Radical reactions with aromatic nitro compounds

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RADICAL REACTIONS WITH AROMATIC NITRO COMPOUNDS

by

John A. Tanaka

A Dissertation Submitted to the Graduate Faculty in Partial Fulfillment of The Requirements for the Degree of DOCTOR OF PHILOSOPHY

Major Subject: Organic Chemistry

Approved:
Signature was redacted for privacy.

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Signature was redacted for privacy.

Head of Major Department
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Dean of Graduate College

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PART I. THE REACTION OF $p$-NITROPHENYL RADICAL

WITH NITROBENZENE
INTRODUCTION

The nature of the substitution of an aromatic nucleus by a free radical is relatively unknown compared with its ionic counterpart. Wide recent interest in this reaction has led to a fairly thorough study of the effect of phenyl radical substitutions on various aromatic substrates. This work was initiated in the hope of furthering the understanding of this reaction by observing the effects of a p-nitro group on the attacking phenyl radical in its reaction with nitrobenzene.

Unlike electrophilic aromatic substitution, this reaction does not give rise to a predominant amount of a few products, but in general gives many products mixed together in a difficultly resolved tar. Since the simple aromatic substitution products often account for less than half of the reaction products, it was thought that characterization of some of these other products would lead to a better understanding of the reaction.
HISTORICAL

Homolytic aromatic substitution, the attack of an aromatic ring by a free radical, has been known for some time. One of the earliest practical uses was the synthesis of unsymmetrical biaryls by the diazo reaction.\(^1\) This general synthesis was further elucidated by Grieve and Hey\(^2\) and Heilbron\(^3\) who used the nitrosoacetylamines as the free radical source. This reaction has been used to synthesize a number of products. The literature for this reaction is reviewed quite extensively in a chapter in *Organic Reactions* by Bachmann and Hoffman\(^4\).

Although the phenyl and substituted phenyl radical has been most extensively studied, other free radicals have also been substituted on aromatic nuclei. Claims have been made for methyl radical substitution, although there is evidence to indicate that addition rather than substitution is taking place.\(^5\) Fieser, Clapp and Daudt\(^6\) decomposed lead tetraacetate to obtain methylated aromatic nitro compounds. Sandin and McCormack\(^7\) decomposed phenyliodosoacetate to methylate trinitrotoluene. Szwarc\(^8,9\) has thermally decomposed acetyl peroxide to study reactivities of aromatic hydrocarbons toward the methyl radical.
The hydroxy radical has been generated in a number of ways. Weiss and co-workers produced hydroxyl radicals from Fenton's reagent and effected substitution on nitrobenzene. Halfpenny and Robinson hydroxylated as well as nitrated toluene, nitrobenzene, dimethylaniline, phenol, anisole, and chlorobenzene using pernitrous acid. Weiss and co-workers have made extensive use of the hydroxyl radical generated by X rays. Reactions of hydroxyl radicals thus generated and benzoic acid, phenols, and chlorobenzene have been reported.

Other radicals which react homolytically with aromatic nuclei are the nitro, amino, benzoylperoxy, benzenesulfonimido, carboxymethyl and 2-cyano-2-propyl radicals. Halfpenny and Robinson's work with nitro radicals from pernitrous acid has already been mentioned. Laville and Waters nitrated quinoline using this same radical source without getting the hydroxy substituted product. According to Seaman, Taylor, and Waters the amino radical from hydroxylamine and titanous ion gives adducts with benzene and toluene which decompose on standing to give ammonia, aniline and diphenyl in the case of benzene and toluidine in the case of toluene. Benzoylperoxy radical from benzoyl peroxide is found to attack anthracene, 3,4′-benzopyrene, and 1,2-benzanthracene in the exposed meso positions by substituting the benzoyl group for a hydrogen.
Dermer and Edmison\textsuperscript{18} report the substitution of benzenesulfonimidoo radical on a series of aromatic compounds. Carboxymethyl radical is ostensibly formed during the irradiation of 3,4-benzpyrene and thioglycolic acid since 5-benzpyreneacetic acid is obtained in good yields.\textsuperscript{19} The 2-cyano-2-propyl radical from azo-bis-isobutyronitrile has been substituted on 9-substituted anthracenes and 3,4-benzpyrene.\textsuperscript{20, 21}

In a development historically similar to the elucidation of electrophilic aromatic substitution, the orientation of substitution in homolytic aromatic substitutions has been actively pursued in recent years. Most of the work has been done using phenyl radicals, although data is also available for the other radicals which undergo homolytic aromatic substitution.

It was noted by the early workers in this field that the orientation effects for homolytic substitutions did not follow the rules of ionic substitutions. Thus Gomberg and Bachmann\textsuperscript{1} reported ortho and para attack on nitrobenzene. Grieve and Hey\textsuperscript{2} found para attack on toluene, chlorobenzene, nitrobenzene, and benzaldehyde. Hey also reported in a subsequent paper published in the same year\textsuperscript{22} that ethyl benzoate gives meta-para substitution while nitrobenzene gives ortho-para and chlorobenzene gives para substitution.

After a lapse of some years, this field has again become quite active. Since several review articles are in press\textsuperscript{23, 24},
an extensive review of the orientation phenomena will not be made here. In general, refinement of technique has made possible a more accurate estimation of the isomer ratios arising from the radical reaction. Ultraviolet and especially infrared spectroscopy have been invaluable aids. By using these tools to determine isomer ratios and by doing competitive experiments in which several substrates are made to compete for the attacking radical, a series of partial rate factors for homolytic substitutions at various positions in various substrates have been determined. Hey and co-workers have been particularly active in this field\textsuperscript{25-36}. Their work as well as that done by others is nicely tabulated by Rondestvedt\textsuperscript{37}, who also extensively discusses the mechanism of the reactions involved. Hey\textsuperscript{38} tabulates data in another review which strikingly points out the insensitivity of the isomer ratios to the method used for generating the radical.

The substituted benzenes are on the whole more reactive than benzene to substitution and all but a few show ortho-para direction with an ortho/para ratio larger than commonly found in electrophilic substitutions.

Very recently workers have started to report on the effects of substituents in the attacking phenyl radical. Hey is quoted by Rondestvedt\textsuperscript{37} as finding little orientation change on the arylation of nitrobenzene by p-tolyl, phenyl, p-bromophenyl, and p-nitrophenyl radicals. The meta substitution
ranged from 9 to 15 per cent. He also finds\textsuperscript{33} that \textit{p}-
chlorophenyl radicals are less reactive than phenyl radicals
to substitution on nitrobenzene and chlorobenzene. Dannley\textsuperscript{39}
reacted phenyl, \textit{p}-chlorophenyl, and \textit{p}-nitrophenyl radical with
benzotrichloride and obtained predominant meta substitution
with all three radicals. Simamura\textsuperscript{40} reacted \textit{p}-anisyl radical
with nitrobenzene and reports relative reactivities of the
ortho: meta: para as 7.24: 0: 8.95 on the basis of a nuclear
position of benzene as unity. DeTar\textsuperscript{41} studied the effects of
both the 3-nitrophenyl and 4-nitrophenyl radical by decom-
posing the diazonium salt in nitrobenzene. The 3-nitrophenyl
radical produced 31 per cent ortho, 25 per cent meta and \textit{h}4
per cent para isomers. The 4-nitrophenyl radical produced
\textit{h}4 per cent ortho, 23 per cent meta and \textit{h}3 per cent para
isomers. Morrison and Sweeney\textsuperscript{42} have indicated that they have
substituted nitrobenzene and anisole with \textit{p}-nitrophenyl
radicals and have found substitution ratios of ortho: meta:
para of 58 per cent: 13 per cent: 29 per cent for nitrobenzene
and 89 per cent: 8 per cent: 3 per cent for anisole.

There has been little in the literature regarding
products other than the primary homolytic aromatic substitution
products formed in these reactions. Almost all the workers
report tar to be produced in these radical reactions.
Rondeسته\textsuperscript{43} mentions that in phenylations with \textit{N}-nitroso-
acetanilide red azo compounds are produced along with biphenyl
fractions. DeTar found on vacuum distillation and chromatography of a reaction mixture of N-nitrosoacetanilide and benzene that he obtained a mixture of azobenzene and biphenyl which he estimated to be 6 per cent azobenzene on the basis of the nitrogen analysis on the mixture. He further isolated the azobenzene by extraction with conc. sulfuric acid and reprecipitation in water.

The nature of the N-nitrosoacylanilides has received attention. Huisgen and DeTar present evidence that the N-nitrosoacylanilides rearranges in a rate determining step to form the aryldiazoacetate. Huisgen has also extensively studied the ionic reactions of N-nitrosoacylanilides by investigating the reactions of these compounds with phenols to form the diazo dyes and with picric acid to form the benzene diazonium picrates. A reaction of interest is the decomposition of N-nitrosoacetanilide in piperidine to form L-phenylazopiperidine. This reaction is reported to proceed explosively when piperidine is added to dry N-nitrosoacetanilide.
EXPERIMENTAL

Compounds Used for the Radical Reaction

**Preparation of nitrosyl chloride**

Nitrosyl chloride was prepared following the procedure described by J. R. Morton and H. W. Wilcox. The apparatus described was modified by substituting a 9 x 17 cm. vessel with a 35/25 socket joint for the main reaction chamber. By using a dropping funnel equipped with a 35/25 ball joint in conjunction with this reaction vessel, it was found that the apparatus could be much more readily handled under the pressures required for the reaction.

The nitrosyl chloride was purified by distillation through a Vigreux column surrounded by a dry ice-acetone bath. The distilled nitrosyl chloride was collected in ampoules with a capacity of approximately 10 ml. and sealed. Each ampoule thus contained enough nitrosyl chloride for preparing one batch of N-nitrosoacetanilide.

**p-nitroacetanilide**

Eastman p-nitroacetanilide was recrystallized twice from ethyl alcohol. The melting point in a Hershberg melting point
apparatus was 114.5°C (uncorrected).

Preparation of \( p \)-nitro-\( N \)-nitrosoacetonilide

The method is a modification of the preparation of \( N \)-nitrosoacetonilide reported by DeTar.\(^{46}\) 18.5 g. of \( p \)-nitroacetonilide, 15 g. of potassium acetate, 35 ml. of glacial acetic acid and 30 ml. of acetic anhydride were added to a 500 ml., 3 neck, round bottom flask. A tubor stirrer was inserted in one neck, a dropping funnel placed in another, and the third neck was stoppered. The mixture was stirred and heated to 70°C, but the slurry never becomes a solution as in the case of acetonilide.\(^{46}\) The finely divided slurry was then cooled to 5°C with an ice bath and a solution of 10 ml. of nitrosyl chloride in 30 ml. of acetic anhydride was slowly added while vigorously stirring. After the addition of the nitrosyl chloride, the reaction mixture was slowly poured on ice. When it was poured rapidly, there was a tendency for the product to oil out. On slow pouring, a yellow solid of \( p \)-nitro-\( N \)-nitrosoacetonilide was obtained. This was immediately filtered on a Büchner funnel and washed with water to melt the ice and wash out the excess acetic acid. A rubber dam was then placed over the Büchner funnel and ice placed on top of the dam while suction was continued. After most of the water has been removed, the yellow solid was dried further by pressing between sheets of filter paper.
About 25 g. of a canary yellow powder was obtained. However, there was some moisture left as was indicated by the small amount of a second phase that immediately formed on dissolving this substance in a solvent such as nitrobenzene. The p-nitro-N-nitrosoacetanilide when placed on a melting point block pre-heated to 65° C. began to decolorize at around 68° C. and decomposed at 71° C.

**Nitrobenzene**

Nitrobenzene from Matheson, Coleman & Bell was used after distillation through a column designed for vacuum distillations. The packing of this column consisted of one-inch lengths of 7 mm. tubing sealed at right angles to each other such that a three foot length of a zig-zag tubing was produced. This packing was then enclosed in a vacuum jacket with silvered walls. The stillhead consisted of a solenoid-activated valve with appropriately placed thermometer inlet and takeoff outlet. The whole head was equipped with a vacuum jacket with silvered walls for higher efficiency.

The distillation was carried out at atmospheric pressure for some batches and under vacuum for others. In all cases a 50 ml. forerun from a charge of 450 ml. of nitrobenzene was discarded. The distillation was always stopped with 50 to 100 ml. left in the pot.
Decomposition of p-nitro-N-nitrosoacetanilide in Nitrobenzene

As soon as the p-nitro-N-nitrosoacetanilide was prepared, it was dissolved in nitrobenzene. Even before the solid was completely dissolved, the nitrobenzene had acquired an orange color. Several droplets of a second phase consisting mostly of water formed at once. In all of the decompositions carried out, the reaction had progressed to a dark, reddish brown color in five minutes. The p-nitro-N-nitrosoacetanilide evidently easily rearranged at room temperatures in nitrobenzene to p-nitroazoacetate which in turn decomposed to p-nitrophenyl radical, nitrogen, and acetoxy radical. In one instance the progress was observed in parallel for the reaction of 7.75 g. of the radical source in 80 ml. of nitrobenzene and 19.00 g. of the radical source in 60 ml. of nitrobenzene. It was observed that after five minutes both solutions had turned a dark reddish brown color, and the reaction with the high concentration of radical source began to evolve bubbles of nitrogen. In ten minutes, the reaction with the high concentration of radical source warmed up appreciably due to the exothermicity of the reaction and began to evolve bubbles vigorously. At this time it was thought wise to moderate this reaction by cooling in ice water. The low radical source concentration reaction at this same time was evolving bubbles only slowly. In the
following five minutes the reaction with the high concentration of radical source had to be moderated four times by cooling in ice water. During this same period, the low concentration reaction warmed up slightly and began to evolve bubbles faster. It was very briefly cooled in ice water to insure that the reaction would not get out of hand. Twenty minutes after the start of the reaction, the high concentration reaction was evolving very little gas. At thirty minutes the low concentration reaction was still slightly warm and evolving nitrogen at a fair rate. After one hour the low concentration reaction was bubbling at a faster rate than the high concentration reaction. At one hour and fifteen minutes, both reactions were essentially finished although there was still a little activity left.

