probably due to traces of inorganic thallous salts, was removed by filtration. The clear filtrate was evaporated to dryness in a vacuum desiccator over calcium chloride. The residue was recrystallized from 50% alcohol (the salt was very soluble in water, but practically insoluble in boiling absolute alcohol). On cooling large shining crystals formed, which after filtration and careful drying weighed 4.5 g., which represented a 78% yield. When the melting point was determined under the microscope, a transition point was found at 260°, at which temperature a momentary liquid wave-front was seen to start from some point in each crystal and pass across and
through the entire crystal, solidification taking place immediately behind this wave-front. The compound then melted properly to a clear liquid phase at 317-320°. The yield was 4.5 g. or 79%.

Anal. Caled. for C₆H₆O₃PTl₂: Tl, 72.5 Found: Tl, 72.3.

The Preparation of Thallous Diphenylphosphonate.
Nine-tenths gram (0.0041 mole) of diphenylphosphonic acid (m. p. 193-195°) was covered with 10 ml. of water and heated to 90°; the compound was quite insoluble even in hot water. The gentle heating was continued while 5.4 ml. (0.0041 mole) of 0.77 N thallous hydroxide solution was added, when the undissolved diphenylphosphonic acid rapidly went into solution, showing that the thallous salt was much more soluble in water than the free acid. The solution was cooled and allowed to stand at 0° for five hours, but no crystals separated, again showing the solubility of the thallous salt in water. The clear solution was accordingly evaporated to dryness in a vacuum desiccator over calcium chloride, and the dry residue was recrystallized from 70% alcohol. The yield was 1.4 g. or 82% of glistening white crystals which melted at 203-205°. A mixed melting point with a specimen of the monothallous phenylphosphonate (m. p. 200-201°) prepared above started to melt at 140° and was nearly all liquid at 150°.

The Preparation of the Thallous Salt of Nitromethane.

Six-tenths gram (0.01 mole) of nitromethane was added to 5 ml. of methanol and titrated by 9.6 ml. (0.01 mole) of 1.04 N thallous hydroxide solution. A canary-yellow precipitate formed immediately, and was filtered and dried. The compound did not have a definite melting point, but decomposed gradually at temperatures above 160°. The compound darkened somewhat on standing, was readily soluble in water, and burned with a small flash but without explosion. The yield was 2.2 g. or 85%.


The Preparation of the Thallous Salt of Nitroethane.

One and five-tenths grams (0.02 mole) of nitroethane was dissolved in 10 ml. of methanol and 26 ml. (0.02 mole) of 0.77 N thallous hydroxide solution was added dropwise; there was no precipitate. The clear solution was evaporated to dryness in a vacuum desiccator over sulfuric acid. The golden-yellow, hard, well-defined crystals thus obtained melted at 80-82° with decomposition and gas evolution. The yield was 4.5 g., which was practically quantitative. Because of the low decomposition temperature no attempt was made to re-crystallize the compound. The compound burned with a flash when heated on a spatula by an open flame, but there was no explosion. A small pile of the salt was placed on an anvil and repeatedly hammered without any noticeable effect.
The Preparation of Thallous Methylmercaptoide. Four and eight-tenths grams (0.1 mole) of methyl mercaptan were dissolved in 20 ml. of methanol and titrated with thallous hydroxide solution until no further formation of the canary-yellow precipitate could be observed. The precipitate was quantitative, as it was very insoluble. It was noticed with this and the other aliphatic mercaptans mentioned below that the vapor alone of the mercaptan was sufficient to give a yellow precipitate with solutions of thallous hydroxide three or four feet distant. Also, the instant a stream of thallous hydroxide was allowed to fall from a burette into the flask containing the volatile aliphatic mercaptan in methanol solution, a solid yellow column sprang like a stalagmite up from the surface of the solution to the tip of the burette. The melting points of the aliphatic merccaptides were rather poor, often with some decomposition, and the thallous aliphatic mercaptides were evidently unstable, since they turned dark on standing in tightly stoppered vials. The aromatic mercaptides, however, were stable, and showed sharp melting points that could readily be used in the identification of these compounds. Thallous methylmercaptoide itself melted at 136-140° with decomposition, the melt turning a striking dark red.


