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STUDIES ON THE REACTION OF p-NITROBENZYLDIMETHYLSULFONIUM ION WITH HYDROXIDE ION

BY

UWE SCHULZ

A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
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FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled

STUDIES ON THE REACTION OF
p-NITROBENZYLDIMETHYLSULFONIUM ION WITH HYDROXIDE ION

submitted by Uwe Schulz, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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Date July 19, 1968

TO MY MOTHER

ACKNOWLEDGEMENTS

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ABSTRACT

A reinvestigation of the reaction of p-nitrobenzyldimethylsulfonium tosylate with sodium hydroxide in aqueous solution at 100° was undertaken. A quantitative yield of p,p'-dinitrostilbene had been reported and a carbene intermediate formed by decomposition of sulfonium ylid had been proposed for the reaction.

In the present work the possibility of a mechanism involving nucleophilic displacement was considered and tested for in mixed product experiments. Reactions of mixtures of p-nitrobenzyldimethylsulfonium ion and excess benzyldimethylsulfonium ion in aqueous sodium hydroxide solution did not afford any p-nitrostilbene, the mixed product under consideration. Thus, operation of an S_N2 mechanism in the reaction leading to p,p'-dinitrostilbene was excluded.

Attempts to isolate the p-nitrobenzyldimethylsulfonium ylid under various conditions failed, pointing to a high reactivity and low concentration of the ylid in aqueous base. The title reaction at low temperatures afforded substantial amounts of p,p'-dinitrostilbene oxide, suggesting oxygen interference with the course of the reaction.

Prompted by observations made in this work and guided by theoretical considerations, an analytical reexamination of the title reaction was conducted. Extensive use of thin layer and gas-liquid chromatography led to results which are in drastic contrast to the reported quantitative yield of p,p'-dinitrostilbene. A total of eight compounds corresponding to a combined yield of approximately 50%

could be identified: *p*,*p*'-dinitro derivatives of stilbene, tolane, bibenzyl, and stilbene oxide and the *p*-nitro derivatives of benzyl alcohol, benzaldehyde, benzoic acid and toluene. The remaining 50% of product are believed to be of polymeric nature. A mechanism involving electron transfer between the sulfonium ylid and the sulfonium salt is proposed and can account for all products. Radical coupling processes and reactions of radicals with nucleophiles are proposed to be operative.

The reaction of the *p*-nitrobenzyldimethylsulfonium ion carrying a methyl substituent in benzylic position with hydroxide ion did not afford dimeric olefinic material, indicating that neither a carbene nor an S_N2 mechanism is operative. Unidentified materials of suspected radical origin were obtained.

Further analytical investigations were conducted concerning the *p*-nitrobenzyldiphenylsulfonium, *p*-nitrobenzylpyridinium and 3,5-dimethyl-4-nitrobenzyl 'onium systems in their respective reactions with aqueous base. The *p*-nitrobenzyldiphenylsulfonium system was distinguished from the corresponding dimethylsulfonium ion in that a quantitative yield of *p*,*p*'-dinitrostilbene with a high proportion of the *cis*- isomer was obtained. Furthermore, the reaction was found to be very fast. Isolation of the sulfonium ylid seemed to be precluded due to rapid decomposition. No conclusive interpretations can be offered, but suggestions involving electron transfer between *p*-nitrobenzyldiphenylsulfonium ylids are advanced.

p-Nitrobenzylpyridinium bromide in aqueous base was found to be converted quantitatively to a mixture of p-azoxybenzaldehyde and p-nitrobenzaldehyde. Although the products are distinctly different from those in the corresponding dimethylsulfonium system, a scheme in close analogy to the mechanistic proposal involving radical intermediates for the title reaction can account for their formation. The basic difference in the two systems is ascribed to the leaving group ability of pyridine in comparison to that of dimethyl sulfide.

Preliminary studies of the reaction of the 3,5-dimethyl-4-nitrobenzylpyridinium ion and the corresponding dimethylsulfonium ion in aqueous base did not show any similarity to the reactions of the corresponding p-nitrobenzyl 'onium ions in aqueous base. These results indicate that coplanarity of the nitro group and the phenyl system are required for electron transfer between ylids and 'onium salts.

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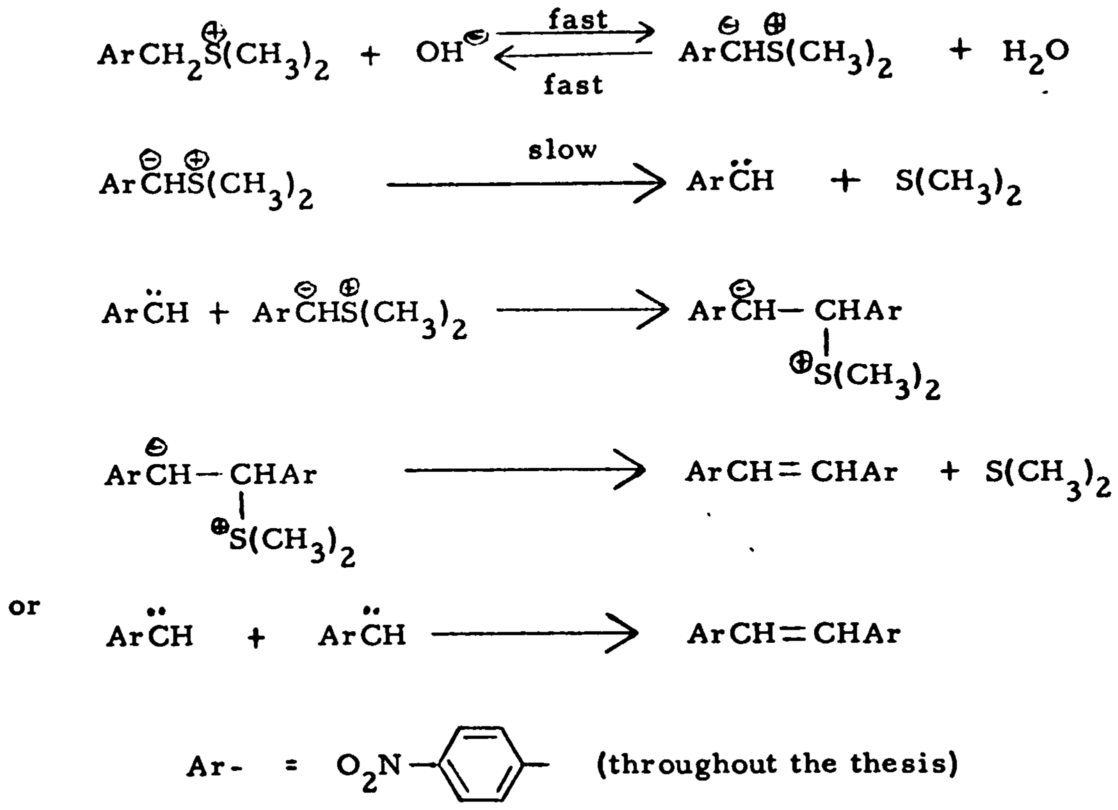
INTRODUCTION

When the present work was begun in May 1965, the choice of the topic was made for two underlying reasons. A very dynamic development in the chemistry of divalent carbene intermediates in the previous decade was about to be followed by a period of critical reexamination. Two comprehensive monographs on carbene chemistry had appeared in 1964 (1, 2), summing up the developments until that time and simultaneously indicating that many questions in the field remained unanswered. In some instances it appeared that carbene intermediates had been invoked unjustifiably and that evidence for their presence was not compelling. Cyclopropane formation, for example, was no longer accepted as a criterion for carbene intermediacy (3). The concept of free divalent species as intermediates in the decomposition of diazo compounds in the condensed phase had also come under attack (4). More recently, it was recognized that the products in metallo-organic initiated α-eliminations were rarely, if ever, due to carbenes, but could well be explained by the intermediacy of α-halocarbanions (5).

At the same time, an intensive research activity began in the field of sulfonium ylids. Even though the isolation of the first sulfonium ylid, fluorenylidenedimethylsulfurane, had been reported as early as 1930 (6), the most recent interest in the field had been prompted by the isolation of the surprisingly stable phenacylidene-methylphenylsulfurane (7), and by the rewarding experience with the synthetically useful phosphonium ylids. Further reports appeared shortly afterwards on the isolation of stable dimethylsulfuranes derived from the following compounds: meldrumic acid (8), barbituric acid (8), cyclopentadiene (9), dicyanomethane (10), and bis(phenylsulfonyl)methane (11). All these sulfonium ylids have sharp melting points and are not sensitive to atmospheric conditions. Reports of sublimation (8) and of inertness (7) to refluxing tetrahydrofuran and refluxing aqueous sodium hydroxide solution stress the stability of these compounds.

This development then, provided the background for the choice of the topic of the present work. In 1961 Swain and Thornton (12) had reported that p-nitrobenzyldimethylsulfonium p-toluenesulfonate (tosylate), when treated with sodium hydroxide in water at 60°, was converted quantitatively to a mixture of cis- and trans-p,p'-dinitrostilbene. They reported the reaction to be first order in hydroxide ion and first order in sulfonium ion and observed that exchange of the benzylic protons for deuterium was rapid as compared to stilbene formation. They rationalized these findings and their data on the sulfur isotope effect by invoking a carbene intermediate formed by spontaneous decomposition of the sulfonium ylid. The reaction pathway as proposed by Swain and Thornton is given in Scheme I. The fact that a quantitative yield of stilbene is obtained would imply that the carbene reacts in a very specific manner with the ylid, to the exclusion of any reaction with other nucleophiles present in aqueous base. In addition, it seemed rather surprising in the light of the recent reports on stable sulfonium ylids, that the p-nitrobenzylidenedimethylsulfurane would decompose spontaneously at 60° in aqueous solution.

SCHEME I



$$ArCH_2\overset{\oplus}{S}(CH_3)_2 + OH^{\ominus} \underset{fast}{\overset{fast}{\rightleftarrows}} Ar\overset{\ominus}{C}H\overset{\oplus}{S}(CH_3)_2 + H_2O$$

$$Ar\overset{\ominus}{C}H\overset{\oplus}{S}(CH_3)_2 \xrightarrow{slow} Ar\ddot{C}H + S(CH_3)_2$$

$$Ar\ddot{C}H + Ar\overset{\ominus}{C}H\overset{\oplus}{S}(CH_3)_2 \longrightarrow Ar\overset{\ominus}{C}H-\underset{{}^{\oplus}S(CH_3)_2}{\underset{|}{CHAr}}$$

$$Ar\overset{\ominus}{C}H-\underset{{}^{\oplus}S(CH_3)_2}{\underset{|}{CHAr}} \longrightarrow ArCH{=}CHAr + S(CH_3)_2$$

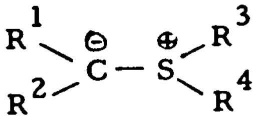
or

$$Ar\ddot{C}H + Ar\ddot{C}H \longrightarrow ArCH{=}CHAr$$

Ar- = O_2N– (throughout the thesis)

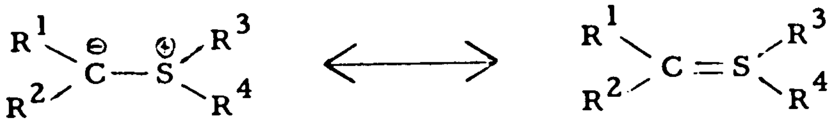
Thus, it was apparent that more work was required to clarify these peculiar features and it was decided to undertake further studies of the above reaction within the scope of a Ph.D. thesis. Prior to experimental work on the chosen topic of research, a survey of the literature of ylids in general and a critical examination of the information presented by Swain and Thornton were undertaken.

The special characteristic of a sulfonium ylid, having the general structure



is the unique stabilization afforded the carbanion by the presence of the adjacent sulfur atom. Whereas normal carbanions are seldom isolable and are very reactive toward atmospheric components, many sulfonium ylids could be isolated as crystalline and stable substances.

Delocalization of the electrons of an ylid carbanion into the vacant 3*d*-orbitals of sulfur is considered a major factor contributing to the stability of the sulfonium ylids (13). In the divalent state, the $3p_y$ and $3p_z$ orbitals of sulfur are filled by electron sharing, but there remain five empty 3*d*-orbitals. It is conceiveable that overlap of a filled 2*p*-orbital of an ylid carbanion with a vacant 3*d*-orbital of sulfur would increase the stability of that carbanion. Effective *p*-*d* π bonding, however, could only result from overlap of the contracted 3*d*-orbitals of sulfur with the adjacent 2*p*-orbital. It is evident also, that the energy of promotion of an electron into a *d*-orbital would be an important factor in determining the effectiveness of the bonding. The promotional energy is related to the nuclear charge so that as the nuclear charge increases, the promotional energy decreases to the point where it requires less energy than is supplied by the resulting bond formation. It therefore would be expected that a high degree of delocalization for a carbanion should occur, if the sulfur atom carried a full unit positive charge as is the case in a sulfonium ylid. Because of the charge neutralization feature of the resonance, a very small contribution of the covalent



structure would represent a substantial amount of energy of stabilization.

Other factors contributing to the stability of sulfonium ylids are the ability of the substituents on carbon to delocalize the negative charge, and the nature of the two substituents on the sulfur atom. In the fluorenylidenedimethylsulfurane the negative charge is delocalized in the aromatic system, and this effect is enhanced further in the 2-nitro and 2,7-dinitro analogues which are both less basic and less nucleophilic and thereby more stable than the parent compound (14). These findings have been substantiated through studies on other sulfonium ylids, and most extensively on phosphonium ylids (15), and thus have general validity. The studies on the phosphonium ylids had simultaneously indicated that electron-withdrawing substituents on the phosphorus atom also exert a stabilizing influence. The same effect would be expected for the sulfur compounds.

A comparison of the physical and chemical properties of sulfonium salts with those of quartenary ammonium salts should provide an estimate of the amount of stability afforded the ylids by utilization of the 3d-orbitals of the heteroatom, since nitrogen is not able to expand its valence shell. It could be assumed that the coulombic effect of a sulfonium and an ammonium group is similar.

Doering and Schreiber (16) have shown that vinyldimethylsulfonium salts undergo typical Michael addition reactions at a rate at least 10^5 times faster than the corresponding vinyltrimethylammonium salts. Another approach to the separation of d-orbital and inductive effects was the determination of the rates for deuteroxide-catalyzed exchange of tetramethylammonium, tetramethylphosphonium, and trimethylsulfonium ions with deuterium oxide, the relative rates being 1, 2.4×10^6 and 2.0×10^7 respectively (17). These results again demonstrate that d-orbital effects strongly stabilize the transition state for carbanion formation and simultaneously allow a comparison between sulfur and phosphorus ylids. Further quantitative data of comparison for sulfur and phosphorus ylids are the reported pK_a values for the corresponding sulfonium and phosphonium salts. The pK_a of 9-fluorenyldimethylsulfonium bromide in 31.7% water-dioxane, determined spectrophotometrically, was shown to be 7.3 (18). Under identical conditions the pK_a for 9-fluorenyltriphenylphosphonium bromide is 7.5 (18). These reports at least indicate that the dimethylsulfonium group provides better stabilization than the corresponding triphenylphosphonium group for an identical adjacent carbanion.

With this information at hand, it was desirable to obtain some estimate of the stability of the p-nitrobenzyldimethylsulfonium ylid under investigation. A survey of the literature of phosphonium ylids actually made the desired data on p-nitrobenzyltriphenylphosphonium ylid available. The isolation of this compound had first been recorded by Kröhnke in 1950 (19), as a red solid of critical stability. Later its method of preparation was improved and the compound was well characterized (20).

Attention is also called to the recent reports on the isolation of unexpectedly stable diazo compounds, a development which paralleled the one mentioned earlier for sulfonium ylids. In fact, for two of the parent compounds of the isolable sulfuranes, reports on the isolation of the corresponding diazo compounds appeared at about the same time. Both, dicyanodiazomethane (21) and bis(phenylsulfonyl)diazomethane (22), are stable and of interest as possible precursors to the corresponding carbenes. The correlation between diazo compounds and sulfur ylids is reflected in their structural features and their chemical behavior. Both classes of intermediates form epoxides from aldehydes and ketones (23, 24), and cyclopropanes from olefinic compounds (23, 25). In his book on ylid chemistry, Johnson (26), pointing out the similarity of ylids and diazo compounds, concludes that diazo compounds can be considered simply a special form of nitrogen ylid.

On the basis of the above relationship, a report on the preparation and isolation of p-nitrophenyldiazomethane was noted with special interest (27). The compound was prepared in aqueous solution, could be recrystallized from acetone, and melted at 80° with decomposition.

After these pertinent data on the correlation of sulfonium and phosphonium ylids on the one hand, and ylids and diazo compounds on the other hand, had been reviewed, closer examination of the original paper by Swain and Thornton (12) seemed to be in order. The authors had based their proposal of the mechanism of the reaction on kinetic studies. It became evident, however, that their kinetic measurements were far from exhaustive. Two kinetic runs were carried out, using two equivalents of sodium hydroxide and one equivalent of the sulfonium salt. Sodium perchlorate was added for constant ionic strength, and the reaction was followed by quenching 10 ml aliquots with hydrochloric acid and back-titrating with sodium hydroxide. No experimental data were given, and the second-order rate constant was simply reported as $2.52 \pm 0.11 \times 10^{-3}$ $l\ M^{-1}\ sec^{-1}$. No experiments were carried out in which the sulfonium salt concentration was either changed or large compared to the base concentration. The organic reactant was found to undergo base-catalyzed deuterium exchange much more rapidly than it formed p,p'-dinitrostilbene, showing that carbanion formation cannot be rate-controlling. The basic reaction solution was slightly orange, presumably due to the presence of the sulfonium ylid. When a pellet of potassium hydroxide was added to the solution, a deep crimson color surrounded it as it dissolved, showing that the red species was present in very low concentration in the orange solution. This observation was the basis for employing the steady state approximation in their treatment of the kinetics. The kinetic order excludes rate-determining reaction between the sulfonium ylid and the sulfonium salt, but is consistent with rate-determining decomposition of the ylid.

In the light of the previous comparison of the stability of sulfonium ylids, phosphonium ylids, and diazo compounds it seems surprising that p-nitrobenzylidenedimethylsulfurane would decompose spontaneously. Furthermore, it seems rather daring to claim the intermediacy of a carbene on account of the amount of rate studies undertaken. Firstly, the carbene proposed, instead of explaining the observed facts in a plausible manner, gives rise to questions regarding its peculiar chemical behavior. Thus, the hydrolysis of chloroform in aqueous sodium hydroxide had been shown to give carbon monoxide and formate ions, formed by nucleophilic attack on dichlorocarbene (28). Since the proposed p-nitrophenylcarbene would be highly electrophilic, mention should also be made of the photolysis of bis(phenylsulfonyl)diazomethane in hydroxylic solvents which in methanol gave rise to the formation of the methyl ether presumably via the highly electrophilic carbene (29). Secondly, the kinetics of the reaction studied by Swain and Thornton (12) might be rather complex and the observed data are only a rough approximation of the actual processes taking place.

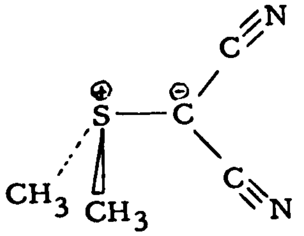
The authors attempted to decide about the fate of the carbene intermediate on the basis of the sulfur isotope effect. The carbene may either dimerize, leading directly to the product, or add to a carbanion, followed by elimination reaction. The measured isotope effect ($k_{32}/k_{34} \doteq 1.0066$) is less than half as large as that observed in the solvolysis of t-butyldimethylsulfonium ions (1.0177). The authors therefore exclude the possibility of rapid dimerization and argue in favor of a rapid attack of a carbene on a carbanion. The arguments used in this connection, however, are objectionable, since they are not in line with the proper treatment of kinetic isotope data. An isotope effect is a useful tool if observed in rate-determining steps and is found to be primary or secondary in nature. A combination of isotope effects of the slow and subsequent fast steps, resulting in a mean isotope effect, is not justified and is not correct. In the reaction under discussion, two molecules of dimethyl sulfide are lost before stilbene is formed. If one molecule of dimethyl sulfide is lost in the rate-controlling step and the other one in a subsequent fast step, the resulting isotope effect would be half the one expected from the slow step, due to the fact that only half the number of molecules of dimethyl sulfide formed make a contribution to the isotope effect. Swain and Thornton, however, average the isotope effects of the slow step (1.0177) and the subsequent fast elimination reaction for which they use the isotope effect 1.0015 found in the reaction of sodium hydroxide with β-phenylethyldimethylsulfonium bromide as a model. The observed value of 1.0066 was considered close enough to the obtained average of 1.0081 to be consistent with the addition of the carbene to the carbanion followed by elimination. After the publication of the paper under discussion, a note of correction appeared in the literature (30) reporting the isotope effect of 1.0015 in the elimination reaction of β-phenylethyldimethylsulfonium bromide with hydroxide ions to be wrong. The correct value was given as 1.0064. In summary, it can be said that it is extremely difficult to base any conclusions as to the reaction mechanism on the observed isotope effect. The only information provided is that a rate-controlling formation of carbene followed by rapid dimerization can be excluded.

Continuing the work on the reaction of p-nitrobenzyldimethylsulfonium tosylate with sodium hydroxide, Thornton and Rothberg (31) studied the reactions of the m-nitrobenzyldimethylsulfonium ion, p-nitrobenzyltrimethylammonium ion, and p-nitrobenzyltriphenylphosphonium ion in aqueous sodium hydroxide solution. The purpose of their study was to determine the factors affecting the p,p'-dinitrostilbene-forming reaction. It was known that unsubstituted, m-chloro-, and p-methylbenzyldimethylsulfonium ions react in aqueous sodium hydroxide solution to give high yields of the corresponding benzyl alcohols (32). The nitro group appeared, then, to be important for carbene formation, so it was of considerable interest to see whether a resonance or an inductive effect dominates. The reaction of m-nitrobenzyldimethylsulfonium bromide with aqueous hydroxide at 100° for 20 hr. yields 5% of m-nitrobenzyl alcohol, 41% of m,m'-dinitrostilbene oxide and a brown tar. Since a m-nitro substituent exerts a stronger inductive effect and a much weaker resonance effect than a p-nitro substituent, it was concluded that a resonance stabilization of the transition state and/or the carbene intermediate is an important factor in determining the nature of the product-forming reaction. A protective cover of nitrogen did not affect the reaction. It was stated that "the mechanism of the reaction is completely unclear, but presumably involves an intermolecular oxidation-reduction reaction. Possibly, carbene reacts with a nitro group of a substrate molecule to form m-nitrobenzaldehyde" which reacts easily with ylid to give stilbene oxide. This is a somewhat peculiar explanation in view of the above mentioned difference in the effect of a p- and m- nitro substituent with regard to carbene formation.

p-Nitrobenzyltrimethylammonium bromide was shown to be inert under identical conditions for 72 hr; p-nitrobenzyltriphenylphosphonium bromide yielded 97% of triphenylphosphine oxide and 56% of p-nitrotoluene. The formation of 0.5% of p,p'-dinitrostilbene was attributed to subsequent reactions of p-nitrotoluene. Thus, it was concluded from these experiments that the combination of the resonance effect of the p-nitro group and d-orbital stabilization of the transition state for proton removal is necessary, but not sufficient, for α-elimination. The combined effect of relatively facile phosphine oxide formation and poor leaving group ability of triphenylphosphine appear to prevent carbene formation.

After the effect of the leaving group had become apparent, the same authors undertook a study of the reactions of some other p-nitrobenzylsulfonium ions with aqueous sodium hydroxide (33). The leaving groups under investigation were phenyl methyl sulfide, p-chlorophenyl methyl sulfide, p-tolyl methyl sulfide, and methyl isopropyl sulfide. The products of reaction of each of the four sulfonium salts with aqueous sodium hydroxide at 60° were examined by chromatographic separation. In each case, a number of products were formed, only some of which could be identified. The yield of the three products which could be identified, *p*-nitrobenzyl alcohol, *p*,*p*'-dinitrostilbene, and *p*,*p*'-dinitrostilbene oxide totalled approximately 35% in roughly equal distribution, with the exception of the methylisopropylsulfonium salt which afforded 48% *p*,*p*'-dinitrostilbene as the only identifiable product. A nitrogen cover did not have a drastic effect in these reactions, but limited the yield of epoxide to a trace. Variation in the yield of *p*,*p*'-dinitrostilbene was relatively small when the substituents in the phenyl ring of the leaving group are varied, indicating that the electrical effect of the substituents is quite small. It was therefore concluded that a steric factor is responsible for the differences between R = C_6H_5, $(CH_3)_2CH$, and CH_3, and the following "attractive hypothesis" was put forward. "The carbene formed will attack the species present in solution by the pathway which requires the least energy. When R = CH_3 the attack on the reversibly-formed ylid requires the least energy and is the predominant reaction or alternatively carbene insertion in a CH bond of the sulfonium ion occurs. However, when the ylid or the sulfonium ion is sufficiently sterically hindered, the carbene could attack other species present (*e*.*g*., insertion reactions or attacks on the double bonds of the leaving group, reaction with oxygen to form *p*-nitrobenzaldehyde and reaction with hydroxide ion and water to form *p*-nitrobenzyl alcohol)".

These explanations are not sound and deserve critical comment. Again they pose more questions than they answer with respect to the facts observed. Firstly, p-nitrophenylcarbene would be highly electrophilic, i.e. the ylid would attack the carbene and this reaction would hardly be subject to a steric effect from the sulfur substituents, at least not as long as one substituent is a methyl group. In this connection mention should be made of a very recent report on the X-ray crystallographic structure of a crystalline sulfonium ylid (34). It was demonstrated that dicyanomethylenedimethylsulfurane has a pyramidal geometry around the sulfur atom. The substituents on the carbon atom are arranged in a plane, and the carbon-sulfur bond and the carbon-carbon bonds are shorter than would be expected for single bonds.



Moreover, if the formation of p-nitrobenzyl alcohol in the study by Rothberg and Thornton is attributed to a reaction of water and hydroxide ions with the carbene, why should such a competing reaction with ylid not take place in the dimethyl system, especially since the ylid concentration is assumed to be small? The authors offer no explanation as to why such a significant amount of unidentified material is formed compared to the quantitative yield of stilbene from the dimethyl sulfonium salt. They mention that no experimental evidence of carbene insertion reactions could be found and that preliminary attempts to trap the hypothetical carbene intermediate had not been successful.

In combination with the preceding critical comments on the studies by Swain and Thornton, it becomes apparent that the carbene intermediacy is at best speculation and that little evidence in its support is presented. Their proposal of a carbene, based on rate studies, could not gain further support from subsequent studies, and indeed became less convincing. The authors themselves seem to admit to this by replacing the term "carbene intermediate" by "proposed" and finally "hypothetical carbene intermediate". However, these studies have shown that the p-nitrobenzyl system exhibits peculiar features which are influenced by the nature of the leaving group.

In this connection, it should be mentioned that the reactions of p-nitrobenzyl chloride with hydroxide ion in aqueous ethanol (35), dioxane or acetone (36) are reported to give p,p'-dinitrostilbene in almost quantitative yield. This behavior is reminiscent of the results obtained from the reaction of p-nitrobenzyldimethylsulfonium tosylate in aqueous base. The reactions of p-nitrobenzyl chloride and related nitrobenzyl halides have been the subject of several reports, and will be referred to briefly in this section.