The decomposition reaction was cooled in ice water periodically in order to help keep the reaction under control. In one particular decomposition involving about 25 g. of p-nitro-N-nitrosoacetanilide in about 75 ml. of nitrobenzene the reaction became so violent when the reaction was not moderated by cooling that about one-half of the reaction mixture was ejected from the flask during the course of the reaction.

The small amount of the second phase forming immediately after the p-nitro-N-nitrosoacetanilide was added to the nitrobenzene increased in amount as the reaction proceeded.
In one experiment involving the decomposition of 18.77 g. of p-nitro-N-nitrosoacetanilide in 60 ml. of nitrobenzene, 1.8 g. of this light yellow colored liquid was isolated. This did not include that amount lost on equipment during separation procedures. On characterization, this liquid was found to have a boiling point of 97° C., a refractive index of 1.3600 at 25° C., gave an acid reaction to litmus, was miscible with water and did not seem to burn.

The qualitative distribution of acetic acid between nitrobenzene and water was determined. Water was added dropwise to a solution of nitrobenzene and glacial acetic acid in a graduate cylinder. A second phase did not form immediately, but as soon as it did, the nitrobenzene layer was found to be substantially less than the original volume of nitrobenzene and glacial acetic acid.

**Fractionation of the Reaction Mixture**

Most of the nitrobenzene was distilled from the reaction mixture for one of the runs. However since this was a slow process it was discontinued.

For all runs the nitrobenzene was customarily removed along with acetic acid by steam distillation. It was found that the nitrobenzene was essentially all stripped off by the time approximately three liters of distillate were collected.
The heterogeneous mixture in the steam distillation flask was then filtered while still hot through a fluted filter. A black tar remained on the filter paper and a yellowish-brown colored aqueous filtrate resulted. After drying off the excess water, the tar was transferred to a flask with acetone as quantitatively as possible. The aqueous filtrate on cooling produced a precipitate which on decolorization with Norite and recrystallization from ethanol gave a yellow solid which was identified as p-nitroacetanilide by its infra-red spectra.

The acetone used to transfer the tar was evaporated and the resulting black residue ground up to a powder in a mortar. This powder was placed in a Soxhlet extractor and extracted for 72 hours with ether. A small amount of crystal plus some dark brown-red tar was extracted out. Identification was not pursued since this was not a profitable method of rectifying the tar. Skelly B was then tried as a solvent for Soxhlet extraction. After more than a week of continuous extraction, a small amount of yellow crystals contaminated with a reddish tar was obtained. Recrystallization of both the Skelly extract and the ether extract was tried with a number of solvents, none of them showing much promise. The Soxhlet extraction was not tried with other solvents because it was felt that they would probably be more non-selective than the above two. In general, this method of isolating
components from the tar was abandoned as being unprofitable.

Paper chromatography using 4,4'-dinitrobiphenyl as a model compound was tried as a possible method of analyzing the components in the tar. Spots of several different concentrations were put on an 8" x 8½" paper. This paper was then placed in a jar for an ascending chromatography using a solvent system of three parts water, four parts pyridine and six parts n-butanol. After the chromatography was complete, the paper was cut into strips such that there was an original spot at the end of each strip. These strips were then cut into squares of approximately 7/8" x 7/8". Each of these squares was then placed in a 10 ml. erlenmeyer flask with 5 ml. of ether. Absorption spectra taken at 3050 Å on the Beckman D. U. showed that all of the dinitrobiphenyl remains on the original spot.

Attempts were made to find a rapid means of detecting the spot. Since the dinitrobiphenyl is in itself non-fluorescent, anthracene was sprayed on the paper containing a spot of dinitrobiphenyl in the hope that the anthracene might complex sufficiently with the dinitrobiphenyl so that it would not be washed off as rapidly as the uncomplexed anthracene. Unfortunately, this was found not to be the case. Ether, which was used as the wash solution, removed all of the anthracene from the paper. Another attempt was made to develop the dinitrobiphenyl spot by reducing the
nitro groups by spraying the spot with titanic chloride, diazotizing the resulting amino groups by spraying with n-butyl nitrite, and coupling the diazo compound by spraying with N-(1 napthyl) ethylene-diamine dihydrochloride. This procedure could not be made to work in two tries. Because there seemed to be no easy way of developing the spot and because the possibilities of finding a good solvent system for moving the spot seemed remote, this approach to a product analysis was also discarded.

The method finally used for fractionating the solid reaction mixture was column chromatography. A 4 x 36 cm. column was filled to approximately 20 cm. with Harshaw alumina. This alumina ranged in particle size from small amounts of 60 to 100 mesh, larger amounts in the 100 to 150 and 150 to 200 mesh sizes, the largest amounts in the 200 to 300 mesh size, and smaller amounts less than the 300 mesh size. There did not seem to be much difference on the effectiveness of the chromatography whether the 150 to 200 mesh size or the mixture was used. The mixture, however, seemed to be somewhat slower due to slower solvent flow. The activity according to Brockman was between II and III. The alumina was used without further activation.

The total solids from the reaction were adsorbed from a concentrated acetone solution on just enough alumina so that when the acetone was dried off, a friable system was obtained.
This was then poured on top of the alumina column and eluted with 1½ to 2 liters of Skelly B. Skelly B did not move any of the reaction products appreciably but did clean the column of small amounts of impurities which were found in some batches of alumina. It also helped remove traces of acetone which might have been left in the product layer.

Characterization of Chromatography Fractions

2,4'-dinitro biphenyl

Authentic 2,4'-dinitro biphenyl was obtained from Eastman Organic Chemicals as the white label product.

4,4'-dinitro biphenyl

The Eastman white label product was used as the sample of authentic 4,4'-dinitro biphenyl.

3,4'-dinitro biphenyl

This compound was prepared by a modification of the method of Scarborough and Waters. Ninety eight grams of Eastman white label p-aminobiphenyl was placed in a 500 ml. round bottom flask and 100 ml. of glacial acetic acid added. A Vigreux column was attached and the mixture refluxed. The temperature at the takeoff was adjusted to 100°C so that the water formed in the amidation reaction would be carried
off. After 6 hours, the mixture was poured into water and the product filtered and dried. The resulting p-acetamido-biphenyl was recrystallized from methanol. The recrys-
tallized p-acetamidobiphenyl, melting point 169-170° C. on the Fisher melting point block, was nitrated by cooling the crystals in ice and pouring in an excess of fuming nitric acid. This reaction was quite vigorous and the flask got quite hot even though it was kept in ice. When the addition was done in the reverse sense by adding small amounts of solid to cold fuming nitric, the dinitration was not complete.

After thirty minutes, the reaction mixture was poured on ice. The resulting yellow solid was recrystallized from glacial acetic acid. The melting point of the product obtained was 235-238° C. The melting point could be raised to 243° C. by recrystallizing this product from acetone. The procedure used to hydrolyze this compound to 4-amino-3,4'-dinitrobiphenyl was identical to that used by Scarborough and Waters. Deamination of the 4-amino-3,4'-dinitrobiphenyl was carried out as follows. A fine slurry of 2.51 g. of 4-amino-3,4'-dinitrobiphenyl in 100 ml. of glacial acetic acid was created by heating the mixture on a steam plate. Two grams of sodium nitrite was dissolved in 55 ml. of cone. sulfuric acid and cooled in an ice bath. To this cooled mixture 5.2 ml. of 30 per cent hypophosphorous acid was added. The re-
sulting mixture was cooled in an ice salt bath and vigorously
stirred. The slurry of 4-amino-3,4'-dinitrobenzophenyl in glacial acetic acid was then slowly added over a period of one-half hour or more. The reaction was stirred for another hour after the addition was complete and then stored in a refrigerator for twenty-four hours. The mixture was then poured on ice and extracted with benzene. The benzene extract was washed with water and evaporated down. The resulting residue was chromatographed on an alumina column. A white solid was obtained by eluting with 5 per cent benzene in Skelly B. When this was recrystallized from acetone, the product was found to have a melting point of 189-190° C. (uncorr.). The melting point reported in the literature is 189° C.

Infrared spectra

The infrared spectra of the authentic 2,4',- 3,4'- and 4,4'-dinitrobenzophenyls were determined on the Baird Associates instrument. The 2,4' isomer exhibited bands at 6.29 μ (w), 6.39 μ (w), 6.65 μ (s), 7.45 μ (s), 11.75 μ (m), 12.7 μ (w), 13.4 μ broad, 14.50 μ (w), and 14.80 μ (w). The 3,4' isomer had bands at 6.2 μ (w), 6.60 μ (s), 7.45 μ (s), 11.40 μ (w), 11.73 μ (m), 12.42 μ (w), 12.95 μ (m), and 13.62 μ (s). The 4,4' isomer showed bands at 6.29 μ (m), 6.65 μ (s), 7.50 μ (s), 11.45 μ (w), 11.80 μ (m), 11.95 μ (m), and 13.6 μ broad. A comparison of these spectra with those of the fractions
bend of the chromatographic column

merkably similar to that of the test washout from the ortogrou

did not match that of 1,4-dinitrotoluene but was re-

The spectrum of the red compound co-eluting with di-

The presence of large amounts of other compounds

sufficiently quantitated to be detected by infrared spectra in

bonds are formed in the reaction, they are not produced in

of the compounds but could not be found. In these cases the

the chromatographed fractions were examined for the presence

The spectrum of 13.40, 13.20, 7.90, and 7.30, and 7.0, 7.5, 6.5,

broad, 10.0, 11.0, 6.0, 8.0, 7.0, 7.5, 6.5, 7.0, 7.5, 6.5, 7.0, 7.5, 6.5,

not characteristic吸收 bands at 5.7, 5.7, 5.7, 5.7, 5.7, 5.7, 5.7, 5.7, 5.7,

samples of 1,4-dinitrotoluene and 1,4-dinitrophenyl-

Toullodet

not characteristic absorption bands of the test washout from

of yellow or orange solids were extracted of the chromatographic-

from the chromatographic column showed that all the early fractions
Isomer ratios from ultraviolet spectra

The ultraviolet spectra of the authentic 2,4',- 3,4'- and 4,4'-dinitro biphenyls were determined on the Beckman Model DU spectrophotometer. Extinction coefficients were determined for each of the isomers at 310 m\(\mu\), 270 m\(\mu\), and 285 m\(\mu\). By determining the absorbency of the dinitro biphenyl isomer mixtures, a system of three equations in three unknowns could be set up and solved for the concentration of each isomer. The results of these determinations are shown on Tables 2, 3, 4, and 5. Only the early dinitro biphenyl mixtures could be analyzed in this fashion since the red compound which overlaps the dinitro biphenyls in the course of chromatography would interfere with the spectrophotometric analysis.

A mixture of 0.1228 g. 4,4'-dinitro biphenyl and 0.0896 g. 2,4'-dinitro biphenyl was put on an alumina chromatography column and eluted with carbon tetrachloride. The 3,4'-dinitro biphenyl was not included since a sufficient quantity was not available at the time this experiment was conducted. The solids in fractions 3 to 32 were combined and analyzed spectrophotometrically. The molar ratio of 4,4' isomer to 2,4' isomer of the original mixture was 1.37. The mixture obtained from the chromatography column gave a spectrophotometrically determined molar ratio of 4,4'/2,4' of 1.38.
Table 1. Reaction of p-nitrophenyl radical and nitrobenzene\(^1,2\)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Fractions</th>
<th>Weight</th>
<th>Nature of product</th>
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<tbody>
<tr>
<td>Skelly B</td>
<td>1 - 28</td>
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<td>None</td>
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<tr>
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<td>29 - 35</td>
<td></td>
<td>I.R. shows 2,4'-dinitrobiphenyl bands</td>
</tr>
<tr>
<td>&quot;</td>
<td>37 - 44</td>
<td></td>
<td>I.R. shows 2,4' - and 4,4' - dinitrobiphenyl bands</td>
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<tr>
<td>&quot;</td>
<td>45 - 51</td>
<td></td>
<td>I.R. shows 4,4'-dinitrobiphenyl bands</td>
</tr>
<tr>
<td>&quot;</td>
<td>52 - 66</td>
<td></td>
<td>Crystallization yields needles, MF 233(^\circ) and powder, MF 130(^\circ)</td>
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<tr>
<td>&quot;</td>
<td>67 - 82</td>
<td></td>
<td></td>
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<tr>
<td>Benzene</td>
<td>83 - 89</td>
<td></td>
<td>First bit of red color comes through</td>
</tr>
<tr>
<td>&quot;</td>
<td>90 - 91</td>
<td></td>
<td>Relatively lots</td>
</tr>
<tr>
<td>&quot;</td>
<td>92</td>
<td></td>
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<td>&quot;</td>
<td>93 - 94</td>
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<td></td>
</tr>
<tr>
<td>Acetone</td>
<td>108</td>
<td></td>
<td>Brown-black solid. I.R. shows p-nitroacetonilide bands plus some others.</td>
</tr>
<tr>
<td>&quot;</td>
<td>109 - 112</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^1\)Approximately 25 g. p-nitro-N-nitrosoacetonilide in 250 cc. nitrobenzene.

