Reactions of some high-molecular-weight fatty acid derivatives

Miles Randolph McCorkle

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REACTIONS OF SOME HIGH-MOLECULAR-WEIGHT FATTY ACID DERIVATIVES

by

Miles R. McCorkle

A Thesis Submitted to the Graduate Faculty for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject Organic Chemistry

Approved:

Signature was redacted for privacy.

In charge of Major work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State College
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ACKNOWLEDGMENT

The author wishes to express his appreciation to Dr. Henry Gilman for valuable suggestions and encouragement given during the progress of these investigations.
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INTRODUCTION

In recent years the attention of organic chemists has turned increasingly to aliphatic chemistry. This has doubtless been partially due to the increasing availability of key compounds for further work. Particularly, the attention of organic chemists has turned to long-chained compounds in which the starting material is usually a naturally occurring fatty acid, i.e., lauric, palmitic, oleic or stearic acids. For example, long-chained alcohols have become available commercially because of recent improvement in methods of catalytic hydrogenation of esters (1). Other examples are the preparation of long-chained nitriles, ketones and amines.

In investigating the reactions of long-chained compounds the question of the limits of homology arises. That is, is there a difference in kind or in degree as one ascends an n-aliphatic series with a given reaction? A review of previous chemistry of long-chained compounds reveals little real difference in many types of reactions. Thus, acid amides are readily dehydrated to nitriles in very good yields up to and including melissamide (C₃₀). In general, it may be said that functional groups in normal aliphatic compounds undergo the same reactions with perhaps some differences in rates. With

regard to this we may state Conant's (2) conclusions from investigations of the rates of reaction of various halides: "In a great variety of reactions a methyl halide is 5 to 20 times more reactive than the ethyl compound which in turn is only about twice as reactive as the other primary straight-chain compounds that do not differ materially from one another, at least, as high in the series as C_{30}H_{61}Cl".

In cases where there appears to be a difference in kind with reactions of normal straight-chained compounds, one may always say that changes in conditions may make the reaction perfectly normal. Thus, the acetoacetic ester condensation is (3) successful for only the first members of the normal aliphatic ester series unless one of the products is removed as the reaction proceeds (ethyl alcohol). Under these conditions the reaction is about equally effective for the \( \alpha \)-aliphatic series of esters, at least as far as ethyl stearate.

In contrast to this view, Whitmore (4) contends that a knowledge of the chemistry of the first two or three members of a series does not necessarily typify the chemistry of the entire series. This is best illustrated by the saturated aliphatic alcohols. The primary, secondary, and tertiary

(3) Briese and McElvain, ibid., 55, 1697 (1933).
alcohols differ considerably in their reactions and methods of preparation. There even appears to be some differences within a primary alcohol series; isobutyl alcohol, \((\text{CH}_3)_{2-}\text{CHCH}_2\text{OH}\), gives most of the reactions of a primary alcohol, but in the preparation of the bromide a considerable amount of \(t\)-butyl bromide is formed. These differences are considered to disappear as one ascends the series. In an \(n\)-aliphatic series of alcohols there appears to be little, if any, difference in reactions or methods of preparation.

This thesis is concerned with an investigation of some of the reactions of long-chained fatty acid derivatives, particularly, the nitriles, ketones, acid chlorides, and alcohols since they are readily available as mentioned in the fore part of this discussion. It was hoped this work would serve two purposes: first, it would make available further compounds which might either be commercially useful themselves, or provide intermediates for use in further synthetic work; and, secondly, the extent and conditions necessary for conducting the reactions might shed further light on the limits of homology.
HISTORICAL

Nitriles. The usual method for preparing nitriles by dehydration of amides with phosphorous pentachloride (5), or thionyl chloride (6) is entirely satisfactory for long-chain nitriles, but the cost of reagents and time consumed in the preparation make this method impractical for obtaining any quantity of material. In view of this a method was developed for the preparation of nitriles from the acid and an excess of ammonia by Ralston, Harwood, and Poole (7) by passing gaseous ammonia into the acid at about the boiling point of the acid. Using this method yields in excess of seventy-five per cent of nitriles from lauric acid up to and including stearic acid may be obtained. The preparation of nitriles containing an odd number of carbon atoms may be accomplished by the interaction of an \( \text{p-alkyl halide} \) and potassium cyanide (8).

Thioamides. Thioamides are generally prepared by one of two methods, the interaction of an amide and phosphorous pentasulfide (9), or the thiohydrolysis of nitriles (10).

(5) Krafft and Stauffer, Ber., 15, 1728 (1882).
Bleyberg and Ulrich, Ber., 64, 2504 (1931).
(9) Hantzsch, Ann., 250, 254 (1889); Hofmann, Ber., 11, 540 (1878).
Of the two methods the latter is much to be preferred as it is more general and gives better yields. In the presence of ammonium hydrosulfide, nitriles add hydrogen sulfide to form thioamides. However, in the absence of ammonium hydrosulfide nitriles do not react with hydrogen sulfide and accordingly, it has been shown that an amidine is formed as an intermediate which reacts further with hydrogen sulfide to form the thioamide (11).

Kindler (10) made a thorough study of catalysts and conditions for the formation of thioamides from nitriles. He found that sodium hydrosulfide and potassium hydrosulfide gave the best yields (80-95 per cent). The reactions are carried out in a closed apparatus in order to prevent loss of hydrogen sulfide. Both aromatic and aliphatic nitriles react to give good yields of thioamides.

**β-Imino-nitriles.** Aliphatic nitriles containing a hydrogen on the α-carbon atom polymerize in the presence of suitable condensing agents to form β-imino-nitriles (12) through the addition of one molecule of the nitrile to a second molecule. The reaction is usually written as follows:

\[
\text{RCH}_2\text{CN} \rightarrow \text{RCHC}=\text{N}-/\text{Na}\left[+ \text{RCH}_2\text{CN} \rightarrow \text{RCH}_2\text{C}=\text{CHR}^\text{CN} \right]_{/\text{Na}}
\]

A variety of condensing agents effect the reaction such as

(11) Bernthsen, Ann., 192, 29 (1878).
as sodium (12), sodium ethoxide (13), and numerous organo-
alkali compounds (14). Ziegler (14) has succeeded in making
a number of large ring compounds by intermolecular condensa-
tion of dinitriles using substituted lithium amides. In
addition, he condensed acetonitrile and $n$-butyronitrile with
the same catalysts and found they gave nearly quantitative
yields of $\beta$-imino-nitriles. The statement was made that the
reaction was equally effective with other nitriles, although
no experimental details were given. Upon mild hydrolysis
the $\beta$-imino-nitriles pass into $\beta$-keto-nitriles which in turn,
upon vigorous hydrolysis, yield symmetrical ketones in fair
yields.

Ketones. In many cases the interaction of a Grignard
reagent with a nitrile gives an excellent yield of ketone
after hydrolysis of the ketamine which is first formed (15).
It has been reported that aliphatic nitriles give poor yields
of ketones with aromatic Grignard reagents (16); beside small
amounts of ketones, there was isolated some tertiary alcohols
and di- and trimolecular products formed by the interaction

(12) E. von Mayer, J. prakt. Chem., (2) 27, 152 (1883);
Holzwart, ibid., 39, 230 (1889).
(14) Ziegler and Ohlinger, Ann., 495, 84 (1932); Ziegler,
Eberle, and Ohlinger, Ann., 504, 94 (1933).
(15) Blaise, Compt. rend., 132, 33 (1900); Moureu and
Mignonac, ibid., 156, 1801 (1913).
Zentr., t, 86 (1923).
of the nitrile. However, it has been shown that by using a ratio of four moles of phenylmagnesium bromide to one mole of nitrile fair yields of ketones (17) may be obtained using the normal aliphatic nitriles from acetonitrile to valeronitrile. The lowest yield reported with a straight-chain nitrile was seventy per cent. Aliphatic Grignard reagents do not usually appear to give as good yields of ketones as do aromatic Grignard reagents (18). Alkyl-aryl ketones have been obtained in excellent yields by the interaction of approximately molecular quantities of aromatic Grignard reagents and lauro- and stearonitrile (19). Likewise, long-chain amides and aromatic Grignard reagents give ketones in fair yields (20).

Long-Chained Secondary and Tertiary Amines. High-molecular-weight amines, both tertiary and secondary, have found considerable use as detergents, flotation agents and in numerous other ways, and in consequence the synthesis of them is described by a number of different methods.

If a high-molecular-weight ester of sulfuric acid is treated with an excess of ammonia, secondary amines are ob-

Zentr., III, 123 (1923)/.
/Cl. A., 2, 1712 (1913)/
tained. Di-n-octadecylamine has been obtained in this manner (21).

It has also been claimed that heating of an alkyl halide with ammonia (aqueous) under pressure gives the secondary amine exclusively (22).

Di-n-tetradecylamine and di-n-hexadecylamine have been synthesized by interaction of the n-alkyl bromide with cyanamide followed by hydrolysis of the dialkylcyanamide (23). No yields were given for any of these preparations.

Walden (24) obtained di-n-hexadecylamine by heating n-hexadecylamine and hexadecyl iodide in a sealed tube. The reaction was apparently complex, as n-hexadecyl- and tri-n-hexadecylamine were also found.

Adkins and co-workers (25) have found that the hydrogenation of acid amides or substituted acid amides, using their copper-chromium oxide catalysts, gives mixtures of primary and secondary amines. For example, hydrogenation of lauramide gave a mixture of di-n-dodecylamine (49 per cent) and n-dodecylamine (48 per cent).

The hydrogenation of ammonium laureate gave a 79 per cent

(22) English Patent, 437, 530 (1935) (Chem. Zentr., I, 3216 (1936)).
(23) Staudinger and Rossler, Ber., 62, 48 (1936).
yield of di-\(n\)-dodecylamine and only 14 per cent of \(n\)-dodecylamine. However, the reaction was not applied to higher amides.

The formation of secondary amines in this type of reaction is attributed to the following reaction:

\[
2R\text{NH}_2 \longrightarrow R_2\text{NH} + \text{NH}_3
\]

It should also be mentioned that the hydrogenation of nitriles gives a mixture of primary and secondary amines \((26)\) and, as will be shown later \((27)\), this method may be adapted to the preparation of long-chain secondary amines.

The formation of secondary amines during the catalytic hydrogenation of nitriles is generally attributed to the following scheme of reactions \((28)\):

\[
\begin{align*}
\text{RC\text{NH} + H}_2 & \longrightarrow \text{RCH=NH} \\
\text{RCH=NH} & \longrightarrow \text{RCH}_2\text{NH}_2 \\
\text{RCH=NH + RCH}_2\text{NH}_2 & \longrightarrow \frac{\text{RCHNHCH}_2\text{R}}{\text{NH}_2} \\
\frac{\text{RCHNHCH}_2\text{R} + \text{H}_2}{\text{NH}_3} & \longrightarrow \frac{\text{RCH}_{2}\text{NHCH}_2\text{R} + \text{NH}_3}{\text{RCH}_{2}\text{NCH}_2\text{R} + \text{H}_2} \longrightarrow \text{RCH}_{2}\text{NHCH}_2\text{R}
\end{align*}
\]

\((27)\) This thesis, page 68.
Frideau (29) prepared tri-n-hexadecylamine by passing a stream of ammonia into heated hexadecyl iodide. The only product isolated was tri-n-hexadecylamine. This reaction has since been applied to the preparation of tri-n-octadecylamine (23).

Tri-n-dodecylamine (30) has been prepared by the interaction of n-dodecyl alcohol, chlorosulfonic acid and ammonia. One of the most convenient methods for the preparation of tertiary amines (31) is by the interaction of two moles of a secondary amine with one mole of an n-alkyl halide. This not only gives excellent yields, but the products are easily isolated. It proceeds according to the following equation:

\[ 2R_2NH + RCl \rightarrow R_3N + R_2NH \cdot HCl \]

Fries Rearrangement of Esters of 4-Hydroxybiphenyl. The first attempt to obtain a Fries rearrangement of an ester of 4-hydroxybiphenyl was made by Blake and Weinkauf (32). By heating a solution of 4-benzoyloxybiphenyl in n-tetrachloroethane with aluminum chloride, they obtained a small yield of what they supposed was 4-hydroxy-4'-benzoylbiphenyl. They offered no proof for this conclusion aside from obtaining a compound from a Friedel-Crafts reaction with 4-methoxybiphenyl

(32) Blake and Weinkauf, ibid., 54, 330 (1932).
and benzoyl chloride, which was identical with the Fries rearrangement product after methylation.

At a later date Hey and Jackson (33) reinvestigated the rearrangement of 4-benzoyloxybiphenyl using essentially the same conditions to effect the reaction as had the previous authors. However, the only product isolated, aside from a little 4-hydroxybiphenyl, was 4-hydroxy-3-benzoylbiphenyl. In order to prove the structure of this product they synthesized it by interacting 4-methoxy-3-biphenylmagnesium bromide and benzaldehyde and oxidizing the carbinol so formed to 4-methoxy-3-benzoylbiphenyl. This compound was identical with the compound obtained by methylation of the Fries rearrangement product from 4-benzoyloxybiphenyl.

From the Friedel-Crafts reaction between 4-methoxybiphenyl and benzoyl chloride they obtained 4-methoxy-4'-benzoylbiphenyl. This was proven by synthesis of the compound from 4-benzoylbiphenyl by nitration, reduction of the nitro group and replacement of the amino group by a hydroxyl through the diazonium reaction. Methylation of this compound gave 4-methoxy-4'-benzoylbiphenyl which was identical with the compound from the Friedel-Crafts synthesis.

In the absence of solvent (34) the product of the Fries

rearrangement of 4-benzoyloxybiphenyl is 4-hydroxy-4'-benzo
ylbiphenyl. No trace of 4-hydroxy-3-benzoxylbiphenyl was
found. In addition to 4-methoxy-4'-benzoxylbiphenyl, the
Friedel-Crafts reaction between 4-methoxybiphenyl and benzoyl
chloride yielded a small amount of 4-methoxy-3-benzoxylbiphenyl.

Fieser and Bradsher (34) in studying the orientation of
4-methoxybiphenyl in the Friedel-Crafts reaction investigated
the Fries rearrangement of 4-acetoxylbiphenyl. They found
the products of rearrangement were 4-hydroxy-4'-acetobiphenyl
and supposedly 4-hydroxy-3-acetobiphenyl. After methylation
these products were identical with the products obtained
from the Friedel-Crafts reaction between 4-methoxybiphenyl
and acetyl chloride. The structure of the 4-methoxy-4'-ace
tobiphenyl obtained from the Friedel-Crafts reaction was
established by oxidation to the known 4-methoxy-4'-carboxy-
biphenyl. However, the position of the aceto group in the
other isomer from the Friedel-Crafts reaction was not es-
tablished, although it was assumed to be 4-methoxy-3-aceto-
biphenyl. Accordingly, the constitution of 4-hydroxy-3-
acetobiphenyl obtained from the Fries rearrangement of 4-
acetoxylbiphenyl is not established.

Sulphonation of Biphenyl and Diphenyl Ether and Deriva-
tives. Sulphonation of biphenyl and diphenyl ether and
derivatives has not been extensively studied. However, it
has been found that biphenyl may be mono- or disulfonated
depending on the conditions. Thus, with concentrated sulfuric acid the principal product is biphenyl-4-sulfonic acid. The position of the sulfonic group was demonstrated by fusion with potassium hydroxide to give the known 4-hydroxybiphenyl. With more vigorous conditions a second sulfonic group was introduced. This sulfonic acid on fusion with potassium hydroxide gives 4,4'-dihydroxybiphenyl, proving the sulfonic acid to be biphenyl-4,4'-disulfonic acid.

On treating 4-nitrobiphenyl with concentrated sulfuric acid 4-nitrobiphenyl-4'-sulfonic acid (35) was obtained. On treating biphenyl-4-sulfonic acid with a mixture of sulfuric acid and nitric acid the same sulfonic acid was obtained which resulted from the sulfonation of 4-nitrobiphenyl, thereby proving the structures of both compounds.

Pollak and co-workers (37) made an investigation of the sulfonation of biphenyl under a variety of conditions. In g-tetrachloroethane, biphenyl is mono-sulfonated by chlorosulfonic acid to give biphenyl-4-sulfonic acid, while with chlorosulfonic acid alone the product is biphenyl-4,4'-disulfonic acid. Under different conditions another product is formed beside the biphenyl-4,4'-disulfonic acid; 2,2'-

(35) Latechinow, Ber., 6, 194 (1873); Kaiser, Ann., 257, 101 (1890).
(36) Gabriel and Damberges, Ber., 13, 1408 (1880).
(37) Pollak and co-workers, Monatsch., 54, 90 (1929); 55, 358 (1930).
biphenylenesulfone-4,4'-disulfonic acid.