Comparative rate studies on the reaction of benzyl chloride and various nitro-substituted benzyl chlorides with sodium hydroxide in 50% aqueous dioxane at 30° showed that second-order kinetics were, at least approximately, obeyed in these cases (36). The relative rates, based on the rate of benzyl chloride, were found to be 35 for *p*-nitrobenzyl chloride and 5 for *o*-nitrobenzyl chloride. 2,4-Dinitrobenzyl chloride reacted immeasureably fast. The products in the reactions of nitro-substituted materials were the corresponding stilbenes, whereas benzyl alcohol was obtained from the unsubstituted chloride. The formation of benzyl alcohol is the result of S_N2 displacement of chloride by hydroxide ion; the analogous reaction is also observed for unsubstituted sulfonium salts (32). To elucidate the nature of the first step in the reaction leading to stilbene, *p*-nitrobenzyl chloride and sodium hydroxide in dioxane-deuterium oxide were allowed to react for 100 min. at 30°, so that about 38% of the chloride should have reacted. Recovered *p*-nitrobenzyl chloride was shown to be 42% deuterated in the benzylic position, indicating the following equilibrium.

$$ArCH_2Cl + OH^{\ominus} \rightleftharpoons Ar\overset{\ominus}{C}HCl + H_2O$$

Formation of *p*-nitrophenyl carbene was suggested to be the rate-determining step.

$$Ar\overset{\ominus}{C}HCl \xrightarrow{\text{slow}} ArCH: + Cl^{\ominus}$$

$$2\ ArCH: \longrightarrow ArCH{=}CHAr$$

Rates were also measured using α-deuterio-*p*-nitrobenzyl chloride as starting material. It was suggested that if the rates of the forward and backward reaction in the above equilibrium are about the same and much greater than the rate of the slow step, α-deuterio-*p*-nitrobenzyl chloride should be substantially converted into p-nitrobenzyl chloride before the reaction proceeds to give stilbene. As a result, no deuterium isotope effect should be observed. The observation of a small effect ($k_H/k_D = 1.28$) was interpreted as an indication that the back-reaction in the equilibrium is of a rate similar to that of the rate-determining step.

Earlier reports in the literature (37, 38) had shown that o-nitrobenzyl chloride in its reaction with aqueous base can give rise to either o-nitrobenzyl alcohol or o,o'-dinitrostilbene, depending on the specific reaction conditions. The reaction of o-nitrobenzyl chloride with potassium carbonate in dilute aqueous solution at reflux affords a 50% yield of the corresponding alcohol (37). If the volume of the solution was decreased, a brown insoluble precipitate was obtained. Lately, this procedure has also been used for the preparation of p-nitrobenzyl alcohol (39). Using potassium hydroxide as base and 98% ethanol as solvent in a concentrated solution, a 50% yield of trans-o,o'-dinitrostilbene was obtained (38) from o-nitrobenzyl chloride.

In a more recent study, Tommila and Savolainen (40) have made similar observations as to the effect of concentration in their study of the reaction of p-nitrobenzyl chloride with methoxide ion in methanol and methanol-dimethylsulfoxide mixtures. When the concentration of reactants is small, the main product in 100% methanol at temperatures ranging from 20° to 60° is p-nitrobenzyl methyl ether. However, when higher concentrations are used, p,p'-dinitrostilbene proves to be the main product. Furthermore, addition of dimethylsulfoxide to the solvent favors stilbene formation. In dilute solution the reaction is first order in p-nitrobenzyl chloride and first order in methoxide ion. It is noticed that the rate of reaction increases substantially when stilbene is the reaction product. The activation entropy for the reaction of p-nitrobenzyl chloride remains nearly constant, and is only very slightly negative, when the dimethylsulfoxide concentration is increased, whereas that for the reaction of benzyl chloride decreases. As the activation energy for the reaction of p-nitrobenzyl chloride is greater than or equal to that of the unsubstituted compound, the high velocity of p,p'-dinitrostilbene formation is due to the only slightly negative activation entropy. These data suggested a loose structure for the transition state of the slow stage of the reaction.

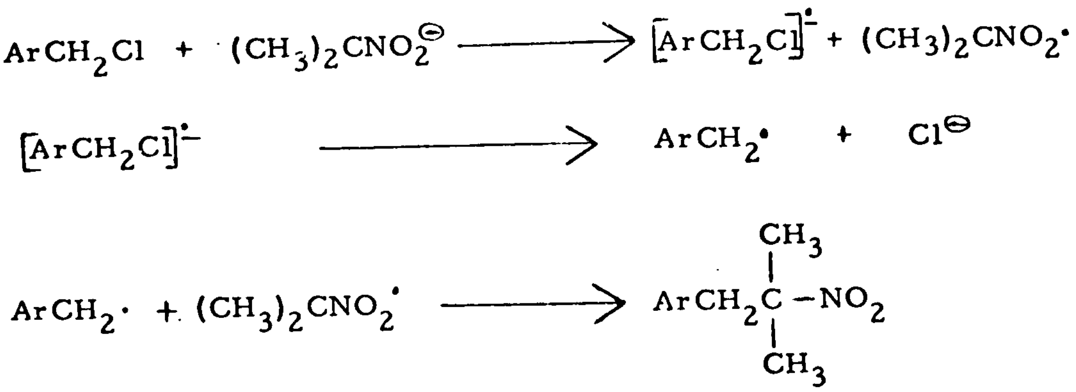
The influence of the concentration on the course of these reactions cannot be fully assessed without further information. However, a mechanism involving the rate-determining decomposition of an anionic intermediate to give carbene is unlikely, as both the formation of an anionic intermediate and the nucleophilic displacement reactions leading to p-nitrobenzyl alcohol and p-nitrobenzyl methyl ether are first order in substrate and first order in base and therefore should not be affected by variations in concentrations. Thus, the observations regarding the effect of changes in the concentration of the solutions point to a higher order in one or two of the two reactants.

Attention is also called to a report (41) of the reaction of p-nitrobenzyl chloride with cyanide ion in dimethylsulfoxide, resulting in the formation of p,p'-dinitrostilbene in high yield. This is contrasted by the course of the corresponding reaction of benzyl chloride which affords phenylacetonitrile almost quantitatively. The latter compound is formed by nucleophilic displacement of chloride ion by the cyanide ion, a process which apparently cannot compete in the case of the p-nitrobenzyl system.

In summary, it can be noted that the mechanism of the various reactions of p-nitrobenzyl chloride leading to p,p'-dinitrostilbene is not very well understood and requires further detailed studies. A similarity to the reactions of p-nitrobenzylsulfonium salts with base, however, seems to emerge.

From the reported studies on the reaction of benzylsulfonium salts and benzyl chlorides in aqueous hydroxide solution it had become evident that the p-nitrobenzyl and, to a lesser degree, the o-nitrobenzyl groups distinguish themselves from other benzylic systems. It was therefore of special interest to see whether such a uniqueness of the o- and p-nitrobenzyl systems had any precedent or analogy in the literature. Indeed, in 1949 (42) a study of the reaction of a series of para-substituted benzyl halides with the sodium salt of 2-nitropropane revealed that only p-nitrobenzyl chloride gives carbon alkylation; benzyl halides substituted in the para position by CN, CF_3, $^{\oplus}N(CH_3)_3$, $CH_3C{=}O$, $CH_3OC{=}O$, Br, and CH_3 give only oxygen alkylation. More recently, it has been found that the uniqueness of the p-nitrobenzyl system depends not only on the p-nitro group but also on the leaving group (43). Thus, whereas p-nitrobenzyl chloride gives 95% carbon alkylation, p-nitrobenzyl iodide gives 81% oxygen alkylation. A comparison of the effect of different leaving groups makes it apparent that carbon alkylation predominates in the p-nitrobenzyl system only when the leaving group is one which is difficultly displaced. This behavior is exemplified by the following leaving groups: trimethylamine, pentachlorobenzoate and chloride ions. Comparative rate studies on the carbon and oxygen alkylation, using various para-substituted benzyl systems, demonstrate that the rate of oxygen alkylation is strongly dependent on the leaving group, whereas the rate of carbon alkylation is relatively insensitive to the leaving group. On the basis of these findings it was proposed that oxygen alkylation, the usual mode of reaction of a nitroparaffin anion with alkyl halide, derives simply from nucleophilic displacement by the oxygen of the anion on the benzylic carbon. In the p-nitrobenzyl series, when the leaving group is one which is difficultly displaced, a second mode of attack by the nitroparaffin anion has a chance to compete and it is this second process which is productive of carbon alkylation. On the basis of their studies of rates and inhibition of carbon alkylation by nitroaromatics in conjuction with electron paramagnetic resonance (e.p.r.) studies, Kornblum and co-workers proposed that carbon alkylation is a radical-anion process involving electron transfer, as shown in Scheme II.

SCHEME II



$$ArCH_2Cl + (CH_3)_2CNO_2^{\ominus} \longrightarrow [ArCH_2Cl]^{\dot{-}} + (CH_3)_2CNO_2^{\bullet}$$

$$[ArCH_2Cl]^{\dot{-}} \longrightarrow ArCH_2^{\bullet} + Cl^{\ominus}$$

$$ArCH_2\cdot + (CH_3)_2CNO_2^{\bullet} \longrightarrow ArCH_2\underset{CH_3}{\overset{CH_3}{C}}-NO_2$$

It should be noted that o-nitrobenzyl chloride and 2,4-dinitrobenzyl chloride also give rise to carbon alkylation, whereas m-nitrobenzyl chloride fails to produce carbon alkylation. Furthermore, the o-nitro group is considerably less effective at fostering carbon alkylation than the p-nitro group.

This proposal of a radical-anion process involving electron transfer for the reactions of nitrobenzylic systems, was made at a time when the chemistry of nitroaromatic compounds in basic solution became subject to a general reappraisal. The groups most active in the field of electron-transfer reactions involving nitro compounds were those of Kornblum (44, 45, 46) and of Russell (47, 48). The ability of nitroaromatics to enter into electron-transfer reactions has been invoked to explain the dimerization of p-nitrotoluene in basic solution, resulting in the formation of p,p'-dinitrobibenzyl and p,p'-dinitrostilbene (48, 49).

Most recently, a paper published by Russell (50) in the series of electron-transfer processes included some studies on the p-nitrobenzyldimethylsulfonium ion. The results of these studies will be discussed in connection with the presentation of the findings obtained in this laboratory in the latter part of the thesis.

Electron-transfer processes, involving oxidation-reduction reactions of the nitro group itself, could give rise to the formation of various functional groups such as nitroso, or azo and azoxy linkages. In this connection, the following note in the literature is of particular interest (51). In the reaction of p-nitrobenzylpyridinium bromide and equimolar amounts of sodium hydroxide in aqueous solution at 25°, p-azoxybenzaldehyde was obtained as the only product.

During review of pertinent literature regarding the characteristics of nitroaromatic systems, a mistake of widely spread reoccurence in various publications was discovered (52). In a review article on the benzoin condensation, o-nitrobenzaldehyde is reported to undergo the normal benzoin condensation, whereas p-nitrobenzaldehyde is reported not to undergo this reaction. The report, therefore, is of interest in connection with the mentioned similarity of ortho- and para-nitrobenzylic systems and their distinctly different behavior from other benzylic systems. It is generally recognized that the ortho-nitro group exerts a much smaller resonance effect compared to the para-nitro group, and this is explained in terms of steric hindrance. This difference in resonance effect is put forward in an interpretation of the reported results of the two nitro-substituted benzaldehydes (53). On closer inspection, however, it becomes evident that the original references cited in the review article either do not even refer to the compounds mentioned, or relate the original findings incorrectly. The plausible manner in which the foregoing erroneous reports are interpreted, probably accounts for their persistence in the literature. Scrutiny of the original literature reveals the following observations. Neither ortho- (54, 55, 56, 57) nor para- (54, 57) nitrobenzaldehydes undergo the benzoin condensation. A claim to the formation of o,o'-dinitrobenzoin (58, 59) was shown to be erroneous (56). The reaction of o-nitrobenzaldehyde with cyanide ions was shown to give rise to formation of o-nitrosobenzoic acid and o-azoxybenzoic acid (54, 55, 56, 57). Only scanty reports on the corresponding reaction of p-nitrobenzaldehyde are available; the products reported are p-nitrobenzoic acid (54, 57), and when ethanol is used as solvent, ethyl p-nitrobenzoate (54). Nitrophenylacetic acid and azobenzoic acid, claimed in the review article to be the products from m- and p-nitrobenzaldehyde, are not mentioned in the references cited.

Against the background of developments outlined in this introduction, a reinvestigation of the reaction of p-nitrobenzyldimethylsulfonium tosylate with sodium hydroxide was undertaken using various approaches. These different approaches, their results and interpretations, and some studies on related p-nitrobenzyl 'onium salts will be the topic of the next chapters of this thesis.

CHAPTER I

MECHANISTIC STUDIES ON THE REACTION OF p-NITROBENZYLDIMETHYLSULFONIUM TOSYLATE WITH HYDROXIDE ION.

The previous investigations on the reaction of p-nitrobenzyldimethylsulfonium tosylate with sodium hydroxide were based on kinetic data (12, 31). However, these studies had failed to provide convincing evidence for a carbene mechanism. A survey of the literature indicated that various examples are known where sulfonium salts and the corresponding halides in their respective reactions with base give rise to formation of dimeric olefinic materials. In these reactions, nucleophilic displacement pathways and carbene intermediates have been suggested. For instance, studies by Hauser and co-workers (60) showed that benzyl chloride and 9-chlorofluorene are converted to dimeric olefins by alkali amides in liquid ammonia. The formation of dimeric olefins was resolved into two consecutive reactions. The first reaction involves the self-alkylation of the halide to form the corresponding dimeric halide, as evidenced by isolation of the latter material, and was followed by dehydrohalogenation to give the dimeric olefin. It had also been reported that cis- and trans-stilbene were obtained from reaction of benzyldiphenylsulfonium fluoroborate with n-butyllithium in tetrahydrofuran at -50° (25). In this case, it was suggested that a carbene mechanism was probably operative; however, a pathway involving nucleophilic displacement could not be excluded.

In another series, a solution of 2-nitrofluorenylidenedimethylsulfurane in nitromethane upon heating afforded 2,2'-dinitrodifluorenylidene (14); the same product was obtained from treatment of 2-nitro-9-bromofluorene with base in t-butyl alcohol solution (61). When benzyltrimethylammonium hydroxide was used as base, kinetics of second order in the substituted 9-bromofluorene were observed, whereas kinetics of first order in the organic halide were obtained, when potassium t-butoxide was employed. Second-order rates suggested nucleophilic attack by the anion on the substrate in the rate-determining step, subsequent β-elimination of hydrogen bromide from the intermediate dimeric halide being very fast. The first-order kinetic behavior was regarded as rate-determining formation of carbene by loss of bromide ion from the 9-bromofluorenyl carbanion. Furthermore, it was observed for other substituted 9-bromofluorenes that rate constants of second order with regard to the organic halide on addition of dimethyl sulfoxide increased at first and that the kinetic form became complex at higher concentrations of additive. Further addition of dimethyl sulfoxide led to kinetics of first order in the substitued 9-bromofluorene.

This last example clearly illustrates that the information based on kinetic studies could not be considered conclusive and it was therefore decided to employ an alternative method of testing for a nucleophilic displacement reaction in the present investigation. It should be mentioned here that more recently a detailed examination of the kinetics in the reaction of 2-substituted 9-bromofluroenes has shown that, for systems obeying the first-order kinetic law, the rate-limiting process is the dissociation of a rapidly-formed ion pair consisting of the carbanion and an alkali-metal cation followed by displacement of the halide ion on the starting material by a carbanion (62).

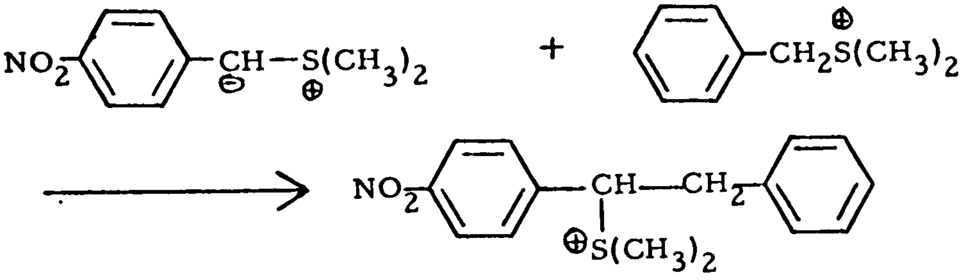
The initial approach in the reexamination of the reaction of p-nitrobenzyldimethylsulfonium tosylate with hydroxide ion was directed at different mechanistic possibilities along the following three lines. Firstly, the reaction of p-nitrobenzyldimethylsulfonium ion with base in the presence of a benzylsulfonium ion would allow formation of an unsymmetrical stilbene, if a nucleophilic displacement reaction is operative. Secondly, the isolation of the p-nitrobenzylidenedimethylsulfurane would provide information regarding the stability of the ylid and its tendency to decompose into a carbene or alternatively to display other modes of reactivity. Thirdly, a p-nitrobenzylsulfonium salt in which one benzylic hydrogen is replaced by a methyl group could provide means of distinguishing between a nucleophilic displacement and a carbene pathway by formation of isomeric olefinic materials which differ in the position of the double bond.

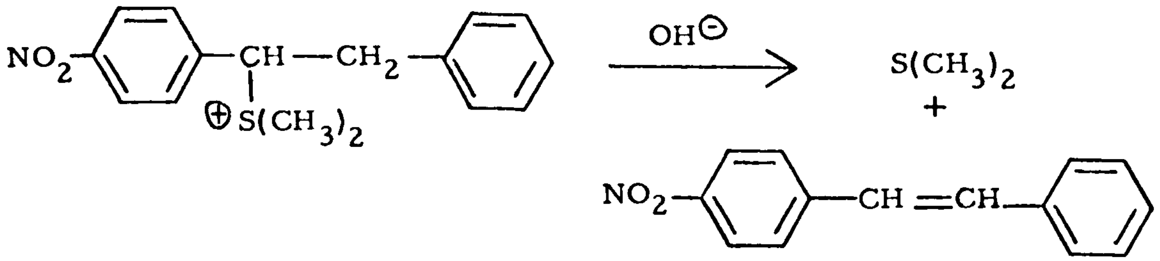
RESULTS

Mixed Product Experiments

A mechanistic pathway involving rate-determing nucleophilic attack of sulfonium ylid on starting material had been discarded by Swain and Thornton (12), since it would require kinetics of second order in p-nitrobenzyldimethylsulfonium ion. In the presence of another benzylsulfonium salt a nucleophilic displacement could lead to formation of an unsymmetrical olefinic material, and this alternative method of testing for such a reaction pathway was employed in this work.

Benzyldimethylsulfonium tosylate was chosen as reaction partner for the following reasons. Its reaction with sodium hydroxide was known to give exclusively benzyl alcohol. The rate of this reaction had been shown to be slower than those for other substituted benzylic systems giving rise to alcohol formation (32). By contrast, in the case of the p-nitrobenzyldimethylsulfonium salt, dimerization at some stage is indicated by the formation of p,p'-dinitrostilbene. These considerations then would suggest the following sequence in the mixed product experiments, if any nucleophilic displacement is operative in the formation of p,p'-dinitrostilbene.



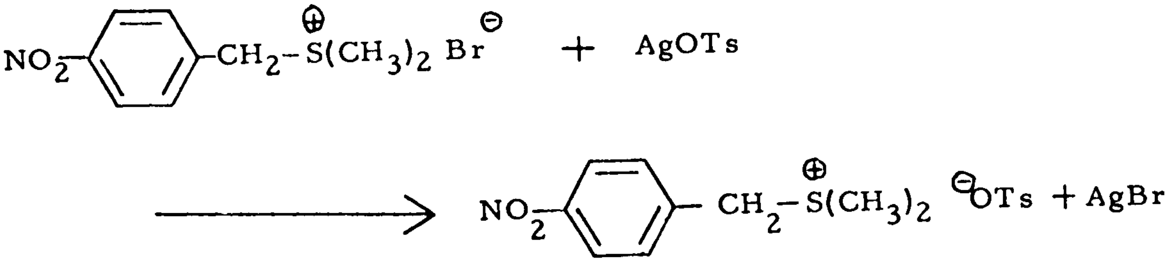


The formation of p-nitrostilbene would point to such a course of the reaction.

The materials needed for such a series of experiments were prepared according to standard procedures in the literature. Benzyldimethylsulfonium tosylate (32) was obtained from reaction of benzyl tosylate (39) and dimethyl sulfide. p-Nitrostilbene (63) was prepared from p-nitrophenylacetic acid and benzaldehyde in the presence of piperidine. p-Nitrobenzyldimethylsulfonium tosylate (12) resulted from reaction of p-nitrobenzyl tosylate (39) with dimethyl sulfide. However, yields in the preparation of the p-nitrobenzyl tosylate from the corresponding alcohol and tosyl chloride were moderate (50%). p,p'-Dinitrostilbene (12) was prepared by reaction of p-nitrobenzyldimethylsulfonium tosylate and sodium hydroxide in aqueous solution at 100°.

Search for a more convenient route to p-nitrobenzyldimethylsulfonium salts brought to mind the bromide. This material is easily obtained in almost quantitative yield from the reaction of p-nitrobenzyl bromide and dimethyl sulfide. However, attempts to recrystallize this salt from hot acetonitrile resulted in the formation of starting material. Apparently the bromide ion is powerful enough a nucleophile to bring about this reversal of reactions. Since the reactions of p-nitrobenzyldimethylsulfonium ions with sodium hydroxide are carried out at 100°, the bromide was not considered a good choice.

It appeared, however, that the bromide could be a convenient precursor to the tosylate according to the following metathesis.



Silver tosylate is prepared simply by stirring equivalent amounts of p-toluenesulfonic acid and silver oxide in acetonitrile (64). A reaction between the two salts in aqueous solution should result in the precipitation of silver bromide, leaving p-nitrobenzyldimethylsulfonium tosylate in solution. Indeed, an 88% yield of pure p-nitrobenzyldimethylsulfonium tosylate was obtained from this reaction, when light was excluded.

Data regarding the rates of S_N2 displacement reactions on p-nitro-substituted and unsubstituted benzylic systems are available in the literature. The rate of the reaction of p-nitrobenzyl chloride with potassium iodide has been reported to be faster by a factor of 6.5 than that of the reaction of benzyl chloride with potassium iodide (65). The reactions of the anion of 2-nitropropane with benzyl iodide and p-nitrobenzyl iodide resulting in oxygen alkylation are found to derive from nucleophilic displacement by the oxygen of the anion on the benzylic carbon and their rates show a ratio of 1 : 3 (43). In view of this difference in rates a six-fold excess of benzylsulfonium salt was employed in all mixed product experiments.

All reactions were carried out at 100° on a steam bath, in analogy to the conditions employed for the formation of p,p'-dinitrostilbene. In the first experiment, one equivalent of an 0.2 N sodium hydroxide solution, based on the amount of p-nitrobenzyldimethylsulfonium salt, was added to a heated aqueous solution which was 0.1 molar with respect to the p-nitrobenzylsulfonium salt and 0.6 molar with respect to the benzylsulfonium salt. The reaction mixture was kept at 100° for one hr and after being cooled was worked up by acidification and filtration. The weight of dried precipitate corresponded to a quantitative yield based on p,p'-dinitrostilbene. A two-fold excess of base was used in a second experiment in view of the fact that the unsubstituted salt also reacts with hydroxide ion. This latter reaction, however, is 300 times slower than that leading to p,p'-dinitrostilbene (12, 32). The amount of precipitate obtained in the second experiment corresponded to a yield of 104% with regard to p,p'-dinitrostilbene. Analysis of the precipitate from the two experiments by infrared and nuclear magnetic resonance (n.m.r.) spectroscopy and thin layer and gas-liquid chromatography (g.l.c.) did not show the presence of p-nitrostilbene as indicated by comparison with an authentic sample of p-nitrostilbene.

In a variation of experimental conditions, the base was added dropwise over a period of 2 hr to the heated salt solution, while the concentrations were unchanged from the second experiment. In a fourth experiment, using identical concentrations, conditions more conducive to mixed product formation were employed. An 0.1 molar solution of p-nitrobenzyldimethylsulfonium salt was added dropwise over a period of 3 hr to the heated solution containing benzyldimethylsulfonium salt and sodium hydroxide. In this last experiment, the p-nitrobenzyldimethylsulfonium ylid, formed instantaneously and present in small quantities, is placed in an environment of high concentration of benzylsulfonium ion and extremely low concentration of p-nitrobenzylsulfonium salt, a situation considered favorable for mixed product formation. However, no p-nitrostilbene could be detected in the precipitate by the mentioned analytical methods. In the last experiment, the aqueous solution was extracted with ether and a small amount of benzyl alcohol was obtained following the concentration of the dried ether layer. An n.m.r. spectrum of the residue which was obtained when the aqueous solution was concentrated to dryness, showed that benzyldimethylsulfonium salt was present.

During the analytical investigation a few observations were made which deserve mention at this point. The weight of the material obtained in the cases where excess base was used exceeded the amount expected for a quantitative yield of p,p'-dinitrostilbene by a few percent. The raw product showed a wide melting range and its infrared spectrum was poorly resolved, much in contrast to spectra of recrystallized trans-p,p'-dinitrostilbene. Furthermore, signals in addition to those assigned to p,p'-dinitrostilbene were observed in the aromatic region of the n.m.r. spectrum. Finally, thin layer chromatography revealed the presence of four impurities in the raw product.

In order to verify that no stilbene nor any other materials observed as impurities in the mixed product experiments are formed in the reaction between benzyldimethylsulfonium tosylate and sodium hydroxide, the two reactants were allowed to react for 1 hr at 100°, and it was shown that benzyl alcohol was the sole product. An exchange experiment using sodium deuteroxide in heavy water demonstrated that the benzylic hydrogens in benzyldimethylsulfonium tosylate were exchanged quantitatively at room temperature within 3 min. This indicates a rapid equilibrium between the benzylsulfonium salt and the ylid and has been confirmed in a very recent study (66).

In connection with the question whether the reaction under investigation could involve nucleophilic displacements and in view of the fact that Hauser (60) had isolated dimeric halides, it was of interest to see whether any intermediate dimeric sulfonium salt could be obtained from a reaction, in which deficient amounts of base were employed. An experiment using half an equivalent of base and one equivalent of p-nitrobenzyldimethylsulfonium salt was carried out for 1 hr at 100°. The precipitate, filtered from the cooled and acidified reaction mixture, corresponded to a 50% yield of p,p'-dinitrostilbene. The n.m.r. spectrum of the residue obtained from concentration of the aqueous phase showed that 50% starting material had been recovered and that no additional peaks could be detected. This result indicates that a possible dimeric intermediate is reacting faster with base than it is being formed.

Attempts to Isolate Ylid

Another objective in conjunction with the mechanistic studies on the reaction of p-nitrobenzyldimethylsulfonium tosylate with aqueous sodium hydroxide was the isolation of the sulfonium ylid. Interest in the isolation of this new compound was especially heightened by the proposal of a carbene intermediate which was thought to arise by spontaneous decomposition of the ylid (12). As mentioned earlier, various reports on the preparation and isolation of sulfonium ylids had appeared in the literature in recent years. Phenacylsulfonium ylids, for instance, had been isolated from the reactions of the corresponding sulfonium salts with triethylamine in aqueous medium at 0-5° (7) and with aqueous sodium hydroxide at 0-5° (7, 67). In the present work, a series of experiments was undertaken using various conditions and a variety of bases of different strength.

A system where the medium could function both as a base and as a nucleophile, was provided when p-nitrobenzyldimethylsulfonium tosylate was dissolved in pyridine. The pyridine solution stayed colorless at room temperature; on heating a red color developed. After 12 hr at reflux no starting material was left in the red solution, as indicated by the n.m.r. spectrum of the residue obtained on rotary evaporation of the mixture. The products obtained were p-nitrobenzylpyridinium tosylate, N-methyl pyridinium tosylate and p-nitrobenzyl methyl sulfide. The concentrated residue was treated with ether and a precipitate was filtered off. p-Nitrobenzylpyridinium tosylate, a new compound, was isolated from the precipitate by repeated recrystallization from methanol-ether and was identified by infrared and n.m.r. spectroscopy in comparison with an authentic sample which was prepared from reaction of p-nitrobenzylpyridinium bromide with silver tosylate. The presence of the N-methyl pyridinium salt was indicated by the signal at τ 5.4 observed in the n.m.r. spectrum of the residue in pyridine solution. Chemical shifts of τ 5.45 in pyridine have been reported for N-methyl pyridinium salts (68). Relative integration of the benzylic methylene and the N-methyl group in the n.m.r. spectrum of the product showed a 70% yield of p-nitrobenzylpyridinium tosylate and a 30% yield of the N-methyl pyridinium tosylate using the tosylate anion as internal standard. p-Nitrobenzyl methyl sulfide was obtained on concentration of the above ether filtrate and was identified by its n.m.r. spectrum, exhibiting an A_2B_2 pattern centered at τ 2.2 and singlets at τ 6.25 and τ 8.0 of required intensities. The results indicate that pyridine is too weak a base to affect proton abstraction. Nucleophilic attack on the benzylic position is favored over attack on the two methyl groups by a factor of 2.3.