\(^2\)Survey experiment. No material balance attempted.
Table 2. Reaction of p-nitrophenyl radical and nitrobenzene1,2

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Fractions</th>
<th>Weight3</th>
<th>Nature of product</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCl4</td>
<td>1 - 6</td>
<td>0.0697</td>
<td>4,4' (20.4%), 2,4' (33.6%), 3,4' (48.6%)</td>
</tr>
<tr>
<td></td>
<td>7 - 16</td>
<td>1.0408</td>
<td></td>
</tr>
<tr>
<td></td>
<td>17 - 23</td>
<td>0.6273</td>
<td>4,4' (28.1%), 2,4' (23.4%), 3,4' (48.6%)</td>
</tr>
<tr>
<td></td>
<td>24 - 35</td>
<td>0.7840</td>
<td>Red crystals and yellow solid</td>
</tr>
<tr>
<td></td>
<td>36 - 46</td>
<td>0.5432</td>
<td></td>
</tr>
<tr>
<td></td>
<td>47 - 54</td>
<td>0.2097</td>
<td></td>
</tr>
<tr>
<td></td>
<td>55 - 62</td>
<td>0.1813</td>
<td></td>
</tr>
<tr>
<td></td>
<td>63 - 81</td>
<td>0.2903</td>
<td></td>
</tr>
</tbody>
</table>

125 g. p-nitro-N-nitrosoacetanilide in approximately 75 ml. nitrobenzene.

2Chromatography of solids from residue remaining in flask after more than half of the reaction mixture lost by ejection from the flask by the vigorous nature of the unmoderated reaction.

33.7463 g. total weight of fractions 1-81.

4Isomer ratios of 4,4', 2,4' and 3,4' dinitrobiphenyls determined from ultraviolet spectra.
Table 3. Reaction of p-nitrophenyl radical and nitrobenzene\(^1,2\)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Fractions</th>
<th>Weight(^3)</th>
<th>Nature of product</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_2)Cl</td>
<td>1 - 8</td>
<td>0.0119</td>
<td></td>
</tr>
<tr>
<td></td>
<td>9 - 13</td>
<td>0.0846</td>
<td></td>
</tr>
<tr>
<td></td>
<td>14 - 24</td>
<td>0.3143</td>
<td>(4,4') (18.6%), (2,4') (25.5%), (3,4') (55.8%)(^4)</td>
</tr>
<tr>
<td></td>
<td>25 - 35</td>
<td>0.2543</td>
<td>Mixtures of isomeric dinitrophenyls</td>
</tr>
<tr>
<td></td>
<td>36 - 47</td>
<td>0.2414</td>
<td>Mixtures of isomeric dinitrophenyls</td>
</tr>
<tr>
<td></td>
<td>48 - 52</td>
<td>0.1013</td>
<td></td>
</tr>
<tr>
<td></td>
<td>53 - 63</td>
<td>0.2493</td>
<td>Red crystals and yellow solid</td>
</tr>
<tr>
<td></td>
<td>64 - 95</td>
<td>0.6466</td>
<td>Red crystals and yellowish solid</td>
</tr>
<tr>
<td></td>
<td>96 - 126</td>
<td>0.5078</td>
<td></td>
</tr>
<tr>
<td></td>
<td>127 - 163</td>
<td>0.4435</td>
<td>Begins to turn gummy</td>
</tr>
<tr>
<td></td>
<td>164 - 174</td>
<td>0.1394</td>
<td></td>
</tr>
<tr>
<td></td>
<td>175 - 186</td>
<td>0.1572</td>
<td></td>
</tr>
<tr>
<td></td>
<td>187 - 198</td>
<td>0.1397</td>
<td></td>
</tr>
<tr>
<td></td>
<td>199 - 211</td>
<td>0.1214</td>
<td></td>
</tr>
</tbody>
</table>

\(^1\) 18.77 g. p-nitro-N-nitroso-acetanilide in 60 ml. of nitrobenzene.

\(^2\) 16.5734 g. solid reaction products produced.

\(^3\) 3.4127 g. Total weight of fractions 1-211.

\(^4\) 1.3020 g. Weight recovered from column except original band.

Isomer ratios of \(4,4'\), \(2,4'\) and \(3,4'\) dinitrophenyls determined from ultraviolet spectra.
<table>
<thead>
<tr>
<th>Solvent</th>
<th>Product</th>
<th>Nature of Product</th>
<th>Reaction Mixture</th>
<th>Weight of Product</th>
<th>Reaction Mixture</th>
<th>Weight of Product</th>
<th>Reaction Mixture</th>
<th>Weight of Product</th>
<th>Reaction Mixture</th>
<th>Weight of Product</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1: Reaction of \( \text{p-nitrophenyl} \) radical and \( \text{nitrobenzene} \)
Table 5. Reaction of p-nitrophenyl radical and nitrobenzene$^{1,2}$

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Fractions</th>
<th>Weight</th>
<th>Nature of product</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCl$_4$</td>
<td>1 - 7</td>
<td>0.0109</td>
<td>4,4' (36.2%), 2,4' (30.0%), 3,4' (33.8%)</td>
</tr>
<tr>
<td></td>
<td>8 - 21</td>
<td>0.4408</td>
<td></td>
</tr>
<tr>
<td></td>
<td>22 - 40</td>
<td>0.4846</td>
<td>4,4' (37.7%), 2,4' (20.8%), 3,4' (41.5%)</td>
</tr>
<tr>
<td></td>
<td>41 - 50</td>
<td>0.1763</td>
<td></td>
</tr>
<tr>
<td></td>
<td>51 - 75</td>
<td>0.4904</td>
<td></td>
</tr>
<tr>
<td></td>
<td>76 - 100</td>
<td>0.2862</td>
<td></td>
</tr>
<tr>
<td></td>
<td>101 - 126</td>
<td>0.2397</td>
<td></td>
</tr>
<tr>
<td></td>
<td>127 - 157</td>
<td>0.2171</td>
<td></td>
</tr>
<tr>
<td></td>
<td>158 - 199</td>
<td>0.2612</td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>200 - 204</td>
<td>0.5496</td>
<td></td>
</tr>
<tr>
<td></td>
<td>205 - 223</td>
<td>0.4712</td>
<td></td>
</tr>
</tbody>
</table>

17.75 g. p-nitro-N-nitrosoacetanilide in 80 ml. of nitrobenzene.

25.5282 g. of solid reaction products produced.

3.6280 g. Total weight of fractions 1-223.
1.7167 g. Weight recovered from alumina in column.
5.3447 g. Total weight of recovered materials.
96.7% Recovery after chromatography of total weight placed on column.
1.0815 g. Weight recovered from original band on column.
20.2% of total recovered material found in original band on column.

$^4$Isomer ratios of 4,4', 2,4' and 3,4' dinitrobenzilphenyl determined from ultraviolet spectra.
| Product | Red | Yellow Powder | Mixture of Red Oxydants and Mixture of Yellow Oxydants with Orange- | Mixture of Isomeric Dinitrophenols | Column
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield</td>
<td>6.5</td>
<td>1.90</td>
<td>1.66</td>
<td>6.35</td>
<td>1 %</td>
</tr>
</tbody>
</table>

Table 6. Reaction of p-Nitrophenyl Radial and Nitrobenzene 1,2
The carbon-tetrachloride-eluted red compound

The red compound co-eluting with the dinitrobenzene tailings was found to fractionally crystallize when an acetone solution was slowly evaporated. These crystals were hand-picked and recrystallized from acetone. Stout red needles were obtained, M.P. 179-181° C. in a Hershberg melting point bath.

Quantitative elemental analysis by Geller Laboratories in Hackensack, New Jersey showed 55.05 per cent carbon, 2.62 per cent hydrogen and 17.81 per cent nitrogen. Oxygen by difference was 24.52 per cent. This indicates that there were three nitro groups to one azo linkage in the molecule. A compound which fitted this requirement was

\[
\text{NO}_2 - \text{C} - \text{NO}_2 - \text{N} = \text{N} - \text{C} - \text{NO}_2
\]

The calculated elemental percentages for a compound of this type with \( \text{C}_{18}\text{H}_{11}\text{N}_{5}\text{O}_6 \) rather closely agreed with that determined for the red compound.

<table>
<thead>
<tr>
<th>Calculated</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 54.96</td>
<td>C 55.05</td>
</tr>
<tr>
<td>H 2.82</td>
<td>H 2.62</td>
</tr>
<tr>
<td>N 17.82</td>
<td>N 17.81</td>
</tr>
<tr>
<td>O 24.43</td>
<td>O 24.52</td>
</tr>
</tbody>
</table>

The ultraviolet spectra was determined on the Beckman DU in acetonitrile solvent. The extinction coefficients for
$\lambda_{\text{max}}$ at 333 ± 2 m$\mu$ was found to be $3.5 \times 10^4$ and for $\lambda_{\text{max}}$ at 450 m$\mu$ was found to be $9.1 \times 10^2$. The infrared showed bands at 6.29 m$\mu$ (w), 6.60 m$\mu$ (M), 7.49 m$\mu$ (s), 11.8 (w), and 13.8 m$\mu$ (w).

**p-nitrophenyl-acetate**

Eastman white label p-nitrophenol was dissolved in excess sodium hydroxide and the resulting solution poured into ice. Excess acetic anhydride was then added. A white solid precipitated which was filtered and recrystallized from aqueous ethyl alcohol. The melting point in a bath was 79–80° C. (Literature 81–82° C.)

**4,4'-dinitroazobenzene**

4,4'-dinitroazobenzene was synthesized after the method of Cook and Jones$^{51}$ by oxidizing p-nitroaniline with potassium or ammonium persulfate. In either case considerable amounts of the corresponding azoxy compound was formed. After three recrystallizations from acetone, the melting point was four degrees low indicating contamination by the azoxy compound. These crystals therefore were chromatographed on an alumina column. Eight of the chromatography fractions were combined and recrystallized again from acetone. Red needles were obtained which melt at 226° C.

The ultraviolet spectra was determined on the Beckman DU in acetonitrile solvent. The extinction coefficients for
\[ \lambda_{\text{max}} \text{ at } 330 \text{ m\textmu} \text{ was } 2.4 \times 10^4 \text{ and for } \lambda_{\text{max}} \text{ at } 450 \text{ m\textmu} \text{ was } 7 \times 10^2. \]

The chromatographic characteristics of this compound were determined by making an artificial mixture of 4,4'-dinitrobiphenyl and 4,4'-dinitroazobenzene and chromatographing under conditions identical to that used for the solid reaction products from the p-nitrophenyl radical and nitrobenzene reaction. It was shown that the dinitroazo- benzene comes through the column mixed with the dinitrobiphenyl. On slow crystallization from acetone, these two compounds also fractionally crystallize. The melting point of the 4,4'-dinitroazobenzene crystals hand picked from the dinitrobenzophenyl crystals was 218-225.5°C in the Hirshberg melting point bath.

The infrared spectrum was determined on the Baird instrument.

Characterization of the Portion Not Eluted from the Column

Tar

That portion of the reaction products which does not move during chromatography will for convenience be referred to as tar. In order to better characterize this rather unpromising black tar, a model countercurrent extraction using concentrated sulfuric acid and chloroform in separatory
funnels was tried. This did not give encouraging enough results to warrant setting up a counter-current extraction setup.

When the original band from the chromatography column of the reaction tabulated in Table 3 was eluted with acetone, a black tar was extracted. Infrared showed bands at 5.92 \( \mu \) (w), 6.28 \( \mu \) (m), 6.60 \( \mu \) (s), 7.45 \( \mu \) (s), 9.05 \( \mu \) (w), and 11.7 \( \mu \) broad. After removal of acetone, the residue was treated with conc. sulfuric acid. The sulfuric acid solution was then extracted with chloroform in a separatory funnel. Within limits of recovery of substances from equipment, etc., the sulfuric acid soluble portion not extracted by chloroform was found to be 5.4602 g., the sulfuric acid insoluble portion to be 0.1954 g. and the portion extracted by chloroform to be 0.7462 g. The chloroform portion fractionally crystallized to yield a small amount (estimated to be 20-30 mg.) of needles plus some uninviting solid. The needles melted at 190-200\(^\circ\) C. on a Fisher melting point block. The infrared spectra indicated only one sharp characteristic band at 6.3 \( \mu \), the others being quite diffuse. The spectra and melting point definitely rule out the possibility that this compound is 2,4'- or 3,4'- dinitrobiphenyl. There is a chance that it might be 4,4' dinitrobiphenyl although the correspondence of bands in the 11 \( \mu \) to 14 \( \mu \) region is not really good.
In order to further test the possibility that the tar contains large amounts of dinitrobenzoyl, a micro spatula full of 2,4'-dinitrobenzoyl and about the same amount of 4,4'-dinitrobenzoyl were put in concentrated sulfuric acid. It was found that some of the solid remained insoluble in the sulfuric acid. Upon extraction of the sulfuric acid with chloroform and evaporation of the chloroform, it was found that 0.1259 g. of residue remained. On pouring the sulfuric acid layer on ice and recovering the resultant precipitate, 0.0112 g. was found to be formed.

Reduction of the tar with tin and hydrochloric acid was tried as a further means of characterizing the tar. If the tar consists of phenyl groups linked in places with azo type linkages, polyamino compounds would be expected. Since these compounds would be expected to be unstable, reduction of 0.4 g. 4,4'-dinitrobenzoyl was carried out by stirring 0.6 g. tin, 10 ml. glacial acetic acid and 2 ml. conc. hydrochloric acid in a 100 ml. round bottom flask in order to obtain the acetylated compound. The product actually isolated was benzidine. The tar itself was reduced in the same manner as the model compound. The solid products were made into a slurry with 6 N sulfuric acid, lead dioxide added and warmed on a water bath at 75° C. The solids from the lead dioxide oxidation were then put in a sublimator and sublimed. No sublimate was obtained. When authentic benzoquinone was put in
the sublimator, it was easily sublimed.