An investigation of the sulfonation of diphenyl ether and some of its derivatives has been made by Suter (38). He found that diphenyl ether may be either mono- or disulfonated depending upon the experimental conditions. The entering sulfonic groups were attached in the case of the mono-sulfonic acid derivative to the 4-position, and in the disulfonic acid product, the entering groups, occupied the 4,4'-positions. Proof of this was obtained by bromination of the sodium salt of the sulfonic acids. The disulfonic acid yielded 4,4'-dibromodiphenyl ether and the monosulfonic acid gave a mixture of 4,4'-dibromodiphenyl ether and sodium 4-bromophenoxybenzene-4'-sulfonate. All attempts to obtain hydroxydiphenyl ethers by fusion with alkalis were unsuccessful, the ether linkage was cleaved in every case.

4-Bromodiphenyl ether on sulfonation with either chlorosulfonic acid, or concentrated sulfuric acid gave 4-bromophenoxybenzene-4'-sulfonic acid.

Sulfonation of Long-Chained Alkyl-Aryl Ketones and Hydrocarbons. The literature contains very little on the sulfonation of long-chained alkyl-aryl ketones, or hydrocarbons. Krafft (39) found that both hexadecyl and octadecylbenzene gave a monosulfonic acid on treatment with

(39) Krafft, Ber., 19, 2984 (1886).
concentrated sulfuric acid. By fusing these products with potassium hydroxide phenols were obtained, although no attempt was made to prove the positions of the groups. Likewise, the same reactions were carried out with 4-methyloctadecylbenzene.

Somewhat later, Adam (40) carried out the same reactions through to the phenol. In addition, he carried out a Friedel-Crafts reaction with anisole, palmitoyl and stearoyl chlorides, and reduced the ketone linkages by the Clemmensen reaction. Upon demethylation, the products were identical with those obtained by sulfonation of n-hexadecyl- and n-octadecylbenzene, followed by fusion with alkalis. Although it was not proven, the sulfonic and hydroxyl groups were assumed to occupy the para position in the benzene ring.

Again in 1936 Seidel and Engelfried (41) repeated the sulfonation of octadecylbenzene. However, as with previous workers no attempt was made to prove the position of the sulfonic group. Attempts to sulfonate stearylphenone were unsuccessful, but 2-stearoylnapthalene readily gave a monosulfonic acid with concentrated sulfuric acid. The position of the entering group was not established.

High-Molecular-Weight Hydrocarbons. A large amount of work has been done with the synthesis and isolation from

(41) Seidel and Engelfried, Ber., 69, 2567 (1936).
natural sources of high-molecular-weight hydrocarbons. Normal aliphatic hydrocarbons occur naturally in a number of materials, notably in waxes, petroleum and coal products. It is the intention of this review to attempt to cover all the high-molecular-weight aliphatic hydrocarbons known. Particular attention will be paid to synthesis, since many of the compounds isolated from natural sources are of somewhat doubtful purity.

Years ago, Krafft (42) synthesized the normal aliphatic hydrocarbons from $n$-undecane to $n$-pentatriacontane. Three general methods were employed in these preparations; reduction of a fatty acid by heating with hydroiodic acid and phosphorous in a sealed tube at $240^\circ$, Wurtz reaction with $n$-alkyl iodides and sodium, and reduction of ketones by first treating with phosphorous pentachloride followed by reduction with hydroiodic acid and phosphorous.

The last mentioned method was the more flexible, since it allowed the ready synthesis of hydrocarbons with both odd and even number of carbon atoms. For example, by the dry distillation of barium stearate ($C_{18}$) he obtained stearone ($C_{35}$), which could then be reduced to $n$-pentatriacontane.

By the dry distillation of barium stearate and barium heptylate he obtained 7-tetracosanone, which on reduction,

(42) Krafft, Ber., 15, 1687, 1713 (1882); Ber., 19, 2218 (1888).
yielded tetracosane.

Table I, gives the compounds prepared, their respective melting points and the methods of preparation used.
<table>
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<td>% Yield</td>
<td>Reaction Description</td>
</tr>
<tr>
<td>-----------------</td>
<td>----------</td>
<td>---------</td>
<td>----------------------------------------------------------</td>
</tr>
<tr>
<td>Eicosane</td>
<td>$C_{20}H_{42}$</td>
<td>36.7</td>
<td>Reduction of 7-eicosanone Wurtz reaction with $n$-decyl iodide</td>
</tr>
<tr>
<td>Heneicosane</td>
<td>$C_{21}H_{44}$</td>
<td>40.4</td>
<td>Reduction of 12-tricosanone</td>
</tr>
<tr>
<td>Docosane</td>
<td>$C_{22}H_{46}$</td>
<td>44.4</td>
<td>&quot; &quot; 7-docosanone</td>
</tr>
<tr>
<td>Tricosane</td>
<td>$C_{23}H_{48}$</td>
<td>47.7</td>
<td>&quot; &quot; laurone</td>
</tr>
<tr>
<td>Tetracosane</td>
<td>$C_{24}H_{50}$</td>
<td>51.1</td>
<td>&quot; &quot; 7-tetracosanone</td>
</tr>
<tr>
<td>Heptacosane</td>
<td>$C_{27}H_{56}$</td>
<td>59.5</td>
<td>&quot; &quot; myristone</td>
</tr>
<tr>
<td>Hentriacontane</td>
<td>$C_{31}H_{64}$</td>
<td>68.1</td>
<td>&quot; &quot; palmitone</td>
</tr>
<tr>
<td>Dotriacontane</td>
<td>$C_{32}H_{66}$</td>
<td>70.0</td>
<td>Wurtz reaction with $n$-hexadecyl iodide</td>
</tr>
<tr>
<td>Pentatriacontane</td>
<td>$C_{35}H_{72}$</td>
<td>74.7</td>
<td>Reduction of stearone</td>
</tr>
</tbody>
</table>
At a later date, Krafft (43) obtained the complete series of hydrocarbons from \( \pi \)-nonadecane to \( \pi \)-hexatriacontane by the distillation of brown coal in very high vacuum.

During the course of work on the proof of structure of some naturally occurring fatty acids, Levene (44) had occasion to synthesize several hydrocarbons. Two general methods were employed; reduction of the \( \pi \)-alkyl iodide with zinc and hydrochloric acid in glacial acetic acid, and coupling of \( \pi \)-alkyl iodides with magnesium by means of the Grignard reaction. The yields from the latter reaction were not very good and there was a considerable waste of Grignard reagent.

It should be said at the outset, that the melting points reported by these investigators were in many cases higher than any reported previous to their work and also in any later work. Consequently, many of these melting points are considered to be incorrect.

The following table gives the compound prepared, their melting points, and the method of preparation employed.

(43) Krafft, Ber., 29, 1323 (1896).
(44) Levene and co-workers, J. Biol. Chem., 10, 477 (1914); 20, 521 (1915).
Table II.
Normal Aliphatic Hydrocarbons (Levene)

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>M. P., °C.</th>
<th>Method of Preparation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexadecane</td>
<td>C\textsubscript{16}H\textsubscript{34}</td>
<td>20</td>
<td>Reduction of ( n )-hexadecyl iodide</td>
</tr>
<tr>
<td>Octadecane</td>
<td>C\textsubscript{18}H\textsubscript{38}</td>
<td>28</td>
<td>&quot; &quot; ( n )-octadecyl iodide</td>
</tr>
<tr>
<td>Eicosane</td>
<td>C\textsubscript{20}H\textsubscript{42}</td>
<td>38</td>
<td>&quot; &quot; ( n )-eicosyl iodide</td>
</tr>
<tr>
<td>Docosane</td>
<td>C\textsubscript{22}H\textsubscript{46}</td>
<td>47</td>
<td>&quot; &quot; ( n )-docosyl iodide</td>
</tr>
<tr>
<td>Tetracosane</td>
<td>C\textsubscript{24}H\textsubscript{50}</td>
<td>54</td>
<td>Action of magnesium on ( n )-dodecyl iodide</td>
</tr>
<tr>
<td>Hexacosane</td>
<td>C\textsubscript{26}H\textsubscript{64}</td>
<td>59-60</td>
<td>Action of magnesium on ( n )-tridecyl iodide</td>
</tr>
<tr>
<td>Octacosane</td>
<td>C\textsubscript{28}H\textsubscript{58}</td>
<td>64-65</td>
<td>Action of magnesium on ( n )-tetradecyl iodide</td>
</tr>
<tr>
<td>Triacontane</td>
<td>C\textsubscript{30}H\textsubscript{62}</td>
<td>69-70</td>
<td>Action of magnesium on ( n )-pentadecyl iodide</td>
</tr>
<tr>
<td>Dotriacontane</td>
<td>C\textsubscript{32}H\textsubscript{66}</td>
<td>74-75</td>
<td>Action of magnesium on ( n )-hexadecyl iodide</td>
</tr>
</tbody>
</table>
### TABLE II (Continued)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Melting Point</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetratriacontane</td>
<td>$C_{34}H_{70}$</td>
<td>76-76.5</td>
<td>Action of magnesium on $n$-heptadecyl iodide</td>
</tr>
<tr>
<td>Hexatriacontane</td>
<td>$C_{36}H_{74}$</td>
<td>78.5</td>
<td>Action of magnesium on $n$-octadecyl iodide</td>
</tr>
</tbody>
</table>
Gascard (45) has obtained a number of hydrocarbons through the Wurtz reaction. Thus, \( n \)-triacontane and \( n \)-hexatriacontane were obtained by the interaction of \( n \)-pentadecyl iodide and \( n \)-octadecyl iodide, respectively, with sodium. The yields from these reactions were rather small. By the reduction of \( n \)-dotriacontanyl iodide with sodium amalgam, dotriacontane was obtained.

With the object of establishing the number of carbon atoms in ceryl, myricyl and lacceryl alcohols, obtained from natural products, he synthesized a number of hydrocarbons. The alcohols were first treated with phosphorous and iodine, followed by reduction which gave the normal hydrocarbon. The melting points were then compared with those of the normal hydrocarbons made by a known reaction. The alcohols proved to have 27, 31 and 32 carbon atoms, respectively, on the basis of this data. Some additional proof was obtained by degrading lacceryl alcohol to myricyl alcohol and the synthesis of dotriacontanoic acid from myricyl iodide through myricyl cyanide.

At a later date the constitution of these products has been questioned (46). From Chinese wax, by fractional

(45) Gascard, Compt. rend., 43, 1484 (1911); 49, 258 (1914); Ann. chim., 9/16, 332 (1921).
distillation of the acetates, there were obtained two products. These respective alcohols were oxidized to acids. Examination of the crystal spacing of the first specimen indicated that it was a mixture of C_{26} and C_{28} acids, and the other sample consisted, therefore, of even higher acids.

The hydrocarbon, however, obtained by reduction of ceryl alcohol from Chinese wax had the same melting point as reported by Gascard. Nevertheless, examination of the crystal spacing showed quite clearly the presence of more than one paraffin, so that the so-called ceryl alcohol is probably a complex mixture of alcohols of a mean molecular weight corresponding to 1-heptacosanol.

In a similar manner, doubt was cast upon the identity of the so-called myricyl alcohol. It, seemingly, was a mixture of alcohols containing up to 34 carbon atoms.

These results, of course, makes it probable that the various derivatives reported in the literature starting from these alcohols are mixtures.

The following table gives the hydrocarbons obtained by Gascard with their melting points, and the method used for their synthesis.
<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>M. P., °C.</th>
<th>Method of Preparation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Octadecane</td>
<td>C\textsubscript{18}H\textsubscript{38}</td>
<td>28</td>
<td>Reduction of \textit{n}-octadecyl iodide</td>
</tr>
<tr>
<td>Hexacosane</td>
<td>C\textsubscript{26}H\textsubscript{54}</td>
<td>56.5</td>
<td>Wurtz reaction with \textit{n}-nonyl iodide</td>
</tr>
<tr>
<td>Heptacosane</td>
<td>C\textsubscript{27}H\textsubscript{56}</td>
<td>59.5</td>
<td>Reduction of ceryl iodide</td>
</tr>
<tr>
<td>Triacontane</td>
<td>C\textsubscript{30}H\textsubscript{62}</td>
<td>65.6-66</td>
<td>Wurtz reaction with \textit{n}-pentadecyl iodide</td>
</tr>
<tr>
<td>Henetriacontane</td>
<td>C\textsubscript{31}H\textsubscript{64}</td>
<td>69.0</td>
<td>Reduction of myricyl iodide</td>
</tr>
<tr>
<td>Dotriacontane</td>
<td>C\textsubscript{32}H\textsubscript{66}</td>
<td>70.5</td>
<td>Reduction of \textit{l}-lacceryl iodide and Wurtz reaction with \textit{n}-hexadecyl iodide</td>
</tr>
<tr>
<td>Tetratriacontane</td>
<td>C\textsubscript{34}H\textsubscript{70}</td>
<td>73.2</td>
<td>Wurtz reaction with \textit{n}-heptadecyl iodide</td>
</tr>
<tr>
<td>Hexatriacontane</td>
<td>C\textsubscript{36}H\textsubscript{74}</td>
<td>76.0</td>
<td>Wurtz reaction with \textit{n}-octadecyl iodide</td>
</tr>
<tr>
<td>Tetrpentatriacontane</td>
<td>C\textsubscript{64}H\textsubscript{110}</td>
<td>96.0</td>
<td>Wurtz reaction with ceryl iodide</td>
</tr>
<tr>
<td>Compound</td>
<td>Formula</td>
<td>Wurtz Reaction with Myriocyl Iodide</td>
<td></td>
</tr>
<tr>
<td>-------------------</td>
<td>-----------</td>
<td>-------------------------------------</td>
<td></td>
</tr>
<tr>
<td>Dodecatriacontane</td>
<td>C_{122}H_{256}</td>
<td>100.6</td>
<td></td>
</tr>
<tr>
<td>Tetradecacontane</td>
<td>C_{124}H_{260}</td>
<td>102.0</td>
<td></td>
</tr>
</tbody>
</table>
By plotting the melting points of the above hydrocarbons against the number of carbon atoms, a smooth curve was obtained, from which the melting points of normal aliphatic hydrocarbons hitherto not prepared could be predicted.

In this connection, others have found that the plot of the melting point of normal aliphatic hydrocarbons against the number of carbon atoms gives a smooth curve. Hildebrand and Wachter (47) have found some of the values given by "International Critical Tables" to be too high. They suggest the following melting points taken from the curve for normal hydrocarbons from C_{19}H_{40} to C_{36}H_{74}; C_{19}H_{40}(m. p. 32\degree), C_{20}H_{42}(m. p. 36.5\degree), C_{21}H_{44}(m. p. 40.5\degree), C_{22}H_{46}(m. p. 44\degree), C_{23}H_{48}(m. p. 47.5\degree), C_{24}H_{50}(m. p. 51\degree), C_{25}H_{52}(m. p. 54\degree), C_{26}H_{54}(m. p. 57\degree), C_{27}H_{56}(m. p. 59.5\degree), C_{28}H_{58}(m. p. 62\degree), C_{29}H_{60}(m. p. 64\degree), C_{30}H_{62}(m. p. 66\degree), C_{31}H_{64}(m. p. 68\degree), C_{32}H_{66}(m. p. 70\degree), C_{33}H_{68}(m. p. 72\degree), C_{34}H_{70}(m. p. 73.5\degree), C_{35}H_{72}(m. p. 75\degree), and C_{36}H_{74}(m. p. 76\degree).

There is no alternation of melting points of the even and odd members of the series, at least, starting with n-nonadecane, although below n-pentadecane there appears to be alternation of the melting points.

The melting points of normal hydrocarbons up to and including n-heptatriacontane, likewise fall upon a smooth

While investigating the scope of the Clemmensen (49) reaction, it was applied to the reduction of some long-chain ketones. Thus, \( n \)-undecane was obtained from 2-hendecanone; \( n \)-nonadecane from 2-nonadecanone; and \( n \)-pentatriacontane from stearone. It should be mentioned that with the longer-chained ketones an extended period of time is required, and large amounts of zinc amalgam and hydrochloric acid, although the yields are very good.

One of the best ways for obtaining extremely pure hydrocarbons is through electrolysis of an appropriate alkali salt of fatty acid. According to Petersen (50), the mechanism is as follows:

\[
\begin{align*}
\text{I.} & \quad 2\text{C}_{11}\text{H}_{23}\text{COOH} \rightarrow 2\text{C}_{11}\text{H}_{23}\text{CO} + \text{H}_2 \\
\text{II.} & \quad 2\text{C}_{11}\text{H}_{23}\text{COOH} + \text{H}_2\text{O} \rightarrow 2\text{C}_{11}\text{H}_{23}\text{COOH} + [\text{O}] \\
\text{III.} & \quad 2\text{C}_{11}\text{H}_{23}\text{COOH} \rightarrow \text{C}_{22}\text{H}_{46} + 2\text{CO}_2
\end{align*}
\]

In addition to the hydrocarbon a small amount of ester is formed, which was accounted for by the following scheme:

\[
2\text{C}_{11}\text{H}_{23}\text{COOH} \rightarrow \text{C}_{11}\text{H}_{23}\text{COOC}_{11}\text{H}_{23} + \text{CO}_2
\]

Using this method the following compounds were prepared; \( n \)-docosane (m. p. 44.4\(^\circ\)), \( n \)-hexacosane (m. p. 56.6\(^\circ\)), \( n \)-triacontane (m. p. 66.1\(^\circ\)), and \( n \)-tetratriacontane (m. p. 72.9\(^\circ\)).