When crystals of p-nitrobenzyldimethylsulfonium tosylate (1.1 g) were added to 30 ml of an aqueous solution containing 1.5 g of potassium carbonate at 0°, the surface of the crystals turned red, indicating formation of the ylid. When all the material had dissolved, only a very slight yellow tinge of the clear solution could be noticed. After stirring the solution for 12 hr at room temperature, a small amount of a grey solid was obtained. The infrared spectrum indicated the absence of p,p'-dinitrostilbene and p-nitrobenzyl alcohol. The mass spectrum showed a parent peak at m/e 286. This pointed to p,p'-dinitrostilbene oxide. An authentic sample of this material was prepared by the reaction of p-nitrobenzyl chloride with p-nitrobenzaldehyde in the presence of potassium carbonate in refluxing methanol, according to the procedure by Bergmann and Hervey (69). Infrared spectroscopy and thin layer chromatography established the identity of the unknown material as trans-p,p'-dinitrostilbene oxide.

This experiment shows that the sulfonium ylid is formed in aqueous carbonate solution as indicated by the fact that a red color is formed when the sulfonium salt is dissolved and by the fact that reaction took place, affording trans-p,p'-dinitrostilbene oxide.

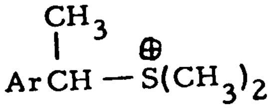
In analogy to the reported isolation of sulfonium ylids (6, 7, 67), attempts were made to isolate the ylid from reaction of the p-nitrobenzyldimethylsulfonium tosylate in aqueous solution containing a large excess of sodium hydroxide. At 0° a bright orange color developed and a yellowish precipitate formed slowly. Filtration after 10 hr at 0° yielded a mixture of p,p'-dinitrostilbene and p,p'-dinitrostilbene oxide. In a second experiment with identical quantities, the aqueous phase was extracted with ether and in a third experiment with methylene chloride. The organic phases, though slightly red, did not produce any material on concentration by rotary evaporation. Evidently, the concentration of the ylid under these conditions is very small. In contrast to the reports on exclusive formation of p,p'-dinitrostilbene at 60° (12) and on the isolation of phenacylsulfonium ylids at 0-5° (7, 67) the p-nitrobenzyldimethylsulfonium ylid afforded in addition to p,p'-dinitrostilbene a product, p,p'-dinitrostilbene oxide, that is believed to result from participation of molecular oxygen at some stage of the reaction.

In a further change of experimental conditions, lower temperature and exclusion of oxygen, a reaction of the p-nitrobenzyldimethylsulfonium tosylate with n-butyllithium was carried out in tetrahydrofuran at -50°. The base was added dropwise, causing instantaneous appearance of a deep red color, presumably due to formation of the ylid. This color, however, disappeared very rapidly indicating the instability of the ylid under these reaction conditions. After 3 hr a high yield of material was obtained. The infrared spectrum showed the presence of trans-p,p'-dinitrostilbene.

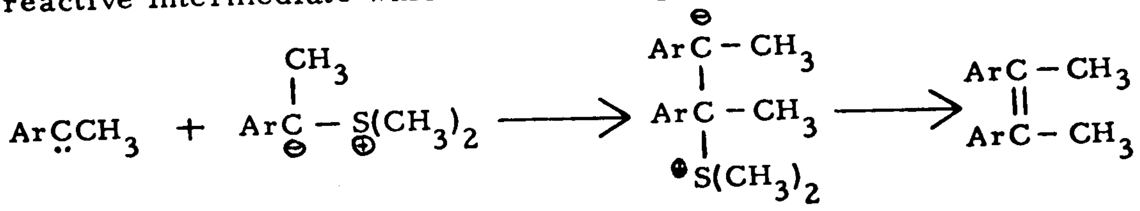
Various other attempts to isolate the ylid, using sodium hydride in pyridine and in tetrahydrofuran under nitrogen at low temperatures met with failure and are not reported. No p,p'-dinitrostilbene was obtained in these systems.

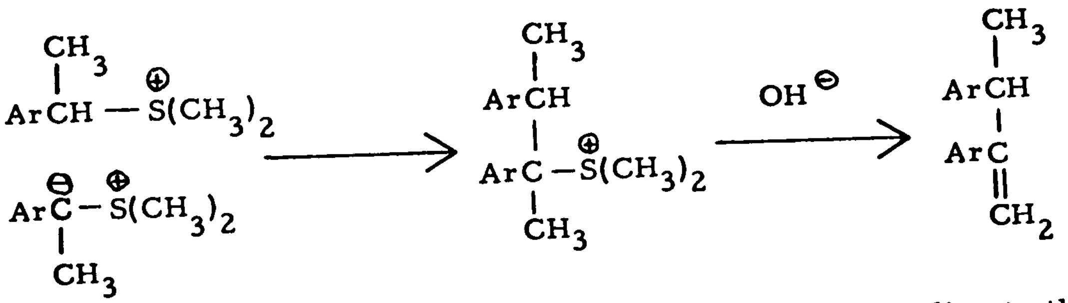
Reaction of 1-p-Nitrophenylethyldimethylsulfonium Ion with Hydroxide Ion

In further studies on the question as to whether the reaction of p-nitrobenzyldimethylsulfonium tosylate with sodium hydroxide proceeds via a pathway involving a carbene intermediate or proceeds via a pathway involving nucleophilic displacement, an investigation on a different, yet closely related system was undertaken. Replacement of one benzylic hydrogen in the p-nitrobenzyl system by a methyl group afforded a system of desired qualities, provided that the reaction of this sulfonium ion with base does not exclusively lead to p-nitrostyrene by attack of hydroxide ion on the β-hydrogens and elimination of dimethyl sulfide. In case of formation of a dimeric olefinic product, the following alternatives are considered. A pathway involving a carbene would give rise to a reactive intermediate which would be expected to give p,p'-dinitro-α,α'-dimethylstilbene in a fast reaction, before protonation would occur. Alternatively, if the reaction would involve a nucleophilic displacement, a dimeric salt would be formed.



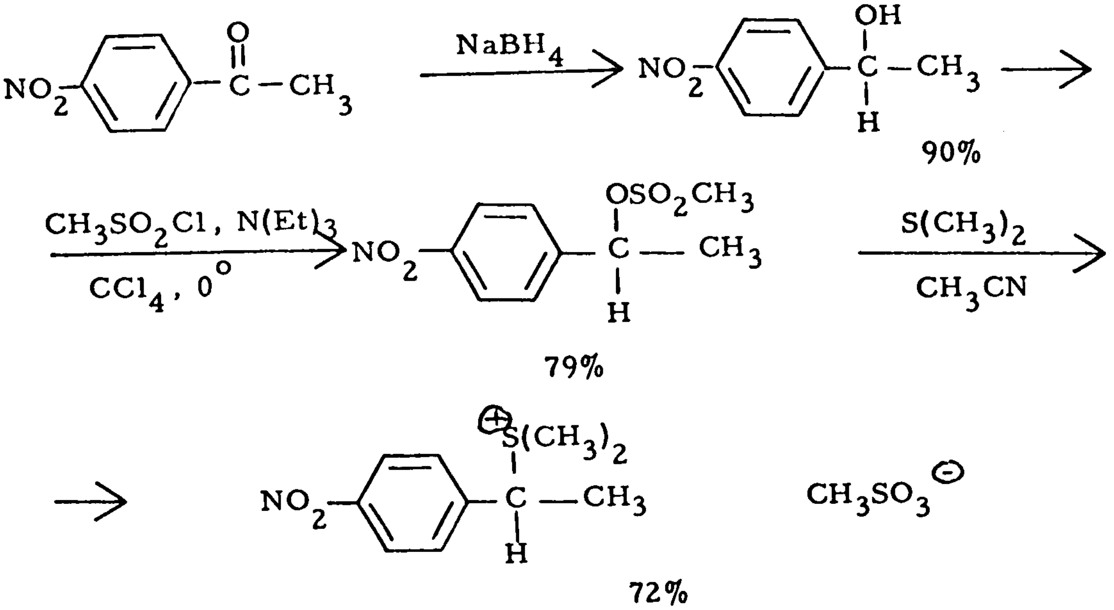
$$\mathrm{Ar}\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}\mathrm{H} - \overset{\oplus}{\mathrm{S}}(\mathrm{CH_3})_2$$





Further action of hydroxide ion on the salt would according to the Hofmann rule be expected to produce predominantly the olefin containing a terminal double bond.

The starting material for this investigation was prepared as indicated in the following sequence.

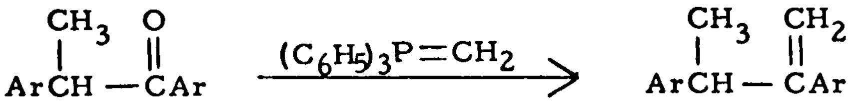


1-p-Nitrophenylethanol was produced in 90% yield by reduction of p-nitroacetophenone with sodium borohydride at room temperature in a solvent mixture of 95% ethanol and tetrahydrofuran. Reaction of this alcohol with methanesulfonyl chloride in dry carbon tetrachloride at 0° in the presence of a slight excess of triethylamine produced the methanesulfonate ester. This material was recrystallized from ethyl acetate-cyclohexane, m.p. 79-80°, and characterized by infrared and n.m.r. spectroscopy and elemental analysis. The corresponding dimethylsulfonium ion was obtained when the ester and a large excess of dimethyl sulfide were allowed to react in a solution of acetonitrile at room temperature for two weeks. Filtration afforded white crystals, m.p. 139-40°, after recrystallization from acetonitrile. The infrared spectrum of this material showed a broad band at 3400 cm^{-1}; a satisfactory analysis was obtained for a hydrated form of the salt with one molecule of water per two molecules of the salt. The n.m.r. spectrum showed the two methyl groups on the sulfur atom to be non-equivalent, due to the neighboring asymmetric carbon.

Preparation of Olefins

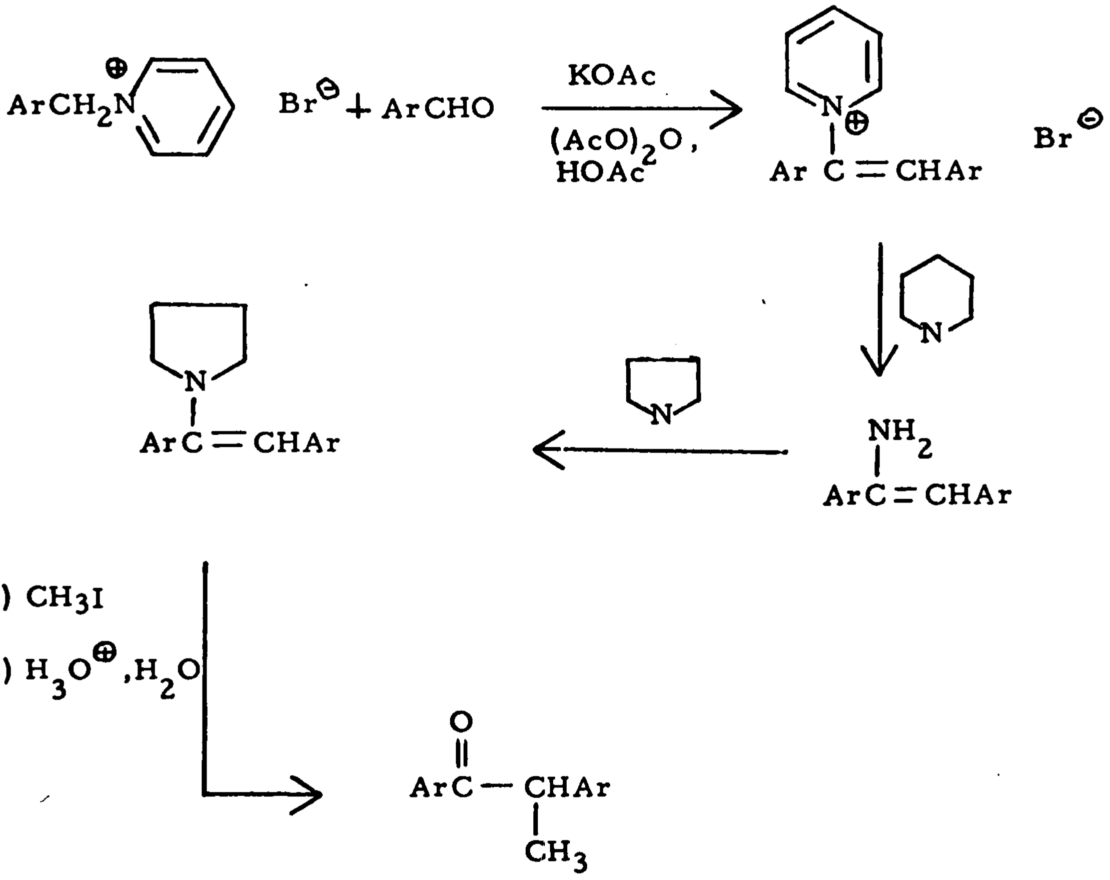
For identification of the considered dimeric olefinic products from the reaction of 1-p-nitrophenylethyldimethylsulfonium methanesulfonate with sodium hydroxide authentic samples of the olefins were needed. p,p'-Dinitro-α,α'-dimethylstilbene was prepared according to procedures in the literature (70). p-Nitroacetophenone was condensed with hydrazine hydrate in ethanol at reflux; a 92% yield of the hydrazone was realized (71). The hydrazone was oxidized by lead dioxide in benzene at room temperature and a stream of sulfur dioxide was passed through the resulting solution. Removal of solvent afforded cyrstalline material, 91% yield, which after recrystallization could be separated into cis- and trans-p,p'-dinitro-α,α'-dimethylstilbene (70).

The preparation of the previously unknown olefinic material which would arise from Hofmann elimination of the dimeric salt was attempted in the following way. For the last step, a Wittig reaction of methylenetriphenylphosphorane with a ketone of required structure was considered a suitable procedure in which the double bond would be introduced specifically in the terminal possition. For the



$$ArCH(CH_3)-C(=O)Ar \xrightarrow{(C_6H_5)_3P=CH_2} ArCH(CH_3)-C(=CH_2)Ar$$

preparation of the depicted ketone the following route was chosen. Benzylpyridinium salts are known to condense with aromatic aldehydes to give N-stilbyl pyridinium salts under conditions similar to those of the Perkin reaction (72). The N-stilbyl pyridinium salts are converted into stilbylamines by action of piperidine in high yield (73). Reaction of the primary amines with pyrrolidine affords pyrrolidine enamines (73). For the specific purposes of the above mentioned synthesis, the following Scheme emerges in which all compounds excluding the last one are known materials.



The pyrrolidine enamine, on methylation and subsequent hydrolysis, could render the desired ketone.

Condensation of p-nitrobenzaldehyde with p-nitrobenzylpyridinium bromide in acetic anhydride containing small amounts of glacial acetic acid at 100° in the presence of potassium acetate afforded the N-stilbyl pyridinium salt in 66.5% yield (72). Conversion of the salt into the primary amine was achieved in 94.5% yield by stirring the salt in piperidine for 1 hr at room temperature (73). Refluxing the amine in pyrrolidine for 12 hr in the presence of catalytic amounts of concentrated hydrochloric acid afforded the pyrrolidine enamine in 68% yield (73). Proper conditions for the last step in the above Scheme were found when N-(p,p'-dinitrostilbyl)pyrrolidine, excess methyl iodide and one equivalent of di-isopropyl ethyl amine were dissolved in acetonitrile and heated in a stainless steel bomb for 60 hr at 80°. The reaction mixture was hydrolyzed with concentrated hydrochloric acid and after purification by column chromatography afforded a 73% yield of product, m.p. 132-133.5°. The material was characterized by infrared and n.m.r. spectroscopy and elemental analysis.

For the preparation of p,p'-dinitro-2,3-diphenyl-1-butene a standard procedure in the literature (74) was employed using tetrahydrofuran as solvent and n-butyllithium as base. After a reaction period of 18 hr no starting material was left and olefin formation had taken place as indicated in the n.m.r. spectrum of the crude product. However, a broad peak at τ7.0 and a large number of signals in the region of τ8.5-9.0 indicated the presence of substantial amounts of side-products. Attempts to obtain pure p,p'-dinitro-2,3-diphenyl-1-butene by column chromatography failed as neither the olefinic material nor the side-products seemed to be homogeneous. The n.m.r. spectrum exhibited a multiplet in the aromatic region, a singlet at τ4.33, a doublet at τ4.53 (J = 1.5 cps), a multiplet at τ5.7 and a doublet at τ 8.41 (J = 7 cps). The signals at τ4.33 and τ4.53 were assigned to the methylene protons and the signal at τ5.7 to the benzylic proton. The multiplet at τ 5.7 showed the features of a quartet (J = 7 cps) of blurred appearance due to coupling of the benzylic hydrogen with the methyl group and with one of the methylene hydrogens. Integration showed the ratio of aromatic to methylene hydrogens to be too large for the desired product. Attempts to purify the olefinic material by sublimation were unsuccessful; the material sublimed, but did not change its composition as indicated by the n.m.r. spectrum. The n.m.r. spectrum of the unsublimed residue exhibited an A_2B_2 pattern centered at τ2.1, a broad peak at τ6.95 and a doublet at τ8.9 in addition to slight impurities; integration showed an approximate ratio of 4:1:3. Comparison with a spectrum of 2,3-diphenylbutane obtained from Mr. T. Gillan in this laboratory, revealed a striking similarity. Indeed, when an authentic sample of p,p-dinitro-2,3-diphenylbutane (75) was prepared, n.m.r. features identical to those of the material in the above reaction became apparent. The residue from sublimation melted at 262-263°, m.p. of meso-p,p'-dinitro-2,3-diphenylbutane

259°. A mixed sample showed a melting point of 255-257°.

Thus it became apparent that the Wittig reaction yielded a complex mixture of compounds. No further attempts were made to establish the identity of the materials, as characteristic n.m.r. features of the olefinic material were on hand for the analytical investigation of the reaction of 1-p-nitrophenylethyldimethylsulfonium salt in basic solution.

The preparation of meso-p,p'-dinitro-2,3-dinitrophenylbutane was done following standard procedures in the literature (75). 1-Phenylethanol was obtained in 89% yield by reduction of acetophenone with lithium aluminum hydride. The alcohol was converted into the chloride by reaction with thionyl chloride in dry benzene at 0°, 90.5%. Reaction of 1-phenylethyl chloride with half an equivalent of magnesium in dry ether afforded 2,3-diphenylbutane in 66% yield (76). Separation of the meso- and the racemic isomers was achieved by recrystallization. Nitration of the meso- compound was carried out at 0° in a mixture of glacial acetic acid and fuming nitric acid, 22% yield (75).

Reaction of 1-p-Nitrophenylethyldimethylsulfonium Methanesulfonate with Sodium Hydroxide

To an 0.1 molar aqueous solution of 1-p-nitrophenylethyldimethylsulfonium methanesulfonate at 100° was added an 0.2 N solution of sodium hydroxide. The solution turned immediately red and later yellowish with formation of oily material. After 2 hr the reaction mixture was cooled, acidified and extracted with ether. A small amount of precipitate was filtered from the ether solution. The infrared spectrum of this material was identical to that of *meso*-*p*,*p*'-dinitro-2,3-diphenylbutane; the n.m.r. spectrum, however, was very complex and could not be interpreted. The ether phase was dried and concentrated, resulting in a syrup-like residue. The n.m.r. spectrum of this residue was complex in the region τ7-9, but indicated the absence of any olefinic material. The infrared spectrum showed features similar to those of *meso*-*p*,*p*'-dinitro-2,3-diphenylbutane and did not indicate the presence of *cis*- or *trans*-*p*,*p*'-dinitro-α,α'-dimethylstilbene. Separation of the residue into components could not be achieved by column chromatography; different fractions showed essentially identical features in the infrared and n.m.r. spectra. Sublimation of the residue afforded a white solid, m.p. 220-240°; the infrared and n.m.r. spectra pointed to *meso*-*p*,*p*'-dinitro-2,3-diphenylbutane. No further analytical work was undertaken. Authentic samples of the two isomers of *p*,*p*'-dinitro-α,α'-dimethylstilbene and of the olefinic material obtained in the Wittig reaction were subjected to conditions of the described reaction and were recovered quantitatively.

In order to establish that the unidentified materials in the above reaction are not secondary products formed by polymerization of *p*-nitrostyrene, the reaction of 1-*p*-nitrophenylethyldimethylsulfonium ion with hydroxide ion was carried out under conditions of steam distillation, since it was known that *p*-nitrostyrene was steam volatile

(77). Only traces of p-nitrostyrene were obtained in the distillate. In a control reaction p-nitrostyrene was formed by reaction of 1-p-nitrophenylethyl chloride in aqueous triethanolamine and isolated by steam distillation in 79% yield. The 1-p-nitrophenylethyl chloride was prepared by reaction of 1-p-nitrophenylethanol with thionyl chloride in benzene solution at 0°. The material was distilled at 105-106°/1 mm and was characterized by the infrared and n.m.r. spectra and elemental analysis.

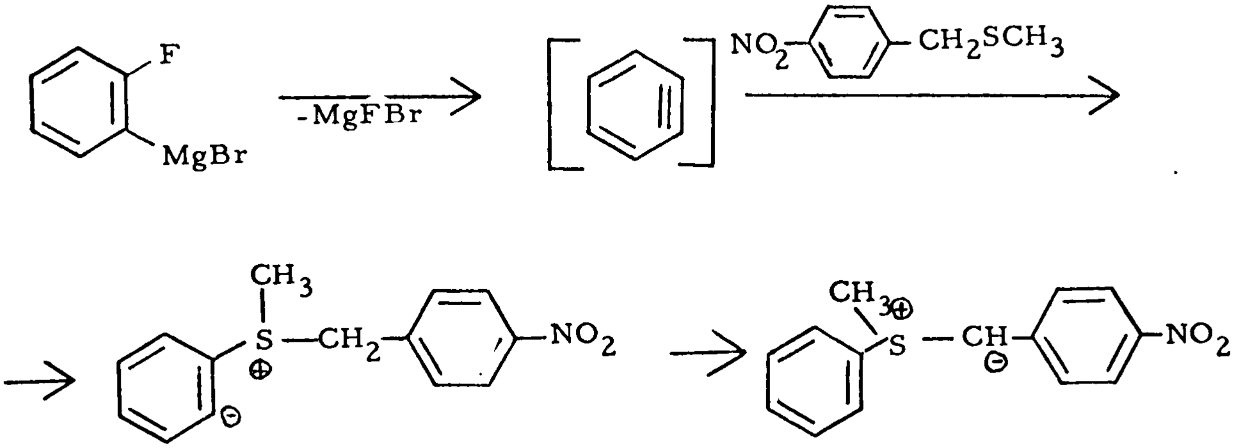
DISCUSSION

The fact that no p-nitrostilbene could be detected in the mixed product experiments indicates that a mechanism involving nucleophilic displacement is not operative in the formation of p,p'-dinitrostilbene in the reaction of p-nitrobenzyldimethylsulfonium ion with aqueous base. Furthermore, a theoretical argument against an S_N2 mechanism can be advanced along the following lines. Benzyldimethylsulfonium tosylate in its reaction with hydroxide ion gives exclusively benzyl alcohol at a rate 300 times slower than the analogous reaction for p-nitrobenzyldimethylsulfonium ion yielding p,p'-dinitrostilbene (12, 32). Deuterium exchange experiments show that the benzyldimethylsulfonium ylid is formed readily. Thus, a possible nucleophilic displacement by the benzyldimethylsulfonium ylid on the starting material is found unable to compete with the attack by hydroxide ion, as shown by the formation of benzyl alcohol and by the failure to observe any stilbene in the reaction of benzyldimethylsulfonium ion with sodium hydroxide. A nucleophilic displacement by ylid on the starting material would be less competitive with hydroxide ion attack in the reaction of the p-nitrobenzyldimethylsulfonium salt with hydroxide ion, since the negative charge is delocalized more effectively in the system carrying the nitro substituent. In fact, it is observed that any possible nucleophilic attack by hydroxide ion to give p-nitrobenzyl alcohol is not competitive with the faster reaction leading to p,p'-dinitrostilbene.

The failure to isolate the p-nitrobenzyldimethylsulfonium ylid at low temperatures in aqueous base is due to an unfavorable position of the acid-base equilibrium between the salt and the ylid, as shown by the attempts to extract the ylid with organic solvents. When the ylid was formed irreversibly in an anhydrous medium at -50°, its instability and high reactivity were much in evidence. However, a high basicity of sulfonium ylids results in general in the formation of the corresponding alcohol in aqueous sodium hydroxide solution. Furthermore, the readiness of the system to react with molecular oxygen once the ylid is formed distinguishes this system from other sulfonium ylids which have been shown to be inert to atmospheric conditions (7, 67) or sensitive only to moisture.

The reported observations on the p-nitrobenzyltriphenylphosphonium ylid revealed that the compound was sensitive to both light (19) and oxygen (20). When p,p'-dinitrobibenzyl was isolated from the reaction of p-nitrobenzyltriphenylphosphonium bromide with aqueous sodium hydroxide, the possibility of a free-radical decomposition process was suspected (20). However, it was concluded that this was not a radical process, but one in which the product distribution is solvent-dependent, since no p,p'-dinitrobibenzyl was detected in 80:20 alcohol-water or in anhydrous ethanol.

Attention should be called to a report (78) on the preparation of sulfonium ylids from the reaction of thioethers with benzyne. Among other systems the reaction of benzyne with p-nitrobenzyl methyl sulfide was investigated. Dropwise addition of p-nitrobenzyl methyl sulfide to a tetrahydrofuran solution of benzyne prepared in situ from



o-fluorophenylmagnesium bromide gave a deeply red colored solution. After 6 hr at reflux, 50% of p-nitrobenzyl methyl sulfide, the starting material, and 20% of phenyl methyl sulfide were isolated. The formation of the latter compound was interpreted as a result of the decomposition of p-nitrobenzylmethylphenylsulfonium ylid to the thioether and p-nitrophenylcarbene. No mention is made as to the fate of p-nitrophenylcarbene. It can be said from experience in this laboratory that it seems difficult to overlook the bright yellow, crystalline p,p'-dinitrostilbene if it is formed.

The described experiment represents excellent conditions for the reaction to proceed according to the mechanism which Swain proposed for the stilbene formation. If the above reaction proceeds via the intermediacy of p-nitrophenylcarbene, this carbene should be attacked by the ylid to give a reactive intermediate and ultimately p,p'-dinitrostilbene. If the reaction does not proceed via p-nitrophenylcarbene, there is no apparent reason why the reaction of p-nitrobenzyldimethylsulfonium tosylate with sodium hydroxide should involve p-nitrophenylcarbene since both reactions without doubt initially give rise to ylids.

The studies on the reaction of aqueous base with the p-nitrobenzyldimethylsulfonium salt in which one benzylic hydrogen is replaced by a methyl group, had failed to provide any conclusive evidence with regard to the mechanism of the reaction. Products expected if a carbene or a nucleophilic displacement mechanism were operative could not be detected. Monomeric olefin formation by elimination was shown to be negligible. The complexity of the product mixture and the infrared and n.m.r. spectroscopic information pointing to the presence of meso-p,p'-dinitro-2,3-diphenylbutane in small amounts are indications that the reaction might involve radical intermediates.

It thus became evident that a reinvestigation of the title reaction of this thesis was in order for the following reasons. No obvious explanation was on hand as to why the p-nitrobenzyl system carrying a methyl substituent in benzylic position would differ so drastically in it reaction with base from the system studied by Swain and Thornton (12). Furthermore, it was not clear why the reactions of p-nitrobenzylmethylphenylsulfonium salts with hydroxide ion gave rise to a complex and largely unidentified mixture of products (33). Thirdly, the analytical thin layer chromatographic studies in connection with the mixed product experiments in this thesis had indicated the presence of impurities and thereby suggested an actually complex course of the reaction studied by Swain and Thornton (12).