2-deutero-3,4'-dinitrobiphenyl

33.8 g. of Eastman white label 2-aminobiphenyl was put in 500 ml. of water and 18 ml. conc. hydrochloric acid added. The mixture was warmed to 50° C. The 2-aminobiphenyl which remained insoluble at this point was put into solution by adding about $\frac{1}{2}$ to 1 ml. of conc. hydrochloric acid at a time until solution was obtained. 23.3 ml. of acetic anhydride was then added to this hot solution. After the flask was shaken briefly, a solution of 30 g. sodium acetate in 100 ml. of water was added. There was an immediate cloudiness followed by a separation of an oily phase. On cooling, the oil phase solidified and long white needles were formed from solution. The solid phase consisting of 2-acetamidobiphenyl was filtered and recrystallized from Skelly B. The melting point on a block was 119.5 to 121° C.

The 2-acetamidobiphenyl was dinitrated to yield 2-acetamido-3,4'-dinitrobiphenyl by the method of Scarborough and Waters. The melting point after one recrystallization from benzene was 208-210° C.

Hydrolysis to the free amine was carried out by placing 5 g. of 2-acetamido-3,4'-dinitrobiphenyl in a 500 ml. round bottom flask along with 200 ml. alcohol and 10 ml. conc. sulfuric acid. The mixture was refluxed for 4.8 hours. During
the course of reflux, a large amount of yellow precipitate formed. At the end of the reflux period the contents of the reaction flask were poured into a sodium carbonate solution. The precipitate of 2-amino-3,4'-dinitrobiphenyl was filtered and recrystallized from alcohol. The melting point in a Hirshberg bath was found to be 235-236°C.

Deuterohypophosphorous acid was prepared by properly equilibrating hypophosphorous acid with D₂O. Thirty per cent Baker and Adamson hypophosphorous acid was concentrated under vacuum at 50-80°C. until water no longer seemed to be collecting in the dry ice trap. Forty-four ml. of this conc. acid was allowed to equilibrate with 50 g. of 90.8 per cent D₂O obtained from Linde. The procedure in general is the same as that used by Grundemeier⁵³ except that longer periods of time were allowed for the removal of water and for equilibration since this work was done at convenient intervals concurrent to other experiments.

Deuterium enriched conc. hydrochloric acid solution was prepared by saturating D₂O with gaseous hydrochloric acid.

The deamination of 2-amino-3,4'-dinitrobiphenyl was carried out in several different runs by a modification of the method described by Alexander and Burge.⁵⁴ In one typical run, 7.37 g. of 2-amino-3,4'-dinitrobiphenyl was made into a slurry by heating with 42 ml. of D₂O and 13.5 ml. of deuterium enriched hydrochloric acid. The slurry was then
cooled in an ice bath and 2.05 g. sodium nitrite in 10 ml.
D₂O was added over a period of one hour. The mixture was
filtered through a coarse sintered glass filter into a filter
flask surrounded by ice. The filtrate was poured into a 250
ml. round bottom flask and sulfamic acid added until a
negative test was obtained with starch-iodide paper. Nitro-
gen was bubbled in for about three minutes in order to sweep
out dissolved oxygen. A solution of 7.1 g. D₂O and 9.4 g.
D₃PO₄ was then added and the reaction mixture stirred for 45
minutes at ice temperatures. After standing in the icebox
for 24 hours, the reaction mixture was then extracted with
ether, the ether extracts evaporated and chromatographed to
get 2-deuterio-3,4'-dinitrophenyl. The products obtained
from various runs were recrystallized from a small amount of
acetone in order to get a homogeneous deuterated sample. A
total of 0.8036 g. melting at 188° C. in a capillary tube was
obtained.

Fate of deuterium in the radical reaction

Because of the "memory" effect of the mass spectrometer,
the deuterium analysis was done for the various fractions
starting from the high deuterium samples and repeated starting
from the low deuterium samples. The results are tabulated in
Table 7.
on the same combustion sample

More than one figure for the same fraction denotes a

deuterium.

Assume that all of the fraction is deuterated.

\[
\begin{array}{cccccc}
\text{Fractions & \% Atom D & \% Atom D & \text{D} & \text{Wt.}\% & \text{D} & \text{Wt.}\%} \\
0^0 & 0.0 & 0.0 & 0.0 & 0.0 & 0.0 & 0.0 \\
0.05 & 0.0 & 0.0 & 0.0 & 0.0 & 0.0 & 0.0 \\
0.10 & (0.0) & (0.0) & 0.0 & 0.0 & 0.0 & 0.0 \\
0.20 & 0.0 & 0.0 & 0.0 & 0.0 & 0.0 & 0.0 \\
0.25 & 0.0 & 0.0 & 0.0 & 0.0 & 0.0 & 0.0 \\
0.50 & 0.0 & 0.0 & 0.0 & 0.0 & 0.0 & 0.0 \\
0.75 & 0.0 & 0.0 & 0.0 & 0.0 & 0.0 & 0.0 \\
0.5 & 0.0 & 0.0 & 0.0 & 0.0 & 0.0 & 0.0 \\
0.75 & 0.0 & 0.0 & 0.0 & 0.0 & 0.0 & 0.0 \\
1.00 & 0.0 & 0.0 & 0.0 & 0.0 & 0.0 & 0.0 \\
\end{array}
\]

Table 6. Deuterium analyses for reaction tabulated on
These results are tabulated in Table 6.

In order to test for the reality of the determination, a sequence of determinations was made for the lowest sample, a second of determinations for the second lowest sample, and a third for the highest sample. The three determinations of each sample were averaged. The average of the last seven per cent determinations gives 0.04.

The other entries in Table 6 are the percentages of the substance eluted from the original column of the chromatograph, tabulated in Table 6.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Percent Eluted</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tier</td>
<td>140.0</td>
</tr>
<tr>
<td>Tier</td>
<td>170.0</td>
</tr>
<tr>
<td>Tier</td>
<td>570.0</td>
</tr>
<tr>
<td>Tier</td>
<td>340.0</td>
</tr>
<tr>
<td>Tier</td>
<td>660.0</td>
</tr>
<tr>
<td>Tier</td>
<td>350.0</td>
</tr>
<tr>
<td>Tier</td>
<td>820.0</td>
</tr>
<tr>
<td>Tier</td>
<td>830.0</td>
</tr>
</tbody>
</table>

Table 6. Determination of dextrotemporin content of "Tier-"
DISCUSSION

This work was initiated to study the effect of substituents on the attacking phenyl radical in homolytic aromatic substitutions. Since the publication of results along these lines by other workers\textsuperscript{40, 41, 37, 42} the major effort has been directed toward the study of the other constituents in the reaction mixture of p-nitrophenyl radical and nitrobenzene. The process of separation involved a chromatography of the product mixture. Since a large amount of the dinitrobi-phenyls formed were eluted from the column before the other constituents began to move, these fractions were spectrophotometrically analyzed for isomer ratios. In general the results seemed to be in agreement with those reported by DeTar.\textsuperscript{41} Since the dinitrobi-phenyl mixture as a whole was not analyzed, it is difficult to check absolute values. For example, the 4,4'-dinitrobi-phenyl percentage is low in all of the fractions checked. This is due to the slow rate of elution of the 4,4' isomer with carbon tetrachloride from an alumina column. The infrared spectrum indicates that the dinitrobi-phenyl co-eluting with the redazo compound is mostly the 4,4' isomer. This is substantiated by the two instances in which two successive fractions of a chromatography were analyzed. The data shown on Tables 2 and 5
indicate that the 4,4' isomer is increasing as the chromatography proceeds. The 3,4' isomer also shows increases according to the ultraviolet analysis of these isomer mixtures. This is not too surprising in view of the "tailing off" of the deuterium samples in the chromatography of the tracer experiment. That there is no indication of this "tailing off" in the infrared is not too disturbing since the mull technique is not sensitive to compounds present in small amounts. One possible discrepancy is the amount of the 2,4' isomer found. In all but one determination (Table 4) the 2,4' isomer was the isomer present in the smallest amount when it is considered that the 4,4' isomer is coming through the column slowly. Since both the infrared and the test chromatography used to check the analytical method for isomer ratios indicate that the 2,4' isomer comes through quite rapidly on elution with carbon tetrachloride, the small amounts in the early fractions would appear to indicate that the 2,4' isomer is present as the smallest amount in the total mixture. DeTar\(^{41}\), however, reports that the 3,4' isomer is present in the smallest amount at 23 per cent followed by 2,4' at 34 per cent and 4,4' at 43 per cent. Hey is reported to have found only 15 per cent of the 3,4' isomer\(^{37}\) and to have obtained an ortho/para ratio not much different from that of phenyl radical substitution on nitrobenzene. Morrison and Sweeney\(^{42}\) have indicated that they
have obtained 58 per cent ortho, 13 per cent meta and 29 per cent para substitution with p-nitrophenyl radicals on nitrobenzene, a result in very good agreement with that of Hey. Since our isomer ratio and that obtained by DeTar do not correlate with Morrison's and Hey's, more work is suggested. At best, the complete acceptance of the results obtained by Hey and Morrison must await the examination of their experimental procedure. There are possibilities that some of the ortho isomer is produced during the isolation procedure from other primary reaction products. This point will be discussed further under the general consideration of reaction mechanisms.

A proposal regarding the nature of homolytic aromatic substitutions must not only attempt to explain the orientation effects but must likewise explain other observable phenomena. For example, p-nitrophenyl acetate could not be identified in the reaction mixture indicating that, if formed, it is only present in minor quantities. The observation by DeTar that acetic acid is found in large quantities and the failure of Hey and Wieland to isolate biphenyls in the decompositions of aryldiazoacetates in many non-aromatic solvents must be consistent with any mechanism proposed. Note must be taken of the repeated failure to identify carbon dioxide as one of the products of aryldiazoacetate decompositions.
The failure to identify p-nitrophenyl acetate in the reaction mixture indicates that the combination of the two free radicals formed in a solvent cage is not of major importance. Since the activation energy for the combination of the two radicals is probably fairly low, some explanation is necessary to explain this lack of radical coupling.

One possible explanation is that the radicals diffuse out of the cage before they have a chance to couple. If this were so, it would seem that Hey\(^2\) and Wieland\(^55\) would have always observed biaryls in the decompositions of these aryl-diazoacetates. There is also the possibility that the free acetoxy radical produced in this manner would decarboxylate giving carbon dioxide. This may not necessarily be true even though the workers in the field have generally discounted the presence of these radicals on the basis of the failure to obtain carbon dioxide. It should be pointed out that the studies of acetyl peroxide decomposition which are used as the analogy for the above reasoning are always carried out at much higher temperatures in order to make the rate determining oxygen-oxygen bond breaking step measurable. In the generation of radicals by the decomposition of nitrosoacetanilides, the temperature for optimum yields of biphenyls was found to be 20° C. \(^57\) At this temperature, the acetoxy radical could conceivably have a long life. Even though some of the objections to the
radical diffusion theory might be rationalized, a more satisfying explanation is that the aryl radical is immediately tied up in some sort of complex with one of the surrounding aromatic solvent molecules or that the aryl radical and acetoxy radical react in a concerted manner with one of the aromatic solvent molecules.

Huisgen\textsuperscript{58} has already proposed a concerted reaction. The following equation is taken from his paper.

\[
\begin{align*}
\text{A} & \quad \overset{N = N}{\rightleftharpoons} \quad \text{B} \\
\text{C} & \quad \overset{N = N}{\rightarrow} \quad \text{C}
\end{align*}
\]

Molecular models show that when a nitrobenzene molecule is placed in an appropriate geometry in relation to the phenyldiazooacetate, the acetoxy group can be oriented such that the nitrogen can be eliminated from the anti aryldiazoacetate leaving the fragments in position such that relatively little geometrical change has to be invoked in order to initiate a termolecular process culminating in the formation of the diaryl and abstraction of the hydrogen by the acetoxy radical. One extreme of the range of configurations possible for the prior orientation (structure B) is the placement of the reacting species such that the aromatic rings are essentially in the positions they will occupy in the
complex intermediate. This would be quite favorable from the standpoint of the energetics of the reaction, but would not lend to an explanation of the orientation effects. On the other extreme, structure B can be pictured with the aromatic rings placed in a face to face orientation as a kind of a complex. This would require a large geometrical change in converting structure B to structure C since the attacking phenyl group must be pivoted 180° C. This formulation probably would not be as energetically favored as that described above, but would have the advantage of allowing rationalizations regarding the orientations observed in substitutions by radicals.

It might be observed that both of these mechanisms are consistent with the observation that all of the homolytic aromatic substitutions studied\textsuperscript{37} are in general rather non-selective in orientation effects. Other than certain cases where exceptions to this lack of selectivity can be readily explained on the basis of steric control, the directional effect exhibited by substituent groups is much less emphatic than those found in electrophilic substitutions. Further than this the face to face complex is more fruitful in justifying isomer ratios. Observations made by Rondestvedt,\textsuperscript{37} among others, that for most of the phenyl radical substitutions the predominant isomer is the ortho substituted product can be explained using this mechanism by a consideration of
timing. If at the moment the aromatic substrate "complexes" with the radical source, the bond about to be broken is stretched such that the fragments have radical character, then arguments such as that applied by Rondestvedt would still be applicable. The p-anisyl radical substitution\(^40\) which is apparently entirely ortho-para on nitrobenzene might be explained by the possible preference for electron-rich ortho and para positions of the methoxy substituted ring to line up with the electron-poor ortho and para positions of the nitro-substituted ring just prior to the termolecular reaction. In the same manner the substitution of p-nitrophenyl radicals on anisole\(^42\) can be rationalized. In this case the substitution at the ortho position is not only favored by this kind of orientation, but is also favored by the electrophilic nature of the p-nitrophenyl radical. This same type of argument applied to the reaction of p-nitrophenyl radical and nitrobenzene would indicate a slight increase of the meta substituted isomer over that of the phenyl radical substitution. Even when the variable results reported for this reaction are considered, this one fact is certainly observed even though the magnitudes do not agree.