(49) Clemmensen, \textit{Ber.}, 46, 1638 (1913).

(50) Petersen, \textit{Z. Elektrochem.}, 12, 141 (1906).
It has long been known that plant waxes contain many substances, notably paraffins and long-chain alcohols, besides true waxes such as ceryl cerotate. In order to identify the components of various waxes, it was necessary to have highly purified synthetic compounds as a standard of comparison. With this in mind, Chibnall and co-workers (51) prepared a number of normal paraffin hydrocarbons.

The hydrocarbons, with uneven number of carbon atoms, were prepared by a Clemmensen reduction of the corresponding ketones, which were prepared from the even number carbon atom acids by heating with iron. Unsymmetrical ketones were obtained by successive reaction, between ethyl sodio-acetoacetates and appropriate \( n \)-alkyl halides, followed by ketone hydrolysis of the disubstituted acetoacetic esters. The Wurtz reaction was used in the synthesis of \( n \)-octacosane, \( n \)-dotriacontane and \( n \)-hexatriacontane. Electrolysis of appropriate fatty acids was used for the synthesis of \( n \)-hexacosane, \( n \)-triacontane, and \( n \)-tetracontane.

The following table gives the hydrocarbons, their melting points and methods of preparation.

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>M. P., °C.</th>
<th>Method of Preparation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexacosane</td>
<td>C₂₅H₅₄</td>
<td>56.4-56.6</td>
<td>Electrolysis of myristic acid</td>
</tr>
<tr>
<td>Heptacosane</td>
<td>C₂₇H₆₆</td>
<td>59.0-59.1</td>
<td>Reduction of myristone</td>
</tr>
<tr>
<td>Octacosane</td>
<td>C₂₈H₆₈</td>
<td>61.4-61.6</td>
<td>Wurtz reaction with n-tetradecyl iodide</td>
</tr>
<tr>
<td>Nonacosane</td>
<td>C₂₉H₆₀</td>
<td>63.4-63.6</td>
<td>Reduction of 10-nonacononone</td>
</tr>
<tr>
<td>Triacontane</td>
<td>C₃₀H₆₂</td>
<td>65.8-65.8</td>
<td>Electrolysis of palmitic acid</td>
</tr>
<tr>
<td>Hentriacontane</td>
<td>C₃₁H₆₄</td>
<td>67.6-67.8</td>
<td>Reduction of palmitone</td>
</tr>
<tr>
<td>Dotriacontane</td>
<td>C₃₂H₆₆</td>
<td>69.5-69.7</td>
<td>Wurtz reaction with n-hexadecyl iodide</td>
</tr>
<tr>
<td>Tetratriacontane</td>
<td>C₃₄H₇₀</td>
<td>72.6-72.8</td>
<td>Electrolysis of stearic acid</td>
</tr>
<tr>
<td>Pentatriacontane</td>
<td>C₃₅H₇₂</td>
<td>74.4-74.6</td>
<td>Reduction of stearone</td>
</tr>
<tr>
<td>Hexatriacontane</td>
<td>C₃₆H₇₄</td>
<td>75.7-75.9</td>
<td>Wurtz reaction with n-octadecyl iodide</td>
</tr>
</tbody>
</table>
According to these authors, melting points and mixed melting points are not a reliable method of determining the purity of hydrocarbons. As an example, a mixture of equimolar parts of \( \text{n} \)-hexacosane and \( \text{n} \)-octacosane melts at the same point at which \( \text{n} \)-heptacosane melts (89.1°). X-Ray pictures were found to be much more reliable, since in some cases in which the melting point was correct, x-ray pictures showed the compound contained an impurity. Further, the x-ray pictures were valuable in giving a clue to the structure of compounds thus leading to their identification by synthesis.

A method for removing impurities from hydrocarbons; such as, ketones, esters, etc., was developed by heating the mixture with concentrated sulfuric acid at 130° for thirty minutes. This process was repeated until the sulfuric acid layer was not blackened by further heating.

Carothers and co-workers (49) synthesized the normal aliphatic hydrocarbons from \( \text{n} \)-icosane to \( \text{n} \)-heptatriacontane by a Wurtz reaction between decamethylene bromide and sodium.

The course of the reaction was written as follows:

\[
\begin{align*}
\text{Br(CH}_2\text{)}_{10}\text{Br} + 2\text{Na} & \rightarrow \text{Br(CH}_2\text{)}_{10}\text{Na} + \text{NaBr} \\
\text{Br(CH}_2\text{)}_{10}\text{Na} + (\text{C}_2\text{H}_5\text{)}_2\text{O} & \rightarrow \text{H(CH}_2\text{)}_{10}\text{Br} + \text{C}_2\text{H}_5\text{ONa} + \text{C}_2\text{H}_4 \\
\text{Br(CH}_2\text{)}_{10}\text{Na} + \text{Br(CH}_2\text{)}_{10}\text{Br} & \rightarrow \text{Br(CH}_2\text{)}_{20}\text{Br} + \text{NaBr} \\
\text{H(CH}_2\text{)}_{10}\text{Br} + 2\text{Na} & \rightarrow \text{H(CH}_2\text{)}_{10}\text{Na} + \text{NaBr}
\end{align*}
\]
According to this scheme, the hydrocarbons present will be composed of a series differing by $\text{H(CH}_2\text{)}_{10}$—. By careful distillation, using a molecular still, the following hydrocarbons were isolated; n-eicosane (m. p. 35-35.6°), n-triacontane (m. p. 65-66°), n-tetracontane (m. p. 80.5-81°), n-pentacontane (m. p. 91.9-92.3°), n-hexacontane (m. p. 98.5-99.3°), and n-heptacontane (m. p. 105-105.5°).

There was a considerable residue left after removal of the n-heptacontane which was not distillable (decomposition), even at a pressure of 0.04 mm. of mercury and a bath temperature of 300°. It was considered probable that n-octacontane and even higher hydrocarbons were present, but they could not be isolated by crystallization. From this data, the authors drew the conclusion that no organic compound with a molecular weight much in excess of 1000 will be distillable. In support of this, the molecular cohesion of n-heptacontane may be calculated, and is about 71,000 calories; and that of n-octa-
contane is 81,000 calories. The heat of separation of the
carbon to carbon bond is 75,000, so therefore, \( n \)-octacontane
should not be distillable on the basis of these facts.

Recently (52), a method for the synthesis of hydro-
carbons has been developed through the use of a modified
Grignard reaction. In the reaction between magnesium and the
\( n \)-alkyl iodides above \( n \)-octyl iodide, it was found the Wurtz
reaction takes place to the extent of from 25-28 per cent.
If the Grignard reagent which was formed was destroyed by io-
dine, according to the following equation; \( \text{RMgI} + \text{I}_2 \rightarrow \text{RI} + \text{MgI}_2 \)
the iodide may then again be reacted with magnesium
to form the Grignard reagent with the attendant Wurtz reaction
again taking place. Repetition of this process five times
gave yields of about 65 per cent of the desired hydrocarbon.

By this method the following paraffins may be prepared;
\( \text{C}_{12}^2 \text{H}_{26}, \text{C}_{14}^2 \text{H}_{30}, \text{C}_{16}^2 \text{H}_{34}, \text{C}_{18}^2 \text{H}_{38}, \text{C}_{24}^2 \text{H}_{50}, \text{C}_{28}^2 \text{H}_{58}, \text{C}_{32}^2 \text{H}_{66}, \text{C}_{36}^2 \text{H}_{74} \)
"etc.

It was mentioned that the obtainment of long-chained com-
ounds in a pure state is a difficult matter, and, at least
with paraffins, mixed melting points are of little value in
determining the purity of a given sample. Apparently, x-ray
and calorimetric methods are to be preferred in measuring
purity.

Incidentally, the purification of hydrocarbons through treatment with 20 per cent oleum was found to be much faster than treatment with concentrated sulfuric acid.

The reduction of primary alcohols (53) with hydrogen over Raney nickel at 250° yields hydrocarbons according to the following scheme:

\[
\begin{align*}
RCH_2OH + H_2 & \rightarrow RH + CH_3OH \\
CH_3OH + H_2 & \rightarrow CH_4 + H_2O
\end{align*}
\]

\(n\)-Undecane, \(n\)-tridecane, and \(n\)-heptadecane were obtained, using this method, in from 80 to 90 per cent yields.

The isolation of normal aliphatic hydrocarbons from natural sources has received a considerable amount of attention. The purity of many of these compounds is extremely doubtful, and it is questionable if the work has demonstrated much aside from showing that the hydrocarbons belong to the \(C_nH_{2n-2}\) series of hydrocarbons.

Mabery (54) has made an extensive study of hydrocarbons in petroleum. He has been able to isolate from Pennsylvania petroleum, hydrocarbons of the \(C_nH_{2n+2}\) series from \(n\)-butane to \(n\)-pentatriacontane. Likewise, from commercial paraffin he obtained hydrocarbons from \(n\)-tricosane to \(n\)-nonacosane. The isolation of these products required many distillations, and with the solid hydrocarbons a number of crystallizations. In

general, the melting points agree fairly well with the synthetic hydrocarbons. However, the specific gravity is often quite different, and it is not unlikely that many are mixtures.

The principal hydrocarbons in Pennsylvania, Ohio and Canadian petroleum boiling below 216° belong to the \( C_n H_{2n+2} \) series. It should also be mentioned that hydrocarbons of the \( C_n H_{2n} \) and \( C_n H_{2n-2} \) series are also present.

Somewhat later, Buchler and Graves (55) found that all the waxes obtained from petroleum belong to the \( C_n H_{2n+2} \) series of hydrocarbons. Fractions were isolated which appeared to have hydrocarbons of at least 43 carbon atoms. The various fractions isolated were not considered to be individual hydrocarbons, but it was said that all the hydrocarbons were straight-chain compounds as their melting points, when plotted against the number of carbon atoms fell on a smooth curve resembling the curve of synthetic hydrocarbons.

Hydrocarbons (56) have been obtained from a variety of sources; such as, beeswax, rose oil, various grasses, apples, sassafras leaves, etc.

\( n \)-Hexahexacontane (57) has been prepared by the electrolysis of potassium tetratriacontanoate. The melting point

was 103.6°, although x-ray pictures indicated it was not quite pure. A Clemmensen reduction of 34-heptahexacontanone gave n-heptahexacone (m. p. 104.1°). Like the above sample, x-ray pictures showed the compound to be impure.

By the hydrogenation of "Farnesol", Fischer (58) obtained a mixture of 2,6,10-trimethyl-12-dodecanol and 2,6,10-trimethylundecane. Treatment of tetrahydro-geranyl bromide with potassium in benzene solution gave 2,6,11,15-tetramethylhexadecane.

The reduction of squalene leads to perhydro-squalene, or 2,6,10,15,19,23-hexamethyltetradecane (59).

Landa and co-workers (60) have synthesized a number of isoparaffins. By reacting ethyl palmitate with methylmagnesium bromide dimethylpentadecylcarbinol was obtained, which on dehydration yielded 2-methylheptadecane-2. 2-Methylheptadecane was prepared from this compound by hydrogenation, using a nickel catalyst. Starting from ethyl behenate, by the same series of reactions, 2-methyltricosane was synthesized.

Ethyl sebacate on reaction with ethylmagnesium bromide gave 2,11-dimethylundecane-diol, which on dehydration gave the diolefin, 2,11-dimethyldodecadiene. This on hydrogenation

(60) Landa and co-workers, Collection Czechoslov. Chem. Commun., 2, 520 (1930); 3, 367 (1931); 5, 184 (1933).
over platinum oxide gave 2,11-dimethyldodecane. Electrolysis of the potassium salt of the half-ester of ethyl sebacate gave diethyl 1,16-hexadecanedicarboxylate, \( C_2H_5OC\left(CH_2\right)_{16}CO_0OC_2H_5 \). On carrying this ester through the same series of reactions as ethyl sebacate 2,19-dimethyl eicosane was obtained.

In exactly the same manner as employed for preparing 2-methylheptadecane, 4-\( n \)-propylnonadecane and 5-\( n \)-butyleicosane were obtained starting from ethyl palmitate and appropriate Grignard reagents (\( n \)-propyl- and \( n \)-butylmagnesium bromides).

In connection with the synthesis of waxes, Grun, Ulbrich, and Krocil (61) obtained some high-molecular-weight hydrocarbons both saturated and unsaturated. The following scheme illustrates the method of preparation:

\[
2C_{17}H_{36}COOH \xrightarrow{Fe} C_{17}H_{35}CC_{17}H_{35} \xrightarrow{H_2} C_{17}H_{35}CHC_{17}H_{35}
\]

\[
C_{17}H_{35}CHC_{17}H_{35} \xrightarrow{-H_2O} C_{17}H_{35}CH = CHC_{16}H_{33} \xrightarrow{H_2} C_{35}H_{72}
\]

The following table gives the compounds prepared and their melting points.

TABLE V.

High-Molecular-Weight Hydrocarbons

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>Melting Point, °C</th>
<th>cis?</th>
<th>trans?</th>
</tr>
</thead>
<tbody>
<tr>
<td>11-Tricosene</td>
<td>C_{23}H_{46}</td>
<td>17-18</td>
<td></td>
<td>1-2</td>
</tr>
<tr>
<td>13-Heptacosene</td>
<td>C_{27}H_{54}</td>
<td>34.2</td>
<td></td>
<td>4.5</td>
</tr>
<tr>
<td>15-Hentriacontene</td>
<td>C_{31}H_{62}</td>
<td>45.2-45.4</td>
<td>liquid b. p.</td>
<td>241-242/2mm.</td>
</tr>
<tr>
<td>17-Pentatriacontene</td>
<td>C_{35}H_{70}</td>
<td>66.5</td>
<td>45-46</td>
<td></td>
</tr>
<tr>
<td>u-Pentatriacontane</td>
<td>C_{35}H_{72}</td>
<td>74.6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Kuhn (62) obtained crocetane, 2,6,11,15-tetramethylhexadecane, through reduction of \( \alpha \)-crocetin.

Karrer and co-workers (63) have made some branch chained hydrocarbons of very high-molecular-weight. By use of the Wurtz reaction, 1-bromo-2,7,11,15-tetramethylhexadecane (bromide of dihydro-phytol) was coupled to give 2,6,10,14, 19,23,27,31-octamethyldotriacontane. In addition to this product, the unsaturated hydrocarbon \( C_{20}H_{40} \) was isolated, which was formed by elimination of hydrogen bromide.

The reduction of bixin yields bixane, or 4,8,13,17-tetramethyleicosane.

By electrolysis of the potassium salt of the mono-methyl ester of perhydrobixin \((\text{CH}_3\text{OOCC}_2\text{H}_{44}\text{COOH})\) the dimolecular compound was isolated, \(\text{CH}_3\text{OOCC}_2\text{H}_{44}\text{C}_2\text{H}_{44}\text{COOCH}_3\). This compound was now reduced to the glycol, which in turn was transformed into the bromide and reduced to the hydrocarbon dibixane, or 4,8,12,16,23,27,31,35-octamethyloctatriacontane.

The dimolecular ester \(\text{CH}_3\text{OOCC}(\text{C}_2\text{H}_{44})_2\text{COOCH}_3\) was partially hydrolyzed to a mixture of the mono-methyl ester and the dibasic acid, the potassium salts of which were electrolyzed. From this the following dimethyl ester was obtained, \(\text{CH}_3\text{OOCC}(\text{C}_2\text{H}_{44})_4\text{COOCH}_3\). This was treated with methylmagnesium bromide, and the resulting glycol reduced to a hydrocarbon, \(\text{C}_{34}\text{H}_{190}\). 2,5,9,13,17,24,28,32,36,41,45,49,53,60,64,68,72,75-octadecamethylhexaheptacontane. This compound was not distillable even at 0.04 mm., some cracking taking place.

In connection with some physical chemistry studies, Strating and Backer (64) synthesized a number of hydrocarbons. \(\pi\)-Heneicosane, and \(\pi\)-tricosane were made by reducing the corresponding ketones by means of the Clemmensen reaction. 13-Methylnpentacosane was prepared by reacting laurylmagnesium (64) Strating and Backer, Rec. trav. chim., 55, 903 (1936).
bromide with ethyl acetate, dehydrating the tertiary alcohol so formed, followed by hydrogenation of the olefin.

2-Methyltricosane was prepared through the same series of reactions from methyl erucate and methylmagnesium bromide.

A number of attempts to reduce 4-butyl n-heptadecyl ketone were unsuccessful, so 2,2-dimethylbutyl n-heptadecyl ketone was reduced, by means of the Clemmensen reaction, to 2,2-dimethyl n-docosane. Cyclohexyl n-heptadecyl ketone was reduced by the same reaction to n-octadecylcyclohexane.

In connection with some studies on the relation between viscosity and constitution, Hugel (65) made some highly branched chain hydrocarbons. Thus, by reacting isoamyl and 2-n-octylmagnesium chloride with ethyl palmitate, disoamyl and di-2-n-octylpentadecyl carbinol were obtained which on dehydration gave olefins in which the position of the double bonds were not proven.