The Preparation of Thallous Ethylmercaptoide. The compound was prepared as above, and decomposed at 96-100°
without melting.

**Anal. Calcd. for C₆H₁₃STl: Tl, 76.8. Found: Tl, 76.4.**

**The Preparation of Thallous n-Butylmercaptide.** The compound was prepared as above, and melted very poorly at 84-90° with decomposition.

**Anal. Calcd. for C₆H₁₃STl: Tl, 69.4. Found: Tl, 69.1.**

**The Preparation of Thallous Thiophenolate.** The compound was prepared by the general method given above. Recrystallized from absolute alcohol, it formed bright yellow needles which melted at 258-260°.

**Anal. Calcd. for C₆H₁₃STl: Tl, 65.2. Found: Tl, 65.0.**

**The Preparation of Thallous p-Thiocresolate.** The compound was prepared by the general method given above. Recrystallized from absolute alcohol, it formed pale yellow crystals which melted at 178-180°.

**Anal. Calcd. for C₆H₁₃STl: Tl, 62.3. Found: Tl, 62.0.**

**The Preparation of Thallous Thio-α-naphtholate.** The compound was prepared by the general method given above. Recrystallized from absolute alcohol, it formed pale yellow crystals which melted at 165-168°.

**Anal. Calcd. for C₁₀H₇STl: Tl, 56.2. Found: Tl, 55.9.**
The Attempted Preparation of Thallous Allylarsonate.

In this attempted preparation a sample of allylarsonic acid purchased from the Eastman Kodak Company was titrated in the usual manner with one equivalent of thallous hydroxide. As furnished, the compound is without a melting-point specification. The melting point, which is widely given in the literature as 128-129°, was found to be 129-135°. The fact that the melting point was high suggested the presence of inorganic matter, which is slow in dissolving in the melt of the allylarsonic acid, which begins to melt at the correct temperature. Actually as much as 10% of the compound was not soluble in water, and when filtered off would neither burn nor melt.

Allylarsonic acid is readily soluble in water, and is stable to one equivalent of sodium hydroxide at the boiling point of the aqueous solution.

One and seven-tenths grams (0.01 mole) of this sample of allylarsonic acid was dissolved in 20 ml. of water, filtered from the insoluble matter and titrated with 23 ml. of 0.436 N thallous hydroxide solution (0.01 mole). Again a small amount of precipitate formed, but this likewise proved to be inorganic. The clear solution was evaporated to dryness, and an oil was thus obtained. After standing one week at 0°, the compound was again dried over sulfuric acid in a vacuum desiccator. Gradually gummy crystals formed. These were covered with 95% alcohol, in which the greater part of the material was quite soluble; the insoluble material
appeared to be inorganic, and was filtered off. On cooling the alcoholic solution a small amount of fine crystals was obtained which melted poorly over a wide range and with decomposition in the neighborhood of 200°.

The Preparation of Thallium Dichloride p-Toluenesulfinate. (I) From Sodium p-Toluenesulfinate. Seventeen and eight-tenths grams (0.1 mole) of sodium p-toluenesulfinate and 38.2 g. (0.1 mole) of thallium trichloride tetrahydrate were each dissolved in the minimum amount of water at 40° and the solutions mixed. There was an immediate precipitate, with a very slight gas evolution and odor of p-toluenesulfonyl chloride. The precipitate was filtered, washed with water, and dried over calcium chloride. It weighed 36 g., which represented an 84% yield of thallium dichloride p-toluenesulfinate melting at 203-205° with decomposition. Qualitative analysis demonstrated the presence of sulfur, chlorine, and thallium. Boiling in water did not eliminate sulfur dioxide with the formation of a carbon-metal linkage, as has been observed with related mercury compounds.31,32,33

Anal. Calcd. for C₁₂H₁₀Cl₂ST₁: T₁, 47.4.
Found: T₁, 47.6.