EXPERIMENTAL

Melting points and boiling points reported are not corrected. Refractive indices were measured on a Bausch and Lomb Abbe-3 L Refractometer. Infrared spectra were recorded on Perkin-Elmer model 421 and model 337 spectrophotometers. Nuclear magnetic resonance spectra were determined with Varian analytical spectrometers, models A-60 and HR-100 with tetramethylsilane (TMS) as internal standard. Electron paramagnetic resonance (e.p.r.) spectra were obtained using a Varian V-4500 e.p.r. spectrometer at 9.5075 ghz. Mass spectra were obtained on an A.E.I. MS-2-H mass spectrometer and on an A.E.I. MS-9 high resolution mass spectrometer at an ionization voltage of 70 eV. Gas-liquid chromatography was carried out on a Varian Aerograph model 90-P gas chromatograph. Calibrated internal standards were used for quantitative g.l.c. analysis. Thin layer chromatography studies were performed on glass plates coated with Silica Gel GF_{254} (E. Merck AG.Darmstadt) and with Aluminum Oxide G (E. Merck AG.). A 275-W General Electric sunlamp was the source of light for irradiation experiments which were conducted in Pyrex equipment.

Benzyl p-Toluenesulfonate (39):

This compound was prepared in 65% yield by dropwise addition of tosyl chloride to a suspension of sodium benzylate in anhydrous ether at -20°, m.p. 56-57° (lit. (39) 58.5-58.9°). The infrared spectrum ($CHCl_3$) showed the following significant bands: 3050, 2950, 1610, 1510, 1465, 1370, 1180, and 1105 cm^{-1}. The n.m.r. spectrum (CCl_4) consisted of a multiplet centered at τ2.6 and singlets at τ5.06 and τ7.62, ratio 9.3 : 1.96 : 3, required 9:2:3.

Benzyldimethylsulfonium Tosylate:

Benzyl tosylate (6 g) was dissolved in dimethyl sulfide, the amount of which was chosen to dissolve all the starting material. The solution turned cloudy due to crystallization of the newly formed sulfonium salt. After 12 hr at room temperature, the salt was filtered off and recrystallized from hot acetonitrile, long needles, m.p. 124-124.5° (lit. (32) 124-124.8°), 6.5 g (88%). The principal infrared bands (KBr) were at: 3020, 2980, 2935, 1600, 1500, 1465, 1440, 1225, 1185, 1120, 1035, 1015, 825, 790, 720 and 685 cm^{-1}. The n.m.r. spectrum (D_2O) exhibited signals at τ2.65 (m), τ5.65 (s), τ7.4 (s), and τ7.82 (s), ratio 9.0 : 1.99 : 6.0 : 3.18, required 9 : 2 : 6 : 3.

p-Nitrostilbene (63):

This material was prepared from p-nitrophenylacetic acid and benzaldehyde in the presence of piperidine, 63% yield, m.p. 156-158° (lit. (63) 155°). The infrared spectrum (KBr) had significant bands at 3085, 3040, 1600, 1520, 1455, 1350, 1120, 1080, 980, 965, 890, 860, 840, 755 and 700 cm^{-1}. The n.m.r. spectrum ($CDCl_3$) exhibited a multiplet centered at τ2.5. The characteristic features of this multiplet are used for identification and are therefore reported here: a doublet at τ1.8 (J = 9 cps) and peaks at τ2.35, τ2.5, τ2.55, τ2.6 and τ2.82.

p-Nitrobenzyl Tosylate (39):

This material was prepared by reaction of tosyl chloride and p-nitrobenzyl alcohol in dry pyridine at -10°, 50% yield, m.p. 101-102° (lit. (39) 105-105.5°) after three recrystallizations from ethyl acetate. The n.m.r. spectrum ($CDCl_3$) showed a multiplet at τ1.7-2.7 and singlets at τ4.8 and τ7.54, ratio 8.3 : 1.92 : 3.03, required 8 : 2 : 3.

p-Nitrobenzyldimethylsulfonium Tosylate:

p-Nitrobenzyl tosylate (5 g) was dissolved in 75 ml of acetonitrile at room temperature. A five-fold excess of dimethyl sulfide was added and the mixture was left at room temperature for 12 hr, followed by 12 hr in the refrigerator. Filtration yielded 4.8 g, 80%, of p-nitrobenzyldimethylsulfonium tosylate, m.p. 138-138.5° (lit. (12) 138-139°). The infrared spectrum (KBr) showed peaks at: 3085, 3020, 2960, 2940, 1605, 1520, 1490, 1440, 1350, 1210, 1190, 1170, 1120, 1110, 1045, 1035, 1020, 890, 860, 820, 740, 720 and 690 cm^{-1}. The n.m.r. spectrum (D_2O) showed a multiplet at τ1.85-3.0 and singlets at τ5.47, τ7.25, and τ7.83, ratio 8 : 1.7 : 6.08 : 3, required 8 : 2 : 6 : 3. Interference from the water signal rendered the integration for the singlet at τ5.47 unreliable.

trans-p,p'-Dinitrostilbene (12):

This material was prepared by addition of 100 ml of 0.2 N aqueous sodium hydroxide solution to a solution of 3.7 g (0.01 mole) in 100 ml of water heated on a steam bath. The reaction mixture was kept at 100° for 1 hr and after being cooled was acidified with concentrated hydrochloric acid. The precipitate was filtered off, and air dried, 1.35 g (100%). After repeated recrystallization from nitrobenzene, bright yellow needles were obtained m.p. 302-304° (lit. (12) 304-306°). The infrared spectrum (KBr) showed the following bands: 3100, 3040, 1600, 1590, 1505, 1375, 1335, 1180, 1110, 980, 970, 960, 865, 855, 760, 710, and 700 cm^{-1}. The material was only sparingly soluble in solvents suitable for an n.m.r. spectrum. A spectrum at low concentration in tetrahydrofuran showed signals closely bunched in the aromatic region at $\tau 1.65$, $\tau 1.8$, $\tau 2.1$, $\tau 2.25$ and $\tau 2.45$.

p-Nitrobenzyldimethylsulfonium Bromide:

p-Nitrobenzyl bromide (5.5 g) was dissolved in a mixture of dimethyl sulfide (30 ml) and acetonitrile (10 ml). After standing at room temperature for 12 hr the white precipitate was filtered off, 6.9 g, 98% yield, m.p. 107-109° (dec.) (lit. (79) 112-113°). The n.m.r. spectrum (D_2O) was characterized by signals at $\tau 2.05$ (m), $\tau 5.36$ (s) and $\tau 7.1$ (s), ratio 3.94 : 6, required 4 : 6 for the signals at $\tau 2.05$ and $\tau 7.1$ respectively. Reliable integration could not be obtained for the singlet at $\tau 5.36$ due to the proximity of the water signal. Attempts to recrystallize the material from hot acetonitrile failed. The product decomposed and gave back starting material, *p*-nitrobenzyl bromide, which was identified by comparison of the infrared and n.m.r. spectra with those of the authentic material.

p-Nitrobenzyldimethylsulfonium Tosylate from Reaction of *p*-Nitrobenzyldimethylsulfonium Bromide with Silver Tosylate:

The success of this procedure is dependent upon the exclusion of light in all operations and the use of exactly stoichiometric quantities. A mixture of 9.5 g (0.05 mole) of *p*-toluenesulfonic acid monohydrate and 5.8 g(0.05 mole) of silver oxide in 200 ml of acetonitrile was stirred magnetically for 30 min. The solution was added slowly with stirring to a solution of 13.9 g (0.05 mole) of *p*-nitrobenzyldimethylsulfonium bromide in a mixture of 200 ml of water and 100 ml of acetonitrile. The precipitate of silver bromide was filtered off in a fluted filter and the filtrate was concentrated by rotary evaporation. The concentrate was recrystallized twice from hot acetonitrile, m.p. 137-138°, 16.2 g, 88% yield.

Mixed Product Experiments:

These experiments were carried out using various conditions and will be described briefly in succession. Detailed analytical methods will be given collectively at the end of the series. In analogy to the procedure by which *p*,*p*'-dinitrostilbene is obtained, 1.1 g of *p*-nitrobenzyldimethylsulfonium tosylate and 5.8 g of benzyldimethylsulfonium tosylate were dissolved in 30 ml of water. The solution was heated on a steam bath and 15 ml of 0.2 N sodium hydroxide solution was added. The mixture was kept on a steam bath for 1 hr, cooled and acidified with concentrated hydrochloric acid. The yellow-brown precipitate was filtered off, air dried, and weighed

(405 mg, 100%). A second experiment was performed under identical conditions except that 30 ml of 0.2 N sodium hydroxide solution were employed, resulting in formation of 420 mg of material. In a third experiment, the same quantities of salts were dissolved in 30 ml of water. To the heated solution was added over a period of 2 hr 30 ml of 0.2 N sodium hydroxide solution; 420 mg (104%) of filtered product was obtained.

Most favorable conditions for the formation of p-nitrostilbene were thought to be provided by the following variation. Benzyldimethylsulfonium tosylate (5.8 g) was dissolved in 30 ml of 0.2 N sodium hydroxide solution, the resulting solution was heated on a steam bath, and 1.1 g of p-nitrobenzyldimethylsulfonium tosylate dissolved in 30 ml of water was added dropwise over a period of 3 hr. After cooling and acidification the salt was filtered off, washed with small amounts of Skelly Solve B and air dried, melting range 155-195°. Its weight (425 mg) amounted to 105% yield based on p,p'-dinitrostilbene. The infrared spectrum (KBr) showed peaks reported for trans-p,p'-dinitrostilbene (80) and no peaks expected for p-nitrostilbene. Due to lack of solubility of the crude product in tetrahydrofuran, a slurry in this solvent was obtained which was filtered; the n.m.r. spectrum of the filtrate showed in addition to the signals of p,p'-dinitrostilbene several weak, poorly resolved signals and a stronger peak at $\tau 2.7$. A comparison with the n.m.r. spectrum of p-nitrostilbene in tetrahydrofuran showed that the additional peaks were not due to the presence of p-nitrostilbene and it was also established that p-nitrostilbene was readily soluble in tetrahydrofuran. A dried ethereal extract of the aqueous solution gave a small amount of pure benzyl alcohol (113 mg) as identified by its n.m.r. spectrum in comparison with authentic material. The aqueous phase was taken to dryness on a steam bath under reduced pressure; the residue contained benzyldimethylsulfonium salt and did not show any traces of p-nitro-substituted starting material, as indicated by the n.m.r. spectrum (D_2O). To check whether the p-nitrobenzyldimethylsulfonium tosylate might have escaped detection in the n.m.r. spectrum of the residue, it was established that the n.m.r. spectrum of an intentionally mixed sample, composed of 7 mg of the substituted and 100 mg of the unsubstituted salt, clearly showed the signal for the methyl groups attached to the sulfur atom of the nitrobenzylic salt at τ 7.25.

Thin layer chromatography studies were performed on glass plates coated with Silica Gel GF_{254} (E. Merck AG. Darmstadt). Samples were applied by spotting dilute solutions of tetrahydrofuran. Chromatograms were developed by solvent ascension to a height of 15 cm using toluene as eluent and the spots were located with an ultraviolet lamp and/or with iodine vapor. Authentic samples of p,p'-dinitrostilbene (R_f 0.54) and p-nitrostilbene (R_f 0.73) were used for comparison. An intentionally mixed sample composed of 6 parts of p-nitrostilbene and 94 parts of p,p'-dinitrostilbene showed that the mononitro compound could be easily detected on a thin layer chromatogram. In none of the reaction products was there any sign of *p*-nitrostilbene. In search for the contaminations indicated by the n.m.r. spectrum, authentic samples of benzyl alcohol (R_f 0.12), *p*-nitrobenzyl alcohol (R_f0.05) and *p*-nitrobenzaldehyde (R_f 0.05) were used. However, none of these materials could be detected. Impurities with the following R_f values were observed: 0.70, 0.60, 0.27 and 0.00. No further attempts were made to identify these materials. G.l.c. analysis (SF-96 column, 245°) confirmed the absence of *p*-nitrostilbene.

Reaction of Benzyldimethylsulfonium Tosylate with Sodium Hydroxide:

Benzyldimethylsulfonium tosylate (3.24 g) was dissolved in 100 ml of 0.2 N sodium hydroxide solution and heated on a steam bath for 1 hr. The slightly cloudy mixture stayed colorless, was cooled and acidified with hydrochloric acid and extracted three times with ether which then was dried over magnesium sulfate. The solvent was removed under vacuum at room temperature. The sole product found was benzyl alcohol as indicated by infrared and n.m.r. spectra which were compared with spectra of authentic material.

Deuterium Exchange of Benzyldimethylsulfonium Ion:

Benzyldimethylsulfonium tosylate (500 mg) was dissolved in 2 ml of a solution of sodium deuteroxide in deuterated water and shaken for 3 min. The reaction was quenched by pouring the solution into a mixture of phosphorus pentoxide in deuterated water. The n.m.r. spectrum of this solution showed peaks at τ2.55, τ7.3 and τ7.7 and no signal for the benzylic hydrogens. Integration, using the aromatic protons as reference, indicated that 25% of the protons of the methyl groups attached to the sulfur had been exchanged.

Reaction of p-Nitrobenzyldimethylsulfonium Tosylate with Half an Equivalent of Sodium Hydroxide:

p-Nitrobenzyldimethylsulfonium tosylate (1.1 g, 3 mmole) was dissolved in 30 ml of water. To the heated solution was added 15 ml of 0.1 N sodium hydroxide solution and the mixture was kept on a steam bath for 1 hr. A yellow precipitate was isolated by filtration, air dried and weighed (204 mg, 50.5%). Its infrared spectrum (KBr) corresponded to that of an authentic sample of trans-p,p'-dinitrostilbene. The aqueous filtrate was neutral and was concentrated by rotary evaporation. The n.m.r. spectrum (D_2O) showed two singlets of equal intensity at τ7.62 and τ7.85 corresponding to the dimethylsulfonium group and the methyl group of the tosylate ion respectively. Thus 50% of the starting material was present; no unidentified peaks were detected.

p-Nitrobenzylpyridinium Bromide:

p-Nitrobenzyl bromide (25 g) was dissolved in 150 ml of pyridine. After shaking the clear solution for 2 min. sudden precipitation set in with evolution of heat. The precipitate was filtered off and treated with anhydrous ether to remove any traces of starting materials, 33.5 g, 98% yield, m.p. 221° (lit. (81) 219°). The n.m.r. spectrum (D_2O) showed a number of signals in the region of τ1.04-2.6 and a singlet at τ4.1, ratio 9.09 : 1.96, required 9 : 2.

p-Nitrobenzylpyridinium Tosylate:

A solution of p-nitrobenzylpyridinium bromide (5.9 g, 0.02 mole) in 100 ml of water was added slowly to 100 ml of an aqueous 0.02 N solution of silver tosylate with exclusion of light. Silver bromide was filtered off on a fluted filter and the filtrate was concentrated under vacuum. Recrystallization from hot acetonitrile yielded white crystals, 7.5 g, 97%, m.p. 171-172°. The infrared spectrum (Nujol) showed peaks at 3130, 3050, 1635, 1605, 1515, 1490, 1345, 1215 1215, 1200, 1185, 1165, 1150, 1120, 1030, 1005, 860, 845, 810, 770, 730 and 675 cm^{-1}. The n.m.r. spectrum (D_2O) showed a large number of signals at τ1.2-3.3 and singlets at τ4.35 and τ8.06, ratio 13.0:2.0:3.07, required 13:2:3.

Anal. Calcd. for $C_{19}H_{18}N_2O_5S$: C, 59.06; H, 4.70; N, 7.25. Found: C, 59.10; H, 4.73; N, 7.01.

Reaction of *p*-Nitrobenzyldimethylsulfonium Tosylate with Pyridine:

p-Nitrobenzyldimethylsulfonium tosylate (1.1 g) was dissolved in 50 ml of dry pyridine and the solution was heated on a steam bath for 12 hr. The solution was concentrated by rotary evaporation and the residue was treated with anhydrous ether. A white precipitate was filtered off, and the filtrate was concentrated under vacuum. A yellow oil (70 mg) was left and its n.m.r. spectrum ($CDCl_3$) showed the following signals: an A_2B_2 pattern centered at τ2.2, and singlets at τ6.25 and τ8.0, ratio 4.16:2:2.96, required for *p*-nitrobenzyl methyl sulfide 4:2:3. The infrared spectrum ($CHCl_3$) had significant peaks at 3070, 2915, 1600, 1520, 1435, 1345, 1105, 1010, 850 and 690 cm^{-1}. Part of the precipitate was recrystallized four times from methanol and ether without changing the melting point of 168-169°.

It was identified as p-nitrobenzylpyridinium tosylate by comparison of the n.m.r. and infrared spectra with those of an authentic sample. The n.m.r. spectrum (D_2O) of another part of the crude precipitate, filtered off after ether treatment, showed a relative intensity of 1.48: 1:3.1 for the benzylic protons (τ4.3), the N-methyl group (τ5.75) and the methyl group of the tosylate anion (τ7.95). This corresponds to a product ratio of 70:30 of p-nitrobenzylpyridinium tosylate to N-methyl pyridinium tosylate. An experiment, with 10 ml of water added under otherwise identical conditions, gave the same ratio of product. The n.m.r. spectrum of the product in pyridine showed the N-methyl group at τ5.4. The amount of sulfide obtained did not correspond to the amount of N-methyl pyridinium salt. This, however, is only a consequence of the work-up of the reaction where substantial amounts of the sulfide could have been lost in the rotary evaporator at 100°/12 mm. A reference (78) to the preparation of p-nitrobenzyl methyl sulfide reports the elemental analysis, but no boiling point data are given.

cis- and trans-p,p'-Dinitrostilbene oxide (69):

p-Nitrobenzyl chloride (8.6 g) and p-nitrobenzaldehyde (8.3 g) were dissolved in 50 ml of methanol, and after addition of 3.5 g of potassium carbonate, the mixture was heated at reflux for 2.5 hr. After the solution had been cooled, the precipitate was filtered off, washed with hot water and dried. The product was dissolved in a small quantity of boiling dioxane. On cooling a white solid precipitated out (4.8 g, 34%) which was recrystallized from hot acetonitrile, m.p.

202-203.5° (lit. (69) 200-201°), trans-p,p'-dinitrostilbene oxide. The infrared spectrum (KBr) had bands at: 3100, 1605, 1595, 1525, 1440, 1395, 1345, 1175, 1100, 1015, 900, 860, 850, 830, 800, 750 and 700 cm^{-1}. The n.m.r. spectrum (deuterated dimethylsulfoxide) showed an A_2B_2 pattern at τ2.1 and a singlet at τ5.7, ratio 8.35: 1.85, required 8:2. The dioxane filtrate was heated again and petroleum ether was added until permanent cloudiness was apparent. The precipitate was the cis- isomer (6 g, 42%) and was recrystallized from glacial acetic acid m.p. 154-156° (lit. (69) 159°). The infrared spectrum (KBr) was characterized by bands at 3100, 1600, 1520, 1435, 1385, 1340, 1170, 1100, 1050, 1010, 905, 880, 855, 840, 820, 790, 745, 740, 730, 700 and 690 cm^{-1}. The signals for the protons of the epoxide ring in the n.m.r. spectrum (acetonitrile) appear at τ5.38 and τ5.83 for the cis- and trans- isomer respectively.

Reaction of p-Nitrobenzyldimethylsulfonium Tosylate in Aqueous Potassium Carbonate Solution:

p-Nitrobenzyldimethylsulfonium tosylate (1.1 g) was dissolved in a solution of 1.5 g of potassium carbonate in 30 ml of water at 0°. An almost colorless solution was obtained which on warming up to room temperature gradually turned cloudy. After 12 hr the precipitate was filtered off (17 mg), m.p. 194-197° and identified as trans-p,p'-dinitrostilbene oxide by its infrared spectrum. The filtrate was acidified with concentrated hydrochloric acid and extracted with ether. The organic phase was dried over magnesium sulfate, concentrated under vacuum, yielding 9 mg of product and was identified as trans-p,p'-dinitrostilbene oxide by its infrared spectrum. Gas-liquid chromatography (SF-96 column, 190°) confirmed the absence of p-nitrobenzyl alcohol, p-nitrobenzaldehyde and p-nitrobenzoic acid. Thin layer chromatography on aluminum oxide G (Merck) (25 ml benzene- 5 ml ether) showed one spot (R_f 0.70) on development with 20% sulfuric acid. Authentic trans-p,p'-dinitrostilbene oxide showed the identical R_f value. A parent peak at m/e 286 in the mass spectrum showed the corresponding molecular weight.

Reaction of p-Nitrobenzyldimethylsulfonium Tosylate with Excess Sodium Hydroxide at 0°:

To a solution of 1.845 g (0.005 mole) of p-nitrobenzyldimethylsulfonium tosylate in 100 ml of water at 0° was added a cooled solution of 4.778 g (0.12 mole) of sodium hydroxide in 100 ml of water. The solution turned red and a light yellow precipitate formed slowly; the mixture was stirred for 10 hr at 0°. Filtration yielded 594 mg of material which by infrared and mass spectroscopy was shown to be a mixture of p,p'-dinitrostilbene and p,p'-dinitrostilbene oxide. The identity of the p,p'-dinitrostilbene oxide was established by the signal at τ 5.95 in the n.m.r. spectrum (nitrobenzene). After several recrystallizations from nitrobenzene pure trans-p,p'-dinitrostilbene (infrared spectrum, m.p.) was obtained. In a second and third experiment under identical conditions the aqueous solutions were extracted with ether and methylene chloride respectively after a reaction period of 5 min. The organic phases showed a slight red color and were concentrated immediately by rotary evaporation at 0°, but did not produce any material.

Reaction of p-Nitrobenzyldimethylsulfonium Tosylate with n-Butyllithium:

To a stirred slurry of 1.936 g (5.23 mole) of p-nitrobenzyldimethylsulfonium tosylate in 50 ml of tetrahydrofuran at -50° under a blanket of nitrogen was added over a period of 1 hr a hexane solution containing 5.3 mmole of n-butyllithium. As each drop of the n-butyllithium solution was added, a deep red color appeared instantaneously, but faded away quickly. The resulting orange slurry was stirred for 2 hr at -50° and then allowed to warm up to room temperature. The mixture was poured into water and after addition of sodium chloride aqueous and organic phase were separated in a separatory funnel. The organic layer was dried over magnesium sulfate and concentrated under vacuum (630 mg,89%),melting range 230-260°. The infrared spectrum showed the presence of trans-p,p'-dinitrostilbene.

1-p-Nitrophenylethanol:

p-Nitroacetophenone (11 g) was dissolved in a mixture of 100 ml of 95% ethanol and 60 ml of tetrahydrofuran. The solution was cooled in an ice bath and stirred magnetically. Sodium borohydride (5.1 g) was added in small protions over a period of 20 min. The mixture containing white viscous lumps was stirred for another 30 min. at room temperature and poured onto 1000 g of cracked ice. The aqueous solution was extracted three times with 100 ml portions of ether. The ether solution was dried over anhydrous potassium carbonate and concentrated on a rotary evaporator. Distillation at 130°/1.5 mm (lit. (82) 137-38/2 mm) gave a yellowish viscous oil, 10 g, 90% yield. The infrared spectrum (film) showed the following significant peaks: 3400 (broad), 2970, 1605, 1515, 1450, 1340, 1190, 1100, 1080, 1000, 890, 845, 745, and 690 cm^{-1}. The n.m.r. spectrum ($CDCl_3$) had an A_2B_2 multiplet centered at $\tau 2.35$, a quartet at $\tau 5.15$ (J = 6.5 cps), a singlet at $\tau 6.75$ (disappearing on deuterium exchange) and a doublet at $\tau 8.56$ (J = 6.5 cps), ratio 3.94 : 0.96 : 0.98 : 3.08, required 4 : 1 : 1 : 3.

1-p-Nitrophenylethyl Methanesulfonate:

1-p-Nitrophenylethanol (3.4 g) was dissolved in 30 ml of carbon tetrachloride at 0°. A solution of methanesulfonyl chloride (2.4 g) in 30 ml of carbon tetrachloride and triethylamine (2.9 ml) were added and the mixture was stirred magnetically for 5 min. Concentration on a rotary evaporator afforded a white residue which was treated with cold water, filtered, and washed with hexane, 3.95 g, 79% yield. The methanesulfonate was recrystallized from ethyl acetate-cyclohexane at room temperature, m.p. 79-80°. The infrared spectrum (Nujol) showed the following significant peaks: 3100, 1600, 1520, 1340, 1310, 1280, 1205, 1160, 1100, 1050, 960, 900, 850, 800, 770, 750 and 690 cm^{-1}. The n.m.r. spectrum ($CDCl_3$) exhibited an A_2B_2 multiplet centered at $\tau 2.25$, a quartet at $\tau 4.3$ (J = 7 cps), a singlet at $\tau 7.15$ and a doublet at $\tau 8.3$ (J = 7 cps), ratio 4.08 : 0.96 : 3.0 : 3.1, required 4 : 1 : 3 : 3.

Anal. Calcd. for $C_9H_{11}NO_5S$: C, 44.08; H, 4.52; N, 5.71.

Found: C, 44.14; H, 4.54; N, 5.88.

1-p-Nitrophenylethyldimethyl Methanesulfonate:

1-p-Nitrophenylethyl methanesulfonate (9 g) was dissolved in 25 ml of acetonitrile in an Erlenmeyer flask equipped with a ground joint stopper. To this solution was added 25 ml of dimethyl sulfide and the stoppered flask was allowed to stand at room temperature. After two weeks a white precipitate was filtered off, 18.4 g, 72%. After recrystallization from acetonitrile the product melted at 139-140°. The infrared spectrum (Nujol) showed bands at 3400 (broad), 3100, 1600, 1520, 1350, 1200, 1100, 1060, 1040, 1010, 980, 865, 855, 775 and 705 cm^{-1}. In spite of repeated recrystallization from acetonitrile no material free of the broad band at 3400 cm^{-1} could be obtained. The n.m.r. spectrum (D_2O) showed a multiplet centered at τ 2.0, a quartet at τ5.07 (J = 7 cps), singlets at τ7.1, τ7.25 and τ7.32 and a doublet at τ8.1 (J = 7 cps), ratio 4.05 : 0.89 : 3.3 : 6 : 2.92, required 4 : 1 : 3 : 6 : 3.

Anal. Calcd. for $C_{11}H_{17}NO_5S_2 \cdot 1/2\, H_2O$: C, 41.74; H, 5.69; N, 4.56. Found: C, 41.74; H, 5.98; N, 4.29.

p-Nitroacetophenone Hydrazone (71):

p-Nitroacetophenone (16.5 g) and hydrazine hydrate (12 g of an 85% solution) was mixed in a 1 liter flask and 350 ml of absolute ethanol was added. After 12 hr at reflux crystalline product, 16.5 g, 92%, was obtained by filtration of the cooled solution, m.p. 148-150° (lit. (71) 149-151°). The infrared spectrum(Nujol) showed significant bands at 3400, 3305, 3210 and 1625 cm^{-1}.

cis- and trans-p,p'-Dinitro-α,α'-dimethylstilbene (70):

p-Nitroacetophenone hydrazone (12 g) and lead dioxide (120 g) were stirred in benzene (600 ml) at room temperature overnight. The mixture was filtered and sulfur dioxide was passed into the red filtrate until the solution turned light yellow. Removal of benzene on a steam bath under reduced pressure gave a solid product which on recrystallization from hot glacial acetic acid afforded trans-p,p'-dinitro-α,α'-dimethylstilbene (5.7 g, 57%) as colorless crystals, m.p. 219-220° (lit. (83) 217°). The infrared spectrum (Nujol) showedthe following bands: 3100, 1590, 1510, 1340, 1310, 1285, 1170, 1100, 1080, 1035, 1010, 850, 780, 750 and 700 cm^{-1}. The n.m.r. spectrum ($CDCl_3$) showed an A_2B_2 pattern centered at $\tau 2.2$ and a singlet at $\tau 8.1$, ration 8.25:5.8, required 8:6.

On slow evaporation at room temperature the mother liquor deposited a mixture of the trans- and cis- isomers, which was filtered off in several fractions, the last of which on recrystallization from acetone yielded the pale yellow cis- isomer, m.p. 151-152° (lit. (83) 155°). The total material recovered from the mother liquor weighed 3.4 g, 34%. The infrared spectrum(Nujol) showed bands at 3080, 1590, 1510, 1340, 1280, 1170, 1100, 850, 750, 715 and 690 cm^{-1}. The n.m.r. spectrum ($CDCl_3$) showed an A_2B_2 pattern centered at $\tau 2.4$ and a singlet at $\tau 7.8$, ratio 8.15:5.95, required 8:6.