In the presence of sodium hydroxide n-octan-2-ol condenses with itself to form di- and tricaprylic alcohols according to the following scheme:

\[
\text{CH}_3\text{(CH}_2\text{)}_5\text{CHCH}_3 + \text{CH}_3\text{(CH}_2\text{)}_4\text{CHCHCH}_3 \rightarrow \text{CH}_3\text{(CH}_2\text{)}_5\text{CHCH}_3 + \text{CH}_3\text{(CH}_2\text{)}_4\text{CHCHCH}_3
\]

(65) Lever, Ann. combustibles liquides, 8, 681 (1933) / C. A., 26, 474 (1934); Hugel, Chimie Ind., 26, 1282 (1933).
ethy] - and 2-hydroxyethylthioacetone were obtained from

ether, 6-g mehythiolthioacetone. In a similar way, 10-
carbon, 10-methylthioacetone. When on reduction the totally yielded the hydra-
neat a wide range of they obtained 10-methylthioacetone-10-o,

from the reaction between petrothane and methylene-

and introducing a part of 1933

of hydrocarbons were then hydrocarbons, up to the

of hydrogenoacetaldehyde, which hydrocarbons, made a complete review of the structure

of synthesis, 67), in connection with the synthesis

under and thence (67)

present.

hydrocarbons of lower molecular weight appeared to be

hydrocarbons containing 71 carbon atoms. Other

tetraed, which on the basis of molecular point and molecular

sure of 10-15 atmospheres a partial pressure of hydrocarbons was ob-

with iron and copper at a temperature of 800° and a press-

of the catalytic treatment (66) of carbon monoxide

teated, 0.766 and 0.469.

of the ethylated ethylenedichlorohydrin hydrocarbons were ob-

so that the ethylated ethylenedichlorohydrin hydrocarbons were ob-

to heat the mixture and then using the mixture reaction with

the hydrocarbons were then transformed into toluene, it - and

double bond was not determined.

these carbonyl on dervitation gave the output.

-17-
palmitone and appropriate Grignard reagents. Palmitone and \( n \)-hexadecylmagnesium bromide react to form 16-\( n \)-hexadecyl-hentriacontan-16-ol, which on reduction through the iodide gave 16-\( n \)-hexadecylhentriacontane.

Attempts to obtain a Wurtz reaction with 16-iodohentriacontane were unsuccessful under a variety of conditions. Myricyl iodide would not react with magnesium and palmitone according to the method originally used by Barbier for conducting reactions between Grignard reagents and functional groups.

Stearone (68) reacts with an excess of ethylmagnesium bromide to give 18-ethylpentatriacontan-18-ol, which on reduction through the iodide gave 18-ethylpentatriacontane.

Recently, Meyer (69) has obtained some long-chain branched hydrocarbons. Through the reaction of 1,2-octadecinylmagnesium bromide with 3,18-eicosanediione, he obtained 19,34-dihydroxy-19,34-diethyldopenpta-17,35-diyne, which on reduction with phosphorous and iodine gave 19,34-diethyldopenptacontane. Heating of the silver salt of 1,2-octadecino gave 17,18,19,20-hexatriacontadiyne.

**Akyly-Aryl Hydrocarbons.** Krafft (70) obtained \( n \)-hexadecyl- and \( n \)-octadecylbenzene by a Wurtz reaction between \( n \)-hexadecyl iodide and iodobenzene, and \( n \)-octadecyl iodide

---

(70) Krafft, *Ber.*, 19, 2987 (1886).
and iodobenzene. At a later date (71) he obtained 2-methylhexadecylbenzene, 3-methylhexadecylbenzene, 4-methylhexadecylbenzene, 1,3-dimethylhexadecylbenzene, and 1,3,5-trimethylhexadecylbenzene by reacting the appropriate aryl halide with n-hexadecyl iodide in the presence of sodium.

Octadecylbenzene has also been obtained by reduction of stearophenone (49), and from a Friedel-Crafts reaction between n-octadecyl bromide and benzene (41).

In studying the polymerization of unsaturated hydrocarbons, Ziegler (72) had occasion to synthesize some alkyl-aryl hydrocarbons. He obtained n-tridecylbenzene and n-heptadecylbenzene by reducing laurophenone and palmitophenone, respectively. The ketones were obtained through a Friedel-Crafts synthesis from the appropriate acid chlorides and benzene.

In connection with a study of the chemical structure of lubricating oils, Mikeska (73) synthesized a large number of hydrocarbons, both alkyl-aryl hydrocarbons and hydroaromatic types. The following table gives the derivatives prepared:

(71) Krafft, Ber., 21, 3181 (1888).
(72) Ziegler, Borsch, and Wollthan, Ann., 511, 13 (1934).
TABLE VI.

Alkyl-Aryl Hydrocarbons

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>M. P. °C.</th>
<th>Hydrocarbon</th>
<th>M. P. °C.</th>
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</thead>
<tbody>
<tr>
<td>C_{18}H_{37}</td>
<td>35-36</td>
<td>C_{4}H_{9}C_{17}H_{35}</td>
<td>31.5</td>
</tr>
<tr>
<td>C_{22}H_{45}</td>
<td>42-44</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C_{4}H_{9}C_{17}H_{35}</td>
<td>38</td>
<td>C_{4}H_{9}(C_{17}H_{35})_{2}</td>
<td>64-66</td>
</tr>
<tr>
<td>C_{4}H_{9}C_{21}H_{43}</td>
<td>32-33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C_{4}H_{9}C_{16}H_{33}</td>
<td>liquid</td>
<td>C_{4}H_{9}C_{17}H_{35}</td>
<td>liquid</td>
</tr>
<tr>
<td>C_{6}H_{9}C_{20}H_{41}</td>
<td>&quot;</td>
<td>C_{22}H_{45}</td>
<td>49-50</td>
</tr>
<tr>
<td>(C_{18}H_{37})_{2}</td>
<td>69-70</td>
<td>C_{4}H_{9}C_{20}H_{41}</td>
<td>51-52</td>
</tr>
<tr>
<td>(C_{18}H_{37})_{3}</td>
<td>46-47</td>
<td></td>
<td>56-58</td>
</tr>
</tbody>
</table>
### TABLE VI (Continued)

<table>
<thead>
<tr>
<th>Chemical Structure 1</th>
<th>Liquid</th>
<th>Chemical Structure 2</th>
<th>Liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}<em>{22}\text{H}</em>{45} )</td>
<td>liquid</td>
<td>( \text{C}<em>{6}\text{H}</em>{13} )</td>
<td>liquid</td>
</tr>
<tr>
<td>( \text{C}<em>{4}\text{H}</em>{9} )</td>
<td></td>
<td>( \text{C}<em>{6}\text{H}</em>{13} )</td>
<td></td>
</tr>
<tr>
<td>( \text{CHC}<em>{17}\text{H}</em>{35} )</td>
<td></td>
<td>( \text{C}<em>{6}\text{H}</em>{13} )</td>
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</tr>
<tr>
<td>( \text{C}<em>{4}\text{H}</em>{9} )</td>
<td></td>
<td>( \text{(C}<em>{6}\text{H}</em>{13}\text{)}_{2} )</td>
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</tr>
<tr>
<td>( \text{CHC}<em>{16}\text{H}</em>{33} )</td>
<td></td>
<td>( \text{(C}<em>{6}\text{H}</em>{13}\text{)}_{3} )</td>
<td></td>
</tr>
<tr>
<td>( \text{CHC}<em>{20}\text{H}</em>{41} )</td>
<td></td>
<td>( \text{(C}<em>{6}\text{H}</em>{13}\text{)}_{3} )</td>
<td></td>
</tr>
<tr>
<td>( \text{CHC}<em>{18}\text{H}</em>{37} )</td>
<td></td>
<td>( \text{(C}<em>{6}\text{H}</em>{13}\text{)}_{3} )</td>
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<tr>
<td>( \text{C}<em>{6}\text{H}</em>{5} )</td>
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<td>( \text{(C}<em>{6}\text{H}</em>{13}\text{)}_{3} )</td>
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</tr>
<tr>
<td>( \text{C}<em>{4}\text{H}</em>{9} )</td>
<td></td>
<td>( \text{(C}<em>{6}\text{H}</em>{13}\text{)}_{3} )</td>
<td></td>
</tr>
<tr>
<td>( \text{CHC}<em>{18}\text{H}</em>{37} )</td>
<td></td>
<td>( \text{(C}<em>{6}\text{H}</em>{13}\text{)}_{3} )</td>
<td></td>
</tr>
<tr>
<td>( \text{C}<em>{4}\text{H}</em>{9} )</td>
<td></td>
<td>( \text{H}_{2} )</td>
<td></td>
</tr>
<tr>
<td>( \text{C}<em>{4}\text{H}</em>{9} )</td>
<td></td>
<td>( \text{H}_{2} )</td>
<td></td>
</tr>
<tr>
<td>( \text{C}<em>{4}\text{H}</em>{9} )</td>
<td></td>
<td>( \text{H}_{2} )</td>
<td></td>
</tr>
<tr>
<td>( \text{C}<em>{4}\text{H}</em>{9} )</td>
<td></td>
<td>( \text{H}_{2} )</td>
<td></td>
</tr>
<tr>
<td>( \text{C}<em>{4}\text{H}</em>{9} )</td>
<td></td>
<td>( \text{H}_{2} )</td>
<td></td>
</tr>
<tr>
<td>( \text{C}<em>{4}\text{H}</em>{9} )</td>
<td></td>
<td>( \text{H}_{2} )</td>
<td></td>
</tr>
<tr>
<td>( \text{C}<em>{4}\text{H}</em>{9} )</td>
<td></td>
<td>( \text{H}_{2} )</td>
<td></td>
</tr>
<tr>
<td>( \text{C}<em>{4}\text{H}</em>{9} )</td>
<td></td>
<td>( \text{H}_{2} )</td>
<td></td>
</tr>
<tr>
<td>( \text{C}<em>{4}\text{H}</em>{9} )</td>
<td></td>
<td>( \text{H}_{2} )</td>
<td></td>
</tr>
<tr>
<td>( \text{C}<em>{4}\text{H}</em>{9} )</td>
<td></td>
<td>( \text{C}<em>{22}\text{H}</em>{45} )</td>
<td></td>
</tr>
</tbody>
</table>

- 29-30
- 43-45
TABLE VI (Continued)

<table>
<thead>
<tr>
<th>Structure</th>
<th>Description</th>
<th>Temperature Range</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Structure 1" /></td>
<td>liquid</td>
<td>35</td>
</tr>
<tr>
<td><img src="image2" alt="Structure 2" /></td>
<td>liquid</td>
<td>43-47</td>
</tr>
<tr>
<td><img src="image3" alt="Structure 3" /></td>
<td>liquid</td>
<td>---</td>
</tr>
<tr>
<td><img src="image4" alt="Structure 4" /></td>
<td>C_{18}H_{37}</td>
<td>77.5-78</td>
</tr>
<tr>
<td><img src="image5" alt="Structure 5" /></td>
<td>C_{18}H_{37}</td>
<td>37-38</td>
</tr>
<tr>
<td><img src="image6" alt="Structure 6" /></td>
<td>C_{18}H_{37}</td>
<td>41.5-43</td>
</tr>
<tr>
<td><img src="image7" alt="Structure 7" /></td>
<td>C_{22}H_{45}</td>
<td>82-84.5</td>
</tr>
</tbody>
</table>
TABLE VI (Continued)

<table>
<thead>
<tr>
<th>Structure</th>
<th>Description</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.jpg" alt="Structure 1" /></td>
<td>$\text{C}_4\text{H}_9\text{COCH}<em>2\text{OH}</em>{41}$</td>
<td>37-39</td>
</tr>
<tr>
<td><img src="image2.jpg" alt="Structure 2" /></td>
<td>$\text{C}_4\text{H}_9\text{CHC}<em>2\text{H}</em>{43}$</td>
<td>44-45</td>
</tr>
<tr>
<td><img src="image3.jpg" alt="Structure 3" /></td>
<td>$\text{C}_4\text{H}_9\text{CHC}<em>2\text{H}</em>{55}$</td>
<td>liquid</td>
</tr>
</tbody>
</table>
The syntheses were accomplished through the Friedel-Crafts reaction, followed by reduction of the ketones according to the Clemmensen reaction. Branched chain hydrocarbons were prepared by reaction of the appropriate ketone with a Grignard reagent, and the alcohols converted to olefins. The olefins were reduced to saturated hydrocarbons or hydroaromatic derivatives. No experimental details were given, nor was there any proof of structure offered.

The hope of the work was to throw some light on the structure of lubricating oils through a variety of physical measurements.

The toxic principal of the fruits of Renghas (74), has been found to be 2,3-dihydroxy-n-pentadecen-10-ylbenzene (renghol). This was shown by the synthesis of 2,3-dimethoxy-n-pentadecylbenzene from the reaction of n-tetradecylmagnesium bromide and benzaldehyde, followed by dehydration and hydrogenation.

This product was identical with the dimethyl ether of dihydrenghol. Ozonization of renghol gave n-valeraldehyde, which was identified as its 2,4-dintrophenylhydrazone, thereby placing the double bond between carbon atoms 10 and 11 in the side chain.

(74) Backer and Haack, Rec. trav. chim., 57, 225 (1938).
The method used for the preparation of lauronitrile is essentially that given by Ralston, Harwood, and Poole (75) for the preparation of stearonitrile.

Preparation of Lauronitrile.

One hundred grams (0.5 mole) of lauric acid was placed in a 1 l. Claisen flask, in one neck of which was an air condenser, and in the other neck an inlet tube for ammonia reaching to the bottom of the flask. The side arm was closed off by a piece of rubber tubing and a clamp. The flask was heated by a bath made from 55 parts of potassium nitrate and 45 parts of sodium nitrate to a temperature of 315-330°. Ammonia was then passed in through a safety trap at such a rate that the acid refluxed gently. Occasionally, the passage of ammonia was halted and the ammonium laurate which solidified in the condenser pushed back into the flask. The reaction was complete in from ten to twelve hours. At the end of this time the flask was set up for vacuum distillation and the nitrile distilled. There was obtained 55-65 g. (61-72 per cent of the theoretical yield) of lauronitrile boiling at 115-130°/3mm. The residue in the flask is a mixture of lauramide and lauric acid and may be left in the flask and used on the next run.

Preparation of Stearmonitrile.

One hundred and fifty grams (0.57 mole) of stearic acid was placed in a 1 l. Claisen flask, in one neck of which was placed an inlet tube for ammonia and a thermometer, in the other a short air condenser. The side arm was closed off. The reaction mixture was then heated to 330-340° internal temperature by a bath of sodium nitrate and potassium nitrate described in the previous experiment. An excess of ammonia was passed in and heating continued for eight to ten hours. Distillation of the contents in vacuum gave 110 g. of stearonitrile (b. p. 160-190°/3mm.). This is a yield of 73 per cent of the theoretical. The nitrile contains only a small amount of acid which may be easily removed by treating with a hot, dilute solution of potassium hydroxide in 50% alcohol (75). The melting point after crystallization from ethanol was 40-41°.

Preparation of 2-n-Decyl-3-iminomyristonitrile, C₁₁H₂₅N₂O₃CH₂NH₂

Phenyllithium (76) was prepared in the usual manner (77), in a 500 cc. three-necked flask fitted with a mercury-sealed stirrer, condenser and a dropping funnel, from 10.8 g. (0.07 mole) of bromobenzene and 0.98 g. (0.14 g. atom) of lithium in 75 cc. of anhydrous ether. When the reaction was complete,

(76) All experiments described in this thesis in which organometallic compounds were used, were conducted in an atmosphere of pure and dry nitrogen.

8.5 g. (0.07 mole) of ethylaniline was added dropwise followed by 9.0 g. (0.05 mole) of lauronitrile all at once, and the reaction refluxed for six hours and then allowed to stand overnight. The reaction was hydrolyzed by the dropwise addition of 50 cc. of water, the layers separated, the ether layer washed once with water and dried with anhydrous sodium sulfate. After removing the ether, the residue was distilled in vacuum. Eight grams of ethylaniline, b. p. 80-90°/15 mm. was recovered followed by 8.0 g. (94%) of the -imino-nitrile boiling at 234-237°/2 mm. Since the compound was somewhat discolored no attempt was made to analyze it, but it was hydrolyzed to the -keto-nitrile.

Preparation of 2-n-Decyl-3-ketomyristonitrile. \( \text{C}_{11}\text{H}_{23}\text{NO} \)

Five grams (0.0275 mole) of 2-n-decyl-3-iminomyristonitrile was hydrolyzed by refluxing with 50 cc. of alcoholic hydrogen chloride for about five minutes, the reaction cooled, diluted with a little water and filtered. Recrystallization of this product from slightly diluted ethanol gave 4.5 g. (90%) of 2-n-decyl-3-ketomyristonitrile, melting at 44-45°.


Preparation of 2-n-Decyl-3-ketomyristamide. \( \text{C}_{11}\text{H}_{23}\text{NOCOONH}_{2} \)

One gram (0.0055 mole) of 2-n-decyl-3-iminomyristonitrile was added to 5 cc. of concentrated sulfuric acid in
a small Erlenmeyer flask and allowed to stand until solution was complete (two to three hours). The reaction was poured into 25 cc. of water, filtered and washed well with water. After one crystallization from ethanol there was obtained 0.9 g. (86%) of product, melting at 114-115°. This melting point may be raised to 115-116° by another crystallization.