This picture of a concerted process for aryldiazoacetate decomposition must also be examined in light of the evidence that phenyl radicals from various sources give rise to products containing the same isomer ratios.\(^38\) Although the
same type of concerted process can be geometrically arranged for compounds like benzoyl peroxide and 1-phenyl-3,3-dimethyltriazene, the homolytic aromatic substitution carried out under Meerwein reaction conditions needs more extensive justification. Under the Meerwein conditions, 2,4'-dichlorobenzenediazonium chloride is decomposed in the presence of benzene and cupric chloride in an aqueous aceton medium. It appears as if the free aryl radical is formed without an accompanying free radical as is the case with azo compounds and peroxides. The following reaction scheme has been written:

(1) \[ \text{CH}_3\text{COCH}_3 + 2 \text{CuCl}_2 \rightarrow 2 \text{CuCl} + \text{ClCH}_2\text{COCH}_3 + \text{HCl} \]

(2) \[ \text{ArN}_2^+ + \text{CuCl}_2^- \rightarrow \text{ArN}=\text{N}^+ + \text{CuCl}_2 \]

(3) \[ \text{ArN}=\text{N}^+ \rightarrow \text{Ar}^* + \text{N}_2 \]

(4) \[ \text{Ar}^* + \text{CuCl}_2 \rightarrow \text{ArCl} + \text{CuCl} \]

(5) \[ \text{Ar}^* + \text{CH}_3\text{COCH}_3 \rightarrow \text{ArH} + \cdot\text{CH}_2\text{COCH}_3 \]

(6) \[ \cdot\text{CH}_2\text{COCH}_3 + \text{CuCl}_2 \rightarrow \text{ClCH}_2\text{COCH}_3 + \text{CuCl} \]

(7) \[ \text{Ar}^* + \cdot\text{C}≡\text{C}^- \rightarrow \text{Ar}-\cdot\text{C}≡\text{C}^* \]

(8) \[ \text{Ar}-\cdot\text{C}≡\text{C}^* + \text{CuCl}_2 \rightarrow \text{Ar}-\cdot\text{C}≡\text{C}^-\text{Cl} + \text{CuCl} \]

(7') \[ \text{Ar}^* + \phi\text{H} \rightarrow \text{Ar}^* \]

(8') \[ \text{Ar}^* + \text{CuCl}_2 \rightarrow \text{ArC}_6\text{H}_5^- + \text{H}^+ + \text{CuCl} \]

This reaction can be made to fit the concerted mechanism picture by considering step (2) as an equilibrium between an ion pair and what can be thought of as a radical pair. This
pair can then be complexed with benzene and the reaction completed with a concerted process in which steps \((7')\) and \((8')\) are combined.

Although a concerted reaction has some merits, the arguments of many of the points are certainly extended. Moreover, the mechanism as it stands provides no means by which polyaryl compounds might be formed other than by successive arylations of the primary product. This in itself is a serious shortcoming in view of the deuterium tracer experiments.

The proposal that the aryl radical is immediately tied up in a loose complex with the aromatic solvent molecules has many attractive features. Once the complex forms it can be readily argued that the acetoxy radical prefers to abstract a hydrogen atom rather than combining with the complexed radical. The orientation problem can be rationalized in a way similar to that used for the concerted reaction mechanism. The explanation for the insensitivity of substitution to the radical source and the justification for the Meerwein condition arylation is much cleaner than for the previous case. However, the most useful feature is that a means is provided whereby products other than the primary substitution products can be postulated or justified. The following reactions can be written:
(1) \[
\text{[Ar}^* \text{[·]}} + R^* \rightarrow \text{Ar} - \text{H} + \text{RH}
\]

(2) \[
\text{[Ar}^* \text{[·]}} + R^* \rightarrow \text{Ar} - \text{H} + \text{H} - \text{R}
\]

(3) \[
\text{[Ar}^* \text{[·]}} + \text{[Ar}^* \text{[·]}} \rightarrow \text{Ar} - \text{H} + \text{H} - \text{H} - \text{Ar}
\]

(4) \[
\text{[Ar}^* \text{[·]}} + \text{[Ar}^* \text{[·]}} \rightarrow \text{Ar} - \text{H} + \text{H} - \text{Ar} + \text{n}
\]

The additions to aromatic compounds have already been postulated for the case of methyl radical by Szwarz.\(^5\) These addition compounds would be expected to be highly colored and to adsorb strongly on alumina, the very characteristics of the tars formed in these radical reactions.

The formation of some of these addition compounds might also explain the low ortho isomer content of the reactions reported here as compared to that of other laboratories. It may be that addition products such as

\[
\text{O}_2\text{N} - \text{Ar} - \text{NO}_2 - \text{H} - \text{O} - \text{C} - \text{CH}_3
\]

become oxidized under severe isolation conditions to produce additional ortho isomer. The procedure used in this laboratory was atmospheric pressure steam distillation followed by a chromatography. The usual procedure reported from the other laboratories is much more drastic. It may be quite informative to treat the tars obtained under mild condition isolations under the more severe conditions to see whether more 2,4'-dinitrobiphenyl is formed.
The loose complex theory does not give a clean explanation for the amount of acetic acid found in these reactions. If it is assumed that a large number of the radical complexes and acetoxy radicals diffused apart so that the products other than the phenyls can be justified, then it must be concluded that the acetoxy radical is a better hydrogen abstractor than a radical complex in order to account for the acetic acid formed.

The appearance of azo compounds in the decompositions of acyl-N-nitrosoanilides have been noted previously by other workers without extensive discussion as to their origin. There are several possible ways in which these azo compounds can be formed. One can conceive of a nitrogen-oxygen homolytic cleavage such that the aryldiazo radical and the acetoxy radical are formed. The acetoxy radical can then be made to abstract a hydrogen atom from solvent with a subsequent collapse of the radical thus formed and the aryldiazo radical. A similar mechanism would involve the combination of an aryldiazo radical and a phenyl radical from the cleavage of another aryldiazoacetate. Another reaction path is possible when nitrobenzene is used as the solvent. A free hydrogen atom can be formed by the phenyl radical displacements of hydrogen from a nuclear position on an aromatic ring. This hydrogen atom can then be made to reduce nitrobenzene to azobenzene. A non-radical path might be a classical
electrophilic coupling of a diazonium ion with an aromatic nucleus. These mechanisms might possibly apply to the formation of azobenzene, but cannot be of general applicability in view of the results of this research. Although authentic 4,4'-dinitroazobenzene was synthesized and characterized under conditions similar to the workup of the radical reaction products, none could be detected in the reaction mixture. The 4,4'-dinitroazobenzene was shown to elute from an alumina column with carbon tetrachloride. The red compound actually found in the carbon tetrachloride eluents was neither the 4,4'-dinitroazobenzene nor azobenzene as could readily be shown by the differences in melting point and infrared spectra. Furthermore, a non-radical electrophilic coupling of a diazonium ion on nitrobenzene is not likely.

The red compound eluted with carbon tetrachloride was shown to be an azo compound on the basis of ultraviolet spectra. The absorption maxima and extinction coefficients seem to fit in with other known azo compounds. The extinction coefficient is calculated using a molecular weight of 393 based on the structure

\[
\begin{align*}
\text{NO}_2 & \quad \text{NO}_2 \\
\text{N} & = \text{N} \\
\text{NO}_2 & \quad \text{NO}_2
\end{align*}
\]

which fits the experimental carbon, hydrogen, nitrogen data.
<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{\text{max}}$</th>
<th>$\lambda_{\text{max}}^2$</th>
<th>$\lambda_{\text{max}}^3$</th>
<th>$\lambda_{\text{max}}^4$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varnothing \text{N} = \text{N} \varnothing$</td>
<td>313</td>
<td>$2 \times 10^4$</td>
<td>$448$</td>
<td>$4 \times 10^2$</td>
<td>60</td>
</tr>
<tr>
<td>$\varnothing \text{N} = \text{N} \varnothing$</td>
<td>335</td>
<td>$3 \times 10^4$</td>
<td>$451$</td>
<td>$9 \times 10^2$</td>
<td>60</td>
</tr>
<tr>
<td>$\text{N}^* = \text{N}$</td>
<td>334</td>
<td>$2.8 \times 10^4$</td>
<td>$450$</td>
<td>$7 \times 10^2$</td>
<td>61</td>
</tr>
<tr>
<td>$\text{NO}_2^* \text{NO}_2$</td>
<td>330</td>
<td>$2.4 \times 10^4$</td>
<td>$450$</td>
<td>$9.1 \times 10^2$</td>
<td></td>
</tr>
<tr>
<td>Red compound</td>
<td>333</td>
<td>$3.5 \times 10^4$</td>
<td>$450$</td>
<td>$9.1 \times 10^2$</td>
<td></td>
</tr>
</tbody>
</table>

The bathochromic shifts in the ultraviolet band have been noted for azo compounds with increasing number of double bonds.\(^6\)\(^2\) It might be noted that the shift was not too large considering that the molecule contained both an extra phenyl group and three nitro groups. This fact might be rationalized by observing that the effects of the two groups work in opposition to each other, the phenyl group in general acting as an electron source and the nitro group as an electron sink. It is unfortunate that by the time these red crystals were hand-picked from a mixture of crystals, obtained by fractional crystallization and recrystallized, there were only milligram quantities available so that further characterization was not feasible.

Since an azo compound was isolated whose presence is not easily explained by reaction mechanisms discussed thus far, it becomes of interest to propose alternate methods by which these azo compounds might be formed during decompositions of aryldiazoacetates. It is therefore suggested that the aryl
diazonium radical must be somehow involved in the reaction. Waters\textsuperscript{63} says that there is no evidence to indicate that there is a methyldiazo radical formed in the decomposition of azomethane. However, it cannot be expected that the symmetric alkyl substituted diazo compound would be a good analogue for an unsymmetric aryl acyl substituted azo compound. Huisgen\textsuperscript{47} reports that N-nitrosoacetanilide reacts with piperidine in ethanol or benzene to yield 1-phenyl-azopiperidine. When piperidine is placed on the crystalline N-nitrosoacetanilide an explosion results. It is proposed that the following chain reaction accounts for the explosive reaction.

\begin{align*}
N=O & \quad \begin{array}{ccc}
\text{N} & \text{H} & \text{N}
\end{array} \\
(1) \quad \phi-N-C-CH_3 & \rightarrow & \phi-N-O-C-CH_3 \\
(2) \quad \phi-N & \rightarrow & \phi^* + N_2 + \cdot O-C-CH_3 \\
(3) \quad \begin{array}{ccc}
\text{N} & \text{H} & \text{N}
\end{array} + CH_3C\equivO & \rightarrow & CH_3C\equivO + \begin{array}{ccc}
\text{N} & \text{H} & \text{N}
\end{array} \\
(4) \quad \begin{array}{ccc}
\text{N} & \text{H} & \text{N}
\end{array} + \phi-N & \rightarrow & \phi-N + \cdot O-C-CH_3
\end{align*}
Step (5) can be thought of as the radical analogue of the ionic mechanisms\(^45, 47, 65, 65\) which have been written for the rearrangement of \(N\)-nitrosoacylanilides to the aryldiazooacetate. Steps (1) and (2) are chain initiating and steps (3) and (5) are the main chain carrying with step (4) as a minor variant. In solution it is likely that the reaction could go entirely by an ionic process, written as shown or with steps (7) and (8) in a concerted process. However,

\[
(6) \quad \phi - N - C - CH_3 \quad \rightarrow \quad \phi - N - O - C - CH_3
\]

\[
(7) \quad \phi - N - 0 - C - CH_3 \quad \rightarrow \quad \phi - N = N^+ + 0 - C - CH_3
\]

\[
(8) \quad \phi - N = N^+ + \quad \rightarrow \quad \phi - N = N - N + H^+
\]

it is also not inconceivable that there is a radical process in solution similar in nature to that proposed for the explosive reaction. In some respects this reaction is faintly reminiscent of the benzoyl peroxide decompositions in the presence of amines such as dimethyl aniline.\(^66, 67, 68\) These reactions can also be written in a completely ionic sense, but it is known that dimethylaniline added to benzoyl peroxide
not only enhances vinyl polymerization reactions but also
gives rise to products indicating formation of free radicals.

A reaction similar to steps (4) and (5) can be written
using an aryl radical in the place of a piperidyl radical,
but this would give rise to 4,4'-dinitroazobenzene in the
case of the decomposition of p-nitro-N-nitrosoacetanilide.
This compound, as has been pointed out, could not be identi­
fied in the reaction mixture. However, if the loose complex
theory discussed earlier is evoked, this problem is neatly
avoided. Writing reaction (5) with a loose complex instead
of a piperidyl radical,

\[
\begin{bmatrix}
\cdot \\
\text{NO}_2
\end{bmatrix} + \text{NO}_2
\] + \text{N} = 0
\xrightarrow{\text{O}_2\text{N}}
\text{H}

an adduct is obtained which can be oxidized to the type of
compound apparently isolated.

There still remains the possibility that the reaction
could have been the result of the addition of an aryl diazo
radical and an aryl radical on the solvent molecule. However,
the above seems more probable in that it is essentially a bi­
molecular reaction involving two fairly abundant species
whereas this latter is a bimolecular or termolecular reaction
involving an aryl diazo radical which probably is not present
in high concentration.
Complete characterization of the azo compound isolated as well as work on the suspected azo compounds obtained as an amorphous solid from the benzene fractions would immeasurably help in testing the hypotheses which have been made.