N-(p,p'-Dinitrostilbyl) Pyridinium Bromide (72):

p-Nitrobenzylpyrinidinum bromide (6 g) and p-nitrobenzaldehyde (4.5 g) were dissolved in a mixture of 75 ml of acetic anhydride and 3 ml of glacial acetic acid containing potassium acetate (2.4 g). The reaction mixture was heated at 70° for 10 hr and concentrated under vacuum. After treatment of the residue with water and ether the product was isolated by concentration of the aqueous phase under vacuum as a crystalline material, 5.9 g, 66.5%, m.p. 310-312° (lit. (72) 299-301°).

_p_,_p_'-Dinitrostilbyl Amine (73):

N-(_p_,_p_'-Dinitrostilbyl) pyridinium bromide (3 g) was stirred magnetically in 20 ml of piperidine for 1 hr. The deep red solution turned viscous and precipitation was completed by addition of ice water. The precipitate was filtered, thoroughly washed with water, and air dried. Recrystallization from hot acetonitrile afforded red needles, 1.85 g, 94.5%, m.p. 175-176° (lit. (73) 174-175°). The n.m.r. spectrum (dimethylsulfoxide) showed a multiplet centered at τ2.05, a broad singlet at τ3.68 and a singlet at τ4.46, ratio 8:1.96:1, required 8:2:1.

N-(_p_,_p_'-Dinitrostilbyl) Pyrrolidine (73):

_p_,_p_'-Dinitrostilbyl amine (2.0 g) was treated for 12 hr with a refluxing mixture of 10 ml of pyrrolidine and 0.2 ml of concentrated hydrochloric acid. Ice water was added to the cooled solution and the precipitate formed was filtered off and washed with water. The product was treated with charcoal and recrystallized from hot acetonitrile, 68% yield, m.p. 182-183°. The preparation of this compound is referred to but not described in the given reference (73). The n.m.r. spectrum (pyridine) showed a singlet at τ4.82 and multiplets at τ7.33 and τ8.6, ratio 1.03 : 3.93 : 3.93 , required 1 : 4 : 4 .

1-p-Nitrophenyl-p-nitropropionophenone:

N-(p,p'-dinitrostilbyl) pyrrolidine (12.5 g), methyl iodide (30 ml), di-isopropyl ethyl amine (4.75 g) and 300 ml of acetonitrile were placed into a stainless steel bomb. The bomb was slowly heated to 80° in an oven and kept at that temperature for 60 hr. The mixture was concentrated on rotary evaporator to a volume of approximately 200 ml and the same amount of water and 8 ml of concentrated hydrochloric acid were added. This mixture was refluxed for 8 hr, cooled and concentrated until free of acetonitrile. The aqueous phase was extracted with ether. The ethereal layer was washed with water, sodium bicarbonate solution, and sodium bisulfite solution successively and dried over magnesium sulfate. The ether was taken off under vacuum and the residue was purified by column chromatography on neutral alumina using benzene as eluent for the alkylated ketone. Traces of the unalkylated ketone were held back and eluted later with chloroform. The yield of the crystalline product amounted to 8 g, 73%. Recrystallization from hot chloroform and Skelly Solve B gave a yellow powder, m.p. 132-133.5°. The infrared spectrum (Nujol) showed bands at 3100, 1680, 1590, 1515, 1400, 1340, 1190, 1100, 960, 850, 780, 740, 705 and 685 cm^{-1}. The n.m.r. spectrum ($CDCl_3$) showed a multiplet centered at τ2.15, a quartet at τ5.1 (J - 7 cps) and a doublet at τ8.35 (J = 7 cps), ratio 8.35 : 0.97 : 3.07, required 8 : 1 : 3 .

Anal. Calcd. for $C_{15}H_{12}N_2O_5$: C, 60.00; H, 4.03; N, 9.33.

Found: C, 59.89; H, 4.20; N, 9.27.

Methyltriphenylphosphonium Bromide (84):

Triphenylphosphine and excess methyl bromide were allowed to react in benzene solution in a stainless steel bomb for 48 hr; filtration afforded the pure phosphonium salt in 87% yield, m.p. 226-227° (lit. (84) 227-229°). The material was stored over phosphorus pentoxide.

Attempts to Prepare p,p'-Dinitro-2,3-diphenylbutene-1:

Methyltriphenylphosphonium bromide (7 mmole) was added to 100 ml of dry tetrahydrofuran in a 250 ml three-necked flask equipped with a reflux condenser surmounted by a drying tube, a gas inlet tube and a dropping funnel. A continuous stream of nitrogen was passed through the system and to the magnetically stirred slurry was added in one portion 4.5 ml of a 15.06% solution of n-butyllithium in hexane (7.1 mmole). After 20 min. a clear solution was obtained and a solution of 2.1 g (7 mmole) of 1-p-nitrophenyl-p-nitropropionophenone in 75 ml of dry tetrahydrofuran was added dropwise over a period of 30 min. The reaction mixture was then heated at reflux temperature for 18 hr and taken to dryness in vacuum. The residue was partitioned between 300 ml of ether and 100 ml of water. The organic phase was washed with water, dried over sodium sulfate and concentrated under vacuum. The n.m.r. spectrum ($CDCl_3$) of the crude product indicated the presence of olefinic material by a singlet at $\tau 4.33$, and a doublet at $\tau 4.53$ (J = 1.5 cps). No starting material could be detected. A large number of signals in the region of τ7.0 and τ8.5-9 pointed to the presence of impurities. Column chromatography on neutral alumina using Skelly Solve B - benzene (70-30 by volume) for elution afforded a solid, 475 mg, 23% yield. This material was not pure as indicated by the n.m.r. spectrum (CDCl$_3$) which showed additional peaks at τ8.5-9.0. The peaks assigned to olefinic product are a multiplet centered at τ2.2, a singlet at τ4.33, a doublet at τ4.53 (J = 1.5 cps), a multiplet at τ5.7 and a doublet at τ8.41 (J = 7 cps). No satisfactory integration could be obtained. Further attempts to purify this material by column chromatography failed; use of more powerful eluents (benzene, chloroform, tetrahydrofuran) resulted in isolation of more olefinic material indicating that the olefinic material was not homogeneous. Sublimation (150°/1 mm) afforded material which contained a terminal double bond (n.m.r.) and melted at 251-253°. The infrared spectrum(Nujol) exhibited significant bands at 3100, 1605, 1590, 1510, 1340, 1180, 1110, 1055, 1010, 995, 960, 855, 770, 755, 700 and 620 cm^{-1}.

<u>1-Phenylethanol:</u>

A solution of acetophenone (0.526 mole) in anhydrous ether (100 ml) was added dropwise to a mechanically stirred slurry of lithium aluminum hydride (0.132 mole) in anhydrous ether (200 ml) at reflux. After 2.5 hr the reaction mixture was worked up by addition of saturated ammonium chloride solution. The ether layer was dried over magnesium sulfate and concentrated under vacuum. The residue was distilled at 90-92°/15 mm (lit. (76) 92-93°/16 mm), 89% yield. The n.m.r. spectrum (CCl_4) showed a singlet at τ2.92, a multiplet at τ5.45 and doublets at τ5.98 (J = 2.5 cps) and τ8.75 (J = 6.5 cps), ratio 5.13 : 1 : 1 : 3.1, required 5 : 1 : 1 : 3.

1-Phenylethyl Chloride:

This material was prepared following the procedure given for the preparation of 1-*p*-nitrophenylethyl chloride (see below). A yield of 90.5% was realized, b.p. 78-80°/14 mm (lit. (85) 73°/11 mm), η_D^{26} = 1.5274. The n.m.r. spectrum ($CDCl_3$) showed a multiplet at τ2.74, a quartet at τ5.03 (J = 7 cps) and a doublet at τ8.30 (J = 7 cps), ratio 4.97 : 1.01 : 3.02, required 5 : 1 : 3.

2,3-Diphenylbutane (76):

1-Phenylethyl chloride (0.6 mole) in dry ether (200 ml) was added to magnesium (0.3 mole) in ether (100 ml) at such a rate that the mixture boiled vigorously. Refluxing was continued overnight and the reaction mixture was worked up by addition of saturated ammonium chloride solution. The ether layer was dried over magnesium sulfate and concentrated under vacuum. The residue was dissolved in boiling methanol and filtration of the cooled solution afforded 40.5% of the *meso*- compound, m.p. 122-123° (lit. (76) 124°). Removal of methanol from the mother liquor afforded the crude racemic material in 25% yield. The n.m.r. spectrum ($CDCl_3$) exhibited a singlet at τ2.85, a broad signal at τ7.25 and a doublet at τ9.0 (J = 6.5 cps), ratio 10 : 2 : 5.84, required 10 : 2 : 6.

meso-*p*,*p*'-Dinitro-2,3-diphenylbutane (75):

2,3-Diphenylbutane (0.086 mole) was dissolved in 50 ml of glacial acetic acid and the solution was cooled in an ice bath. To the magnetically stirred solution was added dropwise an ice-cold mixture of 50 ml of glacial acetic acid and 32 ml of fuming nitric acid. The addition was done at such a rate that the temperature of the reaction medium did not exceed 10°. After complete addition the mixture was stirred at 0° for 10 hr followed by 2 hr at room temperature. The reaction mixture was poured into ice, the precipitate was filtered off and recrystallized from benzene, 5.6 g, 22% yield, m.p. 259° (lit. (75) 256°). The infrared spectrum (Nujol) exhibited significant bands at 3100, 1605, 1590, 1510, 1340, 1180, 1110, 1055, 1010, 955, 960, 855, 770, 755, 700 and 620 cm^{-1}. The n.m.r. spectrum (CDCl$_3$) showed an A_2B_2 pattern centered at $\tau 2.2$, a broad signal at $\tau 7.0$ and a doublet at $\tau 8.92$ (J = 6.5 cps), ratio 10.2 : 2 : 5.9, required 10 : 2 : 6.

Reaction of 1-p-Nitrophenylethyldimethylsulfonium Methanesulfonate with Sodium Hydroxide:

The salt (0.01 mole) was dissolved in 100 ml of water. The solution was heated on a steam bath and 100 ml of 0.2 N sodium hydroxide solution was added. The reaction mixture turned red immediately and was heated at 100° for 2 hr during which time the mixture turned cloudy with a yellow color and formed oily lumps at the bottom of the flask. The mixture was cooled, acidified with concentrated hydrochloric acid and extracted with ether. The flask was thoroughly rinsed with ether. The oily material went into solution and some precipitate was left in the ether solution. Filtration yielded 50 mg of material; the infrared spectrum was identical to that of authentic *meso*-*p*,*p*'-dinitro-2,3-diphenylbutane. However, the n.m.r. spectrum ($CDCl_3$) showed a large number of peaks at τ7-9. The solutions were combined, dried over magnesium sulfate and concentrated under vacuum. Syrup-like material (1.365 g) was obtained; the n.m.r. spectrum ($CDCl_3$) showed a host of signals at τ7-9. Column chromatography on neutral alumina using different eluents (Skelly Solve B-benzene (7-3 and 1-1) and benzene) afforded different fractions the infrared spectra of which were very similar to that of *meso*-*p*,*p*'-dinitro-2,3-diphenylbutane. The n.m.r. spectra were characterized by a complex arrangement of signals. The infrared spectra did not indicate the presence of any *p*,*p*'-dinitro-α,α'-dimethylstilbene, while the n.m.r. spectra did not show the presence of terminal olefins. Sublimation (150°/ 1 mm) of the raw product gave small amounts of the material, m.p. 220-240°. The infrared spectrum showed characteristic features for *meso*-*p*,*p*'-dinitro-2,3-diphenylbutane. More significantly, the n.m.r. spectrum ($CDCl_3$) exhibited all features of the above compound without significant impurities. No integration was feasible due to lack of material.

Slurries of 100 mg of each isomer of *p*,*p*'-dinitro-α,α'-dimethylstilbene in 50 ml of 0.2 N sodium hydroxide solution were stirred magnetically at reflux for 2 hr. The cooled and acidified mixtures gave almost quantitative recovery on filtration, infrared and n.m.r. spectra were confirmatory. The same treatment of 50 mg of olefinic material from the Wittig reaction gave identical results.

Reaction of 1-p-Nitrophenylethyldimethylsulfonium Methanesulfonate with Base under Conditions of Steam Distillation:

The reaction was carried out under conditions as described in the preceeding experiment except that a rapid stream of steam was passed through the solution immediately after addition of base. Distillate was collected over a period of 2 hr and after that time was extracted with methylene chloride. The organic phase was dried over magnesium sulfate and concentrated under vacuum. The n.m.r. spectrum ($CDCl_3$) of the residue (ca. 100 mg) showed weak signals identical to those of p-nitrostyrene and in addition showed signals of undetermined origin at τ 7-9.

1-p-Nitrophenylethyl Chloride:

In a dry 250 ml three-necked flask fitted with a reflux condenser surmounted by a drying tube, a dropping funnel and a magnetic stirring bar was placed 8.5 ml of thionyl chloride. The flask was cooled in an ice bath and 18.8 g of 1-p-nitrophenylethanol dissolved in 15 ml of dry benzene was added dropwise over a period of 1 hr. The reaction mixture was stirred at 0° for another 2 hr and then allowed to warm up to room temperature. Finally it was warmed to 40° and stirred until the evolution of gas ceased (1 hr). The reaction mixture was concentrated by rotary evaporation. Distillation yielded a fore-run (3.8 g, 70-94°/1 mm) consisting of a mixture of p-nitrostyrene and 1-p-nitrophenylethyl chloride in a 70:30 ratio as indicated by the n.m.r. spectrum. The main fraction distilled at 105-106°/1 mm, 12.6 g. The total yield of product amounted to 66%. The infrared spectrum (film) showed significant bands at 3100, 2980, 1600, 1520, 1445, 1340, 1230, 1105, 1040, 1010, 960, 850, 775, 750 and 690 cm^{-1}. The n.m.r. spectrum ($CDCl_3$) exhibited an A_2B_2 pattern centered at τ2.16, a quartet at τ4.85 (J = 7 cps) and a doublet at τ8.18 (J = 7 cps), ratio 4.2 : 0.96 : 2.96, required 4 : 1 : 3.

Anal. Calcd. for $C_8H_8ClNO_2$: C, 51.77; H, 4.34; Cl, 19.10; N, 7.55. Found: C, 51.74; H, 4.48; Cl, 19.28; N, 7.65.

Formation of *p*-Nitrostyrene under Conditions of Steam Distillation (77):

1-*p*-Nitrophenylethyl chloride (4 g), triethanolamine (30 ml) and water (30 ml) were placed in a 500 ml three-necked flask equipped with a steam inlet tube and a distillation condenser. The mixture was heated in a steam bath and a moderate stream of steam was passed into the reaction mixture. After 1 hr the distillate was extracted with ether and the organic phase was dried over magneisum sulfate and concentrated by rotary evaporation, 2.55 g, 79% yield of crude product. The n.m.r. spectrum ($CDCl_3$) showed an A_2B_2 pattern centered at τ2.18, a quartet at τ3.20 (J_{cis} = 10.5 cps, J_{trans} = 18.5 cps), and doublets at τ4.12 (J = 18.5 cps) and τ4.53 (J = 10.5 cps). The four signals of the last two doublets were not sharp due to geminal coupling. Impurities at τ2.7-3.3 excluded satisfactory integration of this region. The ratio of the multiplet at τ2.18 and the doublets at τ4.12 and τ4.53 was 3.95 : 1 : 1.05, required 4 : 1 : 1.

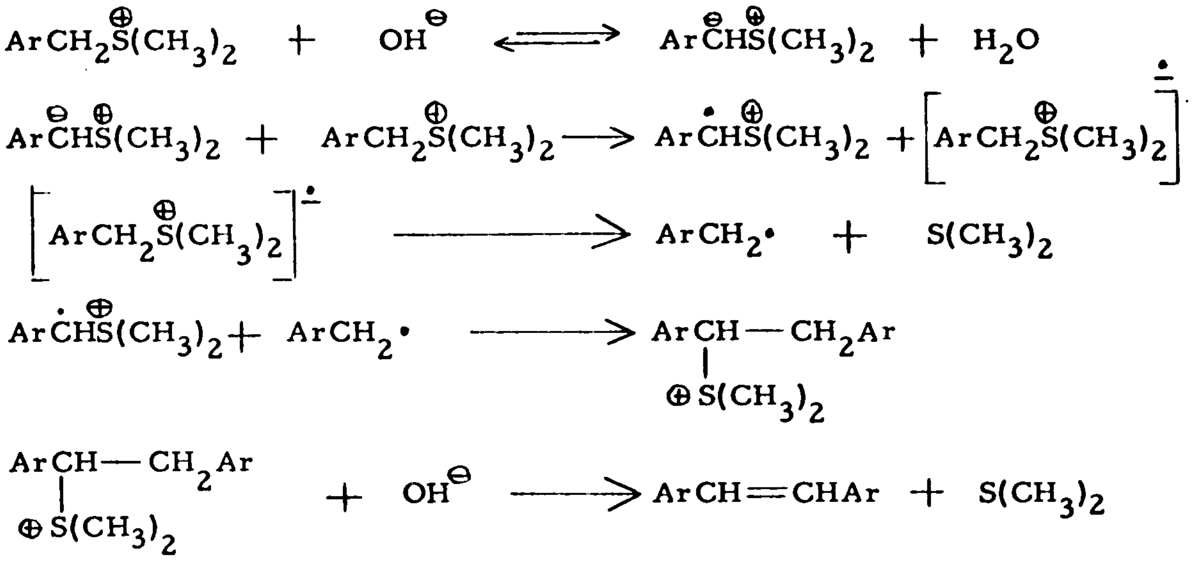
CHAPTER II

ANALYSIS OF THE PRODUCTS FROM REACTIONS OF p-NITROBENZYLDIMETHYLSULFONIUM ION AND SOME RELATED SYSTEMS WITH AQUEOUS BASE

As a consequence and continuation of the studies described in the first chapter it was decided to undertake a careful examination of the products from the reaction of p-nitrobenzyldimethylsulfonium tosylate with sodium hydroxide. This approach of product analysis was extended to reactions of sodium hydroxide with the following related systems: p-nitrobenzyldiphenylsulfonium ion, p-nitrobenzylpyridinium ion and 3,5-dimethyl-4-nitrobenzyl 'onium ions.

Since an S_N2 mechanism had been excluded and a carbene pathway was looked upon rather skeptically in the title reaction of this thesis, a radical process was considered a plausible alternative, especially in the light of the observations made in the study on the methyl substituted p-nitrobenzyl system. Special attention in the analytical work was therefore to be focused on products that would arise from a reaction involving radical intermediates. In analogy to the route proposed (43) for carbon alkylation of 2-nitropropane by p-nitrobenzyl chloride (Scheme II) the following Scheme IIIa could be envisaged.

SCHEME IIIa



$$ArCH_2\overset{\oplus}{S}(CH_3)_2 + OH^{\ominus} \rightleftharpoons Ar\overset{\ominus}{C}H\overset{\oplus}{S}(CH_3)_2 + H_2O$$

$$Ar\overset{\ominus}{C}H\overset{\oplus}{S}(CH_3)_2 + ArCH_2\overset{\oplus}{S}(CH_3)_2 \longrightarrow Ar\overset{\bullet}{C}H\overset{\oplus}{S}(CH_3)_2 + \left[ArCH_2\overset{\oplus}{S}(CH_3)_2\right]^{\overset{\bullet}{-}}$$

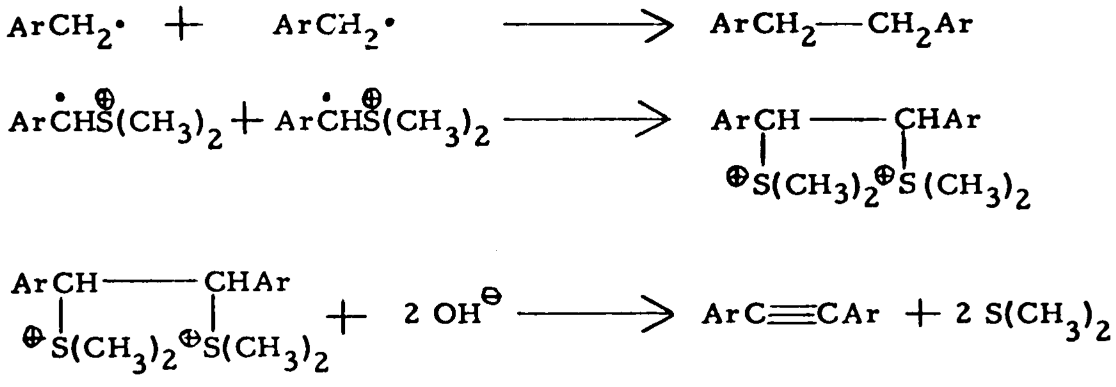
$$\left[ArCH_2\overset{\oplus}{S}(CH_3)_2\right]^{\overset{\bullet}{-}} \longrightarrow ArCH_2\bullet + S(CH_3)_2$$

$$Ar\overset{\bullet}{C}H\overset{\oplus}{S}(CH_3)_2 + ArCH_2\bullet \longrightarrow \underset{\overset{|}{\oplus S(CH_3)_2}}{ArCH}-CH_2Ar$$

$$\underset{\overset{|}{\oplus S(CH_3)_2}}{ArCH}-CH_2Ar + OH^{\ominus} \longrightarrow ArCH=CHAr + S(CH_3)_2$$

It was of particular interest to see whether in the reaction under present investigation coupling of radicals could occur in a manner different from that leading to p,p'-dinitrostilbene. Symmetrical coupling would give rise to p,p'-dinitrobibenzyl and p,p'-dinitrotolane.

SCHEME IIIb



$$ArCH_2\bullet + ArCH_2\bullet \longrightarrow ArCH_2-CH_2Ar$$

$$Ar\overset{\bullet}{C}H\overset{\oplus}{S}(CH_3)_2 + Ar\overset{\bullet}{C}H\overset{\oplus}{S}(CH_3)_2 \longrightarrow \underset{\overset{|}{\oplus S(CH_3)_2}}{ArCH}-\underset{\overset{|}{\oplus S(CH_3)_2}}{CHAr}$$

$$\underset{\overset{|}{\oplus S(CH_3)_2}}{ArCH}-\underset{\overset{|}{\oplus S(CH_3)_2}}{CHAr} + 2\,OH^{\ominus} \longrightarrow ArC\equiv CAr + 2\,S(CH_3)_2$$

RESULTS

Reaction of p-Nitrobenzyldimethylsulfonium Tosylate with Sodium Hydroxide.

In preparation for the analytical investigation, authentic samples of possible products from the reaction of p-nitrobenzyldimethylsulfonium ion with hydroxide ion were needed. p,p'-Dinitrotolane (86) was prepared by light-catalyzed addition of bromine to p,p'-dinitrostilbene (12) and subsequent debromination of the dibromide with potassium hydroxide in an overall yield of 56%. cis-p,p'-Dinitrostilbene (86) was obtained from reaction between p-nitrophenylacetic acid and p-nitrobenzaldehyde in the presence of acetic anhydride and zinc chloride and subsequent decarboxylation in quinoline solution containing small amounts of copper powder. trans-p,p'-Dinitrostilbene resulted from iodine-catalyzed isomerization of the cis-isomer (86). p,p'-Dinitrostilbene oxide was available from earlier studies and the following compounds were available from commercial sources: p,p'-dinitrobibenzyl, p-nitrotoluene, p-nitrobenzaldehyde, p-nitrobenzoic acid, and p-nitrobenzyl alcohol.

Several problems regarding the methods of product analysis arose from the physical properties of trans-p,p'-dinitrostilbene. The compound is only sparingly soluble in most organic solvents, but dissolves readily in hot nitrobenzene. Lack of solubility made it difficult to obtain a well-resolved n.m.r. spectrum for quantitative analysis even at high temperatures and in addition rendered it impossible to use column chromatography as means of good separation.

The high melting point (302-304°) of trans-p,p'-dinitrostilbene combined with its low solubility, initially also seemed to prevent use of gas-liquid chromatography. However, injection of a solution of the material in hot nitrobenzene and use of 5 ft and 18 in columns of 20% SF-96 at 245° surmounted these difficulties. Thin layer chromatography was the method of choice for qualitative identification of products.

It soon became apparent that all three methods, thin layer chromatography, g.l.c. and n.m.r. spectroscopy, were required and were complementary for qualitative and quantitative determination of the various compounds. Identification by mass spectrometry was used for materials which were obtained by preparative thin layer and gas-liquid chromatography.

The material used for product analysis was the crude precipitate from a reaction where a 2 molar solution of sodium hydroxide was added to a solution of p-nitrobenzyldimethylsulfonium tosylate so that the resulting solution was 0.1 molar in salt and 0.2 molar in base. After 1 hr at 100° the reaction mixture was cooled, acidified and the precipitate filtered off.

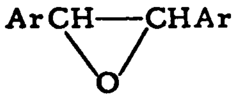
Thin layer chromatograms on the raw product, when analyzed in ultraviolet light, showed the following: trans-p,p'-dinitrostilbene was the only compound noticeable except for a dark residual spot of R_f 0.0-0.1. However, when the raw material was extracted with acetone and the acetone concentrate was analyzed, several spots in the vicinity of trans-p,p'-dinitrostilbene (see Tables IVa-c in experimental section) became apparent. These spots were closely bunched and even overlapping, and in a variety of different eluents on both aluminum oxide and silica gel, their relative positions were interchangeable. Three different eluents were used for identification of each compound. It also became evident that use of different means of detection was advantageous. Ultraviolet irradiation and spraying with 20% sulfuric acid, followed by heating, were used. The compounds detected by thin layer chromatography, were *trans*-*p*,*p*'-dinitrostilbene, *trans*-*p*,*p*'-dinitrostilbene oxide, and traces of *p*,*p*'-dinitrotolane, *p*,*p*'-dinitrobibenzyl and *cis*-*p*,*p*'-dinitrostilbene. In addition, these chromatograms showed a substantial residual spot and trailing in the low R_f value region.

For quantitative evaluation gas-liquid chromatography was used. Internal standards were standardized against a sample of pure *trans*-*p*,*p*'-dinitrostilbene. In a rather surprising turn of events it was found that *trans*-*p*,*p*'-dinitrostilbene was present in about 30-35% yield of the raw material. *cis*-*p*,*p*'-Dinitrostilbene was found to isomerize slowly on the g.l.c. column. It was however confirmed that this compound was present only in traces ($<1\%$) in the reaction under analytical investigation. *p*,*p*'-Dinitrotolane and *p*,*p*'-dinitrobibenzyl had identical retention times and combined, they were present in about 1-2% of the amount of *trans*-*p*,*p*'-dinitrostilbene. A mixture of *p*,*p*'-dinitrotolane and *p*,*p*'-dinitrobibenzyl was obtained by preparative gas-liquid chromatography and the two compounds were identified by their parent peaks in the mass spectrum and by thin layer chromatography. Determination of trans-p,p'-dinitrostilbene oxide was not possible by g.l.c., since the compound seemed to decompose as shown by experiments using authentic material at various temperatures. The amount of trans-p,p'-dinitrostilbene oxide present in the raw product was determined as about 10% by n.m.r. spectroscopy using an internal standard. Gas-liquid chromatography at lower temperature (160°) showed the crude product to contain small amounts of p-nitrobenzaldehyde (2%) and p-nitrotoluene (0.5%). Small amounts of p-nitrobenzyl alcohol (2%), p-nitrobenzaldehyde (0.5%), p-nitrobenzoic acid (2%) and p-nitrotoluene (0.5%) were obtained in the ether extract of the aqueous phase of the reaction mixture. No peaks were observed in the investigation that were not accounted for. Thus, about 50% of the crude product from the reaction of p-nitrobenzyldimethylsulfonium tosylate with sodium hydroxide at 100° had been identified. The results are summarized in Table I.