Preparation of Laurone.

Nine-tenths gram (0.005 mole) of 2-\textit{n}-decyl-3-keto-myristamide was refluxed with 30 cc. of 5 per cent alcoholic potassium hydroxide for eight hours. The reaction was cooled, filtered and the product recrystallized from acetone, removing a small amount of insoluble material. Upon cooling, there was obtained 0.7 g. (89%) of laurone, m. p. 66-67°. A mixed melting point with an authentic sample melting at 64-65° melted at 65-66°.

Preparation of 2-\textit{n}-Hexadecyl-3-iminoarachidonitrile,

\[
\begin{align*}
\text{C}_{16}^{16}\text{H}_{33}^{33} & \\
\text{C}_{17}^{17}\text{H}_{35}^{35}\text{O}^{0}\text{C}^{C} \text{N}^{N} \text{H}^{H}
\end{align*}
\]

Seven-hundredths of a mole of phenyllithium was prepared in the same manner as previously given (78), in a 500 cc. three-necked flask fitted with a mercury-sealed stirrer, condenser and dropping funnel, and to this was added 8.5 g.

(78) This thesis, page 56.
(0.07 mole) of ethylaniline followed by 13.5 g. (0.05 mole) of stearonitrile. The reaction was refluxed for six hours and allowed to stand overnight. Hydrolysis was accomplished by the dropwise addition of 50 cc. of water. The layers were separated, the ether layer washed once with water and dried with anhydrous sodium sulfate. After removing the ether, the ethylaniline was removed in vacuum; 8 g., b. p. 85-92°C/15mm. The residue was crystallized from ethanol to give 13 g. (96%) of the A-1mino-nitrile, melting at 54-55°C.

**Anal.** Calcd. for C_{36}H_{70}N_{2}: N, 5.30. Found: N, 5.60.

**Preparation of 2-n-Hexadecyl-3-ketoarachidonitrile,**

C_{16}H_{33}C=CHCONH_{2}

One gram (0.00185 mole) of 2-n-hexadecyl-3-1minoarachidono-nitrile was refluxed with 50 cc. of alcoholic hydrogen chloride for thirty minutes, cooled and filtered. Recrystallization of the product from acetone gave 0.6 g. (80%) of 2-n-hexadecyl-3-ketoarachidonitrile, melting at 68-69°C.

**Anal.** Calcd. for C_{36}H_{69}ON: N, 2.65. Found: N, 3.05.

**Preparation of 2-n-Hexadecyl-3-ketoarachidamide,**

C_{17}H_{35}C=CHCONH_{2}

To 5 cc. of concentrated sulfuric acid was added 1 g. (0.0018 mole) of 2-n-hexadecyl-3-1minoarachidonitrile, and the reaction allowed to stand at room temperature until
solution was complete. The mixture was poured into 25 cc. of water and filtered, washing well with water. Crystallization of the product from ethanol gave 1 g. (95%), melting at 114-115°.

Anal. Calcd. for C_{36}H_{70}O_{2}N: N, 2.55. Found: N, 2.77.

Preparation of Stearone.

One gram (0.0018 mole) of 2-n-hexadecyl-3-ketoarachidamide was refluxed with 2 g. (0.035 mole) of potassium hydroxide in 30 cc. of ethanol for six hours, cooled and filtered. Recrystallization of the product from ethyl acetate, filtering out a small amount of insoluble material, gave 0.5 g. (55%) of stearone (m. p. and mixed m. p. 85-86°).

Preparation of Thioamides.

The following general procedure was used for the preparation of the thioamides:

One and one-half grams (0.065 g. atom) of sodium was added to 100 cc. of absolute ethanol, and after the sodium had dissolved, the mixture was cooled in an ice-bath and saturated with hydrogen sulfide. This solution was now added to 0.037 mole of the respective nitriles, in an iron bomb which had a glass liner (test tube). The bomb was closed immediately and the temperature raised to 150-160° and kept there for two hours. After cooling to room temperature, the bomb was opened and the contents thoroughly chilled in an
ice-bath and filtered, washing with cold ethanol. The product was crystallized from ethanol.

The following table gives the yields, melting points and analytical data on the thioamides prepared:

**TABLE VII.**

Properties and Analyses of Thiolauroamide, Thiomyristamide, Thiopalmitamide and Thiostearamide.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Melting Point</th>
<th>Yield</th>
<th>Analyses</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Calcd. S : Found: S</td>
</tr>
<tr>
<td>Thiolauroamide</td>
<td>82-83°</td>
<td>63%</td>
<td>14.8 : 14.9</td>
</tr>
<tr>
<td>Thiomyristamide</td>
<td>87-88°</td>
<td>66%</td>
<td>13.1 : 12.9</td>
</tr>
<tr>
<td>Thiopalmitamide</td>
<td>93-94°</td>
<td>66%</td>
<td>11.7 : 12.1</td>
</tr>
<tr>
<td>Thiostearamide</td>
<td>96-97°</td>
<td>63-78%</td>
<td>10.7 : 11.5</td>
</tr>
</tbody>
</table>

Hydrolysis of 1 g. of thiostearamide by refluxing with 25 per cent hydrochloric acid for one hour gave 0.8 g. of stearic acid (m. p. and mixed m. p. 67-68°) after crystallization from ethanol.

**Preparation of p-Phenylphenyl Stearate.**

\[
\begin{align*}
\text{OC}_6H_{17} & \\
\text{S} & \\
\end{align*}
\]

A mixture of 4.25 g. (0.025 mole) of p-phenylphenol and 6.04 g. (0.02 mole) of stearoyl chloride was heated at 120-130°
for six hours, cooled and crystallized from ethanol. The yield of product melting at 73-74° was 6.0 g. (80 per cent of the theoretical).

Anal. Calcd. for \( C_{30}H_{44}O_2 \): C, 82.5; H, 10.1. Found: C, 82.2; H, 9.85.

Fries Rearrangement of p-Phenylphenyl Stearate.

A mixture of 4.35 g. (0.01 mole) of p-phenylphenyl stearate and 4.0 g. (0.025 mole) of aluminum chloride in 40 cc. of carbon disulfide (dried over calcium chloride) was placed in a 250 cc. three-necked flask fitted with a mercury-sealed stirrer and condenser, and refluxed for twenty-four hours. The mixture was poured onto ice and the carbon disulfide removed by steam distillation. The residue was crystallized from petroleum ether (b. p. 60-68°) to give a product melting at 137-139°. Another crystallization from ethyl acetate gave 0.6 g. (14%) of p-(p-hydroxyphenyl)-stearophenone (I), melting at 141-142°. The petroleum ether was removed from the filtrate and the residue crystallized from ethanol several times, removing an oily red impurity by filtration. The yield of o-hydroxy-p-phenylstearophenone (II), melting at 63-64° was 2.0 g. or 40%.

Anal. Calcd. for \( C_{30}H_{44}O_2 \): C, 82.5; H, 10.1. Found: (I) C, 82.3; H, 10.2; (II) C, 82.4; H, 10.3.
Preparation of p-(p-Methoxyphenyl)stearophenone,
\[
\text{CH}_3\text{O} \quad \text{CCl}_6\text{H}_{35}.
\]

The methyl ether of p-(p-hydroxyphenyl)stearophenone was prepared by treating 0.436 g. (0.001 mole) of p-(p-hydroxyphenyl)stearophenone suspended in 20 cc. of acetone and 2.55 g. (0.02 mole) dimethyl sulfate contained in a 250 cc. three-necked flask fitted with a mercury-sealed stirrer, condenser, and a dropping funnel, with a solution of 1.2 g. (0.03 mole) of sodium hydroxide in 10 cc. of water drop-wise. The mixture was refluxed for one hour, cooled, diluted and filtered. Crystallization from ethyl acetate gave 0.4 g. of p-(p-methoxyphenyl)stearophenone, m. p. 115-116\(^\circ\).

**Anal.** Calcd. for C\(_{31}\)H\(_{46}\)O\(_2\): C, 82.0; H, 10.2. Found: C, 82.2; H, 10.3.

Preparation of \(o\)-Methoxy-\(m\)-phenylstearophenone.

\[
\text{CCl}_6\text{H}_{35} \quad \text{OCH}_3.
\]

\(o\)-Methoxy-\(m\)-phenylstearophenone was prepared from 0.436 g. (0.001 mole) of \(o\)-hydroxy-\(m\)-phenylstearophenone exactly as in the preceding experiment. The yield of product after crystallization from ethanol was 0.4 g., melting at 53-54\(^\circ\).

**Anal.** Calcd. for C\(_{31}\)H\(_{46}\)O\(_2\): C, 82.0; H, 10.2. Found: C, 82.0; H, 10.0.
Preparation of p-(p-Methoxyphenyl)stearophenone.

In a 250 cc. three-necked flask fitted with a mercury-sealed stirrer and condenser was placed a mixture of 0.94 g. (0.005 mole) of 4-methoxybiphenyl, 1.5 g. (0.005 mole) of stearoyl chloride in dry carbon disulfide (25 cc.) and 1.33 g. (0.01 mole) of aluminum chloride was added slowly. The reaction was refluxed for six hours, cooled, poured onto ice and the carbon disulfide removed by steam distillation. Crystallization of the residue from ethyl acetate gave 1.4 g. (62%) of p-(p-methoxyphenyl)stearophenone, melting at 115-116°. A mixed melting point with the p-(p-methoxyphenyl)stearophenone obtained above melted at 115-116°. Examination of the mother liquors failed to give any p-methoxy-m-phenyl-stearophenone.

Oxidation of p-(p-Methoxyphenyl)stearophenone.

Three grams (0.0067 mole) of p-(p-methoxyphenyl)-stearophenone was placed in 20 cc. of acetic acid, 10 g. of chromium trioxide dissolved in 10 cc. of water and 20 cc. of acetic acid added, and the reaction refluxed for two hours. The solution was cooled, diluted and filtered. After dissolving the product in dilute sodium hydroxide, a small amount of insoluble material was removed by filtration and the acid was precipitated by acidifying with hydrochloric acid. The product was collected, dried, and esterified by
refluxing with 17 cc. of absolute methanol containing 2 cc. of concentrated sulfuric acid, until solution was complete. On cooling, 0.3 g. of dimethyl terephalate separated, melting at 139-140°. A mixed melting point with an authentic sample (m. p. 139-140°) was not depressed.

Preparation of o-Methoxy-m-phenylstearophenone.

In a 250 cc. three-necked flask fitted with a mercury-sealed stirrer and condenser, was placed 8.5 g. (0.033 mole) of 3-bromo-4-methoxybiphenyl (79) dissolved in 100 cc. of ether, 2 g. (0.08 g. atom) of magnesium, and a crystal of iodine added. After a short period of heating, the reaction started, but it was refluxed for two hours to insure completion, and then 8 g. (0.03 mole) of stearonitrile added. After refluxing for a further two hours the reaction was hydrolyzed with 50 cc. of 10 per cent hydrochloric acid. Removal of the ether and crystallization from ethanol gave 8 g. (59%) of o-methoxy-m-phenylstearophenone, melting at 50-52°. By further crystallization, this melting point was raised to 55-56°. A mixed melting point with the o-methoxy-m-phenylstearophenone, obtained through the Fries rearrangement, likewise, melted at 55-56°.

Preparation of 2-Nonacosanone, \( \text{CH}_3\text{C}_17\text{H}_{35} \).

In a 250 cc. three-necked flask fitted with a mercury-sealed stirrer, condenser and a dropping funnel, was placed 2.42 g. (0.1 g. atom) of magnesium and then methyl bromide was distilled in until the magnesium had all been consumed. To this was now added 21 g. (0.08 mole) of stearonitrile in ether (100 cc.). The reaction was refluxed until the color test was negative. Hydrolysis was accomplished by adding dropwise 100 cc. of 10 per cent hydrochloric acid. The ether layer was separated, washed once with water and dried with anhydrous sodium sulfate. Removal of the ether and distillation of the residue gave 11 g. (47%) of methyl-\( \text{n} \)-heptadecyl ketone (b. p. 160-165\(^\circ\)/3 mm.). A large amount of higher boiling material remained in the flask. It was crystallized once from acetone, but the melting point was indefinite (42-65\(^\circ\)) so it was discarded.

The ketone, after a single crystallization from acetone, melted at 55-56\(^\circ\). Krafft (80), reports the melting point of 2-nonacosanone prepared by the dry distillation of barium acetate, and stearate, as 55-56\(^\circ\).

Preparation of 2-Stearoylnapthalene.

\( \beta \)-Napthylmagnesium bromide was prepared from 4.14 g. (0.02 mole) of \( \beta \)-bromonapthalene and 0.5 g. (0.0225 mole) of (80) Krafft, Ber., 12, 1672 (1879).
magnesium in 75 cc. of anhydrous ether in a 250 cc. three-necked flask fitted with a mercury-sealed stirrer, condenser and a dropping funnel. To this was now added 4.5 g. (0.017 mole) of stearonitrile in 40 cc. of ether and the reaction refluxed for six hours. Hydrolysis was accomplished by the dropwise addition of 40 cc. of 10 per cent hydrochloric acid. After separating the layers, the ether layer was washed once with water and dried with anhydrous sodium sulfate. Removal of the ether and crystallization of the residue from acetone gave 4.5 g. (67%) of ketone, melting at 64-65°. Further crystallization raised this melting point to 65-66°. This compound has been prepared from a Friedel-Crafts reaction (41) between stearoyl chloride and napthalene. The melting point was 66-67°.

**Preparation of p-Phenylstearophenone.**

4-Biphenyllithium was prepared according to the usual procedure (77) from 16.31 g. (0.07 mole) of 4-bromobiphenyl and 1.05 g. (0.15 g. atom) of lithium in 100 cc. of anhydrous ether in a 250 cc. three-necked flask fitted with a mercury-sealed stirrer, condenser and a dropping funnel. To this was now added 13 g. (0.05 mole) of stearonitrile in 50 cc. of anhydrous ether. After refluxing for four hours, the mixture was hydrolyzed with 10 per cent hydrochloric acid, washed once with water and the ether removed. Crystallization of
the residue from ethyl acetate gave 13.5 g. (61%) of ketone, melting at 107-108°. This compound has been prepared by a Friedel-Craft synthesis from stearoyl chloride and biphenyl and melted at 108-109° (19). A mixed melting point of the two compounds was not depressed.

Anal. Calcd. for \( C_{30}H_{44}O \): C, 85.5; H, 10.4. Found: C, 85.3; H, 10.5.

The reductions described in this thesis were performed in an Adkins type hydrogenation machine manufactured by the Parr Instrument Company of Moline, Illinois.

Preparation of Di-\( \text{n} \)-dodecylamine.

Forty grams (0.2 mole) of lauronic tire and 4 g. of copper-chromium oxide (81) were placed in the bomb and hydrogen admitted to twelve atmospheres. The temperature was raised to 200° and maintained at this point for four hours. During this period 0.88 atoms of hydrogen was taken up. The product was dissolved in hot acetone and the catalyst removed by filtration. On cooling, the acetone deposited 38 g. (77.5%) of di-\( \text{n} \)-dodecylamine, melting at 50-51°. Further crystallization raised this melting point to 52-53°. Adkins (26) gives the melting point of di-\( \text{n} \)-dodecylamine as 54-55°. Very recently, Wibaut, has reported di-\( \text{n} \)-dodecylamine with a solidification point of 44.4° (82).

Preparation of Di-\(n\)-octadecylamine.

Twenty grams (0.075 mole) of stearonitrile and 4 g. of copper-chromium oxide catalyst (81) were placed in the bomb under fourteen to fifteen atmospheres of hydrogen and reduced at 210-215° for two hours. After cooling, the bomb was opened and the contents taken up in hot ethanol and filtered through a steam funnel. Cooling and filtration of the alcoholic solution gave 14-15 g. (72-78%) of di-\(n\)-octadecylamine, melting at 71-72°. The compound (21) has been reported to melt at 73-74°.

Di-\(n\)-octadecylamine hydrochloride was prepared by passing hydrogen chloride into an ether solution of the free amine. After crystallization from ethanol it melted at 174-176°.

Anal. Calcd. for \(C_{36}H_{78}N\cdot Cl\): N, 2.52. Found: N, 3.00.

Preparation of \(n\)-Dodecyl Chloride.

In a 250 cc. three-necked flask fitted with a mercury-sealed stirrer, condenser and a dropping funnel, there was placed 18.6 g. (0.1 mole) of \(n\)-dodecanol in 30 cc. of benzene and 0.1 cc. of pyridine. To this was now added 18 g. (0.15 mole) of thionyl chloride dropwise. When the addition was complete the reaction was refluxed for two hours, cooled, and hydrolyzed with water. The layers were separated and the benzene removed. Distillation of the residue gave 18.5 g.
(90%) of n-dodecyl chloride boiling at 100-102°/3mm. n-
Dodecyl chloride has been prepared from n-dodecanol and thionyl
chloride (83).

Preparation of n-Octadecyl Chloride.