The tarry substance remaining on the band of alumina on which the reaction mixture was originally adsorbed will for convenience be referred to as tar. The nature of this tar is of interest in widening our understanding of these radical reactions. Since an azo compound was isolated in the carbon tetrachloride eluted fractions and other azo type compounds might be inferred from the relatively large amounts of red amorphous substances eluted with benzene, the tar was examined for possible azo linkages. This was done by reduction with tin and hydrochloric acid. Under these reduction conditions the nitro groups should be reduced to amino groups and azo linkages reductively cleaved to amino groups.\(^69, 70\) If the tar contains a relatively large number of azo linkages, polyamino biphenyls might be expected. Since these polyaminobiphenyls are expected to be unstable toward air oxidations, indirect means of characterization were attempted. An acetylation of the amino groups in conjunction with reductive cleavage did not work. Consequently, oxidation to more stable products was considered. It is reported that biphenylquinone, a product which can be obtained from oxidation of benzidine, can be oxidized with lead dioxide and dilute sulfuric acid to
benzoquinone.\textsuperscript{71} This latter is a compound which can easily be purified by sublimation and characterized. In the hope that the presence of polyaminobiphenyls could be inferred by the isolation and identification of benzoquinone, the tar was reduced with tin and hydrochloric acid and the reduction products oxidized with lead dioxide and sulfuric acid. The oxidation products were sublimed, but no sublimate was obtained. This is an indication that the tar probably does not contain a large number of azo linkages although it is not positive proof.

The isolation of a small amount of substance from the tar which appears to be \(4,4'=\text{dinitrophenyl}\) might be explained in one of two different ways. It may be that a small amount of the \(4,4'=\text{dinitrophenyl}\) is trapped mechanically in the tar and is not eluted with carbon tetrachloride or benzene. The other possibility is that the \(1,4\) adducts of the radical source to the aromatic substrate, which has already been discussed, may be oxidized in conc. sulfuric acid to the di-nitrophenyl. The present experimental results do not enable a differentiation of the two possibilities.

The deuterium tracer experiment was carried out to test the possibility that the polyphenylated compounds become progressively more reactive as the molecular weight increases. Although this possibility did not seem too likely in view of the rate factor of four for the phenylation of biphenyl,
$C_{12}H_{10}$, obtained by Hey,\textsuperscript{29} it was thought desirable to
definitely eliminate this possibility.

Of the 0.6047 g. of 2-deutero-3,4'-dinitrobinaphthal added
at the start, 0.61 g. is calculated, by making some broad
assumptions, to be recovered in the various fractions. One
of these assumptions involves the use of the atom per cent
deuterium, found when the samples were being analyzed in
order of decreasing deuterium content as the absolute per­
centage value. The other is the assumption that all of the
fractions have the same percentage hydrogen as dinitrobi­
phenyl. The absolute deuterium atom per cent is certain to
be lower than that used for the calculation in view of the
low figures obtained when the samples were analyzed starting
from those lowest in deuterium content. This differential
is due to a "memory" effect of the mass spectrometer which is
caused by adsorption of molecules on the glass surface of the
gas handling system and becomes rather significant when
dealing with small deuterium/hydrogen ratios. The absolute
deuterium atom per cents are probably somewhere in between
the values listed in columns 3 and 4 of Table 7. The high
atom per cent values were arbitrarily selected since it gives
a better material balance than the lower values. The assump­
tion that all the fractions have about the same percentage
hydrogen as dinitrobinaphenyl is also not too good, especially
for the fractions other than those eluted by carbon
tetrachloride. For example, if the hydrogen ratio is assumed to be that of the postulated structure for the azo compound isolated, the apparent amount of the original deuterated dinitrophenyl incorporated in the tar can be calculated to be 0.020 g. Based on the hydrogen ratio of dinitrophenyl, it is 0.026 g. Since the tars are very likely higher molecular weight species, the assumption that the hydrogen ratio is that of dinitrophenyl will lead to high values for the calculation of the amount of deuterated compound incorporated.

In order to calculate the reactivity of the dinitrophenyl, it can be assumed that the dinitrophenyl found in the fractions washed from the alumina column with acetone represents the dinitrophenyl destroyed in the reaction. This accounts for a 0.079 g. loss of the original dinitrophenyl. The molar ratio of nitrobenzene to dinitrophenyl can be calculated from the original amounts used. The nitrobenzene/dinitrophenyl ratio can thus be calculated to be 232. The loss of dinitrophenyl has already been estimated to be 0.079 g. The loss of nitrobenzene can be estimated by assuming that half of the total weight of products formed is from solvent. Subtracting the dinitrophenyl put into the reaction from the 12.7181 g. recovered, 12.1134 g. is obtained as the amount formed. Half of this weight gives an estimation of 6.06 g. of nitrobenzene incorporated in the radical reaction. The ratio of the nitrobenzene consumed to
the dinitrobenzyl consumed is therefore $4.9 \times 10^{-2}/3.2 \times 10^{-4}$ which equals $1.5 \times 10^2$. Since the original molar ratio was $2.32 \times 10^2$, this leads to an estimation for $K_{C_6H_2NO_2}^\text{NO}_4$ of $1.5$. This value is of the order of magnitude found by Hey for the reactivity of biphenyl.

An emphasis should again be made that the preceding calculation is based on a number of assumptions. Some that have not already been specifically pointed out are the assumption disregarding the benzene fractions as not constituting any of the products arising from biphenyl destruction, the assumption that the red compound contained little or no deuterated biphenyl, and the ignoring of the normal deuterium abundance found in nature. The first and third might be serious although the errors would be in opposite directions.

The deuterium tracer experiment definitely indicates that only small amounts of the dinitrobenzyl are destroyed and that the tars are formed by mechanisms other than the consecutive phenylations of polyaryl hydrocarbons.
SUMMARY

The isomer ratio of the dinitro biphenyls formed in the reaction of \( p \)-nitrophenyl radical with nitrobenzene is estimated by chromatographic isolation and ultraviolet analysis. An indication is obtained for a lower ortho content than that reported from other laboratories. It is proposed that this might be explained by a difference in the procedures used for the isolation of the products.

The two compounds, \( p \)-nitro phenyl acetate and \( 4,4' \)-dinitro azobenzene, are neither isolated from the reaction mixture nor identified in any of the fractions. The implications of this fact are discussed.

An azo compound is isolated from the reaction of \( p \)-nitrophenyl radical with nitrobenzene and partially characterized. Speculations are made regarding the method by which compounds of this type are formed.

It is found that crystals which may be \( 4,4' \)-dinitrobi phenyl are recovered from a sulfuric acid treatment of the tar. It is suggested that this might possibly be formed from the tar as a result of the sulfuric acid treatment. In order to further characterize this tar, a sample of 2-deutero-3,4'-dinitrobiphenyl is prepared. The \( p \)-nitrophenyl radical and
nitrobenzene reaction is carried out in the presence of this deuterated dinitrobiophenyl. Very little of the deuterated compound is found to be incorporated in the tar.
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PART II. THE REACTIVITY OF TRIPHENYL METHYL RADICALS TOWARD AROMATIC NITRO COMPOUNDS
INTRODUCTION

Although aromatic nitro compounds are known to retard vinyl polymerization reactions, the mechanism involved is not entirely clear. It was generally supposed that the growing radical chain became substituted on the nucleus of an aromatic nitro compound until evidence was obtained that aromatic nitro compounds with no nuclear positions available for substitution also acted as retarders. This led the workers who observed this effect to postulate an involvement of the nitro group in the retardation mechanism.

The primary purpose of this work is to test the above hypothesis by studying the effects that a known free radical, triphenylmethyl, would have on the nitro group of various aromatic nitro compounds.

Evidence for a triphenylmethyl radical and aromatic nitro compound complex are to be investigated spectrophotometrically. The quantitative aspects of the conversion of triphenylmethyl radical to p-benzhydryltetraphenylmethane and the nature of the reaction of conc. sulfuric acid on ditriphenylmethyl peroxide will be also studied.
HISTORICAL

Aromatic nitro compounds have been observed to decrease the rate of vinyl polymerization reactions. Unlike the inhibitors, they were found neither to suppress the polymerization completely nor to show a definite induction period. This phenomenon was observed and the compounds giving rise to these effects defined as retarders by Foord. Specifically, inhibitors were defined as compounds capable of destroying the free radicals formed in the primary process whereas retarders were defined as compounds which deactivate growing chains thereby reducing overall polymerization rate and reducing the molecular weight of the polymer. This definition has found general acceptance even though there are many compounds which cannot be cleanly classified as one or the other.

Price and Durham found that the polymers formed in the presence of aromatic nitro compounds contained nitrogen. Since Fieser had reported the methylation of aromatic nitro compounds with diacetyl peroxide, Price suggested that the aromatic nitro compound was incorporated in the polymer by a nuclear substitution by the growing polymer chain.

Other workers have since studied the effect of aromatic nitro compounds on vinyl polymerizations. Schulz has
studied the kinetics of polymerization using nitrobenzene and nitrosobenzene as retarders. He found that nitrosobenzene was a strong inhibitor with retarder characteristics. Kolthoff and Bovey\textsuperscript{6} as well as Price and Read\textsuperscript{7} studied the effects of \textit{m}-dinitrobenzene. The latter workers found that several of the \textit{m}-dinitrobenzene molecules were incorporated in the polymer for each initiator fragment used. Hammond and Bartlett\textsuperscript{8} studied the effects of \textit{m}-dinitrobenzene, \textit{o}-dinitrobenzene, \textit{p}-dinitrobenzene, \textit{l,3,5}-trinitrobenzene, dinitrodurene, and nitromethane in allyl acetate polymerizations. Since nitromethane and dinitrodurene, neither of which has replaceable nuclear hydrogen atoms, exhibited a retardation of the allyl acetate polymerization, a suggestion was made that the nitro group is somehow involved in a chain stopping capacity.

In order to test the hypothesis that the nitro group is involved in the retardation mechanism, Hammond and Ravve\textsuperscript{9} studied the reaction of triphenylmethyl radical with nitrobenzene. They reported that after standing 24 hours in diffuse daylight, a product analysis indicated triphenylcarbinol, nitrobenzene, azobenzene, azoxybenzene, nitrosobenzene, biphenyl, and \textit{p}-terphenyl. In the dark, the reaction was said to produce ditriphenylmethyl peroxide instead of triphenylcarbinol along with the same nitrobenzene reduction products. They further reported that nitrosobenzene reacts rapidly with triphenylmethyl to produce azobenzene
and some azoxybenzene along with triphenyloarbinol, biphenyl and terphenyl.

The earlier work with triphenylmethyl radical did not anticipate the results obtained by Hammond and Ravve. Ziegler\textsuperscript{10}, measuring the rate of dissociation of hexaphenylethane in a series of solvents among which was nitrobenzene, reported that the rate was not dependent on the solvent used. There is no mention of possible reactions which may have ensued.

Gomberg\textsuperscript{11} studied the reaction of triphenylmethyl radical with oxygen in a variety of solvents. In nitrobenzene he found that the results were too high. A nitrobenzene blank, however, absorbed several milliliters of oxygen. Once again there is no observation made of any reaction between the solute and solvent. Hey\textsuperscript{12} decomposed phenylazotriphenylmethane in nitrobenzene and was able to isolate no definite compound other than triphenylmethane. Goldschmidt and Christmann\textsuperscript{13} reacted 1.5 g. of nitrosobenzene with 7 g. of hexaphenylethane in benzene solution and reported in addition to triphenylcarbinol a 2.5 g. yield of azoxytetraphenylmethane.

Very recently, Huisgen and Nakaten\textsuperscript{14} have restudied the decomposition of phenylazotriphenylmethane in nitrobenzene and have isolated a 25 per cent yield of nitrobi phenyls. Tri phenylmethane was the other product isolated. There was no mention of finding extensive amounts of nitrobenzene reduction products.
Other than the last mentioned work, the literature in very recent years has not contained further reports on attempted elucidation of the mechanism by which aromatic nitro compounds retard radical reactions.
EXPERIMENTAL

Chemical Materials Used

Triphenylcarbinol

The triphenylcarbinol used was prepared by students using the reaction of phenylmagnesium bromide on benzophenone followed by hydrolysis. Each student had steamdistilled his sample to remove the biphenyls and had recrystallized the residue. In order to be assured of the purity of the product, the combined yield of the class was steamdistilled again and was followed with a decolorization with Norite and three recrystallizations from ethanol. Melting point was 163-164°C (uncorr.) in a Hirshberg melting point bath.

Triphenylchloromethane

Triphenylchloromethane was made from triphenylcarbinol by the method described by Bachmann. It was stored in a vacuum desiccator over soda-lime and paraffin.

The triphenylchloromethane was analyzed for purity by a Volhard titration of the chloride. Approximately 0.7 g. of the triphenylchloromethane was weighed out on an analytical balance. Ten milliliters of absolute ethanol was added which
dissolved the triphenylchloromethane quite slowly. After a solution was obtained, 1 ml. of nitrobenzene, 1 ml. ferric alum indicator, and 5 ml. of 6 N nitric acid was added. An excess of approximately 0.1 N standard silver nitrate solution was added and back titrated with standard potassium thiocyanate solution. These analyses indicated a purity of 96 to 98 per cent for the freshly prepared products. It was also found that after several months storage in a vacuum desiccator the product was still better than 90 per cent triphenylchloromethane.