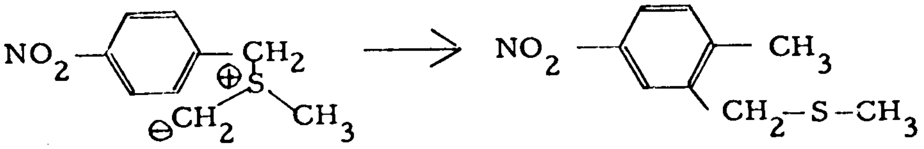
At this point mention should be made of a simple experiment of leading significance. When the crude product was dissolved in the minimum amount of hot nitrobenzene, only trans-p,p'-dinitrostilbene recrystallized on cooling. This finding served as a simple way for the determination of the approximate yield of trans-p,p'-dinitrostilbene and was confirmatory with regard to the results of the g.l.c. analysis. More important, however, is the fact that this behavior of the crude reaction product in nitrobenzene was probably one of the reasons for the erroneous reports of the yields of p,p'-dinitrostilbene (12, 31).

TABLE I

Identified compounds and their respective yields from reaction of *p*-nitrobenzyldimethylsulfonium ion with hydroxide ion in water at 100°.

Compound	Yield (%)
$ArCH=CHAr$	30-35
$ArCH_2-CH_2Ar$	1-2
$ArC\equiv CAr$	
$ArCH_3$	<1.0
	10
$ArCH_2OH$	2
ArCHO	2.5
ArCOOH	2
	~50

In search for other products several possibilities were considered. Sommelet rearrangments of dimethylsulfonium ylids had been reported (87, 88) and in the reaction under investigation such a rearrangement would give rise to the following thioether. No



literature data on this compound were available but it should be conveniently detectable by gas-liquid chromatography and should also have been detected by n.m.r. spectroscopy. Thus its presence in amounts larger than traces was excluded.

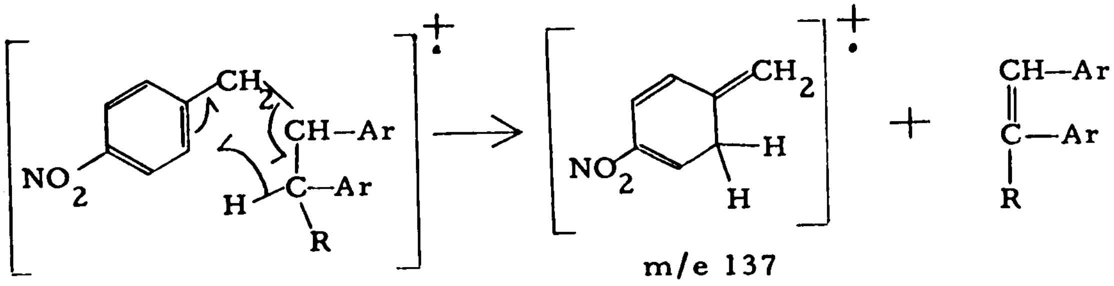
Experiments were carried out to determine the amount of dimethyl sulfide given off in the reaction of the p-nitrobenzyldimethylsulfonium salt with hydroxide ion. Determination was based on the formation of a precipitate in the reaction of dimethyl sulfide with mercuric chloride in aqueous solution (89). An 0.2 molar solution of sodium hydroxide was added dropwise to an 0.1 molar solution of p-nitrobenzyldimethylsulfonium tosylate on the steam bath. The reaction flask was connected by a downward condenser to a series of three flasks which contained mercuric chloride solution. A stream of nitrogen was passed through the system and after 2 hr the white precipitate in the receiving flasks was filtered off, air dried and weighed. In two runs, 82% and 96% yields of dimethyl sulfide were obtained. Experiments with authentic dimethyl sulfide in the same apparatus were carried out by introducing the dimethyl thioether into the cooled system by means of an automatic pipette. The amounts of recovered dimethyl sulfide corresponded to 85-88% yield.

From the determination of the yield of dimethyl sulfide it can be concluded that the reaction of p-nitrobenzyldimethylsulfonium ion with hydroxide ion at 100° produced an almost quantitative yield of dimethyl sulfide. This is confirmed by the failure to observe any thioether, containing the nitrobenzene moiety.

The reaction of p-nitrobenzyl alcohol in 15% aqueous sodium hydroxide for 15 min. at reflux has been shown to afford six derivatives of azobenzene, among them, p-azobenzaldehyde (90). p-Azoxybenzaldehyde was reported to result from reaction of p-nitrobenzylpyridinium bromide in aqueous hydroxide solution (51). Both aldehydes were available from a study described in a following section and analytical studies with regard to their presence in the crude product from the title reaction of this thesis were undertaken. Thin layer chromatography experiments using authentic samples of the two aldehydes and using benzene-ether (5 : 1) as eluent showed that p-azobenzaldehyde (R_f 0.45) and p-azoxybenzaldehyde (R_f 0.3) could not be detected in the crude product. Gas-liquid chromatography at 210° gave sharp peaks for the two authentic aldehydes. The crude reaction product did not show any signs of p-azo- and p-azoxybenzaldehyde.

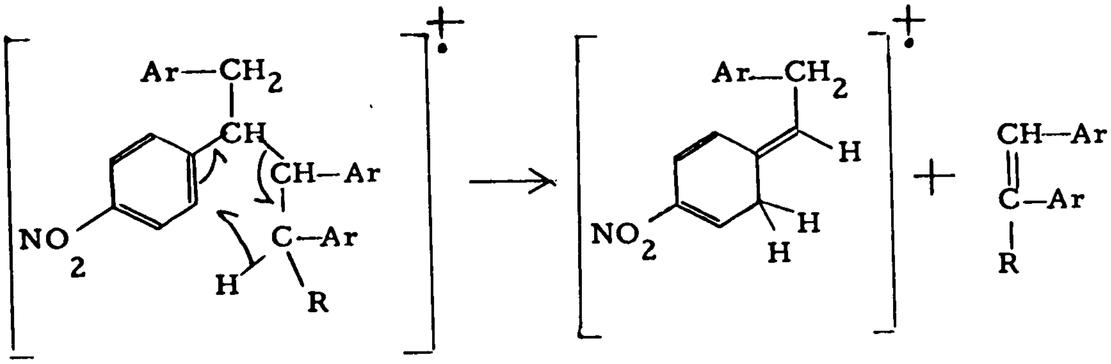
During the analytical work, several observations were made that pointed to a polymeric nature of the unidentified material. Thin layer chromatograms invariably gave a large spot of R_f 0.0 and some trailing in the low R_f value region, when analytical experiments were carried out. Further experiments were undertaken to determine which eluents would move these materials. It was observed that acetone moved all materials; ethyl acetate also moved all materials, but at a slower rate and in a trailing appearance. It was also found that a large amount of acetone would dissolve the crude product. When the crude material was dissolved in hot nitrobenzene, only trans-p,p'-dinitrostilbene would reprecipitate on cooling; it could be separated from the other products by filtration. On concentration of the nitrobenzene solution a yellow material was obtained which on longer standing showed a laquer-like appearance and formed a very hard film on the sides of the flask. The infrared spectrum of this material was very similar to that of trans-p,p'-dinitrostilbene, but showed more pronounced absorption due to the nitro group. The n.m.r. spectrum showed a broad multiplet at τ6-7 assigned to benzylic hydrogens, while the aromatic region was similar to that of p,p'-dinitrostilbene. Integration was not feasible due to low solubility. When compounds obtained on a preparative scale from gas-liquid chromatography were analyzed in the mass spectrum, it was noticed that invariably additional peaks occurred in the region beyond the parent peaks. The column and the mass spectrometer were excluded as sources of these peaks. A collecting tube attached to the gas-liquid chromatograph after trans-p,p'-dinitrostilbene had been collected gradually filled with yellow hard material which in the mass spectrum showed signals up to m/e 460. Preparative thin layer chromatography using benzene as eluent allowed isolation of the material of R_f 0.0. This material melted at 110-120° and when placed in a direct probe of the mass spectrometer at 90° showed practically no ion current while the temperature was raised to 180°. When the sample was heated to 250° a low total ion current resulted, giving rise to a spectrum the main signals of which were at m/e 18, 28, 30, 51, 77, 137, 149 and 150. The intensity beyond the last cited peak was considerably lower and fell off again beyond the last major peaks at m/e 270 and 286. Weak signals were observed up to m/e 450. This behavior is in marked contrast to the properties of *trans*-*p*, *p*'-dinitrostilbene and *p*,*p*'-dinitrobibenzyl when placed into the mass spectrometer. Though its melting point is high (302-304°) *trans*-*p*,*p*'-dinitrostilbene gives a high total ion current at 180° and a clearly defined spectrum. When material of R_f 0.0 was placed into the direct probe of the mass spectrometer at 300°, a strong ion current and a spectrum of high intensity resulted. The most intensive peaks and their relative abundance in relation to the base peaks at m/e 18 and 150 are given: 18 (100), 51 (25), 65 (22), 77 (42), 106 (62), 120 (31), 136 (42), 137 (55), 150 (100), 151 (52), 165 (45), 178 (65), 222 (41), 270 (69), 271 (45), 272 (65), 283 (31), 359 (7) and 420 (14). The last significant peak was at m/e 540 ($<$1); small peaks occurred up to m/e 1000. The peaks at m/e 51, 65 and 77 are typical of aromatic nitro compounds. Most significant with respect to the structure appear to be the peaks at m/e 136, 137, 270, 271 and

272; the m/e 136 ion is assigned to the p-nitrobenzyl radical cation and was shown to be a strong peak in the spectrum of p,p'-dinitrobibenzyl which did not show m/e 137. Thus, the ion at m/e 137 gains special importance with respect to the structure of the material under investigation and is explained by the following rearrangement which requires a γ-hydrogen on the side chain (91).



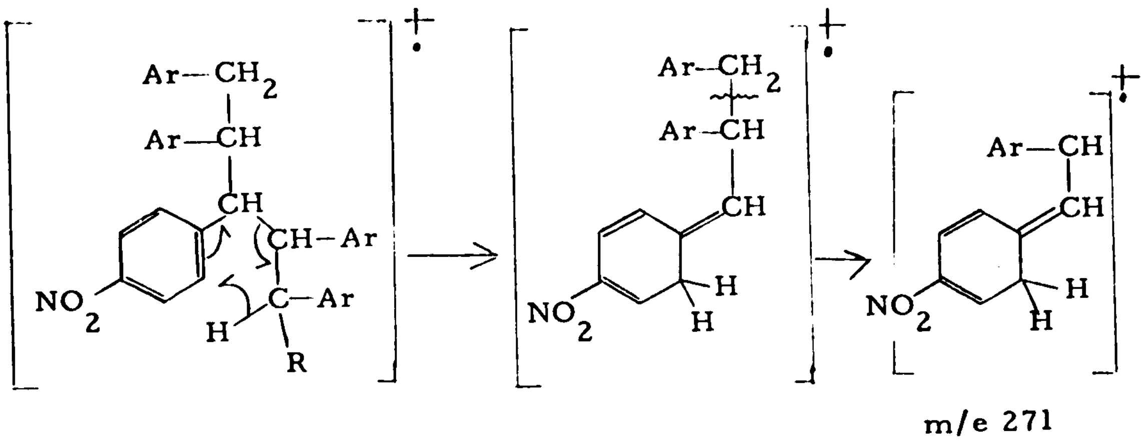
m/e 137

An analogous fragmentation pattern leads to the material of m/e 272.

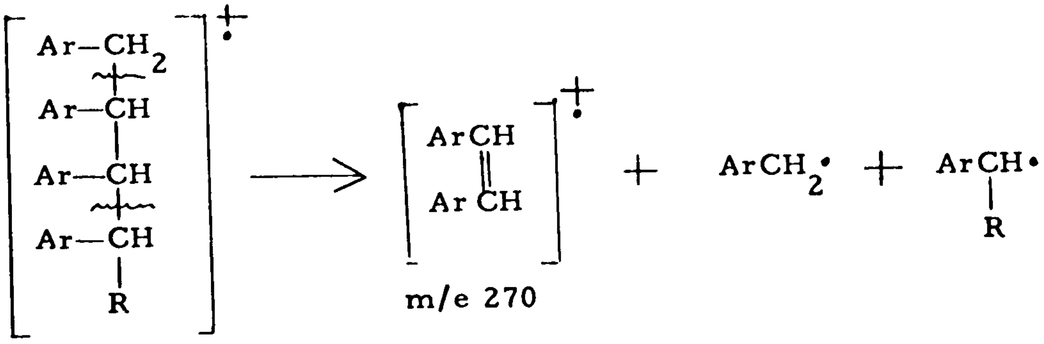


m/e 272

The peak at m/e 271 could arise from rearrangement involving a γ-hydrogen followed by homolytic cleavage of a benzylic bond.



The radical cation of p,p'-dinitrostilbene could be formed by homolytic fission of two benzylic bonds.



Ions at 165 and 178 are also found in the mass spectra of both p,p'-dinitrostilbene and p,p-dinitrobibenzyl. No significant peaks for higher units of m/e 136 were observed that would evidence polymeric material composed of substituted p-nitrobenzyl units. Furthermore, it should be noted that the spectrum was not exactly reproduceable; its basic features remained unchanged, but the relative ratio of abundance was subject to variations dependent upon the lapse of time between introducing the sample and recording the spectrum. Molecular weight determination by vapor pressure osmometry was not feasible due to low solubility of the material of R_f 0.0.

Additional experiments were carried out with regard to the influence of excess oxygen and exclusion of oxygen on the reaction of p-nitrobenzyldimethylsulfonium ion with hydroxide ion at 100°. When the reaction between the salt and hydroxide ion was carried out in dilute solution, 0.01 molar in sulfonium salt, while a rapid stream of air was passed through the reaction mixture, the main product was trans-p,p'-dinitrostilbene oxide (34%). In addition, a total yield of 26% of p-nitrobenzyl alcohol, p-nitrobenzaldehyde and p-nitrobenzoic acid was realized. The amount of trans-p,p'-dinitrostilbene corresponded to 15% yield. Thus, the amount of identifiable products had increased from 50% under normal reaction conditions to 75% in dilution and a stream of air. In an additional experiment it was investigated whether a higher concentration of oxygen would show a further change in product distribution. When the reaction was carried out at a concentration 0.05 molar in salt in a creased flask with high speed stirring in an atmosphere of oxygen, a precipitate was obtained by filtration of the reaction mixture. Thin layer chromatography showed it to be trans-p,p'-dinitrostilbene oxide; no material of R_f 0.0 and no trans-p,p'-dinitrostilbene could be detected. Infrared spectroscopic and g.l.c. analyses were confirmatory. The yield of trans-p,p'-dinitrostilbene oxide amounted to 71%. The filtrate was acidified, extracted with ether, and the ether phase was concentrated. The infrared spectrum showed the material to be p-nitrobenzoic acid with small amounts of p-nitrobenzaldehyde and p-nitrobenzyl alcohol; the total yield of these materials amounted to 24%.

When the reaction was carried out under a protective cover of nitrogen, no change in the yield of trans-p,p'-dinitrostilbene and of p,p'-dinitrotolane and p,p'-dintrobibenzyl was observed compared to the reaction under atmospheric conditions. More significantly, however, the yield of trans-p,p'-dinitrostilbene oxide (10%) remained unchanged. Analytical results are summarized in Table II.

In view of the fact that p-nitrobenzyl alcohol was obtained in small amounts in the reaction of p-nitrobenzyldimethylsulfonium ion with hydroxide ion, it was of interest to see whether the alcohol could have been formed by hydrolysis of the sulfonium salt at 100°. When an aqueous solution of the salt was kept at reflux for 7 hr, no p-nitrobenzyl alcohol could be detected after ether extraction of the cooled solution. Starting material was recovered quantitatively and identified by its n.m.r. spectrum.

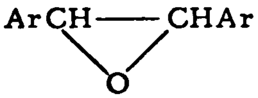
Since only traces of cis-p,p'-dinitrostilbene were obtained in the described reactions, it seemed conceiveable that isomerization might have taken place under reaction conditions. An experiment in which authentic cis-p,p'-dinitrostilbene was subjected to basic reaction conditions for 1 hr demonstrated that no isomerization took place. The cis- isomer was recovered quantitatively and identified by the infrared spectrum.

Reactions of p-Nitrobenzyldiphenylsulfonium Fluoroborate with Base.

In extension of the studies of p-nitrobenzylsulfonium salts with base in cases where the leaving groups were alkyl thioethers and alkyl aryl thioethers (33) it was of interest to learn about the reactions

TABLE II

Summary of the analytical investigations of the reaction of p-nitrobenzyldimethylsulfonium tosylate in aqueous sodium hydroxide solution at 100°.

	reaction conditions, yields (%)			
Compounds	atmospheric conditions	N_2	stream of air	O_2 atmosphere high speed stirrer
ArCH═CHAr	30-35	30-35	15	0
$ArCH_2—CH_2Ar$ ArC≡CAr	1-2	1-2		
$ArCH_3$	<1.0	<1.0		
	10	10	34	71
$ArCH_2OH$	2	2	26	24
ArCHO	2.5	2.5		
ArCOOH	2	2		
	~50	~50	75	95

of the p-nitrobenzyldiphenylsulfonium ion. Since two phenyl groups attached to the sulfur in place of two methyl groups would be expected to have a stabilizing effect on the sulfonium ylid (15), isolation of the p-nitrobenzylidenediphenylsulfurane appeared to be a possibility.

Preparation of p-nitrobenzyldiphenylsulfonium salts had not been reported. In analogy to the preparation of benzyldiphenylsulfonium (25) and alkyldiphenylsulfonium (92) fluoroborates reaction between p-nitrobenzyl bromide, diphenyl sulfide and silver fluoroborate appeared to be the method of choice for the preparation of the p-nitrobenzyldiphenylsulfonium ion. A reaction between these reagents was carried out by slow addition of silver fluoroborate to a solution of excess p-nitrobenzyl bromide in diphenyl sulfide at room temperature. The desired product was separated from the silver bromide by treatment of the filtered precipitate with acetonitrile. The p-nitrobenzyldiphenylsulfonium fluoroborate was isolated by subsequent addition of ether to the acetonitrile solution and was characterized by n.m.r. and infrared spectroscopy and elemental analysis.

In contrast to the p-nitrobenzyldimethylsulfonium tosylate the diphenylsulfonium salt is insoluble in cold water and hydrolyzes readily in hot aqueous solution. The function of diphenyl sulfide as an excellent leaving group became apparent when pyridine was added to a solution of p-nitrobenzyldiphenylsulfonium fluoroborate in acetonitrile. The n.m.r. spectrum of the colorless solution showed a signal for diphenyl sulfide and none for the diphenylsulfonium group.

Since the p-nitrobenzyldiphenylsulfonium fluoroborate was not soluble in water, reactions with sodium hydroxide were carried out in aqueous acetonitrile. These reactions at room temperature were very fast compared to the reaction of the p-nitrobenzyldimethylsulfonium ion with hydroxide ion. Furthermore, the rate of reaction was found to be dependent on the composition of the solvent mixture, being faster in a mixture rich in water. Quantitative yields of mixtures of cis- and trans-p,p'-dinitrostilbene were obtained in these reactions. The cis- isomer was identified by thin layer chromatography, g.l.c. and infrared spectroscopy. The amount of cis-p,p'-dinitrostilbene was as high as 50%. Quantitative yields of p,p'-dinitrostilbene, high amounts of the cis- isomer and very fast reaction rates are features that distinguish the p-nitrobenzyldiphenylsulfonium ion clearly from the p-nitrobenzyl alkyl sulfonium ions in the reactions with hydroxide ion.

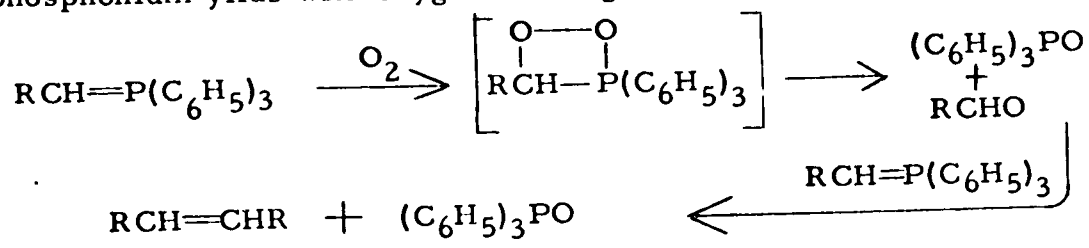
The high reactivity of the diphenylsulfonium ylid was also demonstrated in reactions of p-nitrobenzyldiphenylsulfonium fluoroborate with base in an anhydrous medium. A solution of the p-nitrobenzyldiphenylsulfonium ion in acetonitrile was added slowly with exclusion of light to a slurry of sodium hydride in acetonitrile at room temperature. After 45 min. the reaction mixture was quenched by pouring it into an aqueous solution of excess fluoroboric acid. A yellow precipitate was obtained by filtration and identified as trans-p,p'-dinitrostilbene, 63% yield. On standing, a yellow syrup-like material separated from the filtrate and was shown by thin layer chromatography to be a mixture of material of R_f 0.0 and components of trailing appearance in the low R_f value region. Small amounts of cis- and trans-p,p'-dinitrostilbene could be identified in the syrup-like material by thin layer chromatography and g.l.c. The infrared spectrum of the material showed pronounced absorption due to the nitro group. The material was not identified, but is suspected to be of polymeric nature. More significantly with regard to the reactivity of the ylid, it was established that the reaction had gone to completion. On addition of excess sodium hydroxide to the aqueous filtrate no red color was produced and no yellow precipitate was formed.

Another piece of evidence for the reactivity of the diphenylsulfonium ylid was provided when a reaction between the sulfonium salt and sodium hydride in acetonitrile was monitored by n.m.r. spectroscopy. Immediately after mixing of the reagents a strong peak at τ 3.03 due to diphenyl sulfide appeared. No peaks due to the diphenylsulfonium group at τ 2.58 and to the benzylic protons at τ 4.92 were observed. A singlet at τ 2.86 was present initially in an integration ratio of 1:5 compared to the diphenyl sulfide. The signal slowly weakened and had disappeared after 12 min. No other signals were observed during this time. The singlet of transient existence is believed to be due to the diphenyl group of a reaction intermediate, probably the diphenylsulfonium ylid. Signals expected for the nitroaromatic moiety of the ylid could not be observed. This is not surprising considering the low intensity of the transient signal which is assigned to the diphenylsulfonium group representing ten hydrogen atoms and the fact that monitoring conditions were interfered with by effervescence of the solution and precipitation of p,p'-dinitrostilbene.

The experiments concerning the reactions of p-nitrobenzyldiphenylsulfonium ion with base in aqueous and anhydrous media demonstrated the high reactivity of the p-nitrobenzylidenediphenylsulfurane. It appeared that isolation of the ylid at room temperature was precluded. No further experiments with regard to stability and possible isolation of the ylid were undertaken.

A reaction between p-nitrobenzyldiphenylsulfonium fluoroborate and sodium hydroxide in aqueous acetonitrile in the presence of excess oxygen afforded 67% of p,p'-dinitrostilbene and 29% of p,p'-dinitrostilbene oxide. The formation of the epoxide in the presence of excess oxygen was a feature analogous to the findings in the reaction of p-nitrobenzyldimethylsulfonium ion with hydroxide ion.

In this connection it was of interest whether information could be obtained regarding the interaction between molecular oxygen and the systems consisting of the sulfonium ions and base. In the case of phosphonium ylids a tentative suggestion of a four-membered intermediate had been made by Johnson (93) for the reactions of phosphonium ylids with oxygen which gave rise to dimeric olefins.



$$RCH{=}P(C_6H_5)_3 \xrightarrow{O_2} \left[\begin{array}{c} O{-}O \\ RCH{-}P(C_6H_5)_3 \end{array}\right] \longrightarrow \begin{array}{c}(C_6H_5)_3PO \\ + \\ RCHO\end{array} \xrightarrow{RCH{=}P(C_6H_5)_3} RCH{=}CHR + (C_6H_5)_3PO$$

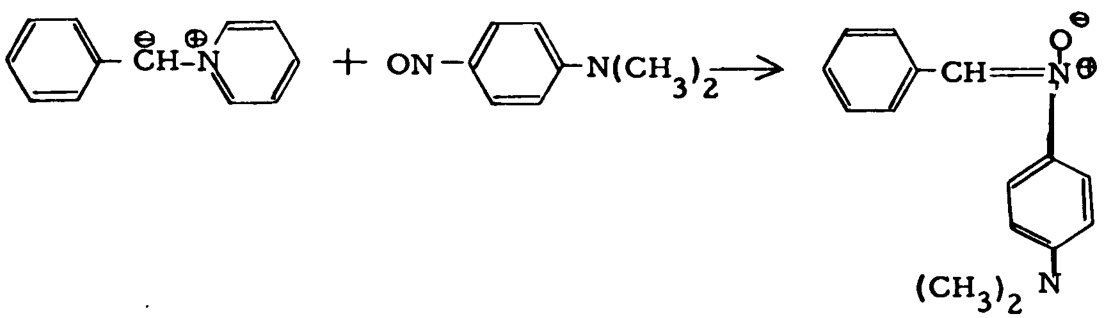
For example, benzylidenetriphenylphosphorane afforded stilbene in 72% yield in the presence of a limited amount of oxygen (94).

Thus, diphenylsulfoxide and dimethylsulfoxide respectively could be expected, if the reactions of phosphonium and sulfonium ylids proceed along similar routes. Since detection of small amounts of dimethylsulfoxide in aqueous solution is difficult, the diphenylsulfonium ion was chosen in search for possible sulfoxide among the reaction products. However, thin layer chromatography and g.l.c. analysis in comparison with authentic diphenylsulfoxide did not reveal the presence of any diphenylsulfoxide in the precipitate or the aqueous phase in the reaction of p-nitrobenzyldiphenylsulfonium ion with sodium hydroxide in the presence of excess oxygen.

Reaction of p-Nitrobenzylpyridinium Bromide with Sodium Hydroxide.

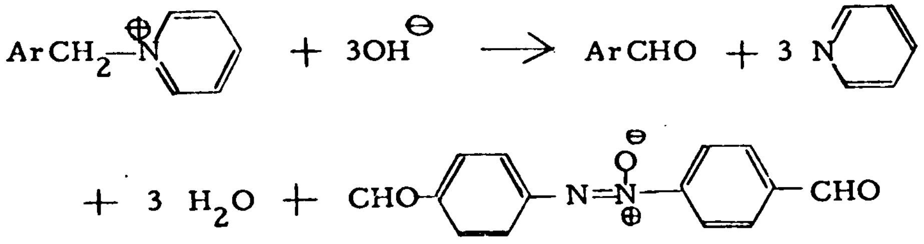
In connection with the study of the reactions of p-nitrobenzylsulfonium salts with aqueous sodium hydroxide, the reports of formation of p-azoxybenzaldehyde from reaction of p-nitrobenzylpyridinium salts with aqueous hydroxide solution were of particular interest (51, 95). It had been known for many years (96) that nitrobenzene is reduced readily to azoxybenzene in a solution of sodium alkoxide in refluxing alcohol. Furthermore, the long-established formation of azoxybenzene from nitrosobenzene and hydroxide ion (97) had most recently been shown by Russell (98, 99) to involve nitrosobenzene radical anions. Russell (99) also demonstrated the intermediacy of radicals in the formation of azoxybenzene from nitrosobenzene and phenylhydroxylamine in the absence of base. Thus, the broad scope of reactions leading to azoxy compounds via radical intermediates became apparent and in extension of the presented proposal (vide infra) of a radical mechanism in the reactions of p-nitrobenzyldimethylsulfonium tosylate with base, it was decided to explore the possibility that the formation of p-azoxybenzaldehyde from reaction of p-nitrobenzylpyridinium ion in aqueous hydroxide solution could involve radical intermediates.

The approach in this investigation was again one of product analysis for the following reasons. The two reports on the reaction of p-nitrobenzylpyridinium ion with sodium hydroxide differed in that one (51) reported p-azoxybenzaldehyde as the sole product, whereas the other report (95) mentioned that substantial amounts of p-nitrobenzaldehyde were formed in addition to the azoxy compound. Furthermore, it was not clear why the reaction of the p-nitrobenzylpyridinium ion should be so conspicuously different from that of p-nitrobenzylsulfonium ions, as both systems contain highly acidic benzylic hydrogens and good leaving groups. This similarity of the two systems is apparent in the reaction of sulfonium (100) and pyridinium (101) ylids with nitroso compounds leading to the formation of nitrones.