(31) Peters, Ber., 38, 2567 (1905).
(II) From p-Toluenesulfinic Acid. One and six-tenths grams (0.01 mole) of p-toluenesulfinic acid and 3.8 g. (0.01 mole) of thallium trichloride tetrahydrate were each dissolved in the minimum amount of water at 40° and the solutions mixed. A precipitate gradually formed, and after it had been allowed to digest for two hours at 0° it was filtered, washed, dried, and weighed: 3.2 g. of material was obtained, which represented a 75% yield of thallium dichloride p-toluenesulfinate which melted at 203-205° with decomposition and showed no depression in a mixed melting point with the thallium dichloride p-toluenesulfinate prepared from sodium p-toluenesulfinate.

The Preparation of Thallous Terephthalate. One and seven-tenths grams (0.01 mole) of pure terephthalic acid was covered with 15 ml. of water and boiled vigorously while titrated with thallous hydroxide solution, using phenolphthalein as an indicator. For an instant just as the end point was reached, everything was in solution, but then the thallous terephthalate rapidly started to separate from the boiling solution, and more separated as the solution was allowed to cool. The yield was 5.2 g. or 91% of shining colorless crystals which did not melt at 340°.

Anal. Calcd. for C₈H₆O₄Tl₂: Tl, 71.4. Found: Tl, 71.3.

The Action of Thallous Formate on Acetone Sodium Bisulfite. One and six-tenths grams (0.01 mole) of acetone
sodium bisulfite was dissolved in a small amount of water and treated with a solution of 2.5 g. (0.01 mole) of thallous formate dissolved in a small amount of water. There was an immediate white precipitate, which would not burn or char. This compound containing no carbon was shown by analysis to be thallous bisulfite.

Anal. Caled. for TlHSO₃: Tl, 71.5. Found: Tl, 71.1.

The Recovery of Thallium. All organic residues, filtrates, filter papers and other similar material containing thallium were placed as they accumulated in a four-liter beaker, and the greater part of the organic matter was destroyed by heating with one liter of nitric acid on the steam-bath. The residue was taken to fumes with sulfuric acid, and any small amount of organic matter remaining was oxidized with hydrogen peroxide. Two or three liters of water were then added, whatever amount was necessary to dissolve the salts at the boiling point, the solution was filtered from insoluble matter (barium sulfate, etc.), the filtrate was reduced to the thallous state by sodium arsenite, and then precipitated by sodium chloride (or bromide, iodide, or other ion which would produce an insoluble thallous salt). The precipitate was washed by decantation (the precipitate was found to be very heavy, and always settled rapidly) five or six times very thoroughly, and then was washed with alcohol several times, filtered and dried. The material may then be used directly for the prepara-
tion of thallium trichloride or other inorganic thallium preparation. From two to three hundred grams of thallous chloride were thus recovered at one time in one operation.
DISCUSSION OF RESULTS