This preparation was carried out in the same apparatus
as the preparation of n-dodecyl chloride. Thirteen and one-
half grams (0.05 mole) of n-octadecanol, 50 cc. of dry ben-
zeine and 0.1 cc. of pyridine were placed in the apparatus and
10 g. (0.075 mole) of thionyl chloride added dropwise. The
reaction was heated until hydrogen chloride was not evolved
copiously (two to three hours) and then 50 cc. of water added
dropwise. The benzene layer was washed once with water and
the benzene removed. Distillation of the residue gave 13.8 g.
(90%) of n-octadecyl chloride boiling at 167-170°/3mm.

The preparation of n-octadecyl chloride from n-octadecanol
and phosphorous pentachloride has been reported by Meyer (68).
However, no yield of product was given.

Preparation of Tri-n-dodecylamine Hydrochloride.

A mixture of 10.6 g. (0.03 mole) of di-n-dodecylamine
and 3.7 g. (0.015 mole) of n-dodecyl chloride was heated at
160-180° for four hours, cooled and thoroughly extracted with
ether, breaking up the solid in order to insure complete
extraction. Filtration of the ether extract gave 6.5 g. of
(83) Rothstein, Bull. soc. chim., 152, 2, 80 (1935).
di-\(\text{\(n\)}\)-dodecylamine hydrobromide, m. p. 208-210°. Neutralization of this hydrobromide with alcoholic potassium hydroxide gave di-\(\text{\(n\)}\)-dodecylamine (m. p. and mixed m. p. 60-51°) quantitatively. Hydrogen chloride was passed into the ether filtrate from the secondary amine hydrobromide and then the ether was removed. Crystallization of the residue from petroleum ether (b. p. 60-88°) gave 8.4 g. (96%) of tri-\(\text{\(n\)}\)-dodecylamine hydrochloride, melting at 75-78°. This melting point was raised to 79-80° by further crystallization.

**Anal.** Calcd. for C_{36}H_{72}NCl: Cl, 6.55. Found: Cl, 6.98, 7.01.

By neutralization of the tertiary amine hydrochloride with alcoholic potassium hydroxide, the free amine, may be obtained (30). It is a liquid, boiling at 260-265°/2mm.

**Preparation of Tri-\(\text{\(n\)}\)-octadecylamine.**

A mixture of 10.4 g. (0.02 mole) of di-\(\text{\(n\)}\)-octadecylamine, and 2.89 g. (0.01 mole) of \(\text{\(n\)}\)-octadecyl chloride was heated at 170-180° (bath) for eight hours, cooled, thoroughly pulverized and extracted with ether. Filtration of the ether extract gave 5.5 g. of di-\(\text{\(n\)}\)-octadecylamine hydrochloride, melting at 165-170°. Neutralization of the hydrochloride gave the free amine (m. p. and mixed m. p. 71-72°). The ether was removed and the residue crystallized from ethyl acetate to give 6.5 g. (85%) of tri-\(\text{\(n\)}\)-octadecylamine, melting
Further crystallization raised this melting point to 53-54°. Staudinger (24) gives the melting point as 54.5°.

**Preparation of Tri-n-octadecylamine Hydrochloride.**

Tri-n-octadecylamine hydrochloride was prepared by dissolving the free amine in ether and passing in hydrogen chloride. Removal of the ether and crystallization of the residue from petroleum ether (b. p. 60-88°) gave the hydrochloride, melting at 96-97°.

**Anal.** Calcd. for C_{54}H_{102}NCl: Cl, 4.48. Found: Cl, 4.75, 4.70.

**Preparation of p-Phenylstearophenone.**

A solution of 15.4 g. (0.01 mole) of biphenyl and 31.8 g. (0.1 mole) of stearoyl chloride was placed in a 500 cc. three-necked flask fitted with a mercury-sealed stirrer, condenser and an apparatus for addition of solids, along with 100 cc. of dry carbon disulfide. To this was now added slowly 27.0 g. (0.2 mole) of aluminum chloride. When the addition was complete the reaction was refluxed for from six to eight hours. After cooling, the mixture was poured onto iced dilute hydrochloric acid, and the carbon disulfide removed by steam distillation. Crystallization of the residue, remaining in the distillation flask, from ethyl acetate gave 38.5 g. (91%) of p-phenylstearophenone, melting at 104-105°. p-Phenoxy-stearophenone (m. p. 62-63°) may be prepared in exactly the
the same manner and about the same yield (90 per cent of the theoretical).

Preparation of 4-Stearoyl-4'-biphenylsulfonic Acid,

\[
\text{SO}_3\text{H} \quad \text{CC}_{17}\text{H}_{35}
\]

In a 250 cc. three-necked flask fitted with a mercury-sealed stirrer and thermometer, was placed 7.0 g. (0.0167 mole) of \( p \)-phenylstearophenone and 50 cc. of concentrated sulfuric acid. The mixture was heated at 50-60\(^\circ\) for twelve hours, cooled, poured onto ice and filtered. The product, after crystallization from ethyl acetate, weighed 6.7 g. (81\%) and melted at 130-135\(^\circ\). Further crystallization raised this melting point to 142-145\(^\circ\). The melting point was not sharp and there was softening at 130\(^\circ\).

**Anal.** Calcd. for \( \text{C}_{30}\text{H}_{44}\text{O}_{4}\text{S} \): S, 6.41. Found: S, 6.75.

Oxidation of 4-Stearoyl-4'-biphenylsulfonic Acid.

A solution of 10 cc. of concentrated nitric acid and 20 cc. of water was refluxed with 1 g. (0.002 mole) of 4-stearoyl-4'-biphenylsulfonic acid for about one hour and filtered hot to remove an insoluble yellow oil. On cooling and filtering 0.31 g. of solid material was collected, which did not melt up to 300\(^\circ\).

**Anal.** Calcd. for \( \text{C}_{13}\text{H}_{10}\text{O}_{5}\text{S} \): S, 11.5. Found: S, 11.7.

The \( p \)-toluidine salt was prepared by refluxing equal
weights of p-toluidine and the sulfonic acid in dilute hydrochloric acid. After crystallization from diluted ethanol the salt melted at 289-290°.

Anal. Calcd. for C_{20}H_{19}O_5NS: N, 3.87. Found: N, 3.64.

Preparation of 4-Sulfo-4'-biphenylcarboxylic Acid.

\[ \text{SO}_3\text{H} \quad \text{CO}_2\text{H} \]

In a small flask carrying a calcium chloride tube was placed 20 cc. of concentrated sulfuric acid and 0.8 g. (0.004 mole) of 4-biphenylcarboxylic acid. This was heated for six hours at 70-80°, cooled and poured onto ice. The precipitated sulfonic acid was filtered. After crystallization from dilute hydrochloric acid, it weighed 0.8 g. which was a 73% yield.

The p-toluidine salt, prepared by heating equal weights of p-toluidine and the sulfonic acid in dilute hydrochloric acid, melted at 289-290°. A mixed melting point with the p-toluidine salt, obtained from the product of the oxidation of 4-stearoyl-4'-biphenylsulfonic acid, was not depressed.

Preparation of 4-Hydroxy-4'-biphenylcarboxylic Acid.

One gram (0.0036 mole) of 4-sulfo-4'-biphenylcarboxylic acid was placed in a small nickel crucible along with 5 g. of solid potassium hydroxide and the crucible heated by a metal-bath at 310-320° for one hour. The temperature was now raised to 360° for five minutes and then the crucible
was cooled to room temperature. The contents of the crucible was dissolved in a small amount of water, and the acid was precipitated by adding an excess of concentrated hydrochloric acid and filtered. After a single crystallization from dilute ethanol it melted at 286-287° and weighed 0.6 g. (78%). Another crystallization from acetic acid raised this to 288-289°. 4-Hydroxy-4′-biphenylcarboxylic acid has been reported to melt at 293-294°, corrected (34).

**Anal. Calcd. for C\textsubscript{13}H\textsubscript{10}O\textsubscript{3}:** C, 72.5; H, 5.1. **Found:** C, 72.9; H, 4.7.

The methyl ester was prepared by saturating a methanol suspension of the acid with dry hydrogen chloride and then refluxing for a short time. After two crystallizations from methanol it melted at 223-224°. Fieser (34) reports a melting point of 224-225°.

**Anal. Calcd. for C\textsubscript{14}H\textsubscript{12}O\textsubscript{3}:** C, 73.4; H, 5.5. **Found:** C, 73.3; H, 5.3.

**Preparation of p-Phenylphenol.**

A mixture of 0.3 g. (0.0014 mole) of 4-hydroxy-4′-biphenylcarboxylic acid, 1 g. calcium oxide, and 0.1 g. of copper powder was intimately mixed and dry distilled in a Pyrex test tube carrying a side arm. The sublimate, which collected on the upper part of the tube, was removed mechanically and crystallized from dilute ethanol. It melted at
160-161° alone and mixed with an authentic sample of p-phenylphenol.

Preparation of a Trisulfonic Acid of p-Phenylstearophenone.

In a 250 cc. three-necked flask containing a mercury-sealed stirrer, was placed 25 cc. of chlorosulfonic acid and the contents cooled to about +5° with an ice-bath. Four and two-tenths grams (0.01 mole) of p-phenylstearophenone was added slowly. The temperature was allowed to rise gradually as the ice-bath melted. After stirring for ten hours, it was heated to 50-60° for six hours. The contents was poured onto iced dilute hydrochloric acid, filtered and washed with slightly diluted hydrochloric acid to remove the sulfuric acid. This compound is soluble in water, but is much less soluble in dilute sulfuric acid or dilute hydrochloric acid. After drying overnight in a vacuum dessicator it weighed 5.5 g. (83%).


Oxidation of the Trisulfonic Acid of p-Phenylstearophenone.

To a mixture of 5 cc. of nitric acid and 10 cc. of water was added 1 g. (0.0015 mole) of the trisulfonic acid and the solution refluxed for about twelve hours. After filtering to remove insoluble matter, the solution was partially neutralized with solid sodium hydroxide. Upon cooling, a
precipitate separated, which after drying weighed 0.3 g. The \( p \)-toluidine salt was prepared by refluxing equal weights of \( p \)-toluidine and the sulfonic acid in dilute hydrochloric acid. After crystallization from dilute ethanol the melting point was 289-290\(^\circ\) alone and mixed with the \( p \)-toluidine salt of 4-sulfo-4'-biphenylcarboxylic acid.

When the sulfonic acid obtained by oxidation of the trisulfonic acid of \( p \)-phenylstearophenone was fused with potassium hydroxide, as described on page 74 of this thesis, 4-hydroxy-4'-biphenylcarboxylic acid (m. p. and mixed m. p. 283-285\(^\circ\)) was isolated; 4-hydroxy-4'-carbomethoxybiphenyl was obtained on esterification, as described on page 75 of this thesis. The melting point and mixed melting point was 220-221\(^\circ\).

**Sulfonation of \( p \)-Phenoxy-stearophenone.**

In a 250 cc. three-necked flask fitted with a mercury-sealed stirrer and thermometer was placed 25 cc. of concentrated sulfuric acid and 5 g. (0.011 mole) of \( p \)-phenoxy-stearophenone and the contents heated to 70-80\(^\circ\) for six hours. After cooling, the contents was poured onto ice, filtered and washed with water. Crystallization from acetone gave 4.5 g. (80\%) of compound, melting at 95-96\(^\circ\).

**Anal. Calcd. for \( C_{30}H_{44}O_5S \):** 3, 5.95. **Found:** 3, 6.45.

The \( p \)-toluidine salt prepared by refluxing equal weights
of p-toluidine and 4-stearoylphenoxybenzenesulfonic acid in dilute hydrochloric acid melted at 155-160° after crystallization from dilute ethanol.

**Anal.** Calcd. for C_{37}H_{54}O_{5}NS: N, 2.24. Found: N, 2.18.

**Oxidation of 4-Stearoylphenoxybenzenesulfonic Acid.**

\[
\text{SO}_{3}H-\text{C}_{17}H_{35}\text{O}-\text{C}_{17}H_{35}\text{O}.
\]

A mixture of 1 g. (0.0019 mole) of 4-stearoylphenoxybenzenesulfonic acid, 2 cc. of nitric acid and 10 cc. of water was placed in a 25 cc. flask, refluxed for twelve hours and filtered hot. After cooling, the solution was partially neutralized with solid sodium hydroxide, again cooled and filtered. The yield of p-sulfophenoxybenzoic acid was 0.4 g. The melting point was indefinite.

**Anal.** Calcd. for C_{13}H_{10}O_{6}S: S, 10.1. Found: S, 10.0.

The p-toluidine salt was prepared by refluxing equal weights of p-toluidine and the sulfonic acid in dilute hydrochloric acid; cooling to precipitate the salt. It melted at 266-267° after crystallization from diluted methanol.

**Anal.** Calcd. for C_{50}H_{18}O_{6}NS: N, 3.69. Found: N, 3.32.

**Preparation of p-Hydroxybenzoic Acid.**

In a nickel crucible was placed 0.9 g. (0.0031 mole) of p-sulfophenoxybenzoic acid and 5 g. of potassium hydroxide
and the mixture heated to 300-310° for one hour by a metal-bath. After cooling, the solid was dissolved in water and extracted with ether. Removal of the ether left 0.2 g. of material which melted at 206-207°. A mixed melting point with p-hydroxybenzoic acid (m. p. 210-211°) melted at 209-210°. The water solution failed to give a test for phenol with ferric chloride.

Preparation of 4-Octadecylbiphenyl.

In a 250 cc. flask was placed 7 g. (0.0167 mole) of p-phenylstearophenone, zinc amalgam (prepared by allowing 50 g. of zinc dust to stand for an hour in 100 cc. of 5 per cent mercuric chloride with occasional shaking), 50 cc. of 20 per cent hydrochloric acid, 25 cc. of acetic acid and 25 cc. of toluene (84). The reaction was refluxed for twelve hours, adding concentrated hydrochloric acid (25 cc.) twice. The two layers were now separated and 50 g. of zinc amalgam added and the above process repeated. The toluene was removed and the residue crystallized twice from acetone. It melted at 76-79°, and weighed 2.5 g. (38%). The reported melting point of this compound is 77.5-78° (73).

Anal. Calcd. for C_{50}H_{46}: C, 88.6; H, 11.4. Found: C, 88.9; H, 11.4.

(84) These are essentially the directions given by Martin, J. Am. Chem. Soc., 58, 1438 (1936), for the reduction of ketones by a modified Clemmensen reaction.
Preparation of Laurone.

A mixture of 20.0 g. (0.1 mole) of lauric acid and 3.4 g. (0.06 g. atom) of iron powder was placed in a 500 cc. three-necked flask which contained an inlet tube for carbon dioxide and an air condenser. After flushing out the flask with carbon dioxide it was heated by a sodium nitrate-potassium nitrate bath to a temperature of 270° (bath) and the temperature gradually raised to 295°. Unless the temperature is raised rather cautiously, there may be a sudden evolution of gas. At about 295° there was a moderate evolution of gas, after which the reaction was heated for thirty minutes at 300°. As soon as the reaction has cooled to room temperature, the air condenser was replaced by a water condenser and the contents extracted by refluxing for thirty minutes with about 100 cc. of acetone. After filtering the solution through a steam funnel, the filtrate was cooled thoroughly under the tap. Filtration gave 15 g. (88 per cent of the theoretical yield) of laurone melting at 63-64°. Further crystallization raised this melting point to 64-65°.

Preparation of Stearone.

In a 500 cc. three-necked flask holding an air condenser and an inlet tube for carbon dioxide was placed 28.4 g. (0.1 mole) of stearic acid and 3.4 g. (0.06 g. atom) of iron powder. The flask was thoroughly flushed out with carbon
dioxide, and then while carbon dioxide was slowly passed in, it was heated gradually to a temperature of 340° (bath) by a sodium nitrate-potassium nitrate bath. At this point there was a vigorous evolution of gas. The heating was continued for thirty minutes at this temperature and then allowed to cool to room temperature. After adding 50 cc. of 20 per cent hydrochloric the contents was carefully heated, finally being brought up to reflux. This served to remove all the iron. When the reaction had cooled the hydrochloric acid was poured off and petroleum ether (b. p. 60-68°) added, and the contents again brought to reflux. A small amount of insoluble material was removed by filtration through a steam funnel. After thoroughly cooling the filtrate under the tap it was filtered. The yield of stearone (m. p. 84-86°) was 20 g. or 80 per cent of the theoretical. Further crystallization raised this melting point to 86-87°.

**Preparation of 14-Heptacosanol, C_{13}H_{27}CHC_{13}H_{27}OH.**

In a 125 cc. Erlenmeyer flask was placed 2 g. (0.005 mole) of myristone and 40 cc. of n-butyl alcohol. After placing the flask under a reflux condenser the contents was brought nearly to reflux and then 2.4 g. (0.10 g. atom) of sodium was added in small pieces at such a rate as to maintain reflux. When the reaction had slowed down somewhat, the solution of the sodium was completed by refluxing.
Hydrolysis was accomplished by the careful addition of about 50 cc. of water. The n-butyl alcohol was removed by distillation and the residue crystallized from acetone. There was obtained 1.8 g. (90%) of product, melting at 79-80°.