Kröhnke (102) had established the reaction of pyridinium ylids with nitroso compounds as a convenient route to sensitive carbonyl compounds which are conveniently obtained by acid hydrolysis of the nitrones. A variety of pyridinium ylids including the one derived from the p-nitrobenzylpyridinium ion, were used (81). In view of this similarity between the sulfonium and pyridinium ylids special attention was to be focused on the possibility that p,p'-dinitrostilbene, for example, could be present in the product of the reaction under investigation.

When the reaction between equivalent amounts of p-nitrobenzylpyridinium bromide and sodium hydroxide in aqueous solution was carried out at room temperature for 24 hr, a yellow precipitate was obtained which was shown to be p-azoxybenzaldehyde containing small amounts of p-nitrobenzaldehyde. The aqueous layer afforded substantial amounts of p-nitrobenzaldehyde. Thin layer and gas-liquid chromatography demonstrated that none of the following compounds were present: p,p'-dinitrostilbene, p,p'-dinitrobibenzyl, p,p'-dinitrotolane, p-nitrotoluene, and p-azobenzaldehyde (103); p-nitrobenzyl alcohol and p-nitrobenzoic acid were found as slight contaminations of the crop of p-nitrobenzaldehyde. The amounts of the two major products corresponded to a quantitative yield. While it was considered fortuitous at first that both materials were obtained in approximately 33 mole percent, repetitions of the experiment confirmed this distribution of products. Determination of the amount of hydroxide ion consumed in the reaction showed that one equivalent of base was used up for one equivalent of *p*-nitrobenzylpyridinium ion and thereby confirmed an earlier report in the literature (95). The following equation accounts for the observed stoichiometry.



Thus, if *p*-nitrobenzaldehyde and *p*-azoxybenzaldehyde are the only products and if the reaction is carried out in a closed system under nitrogen (vide infra), oxidation-reduction considerations require a simple ratio of products.

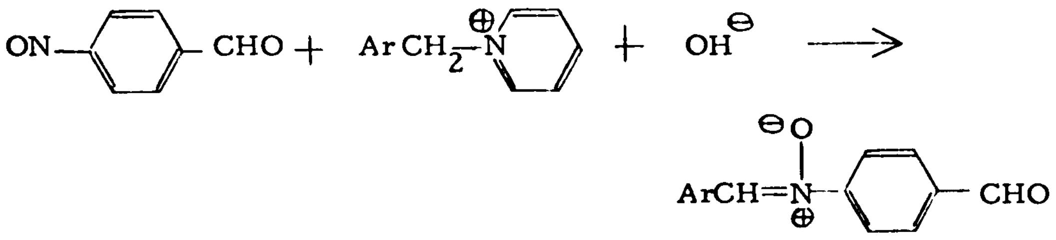
In a variation of reaction conditions, it was demonstrated that a nitrogen cover did not affect the course of the reaction, whereas oxygen inhibited the reaction for several hours, resulting in recovery of starting material. Prolonged exposure of the reaction mixture to oxygen lead to formation of unidentifiable products.

A marked acceleration in the rate of the reaction between *p*-nitrobenzylpyridinium bromide and sodium hydroxide was observed when the reaction was carried out under the influence of light. After 40 min. a quantitative yield of equimolar amounts of *p*-azoxybenzaldehyde and *p*-nitrobenzaldehyde was obtained while under ordinary conditions no sign of precipitation could be detected after a reaction period of 2 hr.

When 0.1 molar solutions of *p*-nitrobenzylpyridinium ion and hydroxide ion were mixed at room temperature in an e.p.r. cell using a flow system, a complex spectrum at a g-value of approximately 2.006 was observed. The spectrum appeared to be the result of the presence of more than one radical species and decayed when the flow of reacting solutions was stopped. When the reactants were allowed to react in approximately 2 molar solutions at a flow rate of zero, a spectrum consisting of three identical and equally intense complex multiplets with a spacing of 13.0 gauss centered at $g = 2.0050$ was observed which decayed within a few minutes. The spectrum showed a minimum of 81 lines and suggested the presence of a nitro radical anion with the unpaired electron on the nitrogen atom and splitting by at least six protons and one nitrogen. No further attempts to elucidate the structure of the species were made, as this would require the use of a computer. Consequently, the obtained e.p.r. spectra were merely taken as a general indication that radical intermediates were present in the reaction of p-nitrobenzylpyridinium ion with hydroxide ion.

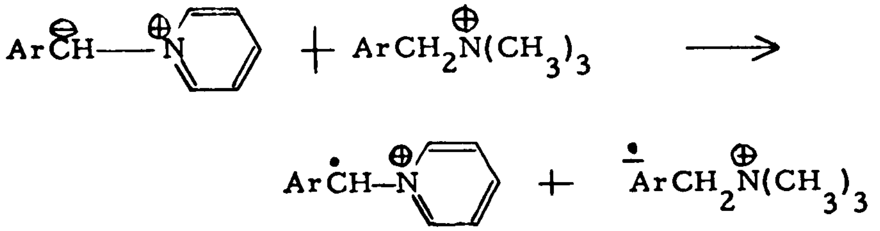
A deuterium exchange experiment in a solution of sodium deuteroxide in heavy water at room temperature indicated that the benzylic hydrogens were exchanged quantitatively within 3 min. This result points to the similarity of the p-nitrobenzylpyridinium and p-nitrobenzylsulfonium systems with regard to the ease of ylid formation.

In the reaction leading to p-azoxybenzaldehyde reduction of the nitro group must take place at some stage of the reaction. It was therefore conceiveable that p-nitrosobenzaldehyde could have been formed as an intermediate. No nitrone had been detected among the reaction products and thus intermediacy of the p-nitrosobenzaldehyde did not seem to be likely. However, it remained to be shown that the reaction of p-nitrosobenzaldehyde with p-nitrobenzylpyridinium ion in the presence of hydroxide ion did produce the nitrone, N-(p-formylphenyl)isoxime of p-nitrobenzaldehyde.



A sample of authentic p-nitrosobenzaldehyde was prepared by reduction of p-nitrobenzaldehyde with zinc in glacial acetic acid followed by oxidation of the intermediate p-hydroxyaminobenzaldehyde with potassium dichromate (104). A reaction between p-nitrosobenzaldehyde and the ylid of the p-nitrobenzylpyridinium ion could not be carried out under the conditions of the reaction of p-nitrobenzylpyridinium bromide with sodium hydroxide, since p-nitrosobenzaldehyde is insoluble in water. Thus, the above reaction was carried out following general procedures for the preparation of nitrones (81). A solvent mixture of 98% ethanol and acetonitrile was employed to insure homogeneity of the solution. Equivalent amounts of reactants with a slight excess of base produced a 66% yield of the nitrone after a reaction period of 24 hr at room temperature. No p-azoxybenzaldehyde could be detected in the reaction product as indicated by g.l.c. analysis. The nitrone was characterized by its infrared spectrum and the melting point of 224-225°. Comparison of the infrared spectrum with that of crude product from the reaction of *p*-nitrobenzylpyridinium bromide with sodium hydroxide before acidification did not show any sign of the presence of the nitrone in the crude product.

In view of the reported inertness of *p*-nitrobenzyltrimethylammonium bromide in aqueous base (31) and the formation of the radical anion of the *p*-nitrobenzyltrimethylammonium ion from reaction of the salt with 2-nitro-2-propyl anion under the influence of light (50), the following question arose. Could the *p*-nitrobenzyltrimethylammonium radical anion undergo a reaction with hydroxide ion? With regard to this question, experiments were conducted employing mixtures of the *p*-nitrobenzylpyridinium and *p*-nitrobenzyltrimethylammonium salts in the presence of base under the influence of light. It was conceiveable that the pyridinium ylid could transfer an electron to the trimethylammonium ion so that the formed radical anion of *p*-nitrobenzyltrimethylammonium ion could react further in the aqueous sodium hydroxide solution.



In a procedure considered superior to that described in the literature (31), p-nitrobenzyltrimethylammonium bromide was prepared in crystalline form and 82% yield by reaction of p-nitrobenzyl bromide with trimethylamine in a dilute ether solution at room temperature.

When mixtures of p-nitrobenzylpyridinium bromide and a five-fold excess of p-nitrobenzyltrimethylammonium bromide were allowed to react with excess hydroxide ion in the presence of a light source for 2 hr, no sign of reactivity of the p-nitrobenzyltrimethylammonium ion could be detected. The reaction between the p-nitrobenzylpyridinium ion and hydroxide ion proceeded in the same manner as in the absence of the p-nitrobenzyltrimethylammonium ion. The n.m.r. spectrum of the residue obtained from concentration of the acidified aqueous phase showed the p-nitrobenzyltrimethylammonium ion as the only material in addition to pyridinium bromide.

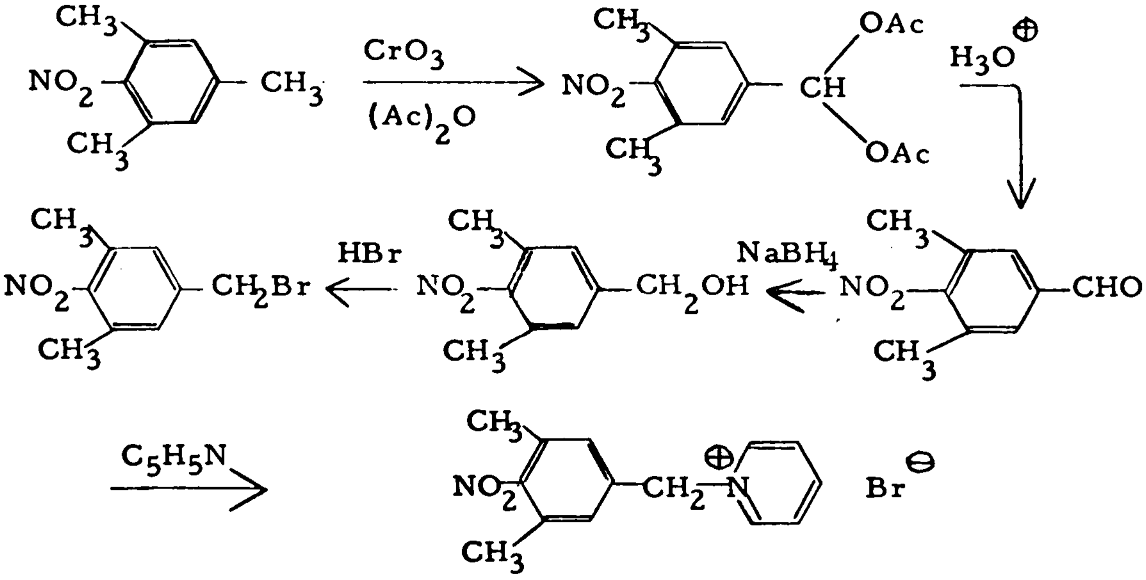
Reactions of 3,5-Dimethyl-4-nitrobenzyl 'Onium Salts with Sodium Hydroxide Ion

In Scheme V (vide infra p. 133) proposed for the reaction of p-nitrobenzylpyridinium bromide in aqueous base the reaction of the protonated form of the radical anion of p-nitrobenzylpyridinium ion with hydroxide ion is a key step leading to the formation of material not containing the nitro group. Loss of hydroxide ion from the nitro group is proposed to proceed in a step involving abstraction of a benzylic hydrogen and formation of a quinoid radical intermediate (step 17 in Scheme V). Coplanarity of the nitro group with the benzene ring would constitute favorable conditions in the transition state of this step of the reaction. If two methyl groups were introduced into the two positions ortho to the nitro group, coplanarity might be rendered difficult.

There is evidence in the literature that introduction of two methyl groups in the two positions ortho to the nitro group affects the spectroscopic properties of the nitro group in aromatic molecules. Ultraviolet studies on Meisenheimer complexes have demonstrated that a nitro group flanked by two methyl groups is completely excluded from participation in resonance (105). Raman spectroscopic studies on nitromesitylene show that the nitro frequency is almost identical to that observed for an unconjugated nitro group (106). These spectroscopic data suggested that the two methyl groups in ortho positions would hinder the nitro group in assuming coplanarity with the phenyl ring, a view also expressed in the literature in connection with studies on the benzoin condensation of 3,5-dimethyl-4-nitrobenzaldehyde (107).

Thus, it was of particular interest to see whether the introduction of two methyl groups into the p-nitrobenzylpyridinium system would affect the reaction of p-nitrobenzylpyridinium ion in aqueous base. Furthermore, introduction of two methyl groups flanking the nitro group would be of general interest with regard to the unique ability of the p-nitrobenzyl system to enter into radical processes.

The preparation of 3,5-dimethyl-4-nitrobenzaldehyde from chromic acid oxidation of nitromesitylene (108) had been reported. This aldehyde seemed to be appropriate starting material for the preparation of the unknown 3,5-dimethyl-4-nitrobenzylpyridinium salt along the following route. Reduction of the aldehyde to the corresponding benzyl alcohol, subsequent formation of the benzyl bromide and finally reaction of the latter compound with pyridine could render the desired material in a convenient manner.



For the preparation of 3,5-dimethyl-4-nitrobenzaldehyde, literature procedures were followed (108). Nitromesitylene was converted into the diacetate of 3,5-dimethyl-4-nitrobenzaldehyde by oxidation with chromic acid in the presence of concentrated sulfuric acid in a mixture of glacial acetic acid and acetic anhydride. The crude diacetate was hydrolyzed in aqueous ethanol containing catalytic amounts of sulfuric acid. The over-all yield of crude aldehyde corresponded to 41.5%. The aldehyde was reduced with sodium borohydride in ethanol solution at room temperature and the crude alcohol was converted into the corresponding bromide by reaction with concentrated hydrobromic acid for 30 min. on a steam bath. The crude bromide was dissolved in a small volume of pyridine and on gentle heating a white precipitate of 3,5-dimethyl-4-nitrobenzylpyridinium bromide was formed, m.p. 251-53°. The over-all yield for the three steps amounted to 62%. The 3,5-dimethyl-4-nitrobenzylpyridinium bromide was characterized by its infrared and n.m.r. spectra and elemental analysis.

With regard to the reactivity of the 3,5-dimethyl-4-nitropyridinium ion towards hydroxide ion, several possibilities had to be considered. Abstraction of a proton from the salt yielding the ylid was expected in the light of the available literature on benzylpyridinium salts (81) and was confirmed by a deuterium exchange experiment, in a solution of sodium deuteroxide in heavy water. After a reaction period of 3 min. at room temperature 63% of the benzylic hydrogens had been exchanged. Thus, any change in mode of reaction of the 3,5-dimethyl-4-nitrobenzylpyridinium ion with hydroxide ion compared to that of the p-nitrobenzylpyridinium ion could be attributed to the effect of the two methyl groups on a stage of the reaction following the ylid formation. To learn about any effect of the methyl groups at a later stage of the reaction was the objective of the investigation, as pointed out earlier with regard to the proposed scheme for the reaction of p-nitrobenzylpyridinium ion with hydroxide ion. Alternatively, it also had to be considered that the hydroxide ion could displace pyridine in the formation of 3,5-dimethyl-4-benzyl alcohol.

After 3,5-dimethyl-4-nitrobenzylpyridinium bromide had been allowed to react with a slight excess of hydroxide ion at room temperature for 60 hr the starting material could be recovered in 83% yield. This was established by n.m.r. analysis using p-nitrobenzyltrimethylammonium bromide as internal standard of the residue obtained from the aqueous solution after acidification and concentration. A slightly yellow color of the solution during the reaction could be noticed, but was rather faint compared to the red color that was observed in the reaction of p-nitrobenzylpyridinium bromide with hydroxide ion which under the employed conditions had led to quantitative formation of products. A trace of an unidentified solid was obtained which in the infrared spectrum showed strong absorption due to the nitro group. No 3,5-dimethyl-4-nitrobenzyl alcohol was formed as demonstrated by the fact that no material was obtained from the ether extract of the aqueous phase.

As irradiation had affected acceleration of the rate of the reaction of p-nitrobenzylpyridinium ion with hydroxide ion, another experiment involving the 3,5-dimethyl-4-nitrobenzylpyridinium ion was carried out under the influence of light. When the 3,5-dimethyl-4-nitrobenzylpyridinium ion and hydroxide ion were allowed to react for 2 hr under irradiation in a nitrogen flushed system, 3,5-dimethyl-4-nitrobenzylpyridinium ion was recovered in 93% yield.

In the reactivity towards hydroxide ion the 3,5-dimethyl-4-nitrobenzylpyridinium ion thus had shown behavior which was expected for benzylpyridinium ions in general and which was in marked contrast to that observed for p-nitrobenzylpyridinium ion. A simple test regarding the question as to whether the 3,5-dimethyl-4-nitrobenzyl system had features that distinguished it from other *para*-substituted benzylic systems was the reaction of the 3,5-dimethyl-4-nitrobenzyldimethylsulfonium ion with hydroxide ion. The reaction of various p-nitrobenzylsulfonium ions with hydroxide ion had given rise to formation of a variety of products as shown in this work and in literature reports (33). By contrast, other benzylic sulfonium ions in reactions with aqueous base had formed exclusively the corresponding benzylic alcohols (32). Thus, 3,5-dimethyl-4-nitrobenzyl alcohol would be expected to be the only product from reaction of the corresponding dimethylsulfonium ion in aqueous base, if the p-nitrobenzyl system carrying two methyl groups in *ortho* position to the nitro group did not exhibit any extraordinary features in its reactivity.

The preparation of the 3,5-dimethyl-4-nitrobenzyldimethylsulfonium ion was achieved using routes analogous to those described for the preparation of the p-nitrobenzyldimethylsulfonium ion. 3,5-Dimethyl-4-nitrobenzyl bromide was dissolved in a mixture of dimethyl sulfide and acetonitrile. After 48 hr the precipitate was filtered off and treated with ether to remove traces of starting material. A 74% yield of 3,5-dimethyl-4-nitrobenzyldimethylsulfonium bromide was realized and the material was identified by its n.m.r. spectrum.

Reaction of the salt with silver tosylate afforded the corresponding sulfonium tosylate in 73% yield. The material was recrystallized from acetonitrile, m.p. 172-74°, and was characterized by its infrared and n.m.r. spectra and elemental analysis.

When the 3,5-dimethyl-4-nitrobenzyldimethylsulfonium tosylate was allowed to react in aqueous sodium hydroxide solution on a steam bath, slow formation of a precipitate took place. After 36 hr the slightly yellowish precipitate was filtered off, m.p. 215-17°. The infrared spectrum showed absorptions due to the nitro group and a number of bands at 880-835 cm^{-1}. The mass spectrum showed a parent peak at m/e 342. The molecular weight pointed to 3,3',5,5'-tetramethyl-4,4'-dinitrostilbene oxide. The pattern of the mass spectrum was compatible with this structure as indicated by comparison with the mass spectrum of *p*,*p*'-dinitrostilbene oxide. The mass spectra of both epoxides were characterized by appearance of cations due to loss of OH(-17), HCO(-29), and OH+NO(-47). No parent peak for the corresponding stilbene was observed. An ether extract of the acidified aqueous reaction mixture afforded small amounts of 3,5-dimethyl-4-nitrobenzyl alcohol as shown by the infrared spectrum of the concentrate. The study of the 3,5-dimethyl-4-nitrobenzyldimethylsulfonium ion is preliminary and was not pursued further, as it became evident that the reaction of this system in aqueous base did not fall into the category of exclusive nucleophilic displacement of dimethyl sulfide by hydroxide ion and did not parallel the reaction of the *p*-nitrobenzyldimethylsulfonium ion in base. It was distinguished from the p-nitrobenzyldimethylsulfonium ion by the fact that no 3,3', 5,5'-tetramethyl-4,4'-dinitrostilbene was obtained in the above reaction. Moreover, the reaction of the 3,5-dimethyl-4-nitrobenzyldimethylsulfonium ion with hydroxide ion was slow compared to the reaction of the corresponding p-nitrobenzylsulfonium ion. 3,5-Dimethyl-4-nitrobenzyldimethylsulfonium ion could be recovered in 45% yield from a reaction with hydroxide ion after 7 hr under conditions where the p-nitrobenzyldimethylsulfonium ion had completely disappeared after 1 hr. The recovery of material was indicated by n.m.r. analysis of the residue obtained from concentration of the acidified aqueous phase of the reaction mixture.

DISCUSSION

Reaction of p-Nitrobenzyldimethylsulfonium Tosylate with Sodium Hydroxide

The investigation into the composition of the product of the title reaction showed that the material which Swain and Thornton (12) reported to be a quantitative yield of p,p'-dinitrostilbene was a complex mixture of compounds. A total of eight different compounds could be identified and these materials were shown to account for half of the product. The remaining 50% of the product are suspected to be of polymeric nature.

Swain and Thornton (12) had weighed the crude precipitate which corresponded to a 100% yield of p,p'-dinitrostilbene and had identified the material after recrystallization from nitrobenzene in the presence of catalytic amounts of iodine as trans-p,p'-dinitrostilbene. It was shown in the present investigation that trans-p,p'-dinitrostilbene is the only component of the crude reaction product that reprecipitates in nitrobenzene on cooling. The fact that the infrared spectrum of the crude product has the same features but in a poorly resolved appearance as the pure trans-p,p'-dinitrostilbene helped to conceal the true nature of the crude product. Thus, only a quantitative comparison of the crude product and the recrystallized material could reveal the imbalance in yield. Reason for concern, however, should have been the wide melting range of the crude product (150-255°) observed by Swain and Thornton. A mixture of cis- and trans-p,p'-

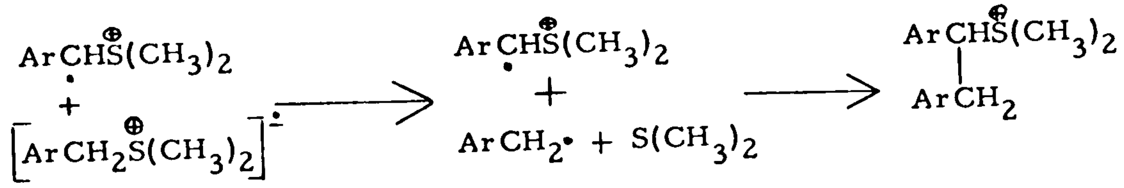
dinitrostilbene was reported and might have been associated with the wide melting range by the authors. Infrared spectroscopic comparisons of the reaction mixture with authentic samples of the cis- and trans-isomers of p,p'-dinitrostilbene (80) would have clearly disclosed the discrepancies.

While caution with respect to the interpretation of these results is in order, two conclusions can be drawn regarding the proposal of a carbene intermediate. Swain and Thornton had based their proposal on kinetic studies which demanded a carbene intermediate in their interpretation. However, in view of the results of the presented product analysis the kinetic studies by Swain and Thornton do not allow any mechanistic conclusions, since in general mechanistic interpretations of rate data are conclusive only when information regarding the stoichiometry and product composition is on hand. Thus, experimental evidence demanding a carbene intermediate does not exist. Secondly, the hypothesis of a carbene of a highly specific nature is rendered untenable in view of the variety of products obtained.

In summary, it can be said that the presented product analysis is in good agreement with the results and observations by Rothberg and Thornton (33). However, a different interpretation of the formation of p-nitrobenzyl alcohol in their studies is suggested. In reactions where aryl alkyl sulfides are the leaving groups, significant amounts of p-nitrobenzyl alcohol were obtained. Formation of the alcohol was rationalized in terms of reaction of the carbene with hydroxide ion or water. To check the possibility that the formation of alcohol was due to nucleophilic attack by water on the sulfonium ion, the authors carried out a blank run of p-nitrobenzylmethylphenylsulfonium ion in water. The salt added to water did not dissolve and the mixture was then heated at 60° for 15 min. to dissolve the salt; an 0.5% yield of alcohol resulted. Corresponding observations were made in this laboratory in connection with studies on p-nitrobenzyldiphenylsulfonium fluoroborate. This salt is insoluble in cold water and inert to it. On heating the salt dissolves and hydrolyzes. Hydrolysis of diphenylsulfonium salts is a general phenomenon (25) and, therefore, hydrolysis of arylmethylsulfonium salts is not unexpected. Thus, the observation that 0.5% of p-nitrobenzyl alcohol was obtained within 15 min. is significant in view of the fact that a 22 hr reaction time in base produced 8-19% of the alcohol. This suggestion of hydrolytic formation of p-nitrobenzyl alcohol is supported by the authors' observation that only traces of alcohol are formed from reaction in base when methyl isopropyl sulfide is the leaving group. The possibility that some alcohol is formed through direct displacement by hydroxide ion on the sulfonium ion cannot be ruled out, however.

The approach to the mechanistic study of the reaction of p-nitrobenzyldimethylsulfonium ion with sodium hydroxide in this work was directed towards the identification of products which might result from radical intermediates. The fact that p,p'-dinitrobibenzyl and p,p'-dinitrotolane were obtained is indeed suggestive of radical intermediates. Both compounds were expected to originate from symmetrical coupling of the respective radicals (Scheme III b, p. 77).

The formation of p,p'-dinitrostilbene could result from direct coupling of the initially formed radicals, followed by elimination of dimethyl sulfide induced by base.

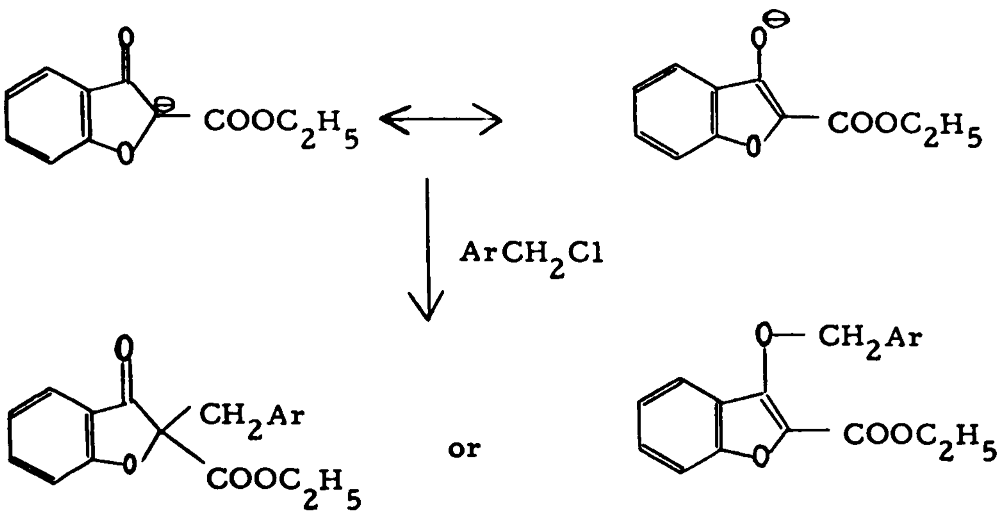


$$\mathrm{Ar\underset{\bullet}{C}H\overset{\oplus}{S}(CH_3)_2} + \left[\mathrm{ArCH_2\overset{\oplus}{S}(CH_3)_2}\right]^{\overset{\bullet}{-}} \longrightarrow \mathrm{Ar\underset{\bullet}{C}H\overset{\oplus}{S}(CH_3)_2} + \mathrm{ArCH_2{\bullet}} + \mathrm{S(CH_3)_2} \longrightarrow \begin{array}{l}\mathrm{Ar\underset{|}{C}H\overset{\oplus}{S}(CH_3)_2}\\ \mathrm{ArCH_2}\end{array}$$

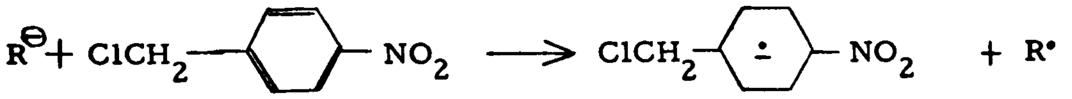
Such a proposal of direct coupling of the initially formed radicals while in each others' proximity can be considered a cage effect and has ample precedence in the decomposition of diazo compounds (109,110).