In general, two methods are available for the synthesis of water-soluble organothallium compounds: the organothallium molecule may be solubilized through the acid radical or "X group" (only \( R_x Tl X \)) compounds are considered in this discussion) or it may be solubilized by the introduction of certain groups into the aromatic nuclei in compounds such as diphenylthallium bromide. Water-solubility in itself is not difficult to attain in the three types of organothallium compounds which are stable enough to be employed pharmacologically: \( RTlX_x \), \( R_x Tl X \) and \( R_x Tl^* \). Very many compounds are known which have the necessary one percent solubility in water, for instance, ethylthallium dibromide, phenylthallium dichloride, diethylthallium chloride, diphenylthallium fluoride, dimethylthallium acetylacetone, or diethylthallium acetoacetate. But some of these compounds, for instance ethylthallium dibromide,\(^{16}\) have been found to be very toxic, while others, such as diphenylthallium fluoride might well be assumed to be toxic, since the compounds are known to ionize into \( R_x Tl^+ \) and \( X^- \), and the fluoride ion is known to be toxic. Although in general \( RTlX_x \) compounds are much more soluble in water than \( R_x Tl X \) compounds, they are also less stable. In some respects the chelate compounds of the type \( R_x Tl^* \) are also rather unstable, and the members of the aliphatic series which are soluble in water (in general,
methyl, ethyl, and in some instances propyl derivatives) are also quite extensively hydrolyzed, the solution really containing the dialkylthallium hydroxide and the chelate compound.

Indeed, it is likely true that the relatively low toxicity of diphenylthallium bromide is due to its great insolubility in water, the thallium thus becoming only very slowly available as an active participant in body processes. This explanation, however, will not hold for dimethylthallium bromide, which is the least toxic of all trivalent thallium compounds tested and reported, and yet it is fairly soluble in water. A similar lack of toxicity has been reported for certain trimethyllead derivatives. One of the most fundamental questions yet to be answered, a question on which the choice of organometallic compounds for therapeutic application must be based, is whether the organometallic molecule exerts its physiological action as an entire molecule, or whether its action is due to a gradual cleavage of the organic groups from the molecule. Probably both modes of action are possible, and they may even be simultaneous. In general, the synthesis of extremely insoluble organothallium compounds, while it might produce non-toxic material, would also in all probability vitiate at the same time any physiological activity the metal might have; the material

would simply be excreted unchanged. Thus, the non-toxic water-soluble type (such as dimethylthallium bromide) is to be preferred to the non-toxic water-insoluble type. An investigation might well be made to determine whether various organometallic compounds are cleaved by the maximum acid and alkaline pH values found anywhere in the body of various animals.

Since there never has been any great difficulty in finding a number of acid radicals ("X groups") whereby dialkylthallium compounds of the type $R_2TLX$ could be made water-soluble, more attention was given to diarylthallium salts. Since the usual starting material is the diarylthallium bromide, the common double-decomposition reaction in pyridine with a silver salt is in general the most direct method of synthesis, but it is not infallible. Diphenylthallium sulfanilate thus was readily prepared from diphenylthallium bromide and silver sulfanilate, both of which are readily soluble in hot pyridine, whereas silver bromide is not. Unfortunately, diphenylthallium sulfanilate was found to be insoluble in water, thus demonstrating that the number of non-toxic acids capable of putting any given diarylthallium base into aqueous solution is certainly limited. Other difficulties are encountered in using this method: certain silver salts are insoluble in pyridine, such as silver sulfamate, while other silver salts react in hot pyridine, such as silver...
aminoacetate, which is considerably reduced by boiling in pyridine. Silver lactate was quite soluble in warm pyridine, and by this method di-2-pyridylthallium lactate was prepared from the insoluble di-2-pyridylthallium chloride. It proved to be quite soluble in water.

Silver saccharide was found to be very soluble in warm pyridine, and dimethyl-, diethyl-, and diphenylthallium saccharides were prepared from the corresponding halides by this double-decomposition method. Dimethyl- and diethyl-thallium saccharides were found to be readily soluble in water, but diphenylthallium saccharide was too insoluble. For comparison, thallous saccharide was prepared: it melted at 228-229° and was very soluble in water.35

It would be interesting to employ thallous salts in those cases where the silver salt was insoluble in pyridine, or was otherwise unsatisfactory. It is entirely possible that thallous salts would be found to be soluble in cases where the corresponding silver salts were insoluble, because the solubility of an inorganic salt in pyridine is probably not a case of simple solution, and thallium has a much stronger coordination force than silver. If some such double-decomposition reaction is not employed, the most general method would be to first prepare the organothallium base from the halide

(35) Studies by Mr. Gordon O'Donnell.
with silver oxide, and then neutralize this with the desired acid, a method which has been widely used, but which requires an additional step.