Preparation of 18-Pentatriacontanol, \( \text{C}_{17}\text{H}_{35}^\text{OH} \text{C}_{17}\text{H}_{35} \).

In a 250 cc. flask was placed 5 g. (0.001 mole) of stearone and 60 cc. of \( \text{n} \)-butyl alcohol and a reflux condenser attached. The contents was heated nearly to boiling and then 5 g. (0.23 g. atom) of sodium added at such a rate as to maintain reflux. When the reaction had subsided somewhat it was refluxed to complete the solution of the sodium. Hydrolysis was accomplished by the careful addition of 70 cc. of water and the alcohol removed by distillation. Recrystallization of the residue in the flask from carbon tetrachloride gave 4.8 g. (96%) of carbinol, m. p. 90-91°.

Preparation of 18-Iodopentatriacontane, \( \text{C}_{17}\text{H}_{35}^\text{I} \text{C}_{17}\text{H}_{35} \).

In a 250 cc. three-necked flask containing a mercury-sealed stirrer and condenser was placed 20 g. (0.04 mole) of 18-pentatriacontanol, 5 g. of phosphorous and 8 g. of iodine. The contents was heated to 130° for five hours and then, after cooling, extracted with carbon tetrachloride. The carbon tetrachloride layer was washed twice with water, once with dilute sodium thiosulfate and finally with water again. Removal of the carbon tetrachloride left a solid, which on
crystallization from a mixture of acetone and ethyl acetate gave 23 g. (94%) of product melting at 41-43°. Further crystallization raised this melting point to 43-44.5°.


**Attempted Preparations of s-Tetra-n-heptadecylethane.**

A mixture of 25 cc. of dry xylene and 3.1 g. (0.005 mole) of 18-iodopentatriacontane was placed in a 125 cc. Erlenmeyer flask under a reflux condenser and refluxed for sixty hours. The sodium was removed by filtration of the hot xylene solution and washed with a little xylene. After removing the xylene under reduced pressure, the residue was crystallized twice from petroleum ether (b. p. 60-88°) to give 0.6 g. of product, m. p. 74-75°. A mixed melting point with n-pentatriacontane was not depressed. The petroleum ether was removed from the filtrates from the two previous crystallizations. The residue had a melting point of 41-55° and this was not altered by further crystallizations from ethyl acetate or acetone. The product contained no halogen.

In a 250 cc. three-necked flask fitted with a mercury-sealed stirrer, condenser and dropping funnel was placed 6.2 g. (0.01 mole) of 18-iodo-n-pentatriacontane, 40 cc. of ether and 2 g. (0.08 g. atom) of magnesium. To this was now added 5.5 g (0.05 mole) of ethyl bromide in 20 cc. of ether dropwise. The reaction started immediately and after it had moderated somewhat it was refluxed for five hours. At this
time 8 g. (0.06 mole) of anhydrous cupric chloride was added and the reaction refluxed for two hours. After standing overnight the reaction was hydrolyzed with 50 cc. of dilute hydrochloric acid. The ether layer was dried with anhydrous sodium sulfate and the ether removed. The residue after crystallization from petroleum ether (b.p. 60-68°) melted at 74-75° and weighed 1.8 g. From the filtrates was isolated 1.5 g. of unchanged starting material melting at 43-45°. A mixed melting between the product melting at 74-75° and n-pentatriacontane was not depressed.

Preparation of n-Pentatriacontane, n-C36H72.

In a 250 cc. three-necked flask containing a mercury-sealed stirrer and condenser was placed 6.2 g. (0.01 mole) of 16-iodopentatriacontane, 40 cc. of glacial acetic acid and 6.5 g. (0.1 mole) of zinc dust. After thoroughly saturating the solution with gaseous hydrogen chloride the reaction was heated till vigorous evolution of hydrogen had subsided (two to three hours). This process was repeated until practically all the zinc dust had dissolved. After diluting with water, the product was filtered and crystallized from petroleum ether (b.p. 60-68°). Three and nine-tenths grams (80%) of product was obtained, melting at 73.5-74.5°. From the mother liquors an additional 0.5 g. was obtained melting at 71-73°.
Preparation of \( n \)-Octadecyl Bromide (85).

A mixture of 27 g. (0.1 mole) of \( n \)-octadecanol, 60 g. of 42 per cent hydrobromic acid and 25 cc. of concentrated sulfuric acid was placed in a 500 cc. round bottom flask under a reflux condenser and refluxed for ten hours. The product was poured into about an equal volume of water and extracted with benzene. After washing the benzene layer with water twice it was filtered and the residue washed with a little benzene. After drying and removing the benzene the residue was distilled in vacuum. There was obtained 29 g. (87%) of \( n \)-octadecyl bromide, b. p. 170-172\( ^\circ \)/3 mm.

Preparation of \( n \)-Tetracosane, \( n \)-C\(_{24}\)H\(_{50}\).

Eight grams (0.032 mole) of \( n \)-dodecyl bromide was dissolved in 30 cc. of ether and added dropwise to a mixture of 0.8 g. (0.033 g. atom) of magnesium, 30 cc. of ether and a crystal of iodine in a 250 cc. three-necked flask fitted with a mercury-sealed stirrer, dropping funnel and condenser. The reaction started almost at once and was heated for three hours to insure completion. To this was now added 4.3 g. (0.032 mole) of anhydrous cupric chloride and the mixture refluxed for two hours and allowed to stand overnight. Hydrolysis was accomplished by the dropwise addition of 10 per cent

\( (85) \) \( n \)-Octadecyl bromide has been prepared in a 91\% yield from octadecanol and dry gaseous hydrobromic acid, ORG. SYN., 15, 24 (1935).
hydrochloric acid. After drying the ether layer with anhydrous sodium sulfate, the ether was removed and the residue distilled in vacuum. There was obtained: 3.5 g., b. p. 95-97°/14 mm. and 2 g., b. p. 140-200°/3 mm. The first fraction had an index of refraction of 1.4235 at 25° and was only very slightly unsaturated to bromine in carbon tetrachloride. The index of refraction of n-dodecane is 1.41952 at 25°. After a single crystallization of the second fraction from acetone, it melted at 50.5-51.5° and weighed 1.2 g. (22%). The reported melting point of n-tetracosane is 51° (47).

**Preparation of 12-n-Dodecyltricosan-12-ol, C_{12}H_{25}C_{11}H_{23}OH.**

Eight grams (0.032 mole) of n-dodecyl bromide was dissolved in 30 cc. of ether and added dropwise to a mixture of 0.8 g. (0.033 g. atom) of magnesium, 20 cc. of ether and a crystal of iodine in a 250 cc. three-necked flask fitted with a mercury-sealed stirrer, dropping funnel and condenser. The reaction started almost at once, but was heated for three hours in order to insure completion. To this was now added 8.5 g. (0.025 mole) of laurone in 40 cc. of dry benzene and the contents refluxed for two hours. After hydrolysis with 50 cc. of 10 per cent hydrochloric acid the ether-benzene solution was dried with anhydrous sodium sulfate and the solvents removed. Distillation of the residue gave 4 g. (b. p.
Redistillation of the second fraction gave 6 g. (37%) of product boiling at 270-275°/2 mm. There appeared to be some dehydration during the distillation, in view of a considerable quantity of lower boiling product in the second distillation.

Anal. Calcd. for C_{35}H_{72}O: C, 82.8; H, 14.3. Found: C, 82.8; H, 14.3.

Preparation of 18-n-Octadecylpentatriacontan-18-ol,
\[ \text{C}_{18}^\text{H}_{35}\text{OH} \]
\[ \text{C}_{17}^\text{H}_{35}\text{O}_{\text{CH}} \]

In a 250 cc. three-necked flask fitted with a mercury-sealed stirrer, reflux condenser and dropping funnel was placed 0.61 g. (0.025 g. atom) of magnesium, a crystal of iodine and 15 cc. of ether. Seven and three-tenths grams (0.022 mole) of n-octadecyl bromide was dissolved in 35 cc. of ether and about 10 cc. of this solution added. After heating for a short time the reaction started, and the remainder of the ether solution was added dropwise. The reaction was heated for three hours and then a warm solution of 7.0 g. (0.014 mole) of stearone in 40 cc. of dry benzene added all at once. After about two hours refluxing the reaction was hydrolyzed with 50 cc. of 10 per cent hydrochloric acid and the solvents removed. About 75 cc. of petroleum ether (b. p. 60-88°) was added and warmed until solution was complete. After thoroughly cooling under the tap
the precipitate was filtered on a fluted filter and washed with a little petroleum ether. When dry it weighed 1.5 g. and melted at 65-80°. Probably, it was a mixture of n-hexatriacontane and stearone. The petroleum ether was removed from the filtrate and the residue crystallized from ethyl acetate to give 9 g. (85%) of carbinol, melting at 56-58°. Further crystallization raised this melting point to 58-59°.

Anal. Calcd. for C_{53}H_{108}O: C, 83.9; H, 14.3. Found: C, 84.1; H, 14.2.

A Zerewitinoff determination on the product melting at 56-58° gave 0.88 active hydrogen.

Preparation of n-Octadecylmagnesium Chloride.

In a 250 cc. three-necked flask containing a mercury-sealed stirrer, reflux condenser and dropping funnel was placed 1 g. (0.04 g. atom) of magnesium, 20 cc. of ether and a crystal of iodine. Ten and thirty-five hundredths grams of n-octadecyl chloride was dissolved in 40 cc. of ether and about 10 cc. of this solution added. After about ten to fifteen minutes refluxing the reaction had not started, so three or four drops of ethyl bromide were added. The reaction started immediately, so the remainder of the ether solution of halide was added dropwise, in the meantime the refluxing of the solution was continued. After five hours heating, the reaction was
considered to be complete. A 5 cc. aliquot was removed for titration (86). The yield of Grignard reagent was 64 per cent. To this was now added 11 g. (0.022 mole) of stearone in 50 cc. of hot benzene at one time. After about an hour of refluxing the solution was hydrolyzed with 50 cc. of 10 per cent hydrochloric acid, the benzene-ether layer separated and the solvents removed. After taking up in petroleum ether as in the previous experiment and filtering, the solution was concentrated and crystallized from ethyl acetate to give 13 g. (86%) of carbinol, melting at 56-58°.

Preparation of 18-Iodo-18-n-octadecylpentatriacontane,

\[
\text{C}_{18}^\text{H}_{37}^\text{I}
\]

\[
\text{C}_{17}^\text{H}_{35}^\text{O} \text{C}_{17}^\text{H}_{35}^\text{I}
\]

In a 250 cc. three-necked flask containing a mercury-sealed stirrer and condenser, was placed 7 g. (0.0105 mole) of 18-n-octadecylpentatriacontan-18-ol, 2 g. of red phosphorous, and 18 g. of iodine. The reaction was heated at 80-85° for eight hours. After cooling, 100 cc. of ether was added and the contents allowed to stand overnight. About 30 cc. of water was now added and the contents allowed to stir until the excess of phosphorous and iodine had reacted. The layers were separated and the ether layer washed with water, sodium thiosulfate solution, and then with water again.

After thoroughly cooling in an ice-bath, the precipitate was filtered and washed with a little cold ether. This precipitate weighed 1 g. and melted at 60-70° with softening at 30°. The ether was removed from the filtrate and the residue crystallized from acetone-ethyl acetate to give 6.5 g. (74%) of product, melting at 29-31°.


The low iodine analysis was probably due to the presence of a small amount of n-pentatriacontane.

Preparation of 18-n-Octadecylpentatriacontane, C₁₇H₃₅CH₁₇H₅₅C₁₆H₃₇

A mixture of 2.5 g. (0.0032 mole) of 18-iodo-18-n-octadecylpentatriacontane, 50 cc. of glacial acetic acid and 5 g. of zinc dust was placed in a 250 cc. three-necked flask containing a mercury-sealed stirrer and condenser. The solution was saturated with gaseous hydrogen chloride and heated until vigorous reaction had subsided. The above process was continued until nearly all the zinc had dissolved. After cooling, the precipitate solidified and was filtered and washed with water. Crystallization from ethyl acetate gave 1.9 g. (80%) of hydrocarbon melting at 43-44.5°. This product was completely soluble in ether at room temperature and on cooling this solution in an ice-bath it crystallized. The melting point was unaltered.

The product was placed in a molecular distillation
apparatus (87), and distilled in a vacuum of considerably less than 1 mm. of mercury. At a bath temperature of 170-200° a small amount (less than 0.1 g.) of product melting at 68-71° was removed. From 210-230° a second fraction was removed melting at 41-56°. The bath temperature was now raised to 240-250° and the remainder of the material removed in three parts. The melting points were as follows: I, m. p. 44-46°; II, m. p. 45-46°; III, m. p. 45-46°. The total weight of these fractions was 1.1 g. A small sample of this material, when dissolved in carbon tetrachloride, required about one more drop of a solution of bromine in carbon tetrachloride than a blank of carbon tetrachloride required to produce the same coloration.


Attempt to Prepare 19,19,20,20-Tetra-n-heptadecyltriocotriacontane.

A mixture of 2.0 g. (0.0026 mole) of 18-iodo-18-n-octa-
decylpentatriacontane, 1 g. of sodium and 30 cc. of dry xylene was refluxed for sixty hours and then filtered hot. After removing the xylene by steam distillation, the residue was crystallized from ethyl acetate to yield 1.5 g. of product.

(87) This consisted of a large pyrex test tube having a side arm and a cold finger condenser. All the connections were ground glass joints.
The product was placed in a molecular distillation
of the residue gave 0.6 g. Of hydrocarbon, melting at 42-46°C, and
removed from the ether from the titration and crystallization
were melted at 74-76°C and were apparently free from impurities. The precipitate
was taken up in 10 cc. of dry ether and filtered. The precipitate
was further crystallized from dry ether. The product was
of 10-α-secadehydroperhydroconocene (724), melting at 43-46°C.
Precipitation II (α-secadehydroperhydroconocene) from ethyl acetate gave 0.6 g.


The product was distilled in vacuum. Precipitation I
reached the melting point at 45-46°C. Although the
melt did not become clear until a temperature of 50°C was
reached, the product was totally dissolved in methanol and
ether. For the most part it melted at 46-46°C. The product was washed with water and crystallized from either
methanol or acetone. The mixture of dry carbon tetrachloride was
passed through a column of activated carbon and allowed to
flow over 10-α-secadehydroperhydroconocene-10-0. The
mixture of dry carbon tetrachloride was filtered and allowed to
crystallize. The compound contained no

melting at 48-48°C. Further crystallization from ether yielded
apparatus and distilled as described on page 91 of this thesis. The following fractions were removed: I, m. p. 70-72°; II, m. p. 40-65°; III, IV and V, melted at 42-44° and weighed 2.5 g. This compound, when dissolved in carbon tetrachloride, readily decolorized a solution of bromine in carbon tetrachloride.

Anal. Calcd. for C$_{53}$H$_{106}$: C, 85.8; H, 14.2. Found: C, 85.9; H, 14.2.
DISCUSSION OF RESULTS

This thesis has been principally concerned with the application of known reactions to high-molecular-weight fatty acid derivatives. Of necessity, this type of an investigation involves the preparation of a number of intermediates, some of which, of course, have been previously described in the literature. In some few cases, these known preparations have been redescribed in this thesis, particularly, when the methods have been modified to any extent.

Lauronitrile and stearonitrile were prepared by a slight modification of the method described by Ralston, Harwood, and Poole (75). The apparatus employed by these investigators consisted of a Claisen flask, in one neck of which there was an inlet tube for ammonia, and in the other neck there was a tube containing aluminum oxide heated to a temperature of 330-360°. This served to transform any ammonium stearate, which was carried up by the ammonia, into stearonitrile. It was found that this tube could be replaced by an ordinary air condenser. The yields, using this method, were about 8-10 per cent lower, but the set-up was greatly simplified.

Although secondary long-chained amines have been made by a number of different methods (88), their synthesis from nitriles by catalytic hydrogenation has not been reported.

The availability of lauro- and stearonitrile made these compounds the logical choice for such a reaction. In the presence of Adkins' copper-chromium oxide catalyst, di-\(n\)-dodecyl and di-\(n\)-octadecylamine were obtained consistently in from 74-78\% yields.

Since, as has been shown in this thesis (89), \(n\)-dodecyl- and \(n\)-octadecyl chloride may be synthesized in excellent yields from the readily available \(n\)-dodecanol and \(n\)-octadecanol, the synthesis of tri-\(n\)-dodecylamine and tri-\(n\)-octadecylamine by the interaction of two moles of the appropriate secondary amine with one mole of the appropriate \(n\)-alkyl chloride was considered worth while. Tri-\(n\)-dodecyl- and tri-\(n\)-octadecylamine were obtained by this reaction in rather good yields.