Triphenylmethyl radical

The triphenylmethyl radical was prepared in benzene solution from triphenylchloromethane and mercury using the procedure of Rudesill.\textsuperscript{16} It was analyzed using the benzoyl peroxide titration procedure described by Hammond\textsuperscript{17} as well as the oxygen absorption method first described by Gomberg.\textsuperscript{11}

An apparatus was constructed in which the gas burettes, manifold, and reaction flask were all fitted with a water jacket such that thermostatted water could be circulated. The trityl radical solution was taken from the reaction apparatus with a hypodermic syringe and injected into the reaction vessel. The trityl solution was stirred using a magnetic stirrer, and the pressure within the apparatus was
kept constant by adjusting a mercury reservoir. The trityl radical concentration was calculated assuming a stoichiometry of two trityl radicals and one molecule of oxygen. This method of analysis was used routinely because of its convenience and rapidity.

**Nitrobenzene**

Nitrobenzene from Matheson, Coleman and Bell was used after distillation under vacuum through a helix-packed column.

**Benzene**

Thiophene-free benzene was distilled through a five foot long helix-packed column at a reflux ratio of 1 to 15. Boiling point was 79-79.5° C. The solvent was stored over sodium.

For later work the thiophene free benzene was distilled through an 1" diameter, 30 plate Oldershaw column. The distillation was conducted under a nitrogen atmosphere, and the distillate was caught in a receiver which allowed the various fractions to be sealed off under nitrogen. The boiling point was 80.0° C. (uncorr.).
**Acetone**

The acetone distillation was carried out with an Oldershaw as described for benzene. The boiling point was $57^\circ$ C.

**Pentane**

Pentane was obtained from Phillips as 99 per cent normal pentane.

**Argon**

The argon was obtained from Matheson. The mass spectrometer analysis showed no detectable water or oxygen. This indicated that the oxygen content was less than one part in twenty thousand. Nitrogen was the main impurity. Krypton was the only other impurity present in detectable amounts.

**Nitrosobenzene**

Nitrosobenzene was prepared by the procedure described by Coleman, McGloskey and Stuart.\textsuperscript{18} It was recrystallized from alcohol and dried in a desiccator over calcium chloride and calcium sulfate. A portion was sublimed. The sublimed material and the substance recrystallized from alcohol showed the same infrared absorptions at $6.25\mu$ (w), $6.60\mu$ (w), $6.72\mu$ (m), $7.72\mu$ (w), $8.35\mu$ (m), $8.52\mu$ (w), $8.60\mu$ (w), $9.00\mu$ (w), $9.32\mu$ (w), $9.80\mu$ (w), $10.55\mu$ (s), $10.85\mu$ (w),
12.80 μ (s), 13.08 μ (s), 14.52 μ (s) and 15.08 μ (s).

**Trinitrobenzene**

Trinitrobenzene was obtained from Eastman Organic Chemicals as the white label product.

**Hexaphenylethane**

Attempts were made to prepare crystalline hexaphenylethane by an apparatus similar to that of Gomberg and Cone. No crystalline material could be obtained which would absorb oxygen.

A vacuum system was constructed consisting of a Welch Duo-Seal fore pump, an Eck and Kreb mercury diffusion pump, a mercury safety switch, a McLeod gauge, three dry ice traps each capable of being isolated from the system by stopcocks, and the sample manipulation system. The sample manipulation system consisted of two flasks separated by a sintered glass disc and three solvent flasks.

Pentane was distilled into a solvent flask under argon. Acetone obtained from the Oldershaw fractionation was opened and placed in the system just prior to use. Chloroform, Mallinkrodt analytical reagent containing 0.75 per cent ethanol as a preservative, was dried over calcium chloride and distilled into a solvent flask after removing a large forerun. Since ethanol and chloroform are reported to
azetrop at 59.3°C, enough forerun was discarded so that there was theoretically no ethanol remaining. After the introduction of these solvents into the system, each was degassed by evacuation.

The triphenylmethyl radical was prepared in benzene solution and transferred to the vacuum system using a syringe. The benzene was removed under vacuum and the residue washed with acetone. The acetone transfer was accomplished by cooling the residue and warming the acetone flask with a glasscol. After a sufficient amount of acetone was distilled over to the residue, the mixture was broken up by stirring with a magnetic stirrer and the acetone removed by creating an uneven pressure with solvent vapor pressures regulated with stopcocks so as to force the acetone through the sintered glass plate to the second flask. This filtration was often complicated by the disc becoming stopped up. The remaining residue of hexaphenylethane was dissolved in chloroform which, like acetone, was distilled into the reaction flask. After the solution was complete, the chloroform volume was reduced by about one-half and some four times this volume of hexane was added. A poor yield of crystals resulted. The solvent was taken off in the same manner as acetone. The residue was dried by continued evacuation and analyzed in toluene by oxygen absorption. The highest purity obtained for the various samples prepared in this manner was 90 per cent. However,
most of the samples only analyzed to about 70 per cent hexa-
phenylethane by oxygen uptake.

The hexaphenylethane was fused with sodium to test for
chlorine. There was essentially no chlorine present which
indicated that no trityl chloride was present as the con-
taminant.

Since high purity hexaphenylethane could not be consis-
tently obtained by the crystallization methods, most of the
vacuum line experiments were done using the residue after
benzene removal without further attempts at purification.

The Quenching of Triphenylmethyl Radical

Reaction with methanol

In searching for a clean quantitative quenching method
for triphenylmethyl radicals, an attempt was made to convert
the free radical to triphenylmethyl methyl ether by intro-
ducing methanol, iodine and pyridine. A benzene solution of
triphenylmethyl radical which had remained unused for a month
after it had been prepared was analyzed for radical concen-
tration by titration with oxygen. A solution of methanol,
iodine and pyridine was prepared such that there was an
equal molar concentration of each reagent. The iodine was
titrated with sodium thiosulfate and a volume of the quenching
solution, slightly in excess of the theoretical value was
added to the radical solution.

After several hours, the reaction mixture was washed with several portions of water and thiosulfate solution. The benzene layer was dried, the benzene stripped off under vacuum and the residue chromatographed. No triphenylmethyl methyl ether could be detected in the reaction products. The chromatography fractions yielded 1.0561 g. of triphenylmethane and 0.3402 g. of \( p \)-benzhydryltetraphenylmethane. A total of 2.8160 g. were recovered over a range of 118 fractions.

**Reaction with ethanol**

A freshly prepared benzene solution of triphenylmethyl radical was quenched using ethanol, iodine and pyridine in the same manner as the analogous quenching with methanol. The various fractions were not weighed, but it was observed that a relatively large amount of triphenylmethyl ethyl ether was recovered. However, there was still a surprising amount of \( p \)-benzhydryltetraphenylmethane as well as lesser amounts of triphenylcarbinol isolated. These three compounds seemed to account for most of the solid products obtained from 203 fractions.

**Reaction with N-acetylethanolamine**

The triphenylmethyl radical quenching was tried using the same procedure as that described for the methanol method.
except that N-acetylene was used as the alcohol. The N-acetylene amine was prepared from ethanolamine by the method of Wenker. Chromatography yielded only oily and colored products the characterization of which was not attempted.

Reaction with molecular oxygen

Gomberg's statement that triphenylmethyl radical does not yield ditriphenylmethyl peroxide quantitatively has been confirmed. Crystallization of hexaphenylethane from a triphenylmethyl radical solution in benzene was attempted in an argon flushed dry box. It was found that enough oxygen was present to slowly convert the radical to the peroxide. The peroxide was separated from the acetone soluble portion and found to weigh 0.5412 g. The oil resulting from the red colored acetone solution was found to weigh 1.1470 g.

The Rate of Triphenylmethyl Activity Loss in the Presence of Aromatic Nitro Compounds

Nitrobenzene

An equimolar amount of nitrobenzene was added to a benzene solution of triphenylmethyl radical. Aliquots taken out at intervals up to 159 hours gave a scattering of values for radical activity by oxygen titration. No trend, indicating a
decrease of radical concentration, was observed. After two months, the solution still absorbed oxygen.

Nitrobenzene was distilled into a flask containing solid hexaphenylethane. The nitrobenzene was then removed by room temperature evaporation under vacuum. After ten days, 27.2 per cent of the weight of the resulting solid seems to be triphenylmethyl radical on the basis of oxygen titration. In an identical experiment, vacuum was applied to the nitrobenzene-triphenylmethyl radical mixture for thirty days. The main amount of nitrobenzene was removed in six days, but small amounts were continuously collecting in the dry ice traps for the length of the experiment. At the end of thirty days, the solid residue was found to be 32.4 per cent triphenylmethyl radical by oxygen absorption.

**Nitrosobenzene**

Equimolar amounts of a benzene solution of triphenylmethyl radical and solid nitrosobenzene were mixed. The radical activity decreased to about one-fourth of the original in ten hours but remained essentially constant thereafter. The mixture still absorbed oxygen after two weeks.

**Trinitrobenzene**

An excess of trinitrobenzene was mixed with triphenylmethyl radical in benzene solution. The radical activity
decreased about one-third in the first ten hours but remained essentially constant for the following thirty hours.

Products Arising from Triphenylmethyl Radical and Aromatic Nitro Compounds

Nitrobenzene

**Mixture I.** An equimolar solution of nitrobenzene and triphenylmethyl radical in benzene was kept in a rubber-stoppered erlenmeyer flask which was also equipped with a syringe stopple so that samples could be removed for kinetic studies. The portion not used for the kinetic determinations was allowed to stand in the laboratory until the benzene was lost through the rubber stopper and stopple. The solid residue was titurated with acetone to separate 0.1562 g. of insoluble ditriphenylmethyl peroxide. The acetone was evaporated from the acetone soluble portion and the residue steamdistilled. Of the 0.196 g. of nitrobenzene originally introduced, 0.165 g. was recovered from the steam distillate. This nitrobenzene was shown by refractive index measurements to contain at most 5\(\frac{1}{2}\) per cent biphenyl. From the residue remaining after removal of nitrobenzene, 0.6526 g. triphenylmethane, 0.2409 g. \(p\)-benzydroltetraphenylmethane, and 0.8680 g. triphenylcarbinol were recovered.

**Mixture II.** A solid residue was obtained in a vacuum
line, room temperature evaporation of nitrobenzene from a mixture of hexaphenylethane and nitrobenzene. This sticky yellow residue on exposure to air turned into a black tar. Titration with acetone separated 0.2394 g. of ditriphenylmethyl peroxide. Chromatography of the acetone soluble portion yielded 0.2053 g. triphenylmethane, 0.2088 g. of $\beta$-benzhydryltetraphenylmethane, 0.8796 g. of triphenylcarbinol and 0.3785 g. of unidentified solids.

**Mixture III.** A solid residue obtained in the vacuum line after thirty days of constant evacuation of the nitrobenzene hexaphenylethane was exposed to air. The dry yellow solid began to acquire an orange color on the surface after one day. After three days, the surface became sticky but interior portions remained a dry yellow solid. The solids were taken up in acetone and insoluble portion filtered off as 2.52 g. of ditriphenylmethyl peroxide. After stripping off the acetone, the residue was vacuum distilled to yield 0.0632 g. of nitrobenzene. Chromatography of the distillation residue yielded 0.3696 g. of triphenylmethane, 0.2357 g. of $\beta$-benzhydryltetraphenylmethane, and approximately 0.58 g. of fractions which appeared to be triphenylcarbinol. Some 78 per cent of the acetone soluble solids were recovered after the various separation procedures.

**Mixture IV.** A hexaphenylethane-nitrobenzene residue of 5.0614 g. obtained after 62 days in the vacuum line was
analyzed for products. The acetone insoluble portion which was assumed to be ditriphenylmethyl peroxide weighed 1.3334 g. The acetone soluble portion of 3.7280 g. was chromatographed to yield 0.8608 g. of triphenylmethane, 0.3197 g. of triphenylearbinol, and 0.8177 g. of $p$-benzhydryltetra phenylmethane along with unidentified products.

**Mixture V.** Triphenylmethyl radical was prepared with a regular stock solution of benzene. A slight excess of nitrobenzene was added and $\frac{1}{2}$ ml. of air was purposely admitted into the reaction chamber. After three days the benzene solution was poured directly on an alumina column made up with Skelly B and the elution carried out with Skelly B. The chromatography indicated large amounts of ditriphenylmethyl peroxide and $p$-benzhydryltetra phenylmethane along with triphenylearbinol and small amounts of other products. Triphenylmethane was not isolated as such. There were no colored products formed to indicate the formation of reduction products of nitrobenzene.

**Nitrosobenzene**

A mixture of equimolar amounts of nitrosobenzene and triphenylmethyl radical yielded azoxybenzene, $p$-benzhydryltetra phenylmethane, triphenylearbinol, triphenylmethane and possibly tetra phenylmethane. No azobenzene was isolated.
Triphenylmethyl Radical Complexes with Aromatic Nitro Compounds

Attempts were made to detect a complex of the triphenylmethyl radical with aromatic nitro compounds. The yellow solid obtained from hexaphenylethane and nitrobenzene in the vacuum line was suspected of being such a complex since it decomposed in air to a sticky substance smelling strongly of nitrobenzene. This yellow solid was mixed with potassium bromide and made into a salt pellet. The infrared spectrum was characteristic of ditriphenylmethyl peroxide and nitrobenzene. Apparently the solid could not be taken through the pellet-making process without decomposition.