The other general method whereby organothallium compounds of the type \(R_2TlX\) may be made water-soluble is to modify the "R group". Again, the chief present consideration will be confined to diarylthallium salts. Challenger and Rothstein showed\(^5\) that the nitration of diphenylthallium nitrate takes place in the meta-position, but they did not attempt to isolate any organothallium compound from this reaction, but instead cleaved the entire reaction mixture with bromine and isolated \(m\)-nitrobenzene. Mel'nikov and Rokitskaya\(^7\) were unable to isolate any \(di-m\)-nitrophenylthallium salt from the nitration of diphenylthallium bromide, but their reaction temperature was probably too high. However, by employing the proper conditions it has been found possible in the present studies to carry out this direct nitration in reasonable yield. The compound, however, is more readily prepared from \(m\)-nitrophenylboric acid in the customary manner with aqueous thallium trichloride. The corresponding \(di-m\)-aminophenylthallium salt has never been prepared, and great difficulties would have to be faced in the synthesis of this compound.

Two methods are open for the synthesis of \(di-m\)-aminophenyl-thallium chloride: (1) the reduction of \(di-m\)-nitrophenylthallium chloride, and (2) the reaction between thallium trichloride and
m-aminophenylboric acid. Di-m-nitrophenylthallium chloride is very insoluble; in fact, the only solvent in which it has any appreciable solubility is pyridine, which is a poor solvent for reductions, either direct catalytic reduction by hydrogen, or by more usual reductions using the common inorganic reducing agents. In the second instance, thallium trichloride is known to exert a strong oxidizing effect on aniline and related derivatives (see p. 98) with the formation of chlorinated dyes.

The direct sulfonation of an organothallium compound has not previously been attempted. It has been found possible, however, to take advantage of the great insolubility of R₃TLX compounds and their resistance to acid cleavage to directly sulfonate diphenylthallium bromide, once in each aromatic nucleus, in the meta-position. The extreme insolubility in water of diphenylthallium bromide is thus reduced to a point where the compound may be easily re-crystallized from water. At low temperatures there does not appear to be any very great tendency for fuming sulfuric acid to cleave diphenylthallium bromide. However, an exchange of salt radicals does take place, and the final product is di-2-(4-sulfotoluene)thallium sulfate. The compound is readily soluble in sodium hydroxide solution, may be titrated with standard base to a good end-point with phenolphthalein,

and the sodium salt thus obtained is readily soluble in water.

The position of sulfonation was established by cleaving the di-2-(4-sulfotoluene)thallium sulfate by bromine. The thallous salt of the χ-bromotoluenesulfonic acid thus obtained gave no depression in a mixed melting point with an authentic sample of thallous 2-bromotoluene-4-sulfonate.

The discovery that the thallous salts of sulfonic acids possess sharp melting points and melt without decomposition opened up some important possibilities. A variety of thallous salts of different sulfonic acids was prepared\(^\text{37}\) and without exception they all showed good melting points, usually without decomposition. Two general methods of preparation were used, depending on whether the starting material was in the form of the free sulfonic acid or as a sodium sulfonate. When the starting material was in the form of the free sulfonic acid, titration with thallous hydroxide invariably gave a good derivative. When resort had to be made to the double decomposition between thallous formate and a sodium sulfonate, in a few cases the thallous sulfonate was just as soluble as the sodium sulfonate, and no precipitate could be obtained; such was the case, for example, with sodium benzenesulfonate. Thallous benzenesulfonate was prepared, however, by the direct

titration of benzenesulfonic acid, and the compound proved to
be extremely soluble in water.