In connection with other studies, the need arose for the \(\beta\)-imino-nitriles which could possibly be obtained by the condensation of lauronitrile and stearonitrile with themselves. Accordingly, the synthesis was attempted through the use of phenylethyllithium amide \((C_8H_5NC_8H_5)\text{Li}\) in ether solution. 2-\(n\)-Decyl-3-iminomyristonitrile was obtained in nearly quantitative yields from lauronitrile, and 2-\(n\)-hexadecyl-3-imino-arachidonitrile was obtained in nearly as good yields from stearonitrile. These compounds on hydrolysis with concentrated sulfuric acid gave the corresponding \(\beta\)-keto-amides, which in

(89) This thesis, page 69.
turn gave the ketones, laurone and stearone, respectively, on hydrolysis with alcoholic potassium hydroxide. This established the structure of both compounds. Mild hydrolysis gave, in each case, the expected \( \beta \)-keto-nitrile.

A series of thioamides were prepared from thiolauramide up to and including thiostearamide, by the thiohydrolysis of the respective nitriles with hydrogen sulfide using sodium hydrosulfide as a catalyst. They were identified by analysis. It was hoped that compounds of this type might be useful as flotation agents.

Since the Friedel-Crafts reaction between napthalene and stearoyl chloride gives a mixture of 1- and 2-stearoyl-napthalene (41), the synthesis of these compounds by another method was deemed of interest. The preparation of \( \alpha \)-stearoyl-napthalene by the reaction of \( \alpha \)-napthylmagnesium bromide with stearonitrile has been previously reported (19). \( \beta \)-Napthylmagnesium bromide and stearonitrile gave \( \beta \)-stearoylnapthalene in fair yields. The melting point agreed with that of Seidel and Engelfried for their supposed 2-stearoylnapthalene, for which no structure proof was offered. In this connection the structure of 2-phenylstearophenone obtained from a Friedel-Crafts reaction between stearoyl chloride and biphenyl was proven by synthesis from 4-biphenyllithium and stearonitrile.

The Fries rearrangement of phenolic esters gives hydroxyketones in rather good yields in many cases. Compounds of
this type are of interest as germicides. With this in mind, the Fries rearrangement of \( p \)-phenylphenyl stearate was attempted.

Usually rearrangements of this type are brought about by mixing the ester and aluminum chloride in carbon disulfide, and after removing the carbon disulfide the reactants are heated at a temperature of 100-150\(^\circ\) for a short period of time. However, with \( p \)-phenylphenyl stearate the rearrangement took place on simply refluxing the carbon disulfide solution of the ester and aluminum chloride. As was to be expected, two products were formed; \( o \)-methoxy-\( m \)-phenyl-stearophenone and \( p \)-(\( p \)-methoxyphenyl)stearophenone. Separation of these substances was accomplished rather easily by their difference in solubility in petroleum ether; the para isomer, as might be predicted, was much less soluble.

Upon oxidation with chromium trioxide, \( p \)-(\( p \)-methoxy-phenyl)stearophenone gave terephthalic acid, which was identified as dimethyl terephthalate. The formation of terephthalic acid proves the stearoyl group occupies the para-position in the biphenyl nucleus. Since the ring containing the hydroxyl was degraded to a carboxyl group on oxidation, the hydroxyl must occupy the para-position in the other benzene ring in the biphenyl nucleus. Accordingly, the constitution of the compound is \( p \)-(\( p \)-methoxyphenyl)stearophenone.

The structure of \( o \)-hydroxy-\( m \)-phenylstearophenone was
established by the synthesis of \( \alpha \)-methoxy-\( m \)-phenylstearophenone from the known \( 4 \)-methoxy-\( 3 \)-biphenylmagnesium bromide and stearonitrile, and was identical (mixed m. p.) with the product obtained by methylation of \( \alpha \)-hydroxyl-\( m \)-phenylstearophenone from the Fries rearrangement.

Although the formation of the ortho and para isomers has been observed with the Fries rearrangement of \( p \)-acetoxy-biphenyl, the constitution of the ortho product was not established (16). With \( p \)-phenylphenyl benzoate both ortho and para migration has been observed and the positions proven (33). However, both products were not observed from a single reaction, but under different conditions the ortho and para isomers are each obtained.

As is well known the introduction of sulfonic groups into an organic compound increases its solubility in water. With this in mind, it was decided to undertake the sulfonation of long-chained alkyl-aryl ketones. \( p \)-Phenylstearophenone and \( p \)-phenoxystearophenone were used as they seemingly would be easier to sulfonate and would also offer less chance for the formation of isomers.

Under comparatively mild conditions the ketones were sulfonated in rather good yields. In each case with concentrated sulfuric acid a monosulfonic acid was formed. In neither of these instances were the sulfonic acids, or their sodium salts, soluble in water to any extent, although the
solubility without doubt had been increased.

With \( p \)-phenylstearophenone the product was shown to be 4-stearoyl-4'-biphenylsulfonic acid by oxidation to 4-sulfo-4'-biphenylcarboxylic acid. This acid was obtained by the sulfonation of 4-biphenylcarboxylic acid. The products were shown to be identical by a mixed melting point of the \( p \)-toluidine salts. In order to prove the position of the sulfonic group in 4-sulfo-4'-biphenylcarboxylic acid it was fused with potassium hydroxide to give 4-hydroxy-4'-biphenylcarboxylic acid. The melting point agreed with that of 4-hydroxy-4'-biphenylcarboxylic acid obtained by Fieser by a different method (33). However, in order to establish the structure beyond a doubt, the 4-hydroxy-4'-biphenylcarboxylic acid was decarboxylated to the known \( p \)-phenylphenol. A mixed melting point determination with an authentic sample proved the substances to be identical.

Sulfonation of \( p \)-phenylstearophenone with chlorosulfonic acid gave a trisulfonic acid which was water-soluble. On oxidation, 4-sulfo-4'-biphenylcarboxylic acid was obtained which indicates that two sulfonic groups are located in the side chain. No attempt was made to ascertain the points at which these sulfonic groups were attached. However, it is entirely possible they are in the alpha, alpha-positions for these positions would probably be easily substituted (90).

With $p$-phenoxy stearophenone, the location of the sulfonic group was not entirely established. By oxidation with very dilute nitric acid, the 4-stearoylphenoxybenzenesulfonic acid gave 4-sulfophenoxybenzoic acid. Fusion of this product with potassium hydroxide cleaved the ether linkage, resulting in the formation of $p$-hydroxybenzoic acid. This only proves the stearoyl and sulfonic groups are in opposite benzene rings in the 4-stearoylphenoxybenzenesulfonic acid. In view of previous investigations, it is likely that the sulfonic group is in the para-position, as the introduction of a sulfonic group into $p$-bromodiphenyl ether gives 4-(4-bromophenoxy)benzenesulfonic acid (38).

Organic chemists have always been interested in hydrocarbons. Doubtless this has been partially due to the large number of compounds of this type which occur naturally, and the many uses to which they may be put. In recent years they have been particularly concerned with high-molecular-weight hydrocarbons because of their use in physico-chemical experiments, as well as, their biological significance. In addition, high-molecular-weight hydrocarbons have been used for viscosity measurements. The study of lubricating oils has also prompted the synthesis of a number of high-molecular-weight hydrocarbons. Before beginning a study of problems of these types, it is necessary to work out the preparation of a number of intermediates as well as to obtain considerable amounts
of the final products. With this in mind, a start has been made on the synthesis of some high-molecular-weight compounds.

The synthesis of symmetrical ketones through heating of a fatty acid with iron powder has been known for a long time (91). However, many of the directions given in the literature are rather brief, and in some cases they are not applicable to the synthesis of relatively small amounts of ketones. It has been found that by heating lauric and stearic acid with iron powder in an atmosphere of carbon dioxide, yields of from 80-90% of the symmetrical ketones, laurone and stearone are obtained. It was also found to be advantageous to remove the iron present by heating with diluted hydrochloric acid before attempting to crystallize the ketones. This served to remove largely the color from the products.

The reduction of myristone and stearone to secondary alcohols by sodium and n-butyl alcohol was found to proceed in very good yields. By the treatment of 18-pentatriacontanol with phosphorous and iodine, 18-iodopentatriacontane was formed. In the hope of obtaining a symmetrical tetra-substituted ethane, attempts were made to couple 18-iodopentatriacontane by the Wurtz reaction, and by reaction of the Grignard reagent with cupric chloride. However, in neither case was the desired compound isolated, but instead n-pentatriacontane was obtained along with other lower melting products and

18-iodopentatriacontane. This was not particularly surprising for Suida and Planckh (67) have observed corresponding products in attempting to couple 18-iodohentriacontane.

Incidentally, the coupling of \( \eta \)-dodecylmagnesium bromide with cupric chloride gave only a 22% yield of \( \eta \)-tetracosane, so evidently this reaction is not applicable in effecting coupling of high-molecular-weight Grignard reagents. The extent to which \( \eta \)-tetracosane is formed during the preparation of \( \eta \)-dodecylmagnesium bromide is probably 10-15%, in view of the amount formed when \( \eta \)-dodecylmagnesium iodide is prepared (23%) (52).

According to Suida and Planckh, the interaction of \( \eta \)-hexadecyl bromide, magnesium and palmitone, using the Barbier procedure, gave a very small yield of tertiary alcohol; starting with 63 g. palmitone and 26 g. of cetyl bromide only 3.2 g. of carbinol was obtained.

However, as has been shown in this thesis (92), the synthesis of 18-octadecyl-18-pentatriacontanol from either \( \eta \)-octadecylmagnesium bromide, or \( \eta \)-octadecylmagnesium chloride and stearone gave excellent yields (86% based on the ketone used) of the tertiary carbinol. Incidentally, the use of \( \eta \)-alkyl chlorides for the preparation of long-chained Grignard reagents appears to be preferable, because of the greater extent to which the Wurtz reaction takes place when either the

(92) This thesis, page 87.
\textit{p}-alkyl bromides or iodides are used. The \textit{p}-pentatriacon-
tane formed when \textit{p}-octadecylmagnesium bromide was used was
very difficult to remove and was present in considerable
quantities (10-15\%). It is likely that with \textit{p}-octadecyl-
magnesium chloride there is only about 5\% of \textit{p}-pentatria-
contane present, since with \textit{p}-dodecylmagnesium chloride the
Wurtz reaction takes place to about that extent (52). By
titrations, the yield of \textit{p}-octadecylmagnesium chloride was
64\%, but without doubt this yield can be improved.

\textit{18-Octadecyl-18-pentatriaconanol} was easily transformed
into \textit{18-octadecyl-18-iodopentatriaconante} by means of phos-
phorous and iodine. On reduction with zinc and hydrochloric
acid, \textit{18-octadecylpentatriaconante} was formed in fairly good
yields. This is the largest hydrocarbon of this type known.

In the hope of forming a hexa-substituted ethane, \textit{18-
octadecyl-18-iodopentatriaconante} was reacted with sodium in
a Wurtz reaction. The product obtained was halogen free and
melted at 41-43^\circ. It was also unsaturated. By dehydration
of \textit{18-octadecyl-18-pentatriaconanol}, \textit{18-octadecylpentatria-
contene} was formed. It melted at 42-44^\circ and quite possibly
is a mixture of olefins, since dehydration of the carbinol
could possibly give two olefins. A mixed melting point with
\textit{18-octadecylpentatriaconante} (m. p. 45-46^\circ) melted at 43-45^\circ.

The value of mixed melting points with high-molecular-
weight aliphatic compounds is uncertain. As mentioned earlier
in this thesis (51), mixed melting points between n-aliphatic hydrocarbons are not of any value. In general, it may be safely said, that aliphatic compounds of high-molecular-weight do not show as large a depression of melting point in mixed melting point determinations (93), as do many other types of compounds.

On the basis of the mixed melting point and the fact that the mixture is unsaturated, it is not unlikely the products of the Wurtz reaction are the disproportionation products, 18-octadecylpentatriacontene and 18-octadecylpentatriacontane. Disproportionation reactions are frequently observed in attempting to synthesize hydrocarbons by the Wurtz reaction with high-molecular-weight alkyl halides (63) (52). Without doubt, the hexa-substituted ethane would have a considerably higher melting point than the tertiary hydrocarbon.

Before beginning a discussion of homology or the limits of it, it is well to define the word homology. According to Dr. Austin M. Patterson (94) the meaning of homology with regard to chemistry is defined as follows: "The relation existing between the compounds of a series whose successive members possess, in addition to similarity of structure a

regular difference in formula." Now according to this definition primary, secondary, and tertiary aliphatic alcohols can not be considered as members of a single homologous series, for they are not structurally similar, and in fact are known as structural isomers. In reality then these compounds should belong to three homologous series. Of course, this is applicable to other aliphatic series; hydrocarbons, alkyl halides, acids, etc.

Seemingly, Whitmore (4) has considered the entire classes of aliphatic hydrocarbons, alcohols, etc., as belonging to one homologous series each. With this classification a great many irregularities are observed in the preparation, reactions and properties of the various compounds as one ascends such a series. However, if one considers as an example of a homologous series the normal aliphatic alcohols, it is observed that there are regular variations of the physical and chemical properties.

By far the greater number of compounds in this thesis are normal aliphatic compounds, and therefore, few conclusions can be drawn except with regard to a normal aliphatic series. At the outset it may be said that no pronounced irregularities were observed in the preparation or reactions of these long-chained compounds.

In the preparation of the series of thioamides from thiolauramide to thiostearamide no irregularities were observed
either in the preparation or the properties of the compounds. As a matter of fact, the directions are nearly identical with those used in the preparation of other thioamides both aliphatic and aromatic.

The condensation of acetonitrile and n-butyronitrile to form β-imino-nitriles proceeds under identical conditions with those described in this thesis for the preparation of β-imino-nitriles from lauronicnitrile and stearonitrile and the yields are comparable.

It is interesting to observe that several attempts to obtain a Reformatsky reaction with either ethyl α-bromo-laurate or α-stearate were unsuccessful (95). This is in marked contrast to the reactivity of theα-carbon atoms in lauronitrile and stearonitrile in the formation of β-imino-nitriles.

n-Dodecylmagnesium chloride (52) has been prepared in excellent yields (91%) and although the yield of n-octadecylmagnesium chloride was only 64% in a single experiment, no great weight can be placed upon this, for it is possible different conditions would improve this yield.

Ketones, such as laurone and stearone react with long-chained Grignard reagents under strictly comparable conditions with the conditions employed for the preparation of other tertiary alcohols by a similar reaction. In addition, there

(95) Unpublished work by Dr. Henry Gilman and the author of this thesis.
appears to be no great change in the rate of reaction for
in a very short time (less than an hour) after adding an
excess of ketone to the Grignard reagent the color test for
organometallics is negative. So far as was investigated in
this thesis, the reactions of the high-molecular-weight
tertiary alcohols were comparable to those of lower molecu-
lar weight. They were readily dehydrated to olefins and
formed iodides which were easily reduced.

No differences were observed in the preparation or
yields of long-chained secondary amines by hydrogenation of
nitriles than are observed with other nitriles. In addition,
the secondary amines readily reacted with \( p \)-alkyl halides
to form tertiary amines which is characteristic of the other
shorter-chained \( p \)-alkyl halides and secondary amines.

No difficulties were observed in the Fries rearrange-
ment of \( p \)-phenylphenyl stearate, and as a matter of fact, the
yields were superior to those obtained with either the benzo-
ate or acetate. However, this can probably be attributed
to the somewhat more drastic conditions employed to effect
these rearrangements.

From this discussion it appears that there are no pro-
nounced irregularities in either the reactions or prepara-
tions of the compounds investigated in comparison with similar
reactions and the properties of shorter-chained compounds.
This, of course, is by no means conclusive and it is
conceivable that with compounds of longer-chain length and higher molecular weight differences may be observed. In fact the investigation of compounds of this chain length (C₁₂-C₁₈) is by no means complete, and there are many more reactions to be carried out before any exact conclusions may be drawn.

Note on Nomenclature. In a personal communication from Dr. E. J. Crane and Dr. Leonard T. Capell of the Editorial staff of Chemical Abstracts, dated July 6, 1938, these authorities give the following preferred names for certain alkylaryl ketones and derivatives included in this thesis; 2-methoxy-5-phenylstearophenone (96), 2-hydroxy-5-phenylstearophenone (96), 4'-stearyl-4-biphenylsulfonic acid (97) and 4'-sulfo-4-biphenylcarboxylic acid (97). The various other ketones and derivatives are correctly named according to these authorities.

(96) This thesis, pages 62, 63 and 65.
(97) This thesis, pages 73 and 74.
SUMMARY

The preparation of aliphatic nitriles, thioamides, $eta$-imino-nitriles, ketones, long-chained secondary and tertiary amines; the Fries rearrangement of esters of $p$-phenyl-phenol, sulfonation of biphenyl, diphenyl ether and derivatives, long-chained alkyl-aryl ketones and hydrocarbons have been discussed.

A review of the literature pertaining to high-molecular-weight hydrocarbons has been made.

The synthesis of a number of high-molecular-weight fatty acid derivatives has been accomplished: $eta$-imino-nitriles, secondary and tertiary amines, alkyl-aryl ketones, sulfonic acids of alkyl-aryl ketones and some alcohols, iodides and hydrocarbons.

Some improvements have been made in the preparations of laurone and stearone, and the preparation of $n$-dodecyl chloride, $n$-octadecyl chloride and bromide has been described.

A discussion of the limits of homology has been made with regard to normal aliphatic compounds.