Ultraviolet spectra of aromatic nitro compounds and triphenylmethyl radical in benzene solution were determined on the Cary spectrophotometer. The spectrophotometer cell was fitted with a rubber stopple and flushed with nitrogen by alternately evacuating and introducing nitrogen by means of a hypodermic needle attached to a two way stopcock. The nitrogen was then displaced by injecting the solutions of radical and aromatic nitro compound with a hypodermic syringe. Spectra determined in this way showed no changes in the triphenylmethyl radical absorption with addition of aromatic nitro compounds. The following combinations were examined:
<table>
<thead>
<tr>
<th>Aromatic Nitro Compound</th>
<th>Concentration (m/l)</th>
<th>Radical conc. (m/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>m-dinitrobiphenyl</td>
<td>$9.92 \times 10^{-3}$</td>
<td>$8.9 \times 10^{-2}$</td>
</tr>
<tr>
<td>1,3,5-trinitrobenzene</td>
<td>$9.85 \times 10^{-3}$</td>
<td>$8.9 \times 10^{-2}$</td>
</tr>
<tr>
<td>nitrobenzene</td>
<td>$7.08 \times 10^{-1}$</td>
<td>$8.9 \times 10^{-2}$</td>
</tr>
<tr>
<td>nitrobenzene</td>
<td>$9.82 \times 10^{-3}$</td>
<td>$8.9 \times 10^{-2}$</td>
</tr>
</tbody>
</table>

**Reaction of Triphenylmethyl Radical with Hydrochloric Acid**

Gomberg$^{22}$ reported a condensation of triphenylmethyl radical to hexaphenylethane with hydrochloric acid. The compound which he assumed to be hexaphenylethane was in reality p-benzhydryltetraphenylethane.$^{23}$ Since this latter compound is isolable, the quantitative aspects of the reaction was investigated with an analytical method for triphenylmethyl radical in mind.

Two ml. of radical solution was placed in a flask containing about 10 ml. benzene and previously flushed with dry hydrochloric acid. Within a half hour the benzene solution had decolorized completely. After 1$\frac{1}{2}$ hours, the benzene solution was opened to the air and the benzene removed. The solid residue was chromatographed on an 1 cm. x 5 cm. alumina column. The first 70 ml. of Skelly B eluant brought down 0.0053 g. of triphenylethane. The next 300 ml. of Skelly
eluant and 200 ml. Skelly-benzene eluant brought down 0.1401 g. \( p \)-benzhydryltetraphenylmethane. The pure benzene eluant which followed brought down 0.0482 g. triphenylcarbinol. Assuming that all the triphenylmethyl radical was converted to \( p \)-benzhydryltetraphenylmethane by hydrochloric acid, the concentration of the sample analyzed would be \( 2.88 \times 10^{-4} \) molar. This same sample when analyzed by oxygen absorption was determined to be \( 2.69 \times 10^{-4} \) molar.

Reaction of Ditriphenylmethyl Peroxide with Concentrated Sulfuric Acid

Gomberg\(^{11}\) stated that conc. sulfuric acid and ditriphenylmethyl peroxide gives an 80 per cent yield of triphenylcarbinol. This work was repeated. A sample of 1.5798 g. of ditriphenylmethyl peroxide was dried under vacuum. The weight remained constant. Twenty five ml. of conc. sulfuric acid was added to this sample of peroxide. The mixture turned black almost immediately. No noticeable exothermic effect was noted. After \( \frac{1}{2} \) hour, the very dark colored solution was poured on ice. A light brown precipitate resulted. The precipitate was filtered and dissolved in ether. The ether solution was washed with dilute potassium hydroxide solution, dried over calcium chloride and concentrated. The first drop of crystals, dried overnight
in a vacuum desiccator, weighed 0.7070 g. and was identified as triphenylcarbinol. The second crop, also mainly triphenylcarbinol, weighed 0.2377 g. The third crop weighed 0.4040 g. The triphenylcarbinol from the three crops accounted for an 85 per cent yield. Estimating the amount of triphenylcarbinol not isolated in these first crystallizations, it was guessed that the carbinol yield is around 87-90 per cent.

The potassium hydroxide wash was acidified and extracted with ether. The ether solution decolorized bromine in carbon tetrachloride giving off HBr. A dark colored solid weighing 0.0908 g. was obtained. This dark compound on sublimation yielded only a trace of sublimate. The residue, however, was found to decolorize bromine.

The amount of benzophenone present was estimated using Beer's law on a peak at 4.5 μ. According to this calculation there was 0.0136 g. of benzophenone formed.
DISCUSSION

The determination of the rate of decrease of triphenylmethyl radical activity in the presence of nitrobenzene has shown that the reaction, if any, is extremely slow. The early decrease in radical activity in the presence of tri-nitrobenzene and nitrosobenzene may or may not be real. This effect might well be caused by a diffusion of oxygen into the system. In any case, it has been established that triphenylmethyl radical and the aromatic nitrogen compounds mentioned can coexist for long periods of time without dramatic changes taking place. This is in sharp contrast to the inference by Hammond and Ravve\textsuperscript{9} that the reaction of triphenylmethyl radical and nitrobenzene is quantitatively complete after 24 hours. There is also a serious discrepancy in the products obtained by Ravve and that obtained in this series of experiments. Whereas Ravve reports a series of nitrobenzene reduction products, none was ever detected in these experiments. The product analysis of the nitrosobenzene and triphenylmethyl radical mixture yielded azoxybenzene. However, this is not unexpected since nitrosobenzene on decomposition in the laboratory at room temperatures produces a black tar which can be chromatographed to yield large amounts of
It is interesting to note that the major products isolated from mixtures of nitrobenzene and triphenylmethyl radical were ditriphenylmethyl peroxide, triphenylmethane, triphenylcarbinol, \( p \)-benzhydryltetraphenyldimethane and nitrobenzene. The nitrobenzene was shown in one instance to be recovered quantitatively within limits of experimental techniques. The other products are all obtainable from triphenylmethyl radical in the absence of aromatic nitro compounds as was shown in the product analysis of the hydrochloric acid treatment of triphenylmethyl radical. The peroxide is undoubtedly formed by the reaction of the free radical with oxygen in the atmosphere. The triphenylmethane and triphenylcarbinol appear to be the reduction and oxidation products of triphenylmethyl radical. The \( p \)-benzhydryltetraphenyldimethane is a disproportionation product. The reason for the production of these particular compounds is as yet not clear.

Some type of molecular complex for triphenylmethyl radical and nitrobenzene was postulated on the following basis. Nitrobenzene was removed from hexaphenylethane with some difficulty. The excess nitrobenzene was removed fairly readily; but once enough was removed so that the solid formed, further removal was so slow that nitrobenzene was still being taken off at the end of two months. It was also observed
that the solid on exposure to air released nitrobenzene so that it could be readily distinguished by its odor.

A postulation of a radical-aromatic complex is not original. Gomberg\textsuperscript{24} stated that hexaphenylethane formed a 1 to 1 complex with benzene, toluene, ethybenzene, m-xylene, o-xylene, and p-xylene. His evidence was the loss in weight on heating a sample of what he considered to be a complex. Goodwin, Johnson and Witkop\textsuperscript{25} have isolated a compound which they postulate to be a complex of hexaphenylethane with an ozonide on the basis of the infrared spectrum. Mayo\textsuperscript{26} postulated a complex of a hydrogen atom or substituted benzyl radical with the aromatic solvent in order to explain reduction in molecular weight of styrene without incorporation of the solvent molecule. Leffler and Hubbard\textsuperscript{27} assumed a complex formation of trinitrobenzene and triphenylmethyl radical in their discussion of the transition state configuration for the dissociation of hexaphenylethane. Boozer and Hammond\textsuperscript{28} found that a complex of the peroxy radical and inhibitor could account for the behavior of inhibitors in air oxidation studies.

Attempts were made to detect these complexes by spectroscopic means without success. It was thought that the infrared spectra might be helpful since Kross and Fassel\textsuperscript{29} have studied the effects of complex formation on the nitro asymmetric stretching and the out-of-plane C-H bending vibrations
of picric acid. However, it was not found possible to obtain a spectrum before the hexaphenylethane decomposed in air to the peroxide. The ultraviolet spectrum of nitrobenzene and triphenylmethyl radical in benzene showed the same spectrum as the benzene solution of triphenylmethyl radical. This was observed for a concentration range of nitrobenzene ranging from 0.1 to 14 times the concentration of triphenylmethyl radicals. The absorption peaks were essentially the same as those observed by Lewis.\textsuperscript{30} Trinitrobenzene and dinitrobi-phenyl also failed to affect the triphenylmethyl radical spectrum. The failure of these aromatic nitro compounds to affect the triphenylmethyl radical spectrum indicates that the complex in benzene solution, if formed, is an extremely loose one. It might prove more rewarding to look for complexing evidence in a non-aromatic solvent.

The quenching of triphenylmethyl radical with an alcohol, iodine and pyridine, did not seem to be a clean reaction. Molecular iodine and triphenylmethyl radical should react readily since there is apparently very little activation energy involved.\textsuperscript{31} The triphenylmethyl iodide should in turn undergo a nucleophilic displacement by ethanol with pyridine acting as the base to pick up the proton. Despite this apparently clean path, the reaction products indicated that there are probably complications involved. The relatively large amounts of p-benzhydryltetraphenylmethanes which
are formed meant that something was aiding a disproportion of this kind.

The reaction of N-acetylethanolamine with triphenylmethyl radical was an extremely poor one. This is not at all surprising in view of the results with simple alcohols. However, at the time the experiment was conducted, the nature of the ethanol and methanol reactions was not yet well understood. The more complex alcohol was used in hopes of obtaining a quench product which would not elute from the alumina column very readily and thus permit the separation of the hydrocarbon products formed in the triphenylmethyl radical and aromatic nitro compound mixtures.

The reaction of triphenylmethyl radical with oxygen is another reaction which is seemingly clean cut, but in actuality is not. The quantitative amount of the non-peroxide fraction obtained from the triphenylmethyl radical solution which became oxidized in the dry box may be in error since all the acetone might not have been completely removed. However, in general, significant amounts of non-peroxide substances are always obtained. This has not only been observed by a number of the early workers\textsuperscript{11, 32, 33} but has recently received extensive study by Lichtin.\textsuperscript{34}

One of the cleanest reactions, product-wise, observed for triphenylmethyl radicals seems to be the disproportionation to 2-benzhydrolyltetraphenylmethane with hydrochloric
acid. This reaction might well be used to analyze for triphenylmethyl radical except that the procedure is slow and subject to the inherent quantitative errors of chromatographic processes and gravimetric analysis.

The ditriphenylmethyl peroxide and sulfuric acid reaction is interesting in that the yield of triphenylcarbinol is much higher than expected. It might be guessed that the reaction proceeds in the following manner:

\[ \text{C}_3\text{COOC}_3 + \text{H}^+ \rightarrow \text{C}_3\text{COH} + \text{C}_3\text{CO}^+ \]
\[ \text{C}_3\text{CO}^+ \rightarrow \text{C}_2\text{CO} \]
\[ \text{C}_2\text{CO} + \text{HOH} \rightarrow \text{C}_2\text{C}=\text{O} \]
\[ + \text{OH} \quad \text{H} \]
\[ \text{C}_2\text{C}=\text{O} \rightarrow \text{C}_2\text{C} = \text{O} \quad + \text{H}^+ \]
\[ + \text{OH} \quad \text{OH} \quad \text{H} \]
\[ \text{C}_2\text{C} = \text{O} \rightarrow \text{C}_2\text{C} = \text{O} + \text{HQ} \]
\[ \text{OH} \]

If this reaction scheme is followed, the yield of triphenylcarbinol should never exceed one molecule for one molecule of peroxide. It has been found that almost 2 molecules of triphenyl carbinol are obtained from one molecule of the peroxide. This result, plus the fact that neither benzo-phenone nor phenol could be isolated from the reaction mixture, rules out the possibility that the expected reaction
mechanism is an important one.

A mechanism which would account for the large yield of triphenylcarbinol is the solvolysis of ditriphenylmethyl peroxide to two triphenylmethyl carbonium ions plus hydrogen peroxide. The triphenylmethyl carbonium ion on being poured on ice forms triphenylcarbinol. The hydrogen peroxide in conc. sulfuric acid is essentially the same thing as Caro's acid, a well-known species. The presence of a strong oxidizing species of this kind helps to explain the formation of small amounts of high molecular weight phenolic compounds which seem to be formed. In general, this was a rather interesting sidelight in the study of the reactivities of aromatic nitro compounds toward triphenylmethyl radical.
SUMMARY

The reactivity of triphenylmethyl radical toward nitro-benzene was found to be negligible. The reactivity of the radical toward trinitrobenzene and nitrosobenzene must also be negligible since radical activity was maintained for long periods of time in the presence of these compounds. Careful product analysis showed no evidence of nitrobenzene or tri-nitrobenzene reduction products. Nitrosobenzene forms azoxybenzene, but this was found to occur with or without the presence of triphenylmethyl radical.

Spectroscopic evidence was sought for a triphenylmethyl radical and aromatic nitro compound complex without success. The infrared spectra could not be obtained for technical reasons, and the ultraviolet spectra in benzene solution did not show evidences of complexing.

The quenching reaction of triphenylmethyl radical with an alcohol, iodine and pyridine was found not to give the triphenylmethyl alkyl ether stoichiometrically. The reaction of triphenylmethyl radical with hydrochloric acid to give p-benzhydryltetraphenylmethane was found to be a much cleaner reaction.

The reaction of ditriphenylmethyl peroxide with cons.
sulfuric acid gave unexpectedly large yields of triphenyl-carbinol. A mechanism for the reaction was proposed.


22. Gomberg, Ber., 36, 376 (1903)

23. Weickel, Ann., 372, 8 (1909)

24. Gomberg and Cone, Ber., 38, 1333 (1905)


29. Kross and Fassel, Private communication, Institute for Atomic Research and Department of Chemistry, Iowa State College (1956)


32. Gomberg, Ber., 34, 2726 (1901)


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