If the thallous hydroxide solution is first standardized,
the process of preparing a derivative of a sulfonic acid also
provides a neutral equivalent on the compound. The thallous
sulfonate can then readily be alkylated, for instance with
methyl iodide, to obtain another derivative. Generally, the
compounds crystallize very well, can be easily recrystallized
from water or various water-alcohol mixtures, exhibit a
variety of melting points, possess a wide range of solubilities,
and show large depressions in mixed melting point determinations.
It was found that very small amounts of material could readily
be characterized by this simple and quick method. No record
could be found in the literature of the preparation of any
thallous sulfonate, although a large number of various types
of thallous salts has been recorded, many of which also show
excellent melting point characteristics.

No alkylsulfonic acid was available for direct titration
with thallous hydroxide solution. Accordingly, the only
method used was the double decomposition between thallous
formate and a sodium sulfonate. Several attempts to obtain
thallous n-butylsulfonate by this method were unsuccessful;
an inorganic precipitate was obtained, and no pure thallous
salt could be isolated. Thallous laurylsulfonate, however,
was obtained by this method, although not in very good yield.
The melting point phenomena observed under the microscope made
it seems very probable that this compound forms liquid crystals, and really has two melting points, as has been observed by several workers for all the thallous salts of the fatty acids above butyric.\textsuperscript{38,39,40,41} Further work on several compounds, preferably with the aid of the polarizing microscope, would be necessary to establish this point definitely.

Lead, mercury, and silver salts were made of several aromatic sulfonic acids. Although these heavy metal salts were all known, no record could be found of attempts to take their melting points. Actually it was found that such salts do not melt at 350° and the belief in the apparently unique property of thallium was strengthened. The bivalent nature of lead and mercuric mercury is also a disadvantage. On several grounds it could be predicted that the cesium salts might most nearly approach the thallous sulfonates in melting point and solubility characteristics.

The work on the preparation of thallous salts was extended to include some of the related acids. Salts of sulfinic, and phosphonic acids were prepared, and many other obvious possibilities await trial. Both the mono- and dithallous salts of phenylphosphonic acid were obtained, and

\begin{enumerate}
\item[(38)] Vorländer, \textit{Ber.}, \textbf{43}, 3120 (1910).
\item[(39)] Holde and Selim, \textit{Ber.}, \textbf{58}, 523 (1925).
\item[(40)] Holde and Takehara, \textit{Ber.}, \textbf{58}, 1788 (1925).
\item[(41)] Walter, \textit{Ber.}, \textbf{59}, 962 (1926).
\end{enumerate}
both possessed good melting points.

The alkyl mercaptans formed very insoluble thallous salts, but the melting points were poor. These salts, however, would provide a ready method for the detection and separation of a mercaptan in mixtures with neutral components. The thallous salts of aromatic thiophenols, in sharp contrast, were stable well-defined crystalline bodies with satisfactory melting points.

Nitromethane gave a crystalline thallous salt which did not melt; nitroethane, one which melted with decomposition. The usefulness of this class of thallous salts would thus appear to be limited. Trinitrobenzene formed blood-red thallous salts of rather indefinite composition: the amount of thallium in the salt was regularly increased as the trinitrobenzene was treated with an increasing number of equivalents of thallium. These compounds were all somewhat explosive, but in varying degree.

It was hoped that the thallous salt of terephthalic acid would melt, and that it would thus be possible to derivatize this troublesome compound more rapidly and easily than at present may be done by the preparation of the methyl ester. Thallous terephthalate did not melt at 340°. Thallous oxalate melted with decomposition in the neighborhood of 320°.

Attempts to prepare organothallium compounds directly from thallous sulfate, using either methylmagnesium chloride or α-naphthyllithium, were unsuccessful. Thallous sulfate
is completely insoluble in ether, and could be refluxed for long periods with active organometallic compounds without the slightest sign of action. It would be of some advantage if the commercially available form of thallium, thallous sulfate, could be used directly in the preparation of organothallium compounds, without first being converted to the chloride or trichloride, but its action appears to be unlike that of the halides.

It was likewise without success that attempts were made to react diazomethane with thallium trichloride in ether solution. This is somewhat surprising, since mercuric chloride is nearly insoluble in ether and yet reacts as a suspension to give high yields of chloromethylmercury chloride, whereas thallium trichloride is completely soluble in ether, and yet gives no sign of reaction. It had been intended to extend this reaction, if successful, to the introduction of the \(\beta\)-chloroethyl group into organothallium compounds.

The preparation of organolead compounds containing diazo linkages has been carried out with striking success. Similar efforts to obtain related organotin compounds were not very fruitful. This is distinctly unusual, and at the present not completely explainable, for in general it is true that many reactions have been found to take place with tin,

but not with lead; the converse of this statement, that
reactions that take place with lead do not take place with
tin—with the exception of cleavage reactions—rarely has been
found to hold good.

On the contrary, this very resistance of tin compounds
to acid cleavage should make it easier to obtain diazo com-
ounds. The same may be said for thallium compounds of the
type R₄TLX, which are very much more resistant to acid
cleavage than are lead compounds; yet in the only case where
any action was observed with R₄TLX compounds, the reaction
was demonstrated to be that of cleavage. Two major difficulties
(omitting such considerations as inherent chemical reactivity
toward the coupling reaction, since it is still unknown
whether the presence of a metal increases or decreases the
tendency to undergo coupling) stand in the way of preparing
organothallium compounds containing the diazo linkage: (1)
the difficulty of preparing starting materials which would be
likely to undergo ready coupling, and (2) the insolubility of
R₄TLX compounds in nearly all solvents. When a fourth group,
such as o-hydroxyphenyl or p-aminophenyl, is added to an
R₄PbX compound there are in general only two simple
possibilities: either a lead-carbon linkage results or a lead-
oxygen (or lead nitrogen) bond is formed. Probably both
reactions take place, with the former predominating, but the
second has been little investigated. Such an investigation
would require the preparation of such typical compounds as
triphenyllead phenoxide and triphenyllead N-anilide. With thallium the case is more complicated, since the usual starting material is thallium trichloride, which has three valences which may be substituted either by a carbon-bond or by an oxygen-bond, or—as is more likely—by a combination of such bonds. The yield in the preparation of di-o-hydroxyphenylthallium bromide was only 15%, and this particular application of the halogen-metal interconversion reaction was abandoned; this meant that the compounds which could be more readily prepared in higher yields, such as di-p-dimethylaminophenylthallium bromide, di-o-anisylthallium bromide, and di-p-anisylthallium bromide, were subjected to the action of diazonium salts, although it is reasonable to believe that they would be less reactive toward coupling.

The second difficulty, the great insolubility of R₂T₅X compounds in most solvents, also could not be satisfactorily met. In several experiments ethyl acetate was used as a solvent, partly because R₂T₅X compounds do have some small solubility in this solvent, which does not interfere in the coupling reaction of a diazonium salt, and partly because it had been successfully used with lead compounds. Pyridine was also used, but a gradual reaction of this solvent with the diazonium salt was noticed.

The reaction of di-p-dimethylaminophenylthallium bromide with p-nitrobenzenediazonium chloride to give 4'-nitro-4-dimethylaminoazobenzene, i. e., a cleavage product
is very interesting, since a parallel experiment containing exactly the same substances with the exception of sodium nitrite showed no cleavage. In other words, the acid present apparently was not responsible for the cleavage as such, and it may be assumed that the p-nitrobenzenediazonium chloride, either directly or indirectly, itself functioned as a cleavage agent. Much further work would, of course, be necessary to confirm this assumption.

In conclusion it might be mentioned that the double-decomposition reaction between acetone sodium bisulfite and thallous formate gave a precipitate of thallous bisulfite. Until further experiments are conducted on related aldehyde and ketone bisulfite addition products, and the absence of such impurities as sodium bisulfite is demonstrated, it would be hasty to assume that a carbon-sulfur linkage is not present, as is now generally believed. It should be pointed out, however, that thallium might be a powerful tool in such investigations, for the probability is high that melting point determinations could be made on various isomeric structures and mixed melting points would then afford positive identification.

SUMMARY

By means of the double-decomposition reaction between a diarylthallium halide and a silver salt of a water-soluble acid various diarylthallium salts have been prepared which have some slight solubility in water; but it was shown that the choice of acids is limited if both the criteria of water-solubility and non-toxicity are to be met. Certain salts, moreover, could not be prepared by this reaction.

The direct nitration and sulfonation of an \( \text{R}_\text{2} \text{TLX} \) compound was successfully carried out for the first time, and the position of substitution was carefully established. It was found that \( \text{di-}^m\text{-nitrophenylthallium chloride} \) was prepared more readily and in better yields, however, by the reaction between \( m\text{-nitrophenylboric acid} \) and thallium trichloride in aqueous solution. \( \text{Di-}^2\text{-}^4\text{-sulfotoluene} \text{thallium sulfate} \) was found to have a very favorable solubility in water, and its sodium salt was readily prepared by direct titration, and was found to be stable and easily soluble in water. The use of the thallous salt of \( 2\text{-bromotoluene-4-sulfonic acid} \) as a derivative of a sulfonic acid—since it possessed a sharp melting point—led to the preparation of several thallous sulfonates, all of which were found to possess excellent melting points. The work was then extended to include thallous salts of sulfinic acids, mono- and disubstituted
phosphonic acids, all of which likewise proved to be suitable derivatives.

Carefully detailed conditions were worked out for the preparation of thallous hydroxide and thallous ethoxide in one-hundred gram quantities. Diethylthallium ethoxide was prepared from diethylthallium chloride and thallous ethoxide, also by using the cheaper sodium ethoxide. The compound could be readily distilled, but was immediately hydrolyzed by contact with water.

2-Pyridyllithium, when reacted with thallium trichloride, gave di-2-pyridyldithallium chloride in very good yield. Various thallium tribromide and trichloride complexes of pyridine, 2-aminopyridine, 2-bromopyridine, cysteine, and related compounds were prepared and their melting points determined. Useful solubility data were also obtained, which were compared with the solubility of di-2-pyridyldithallium chloride. Various organolithium compounds with functional groups were prepared by the interconversion of the corresponding halides, but they gave only very low yields of \( \text{R}_\text{X} \text{TI} \text{X} \) compounds when reacted with thallium trichloride. For instance, di-o-hydroxyphenylthallium bromide was obtained in 15% yield by this reaction.

Amino and phenolic compounds were desired as starting material for the preparation of \( \text{R}_\text{X} \text{TLX} \) compounds containing the diazo linkage. The low yields of these compounds as obtained
via the halogen-metal interconversion reaction made it seem more expedient to prepare such compounds as were available by the direct Grignard reaction, although it was believed they would be less reactive toward the coupling reaction. Di-ortho- and di-p-anisylthallium bromide and di-ortho- and di-p-dimethylaminophenylthallium bromide were prepared, but they could not be made to undergo coupling with p-nitrobenzenediazonium chloride. The diazonium salt apparently cleaved di-p-dimethylaminophenylthallium bromide, since the product isolated from the reaction was 4'-nitro-4-dimethylaminoazobenzene. Di-p-dimethylaminophenylthallium bromide was shown to be stable to the same acid concentrations employed in the reaction with p-nitrobenzenediazonium chloride.

The reaction of thallous hydroxide with several nitroparaffins, alkyl mercaptans, thiophenols, dibasic acids, allylarsonic acid, and acetone sodium bisulfite is also recorded.