The distribution of these three products resulting from direct coupling of the initially formed radicals can be regarded as evidence for a cage reaction. If the products were formed by coupling on a statistical basis, 50% of p,p'-dinitrostilbene, 25% of p,p'-dinitrotolane and 25% of p,p'-dinitrobibenzyl out of the total of these three compounds would be expected. The observed product ratio between these compounds, however, is found to be approximately 95% of p,p'-dinitrostilbene to 3-6% of the sum of p,p'-dinitrotolane and p,p'-dinitrobibenzyl.

While this work was in progress, papers by Kornblum (44,45) and Russell (111) appeared in which they independently reached the conclusion that the reaction of the 2-nitro-2-propyl anion with p-nitrobenzyl chloride is a radical chain process involving the attack of the p-nitrobenzyl radical upon the 2-nitro-2-propyl anion. Kornblum (45) studied the effect of cupric chloride on the reaction between the sodium salt of 2-carbethoxy-coumaran-3-one and p-nitrobenzyl chloride, a reaction for which a radical-anion process had been proposed in the formation of carbon alkylation product (44). It was



found that minute amounts of cupric chloride were able to supress the radical-anion reaction while allowing the S_N2 displacement reaction leading to oxygen-alkylate to proceed unchecked. A chain process was proposed :



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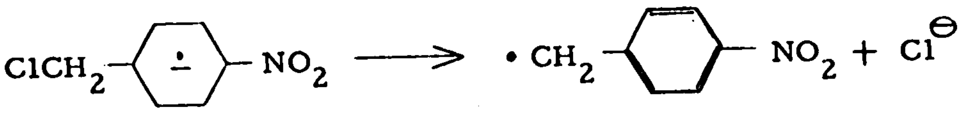
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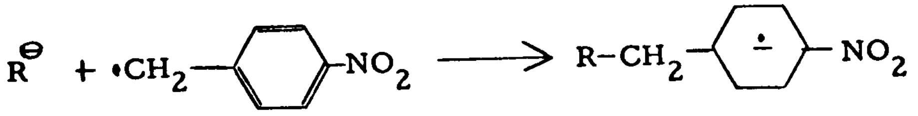
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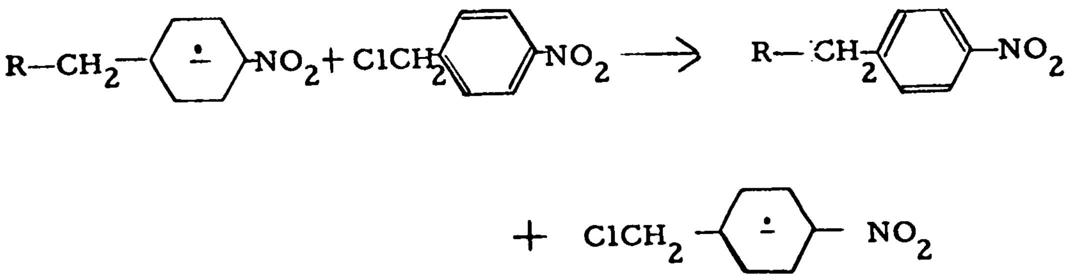
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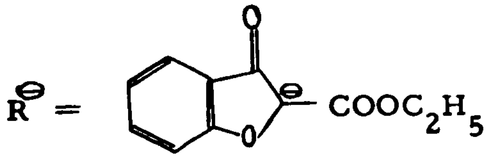
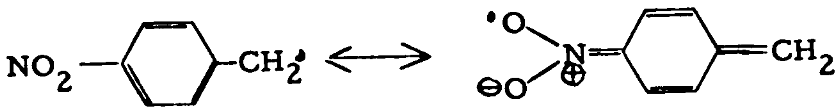


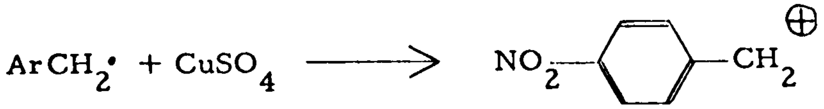
The radical anion of p-nitrobenzyl chloride was assumed to perpetuate the chain by undergoing step 2. Step 3 was considered the key reaction of this chain sequence. The reasonableness of step 3 was pointed out when the various resonance forms contributing to the p-nitrobenzyl radical were considered. It was suggested then



that step 3 resembles the Michael addition of anion $R^{\ominus}$ to a conjugated nitroolefin. Furthermore, it was found that cupric chloride is a far better supressor of carbon alkylation than is cupric sulfate. The proposed chain mechanism provided a simple basis for understanding this disparity in the ability of cupric chloride and cupric sulfate to affect the reaction leading to carbon alkylation. Ligand-transfer oxidation by cupric chloride in the case of p-nitrobenzyl radical should

$$ArCH_2\cdot + CuCl_2 \longrightarrow ArCH_2Cl + CuCl$$

be facile whereas electron-transfer oxidation to the p-nitrobenzyl

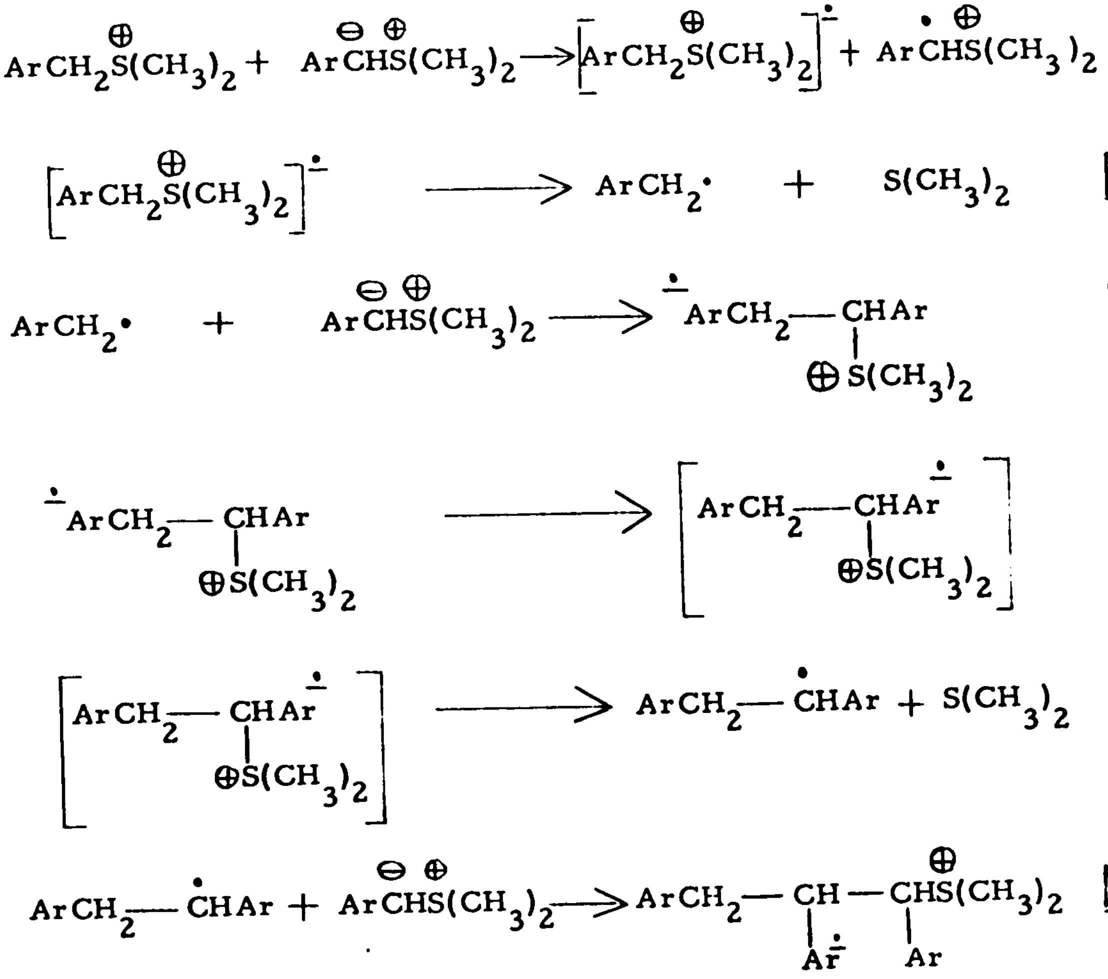


carbonium ion by cupric sulfate should not take place readily.

The study by Russell (111) was undertaken in a series of examinations of reactions of carbanions stable to molecular oxygen. In the presence of oxygen, free radicals formed should be trapped to yield oxidation products rather than coupled products. The 2-nitro-2-propyl anion was found to be stable to oxygen. In the reaction of the 2-nitro-2-propyl anion with p-nitrobenzyl chloride coupled products are not formed in the presence of oxygen. Instead, the 2-nitro-2-propyl anion is converted to acetone and nitrite ion by a free-radical chain oxidation with the absorption of 0.5 mole of oxygen per mole of 2-nitropropane.

If the mechanistic scheme of a radical chain process involving attack of the p-nitrobenzyl radical on the 2-nitro-2-propyl anion would be applied to the reaction under investigation, the following sequence of steps can be written as shown in Scheme IV.

SCHEME IV



$$\mathrm{ArCH_2\overset{\oplus}{S}(CH_3)_2 + Ar\overset{\ominus}{C}H\overset{\oplus}{S}(CH_3)_2 \longrightarrow \left[ArCH_2\overset{\oplus}{S}(CH_3)_2\right]^{\dot{-}} + Ar\overset{\bullet}{C}H\overset{\oplus}{S}(CH_3)_2} \quad [5]$$

$$\mathrm{\left[ArCH_2\overset{\oplus}{S}(CH_3)_2\right]^{\dot{-}} \longrightarrow ArCH_2^{\bullet} + S(CH_3)_2} \quad [6]$$

$$\mathrm{ArCH_2^{\bullet} + Ar\overset{\ominus}{C}H\overset{\oplus}{S}(CH_3)_2 \longrightarrow {}^{\dot{-}}ArCH_2-\underset{\overset{|}{\oplus S(CH_3)_2}}{CHAr}} \quad [7]$$

$$\mathrm{{}^{\dot{-}}ArCH_2-\underset{\overset{|}{\oplus S(CH_3)_2}}{CHAr} \longrightarrow \left[ArCH_2-\underset{\overset{|}{\oplus S(CH_3)_2}}{CHAr^{\dot{-}}}\right]} \quad [8]$$

$$\mathrm{\left[ArCH_2-\underset{\overset{|}{\oplus S(CH_3)_2}}{CHAr^{\dot{-}}}\right] \longrightarrow ArCH_2-\overset{\bullet}{C}HAr + S(CH_3)_2} \quad [9]$$

$$\mathrm{ArCH_2-\overset{\bullet}{C}HAr + Ar\overset{\ominus}{C}H\overset{\oplus}{S}(CH_3)_2 \longrightarrow ArCH_2-\underset{\overset{|}{Ar^{\dot{-}}}}{CH}-\underset{\overset{|}{Ar}}{CH}\overset{\oplus}{S}(CH_3)_2} \quad [10]$$

The intermediate obtained in step 7 is distinguished from the analogous intermediate in the reaction studied by Kornblum (45) and Russell (111) by the fact that the molecule contains a good leaving group. In addition, owing to the presence of an extra electron, this molecule has all the requirements for a reaction to occur in analogy to step 6. An intramolecular electron transfer (step 8) would result in loss of dimethyl sulfide and formation of a p,p'-dinitrobibenzyl radical (step 9). This new radical in turn could undergo reaction with another molecule of the sulfonium ylid and again via intramolecular electron transfer give rise to a radical of higher molecular weight but similar structure as the preceding one. This sequence constitutes a radical chain process and would lead to polymeric material.

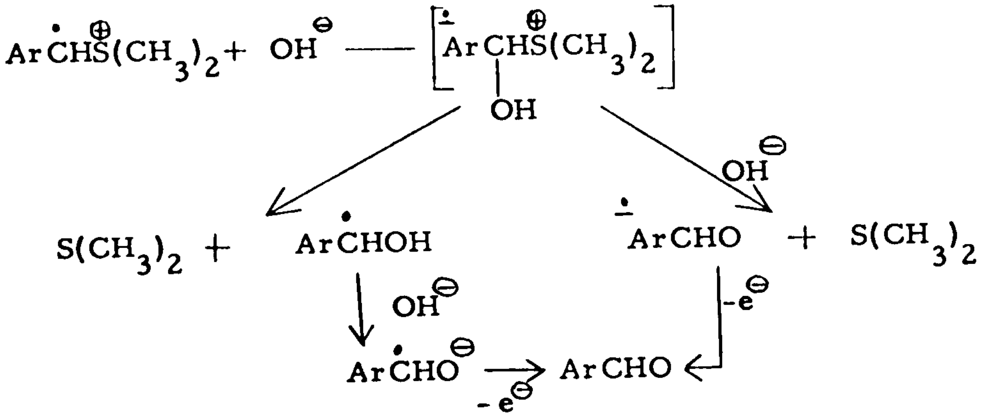
It should be noted that the information with regard to the unidentified product, as presented in the result section, is considered suggestive of and compatible with a polymeric nature of the material. However, no conclusive evidence could be obtained. Furthermore, the nature of the processes leading to termination of the chain and the chain length are unknown and will not be discussed in this work.

In light of the presented proposal of a cage reaction leading to p,p'-dinitrostilbene and a chain reaction leading to polymeric material, only small amounts of symmetrical coupling products would be expected. In fact, the total amount of p,p'-dinitrotolane and p,p'-dinitrobibenzyl was found to be in the order of 1-2%. Exact knowledge of the absolute amounts of these two materials separately would not constitute a mechanistic tool, as both radicals can undergo a number of reactions.

If the reaction leading to unidentified polymeric material involves a radical chain process, the presence of oxygen should have a marked effect on the amount of polymeric material formed. This is in fact observed when the reactions of p-nitrobenzyldimethylsulfonium ion with hydroxide ion are carried out in the presence of excess oxygen. A rapid stream of air through the solution containing the reactants reduced the amount of unidentified material from 50% to 25% of the product mixture. A reaction in oxygen atmosphere did not produce any material of R_f 0.0 in the thin layer chromatogram under analytical conditions. It was also demonstrated that the yield of p,p'-dinitrostilbene was dependent upon the amount of oxygen present. The reaction in the presence of a stream of air yielded 15% compared to 30-35% of p,p'-dinitrostilbene under atmospheric conditions and no p,p'-dinitrostilbene was obtained in the reaction under an oxygen atmosphere. This finding does not militate against the proposal of a cage reaction leading to p,p'-dinitrostilbene. It could simply mean that a reaction between the ylid and oxygen, involving an electron transfer from the ylid to oxygen, is competing successfully with an electron transfer from the ylid to the sulfonium salt. In a pure oxygen atmosphere the reaction between the ylid and oxygen is the predominant one. Extensive research by Russell has provided ample evidence for reactions of anions with oxygen involving electron transfer (112).

The reactions under atmospheric conditions and under a nitrogen atmosphere gave rise to identical products and their relative abundance was not affected. Apparently, oxygen does not interfere with the course of the reaction under atmospheric conditions. This could be explained by the fact that at 100° evaporation of the aqueous solvent provides a protective cover against the atmosphere, especially since the reaction mixtures are not stirred.

A further indication of the presence of radical intermediates is the formation of p,p'-dinitrostilbene oxide when the reaction between p-nitrobenzyldimethylsulfonium ion and hydroxide ion was carried out under nitrogen. The formation of the epoxide is believed to be due to reaction of sulfonium ylid with p-nitrobenzaldehyde. Thus, the question arises how the aldehyde is formed. The following mode of formation is proposed. Reaction between the



radical cation and hydroxide ion leads to a reactive intermediate for which two routes involving proton abstraction by hydroxide ion, loss of dimethyl sulfide and loss of an electron in different orders are available, leading to p-nitrobenzaldehyde. The proposed route to p-nitrobenzaldehyde finds an analogy in the reaction of p-nitrobenzylpyridinium bromide with hydroxide ion under nitrogen. Furthermore, electrostatic considerations make the reaction between the radical cation and hydroxide ion plausible. Steric and electrostatic reasons might be responsible for the fact that the hydroxide ion is evidently successfully competing with the sulfonium ylid in the reaction with the cation radical. The reaction between the sulfonium ylid and the cation radical would lead to polymeric material. In the reaction of the p-nitrobenzyl radical with nucleophiles the hydroxide ion apparently is less able to compete with the ylid as indicated by the low amount of p-nitrobenzyl alcohol formed.

With regard to the proposed carbene mechanism it can be said that the fact that p,p'-dinitrostilbene oxide is obtained from the reaction under nitrogen argues against a carbene intermediate. The reaction of a carbene with hydroxide ion would lead to p-nitrobenzyl alcohol and would not provide any explanation for the formation of p-nitrobenzaldehyde.

On the other hand, how well justified is the proposal of a chain reaction as outlined earlier, leading to what is believed to be polymeric material? If any radical intermediates are involved in the reaction and if the reaction of radicals with anions is an accepted fact, then it seems that a radical chain process in the reaction under investigation is only a logical extension of the proposal by Kornblum (45) and Russell (111) for the reactions of p-nitrobenzyl chloride. Moreover, in a recent study Russell (50) has presented evidence that the p-nitrobenzyldimethylsulfonium ion is capable of undergoing a radical reaction in analogy to p-nitrobenzyl chloride.

Most recently, the reaction of p-nitrobenzyldimethylsulfonium bromide with aqueous base has been investigated by Russell (50) to determine whether the process leading to p,p'-dinitrostilbene proceeds via a free-radical chain mechanism involving the coupling of the p-nitrobenzyl radical with a molecule of ylid similar to the reaction of p-nitrobenzyl chloride with the 2-nitro-2-propyl anion.

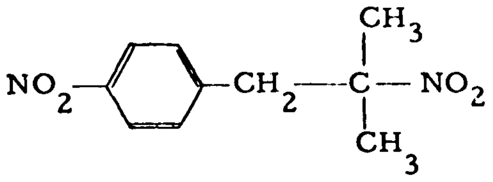
The reaction was found to be catalyzed markedly by light at 12.5° in 50% aqueous ethanol under nitrogen. It was observed that the rate of reaction increased as the percent of alcohol in the solvent was increased. Simultaneously, increasing the percent alcohol resulted in a decreased yield of p,p'-dinitrostilbene. No details were given on the method of identification of p,p'-dinitrostilbene and no side-products were mentioned. Apparently, Russell did not notice anything in disagreement with the claims of exclusive formation of p,p'-dinitrostilbene by Swain and Thornton. When the reaction was carried out in an oxygen atmosphere, yields of 68% of p,p'-dinitrostilbene oxide and 23% of crude p-nitrobenzoic acid were realized. There was no affect on the rate of reaction when a large excess of nitrobenzene was present in solution.

Application of electron paramagnetic resonance techniques satisfactory for the production and detection of the radical anion of the p-nitrobenzyltrimethylammonium ion failed to produce the spectrum of the radical anion of the p-nitrobenzyldimethylsulfonium ion. It was concluded that the sulfonium radical anion must decompose readily to

$$\left[\mathrm{ArCH_2\overset{\oplus}{S}(CH_3)_2}\right]^{\overset{\bullet}{-}} \longrightarrow \mathrm{ArCH_2{\cdot}} + \mathrm{S(CH_3)_2}$$

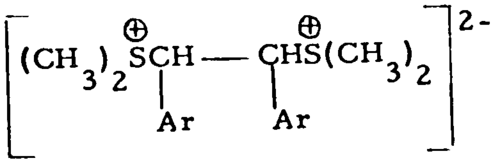
the p-nitrobenzyl radical and dimethyl sulfide.

The reaction of the lithium salt of 2-nitropropane with *p*-nitrobenzyldimethylsulfonium bromide in ethanol produced the carbon-alkylated coupled product in good yield. Moreover, just as with *p*-nitrobenzyl chloride the reaction can be catalyzed by light and inhibited by hexaphenylethane for periods of time dependent upon the concentration of the inhibitor. It was also noted that the yield of coupled product was dependent upon the concentration of inhibitor. This was interpreted as an indication that another process was occurring which consumed reactants but was not affected by the free-radical inhibitor. It was reported that this competing reaction resulted in formation of *p*,*p*'-dinitrostilbene, possibly via a carbene mechanism. The author concluded that in the reaction of *p*-nitrobenzyldimethylsulfonium bromide with aqueous base a free-radical chain mechanism probably is not operative, while the carbene mechanism is not excluded by any of the results.



Do these observations by Russell argue against a radical process and in favor of a carbene intermediate? The fact that *p*,*p*'-dinitrostilbene is formed in the reaction between the lithium salt of 2-nitropropane and *p*-nitrobenzyldimethylsulfonium bromide shows that the sulfonium ylid is formed. The ylid then could compete with the 2-nitro-2-propyl anion to transfer an electron to the sulfonium salt. Thus, the fact that stilbene is obtained in the presence of inhibitor does not exclude a radical pathway if a cage effect is plausible. That a cage effect is not unlikely is indicated by the fact that Russell was not able to achieve any substantial inhibition in the reaction between the sulfonium salt and hydroxide ion.

A suggestion avoiding the necessity of postulating a carbene that does not react with hydroxide ion was put forward by Russell in analogy to the coupling of *p*-nitrotoluene in basic solution to yield *p*,*p*'-dinitrobibenzyl (49). The author suggested the following intermediate, but did not offer any detailed explanation as to how it arises.



$$\left[(CH_3)_2\overset{\oplus}{S}\underset{\displaystyle Ar}{CH}-\underset{\displaystyle Ar}{CH}\overset{\oplus}{S}(CH_3)_2\right]^{2-}$$

However, it was noted that such an analogy has shortcomings in that oxygen increases the yield of *p*,*p*'-dinitrobibenzyl in the coupling of *p*-nitrotoluene, whereas it changes the course of the reaction in the case of the sulfonium salt.

In this connection the validity and reasonableness of a carbene mechanism proposed by Swain and Thornton and considered an alternative to a radical chain process by Russell is to be discussed. The product analysis in this work has shown that the rate studies performed by Swain and Thornton (12) cannot be advanced for any interpretations. These rate data had been the only evidence demanding a carbene intermediate. Attempts by Rothberg and Thornton (33) to provide additional evidence for a carbene intermediate in the form of insertion products or materials containing a cyclopropane ring had met with failure. Absence of substantial amounts of p-nitrobenzyl alcohol had been an intriguing feature of a carbene hypothesis and had led to debatable interpretations when alcohol was formed (33).

In view of the presented product analysis, what merits does a carbene intermediate have? A reasoning that the stilbene formation alone is due to carbene intermediacy while the other observed products are formed by other pathways does not seem justified. How, then, could the formation of p,p'-dinitrotolane and p,p'-dinitrobibenzyl be interpreted? The only instance where a carbene intermediacy in the decomposition of sulfonium ylids seems to be generally accepted gave a clean reaction (67,113). Phenacylidenedimethylsulfurane, thermally stable in boiling benzene, on photolysis in benzene led to nearly quantitative yield of 1,2,3-tribenzoylcyclopropane.

The conclusion by Russell (50) that the reaction leading to p,p'-dinitrostilbene may indeed proceed via a carbene can be commented upon critically in the sense that no explanation is offered as to why a change in mechanism from radical to carbene intermediacy seems plausible to the author, when the reaction partner for the p-nitrobenzyldimethylsulfonium ion is changed from 2-nitro-2-propyl anion to the anion of the p-nitrobenzyldimethylsulfonium ion. Such an explanation could be expected in view of the fact that the studies by Russell were motivated by possible similarities between reactions of 2-nitro-2-propyl anion with p-nitrobenzyl chloride and the reaction of the sulfonium ylid with the sulfonium ion.

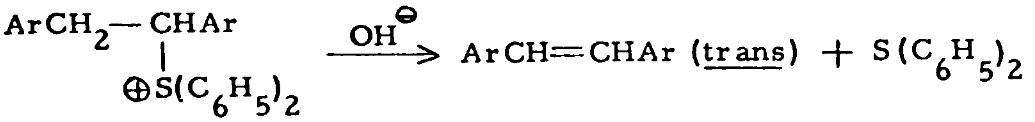
Drawing from the findings in this work one has to be especially careful in assessing the validity of a carbene hypothesis as one is not in a position to reiterate the claims by Swain which seemingly have found acceptance in the literature. Considering the reviewed literature and observations and results in this work, no evidence suggestive of a carbene intermediate can be advanced. However, no direct evidence against a carbene intermediacy has been found either.

Summarizing these studies on the reaction of p-nitrobenzyldimethylsulfonium ion with hydroxide ion in this work, it can be said that the proposed radical mechanism can account for all products observed in a plausible manner. While the studies by Kornblum provide mechanistic precedence for the mechanism proposed in this work, the particular system under investigation constitutes a new type of reaction in which chain and direct coupling reactions are competing with each other. Some of the factors governing the relative proportion of direct coupling and chain processes are the stability of the various radical intermediates, the efficiency of the cage, and the reactivity of the ylid, either as an electron donor or as a nucleophile. However, no studies pertaining to these aspects were undertaken in the present work.

Reactions of p-Nitrobenzyldiphenylsulfonium Fluoroborate with Base

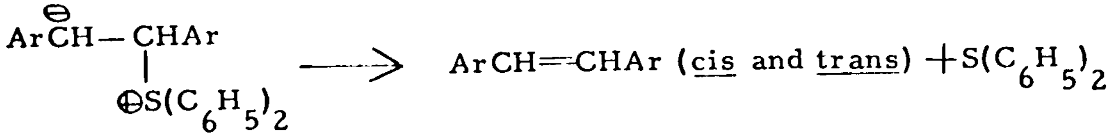
The studies on the p-nitrobenzyldiphenylsulfonium system were undertaken, as pointed out earlier, in extension of investigations on the corresponding dimethyl- and alkylphenylsulfonium systems (33). While the ease of hydrolysis of the *p*-nitrobenzyldiphenylsulfonium ion is in line with literature reports (25), the results from the reaction of the diphenylsulfonium ion with hydroxide ion are in distinct contrast to those obtained from reactions of the *p*-nitrobenzylsulfonium ions mentioned above.

In the reaction of the *p*-nitrobenzyldiphenylsulfonium salt with hydroxide ion three striking features deserve comment: the rate of reaction, the quantitative yield of identified products and the large amount of *cis*-*p*,*p*'-dinitrostilbene formed. The fact that the reaction is very much faster than that of the corresponding dimethylsulfonium ion is surprising. The first intermediate in the reaction, the sulfonium ylid, is expected to be more stable in the case where the two sulfur substituents are phenyl groups in analogy to the observations on phosphonium ylids (15). The fact that a yield of up to 50% of *cis*-*p*,*p*'-dinitrostilbene is obtained, seems to exclude a mechanism involving elimination of diphenyl sulfide from a dimeric sulfonium salt. Such



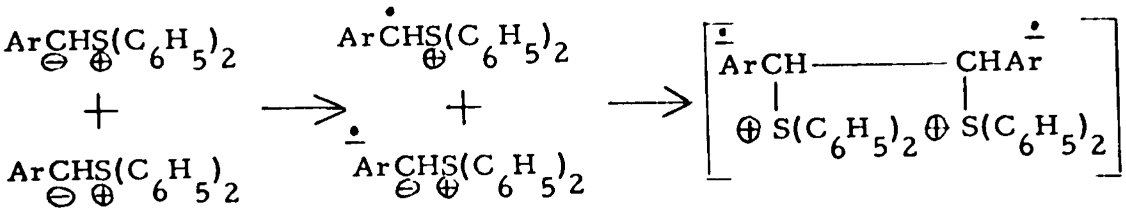
$$\mathrm{ArCH_2{-}\underset{\oplus S(C_6H_5)_2}{\underset{|}{C}}HAr} \xrightarrow{OH^{\ominus}} \mathrm{ArCH{=}CHAr}\ (\underline{\mathrm{trans}}) + \mathrm{S(C_6H_5)_2}$$

an elimination would be expected to give predominantly the *trans*-isomer. Formation of *cis*-*p*,*p*'-dinitrostilbene from a highly reactive intermediate, however, appears plausible. A reactive intermediate could be the following anion of the sulfonium salt which could arise from a carbene pathway as proposed by Swain (12).



$$\mathrm{Ar\overset{\ominus}{C}H{-}\underset{\oplus S(C_6H_5)_2}{CHAr}} \longrightarrow \mathrm{ArCH{=}CHAr}\ (\underline{\text{cis}}\ \text{and}\ \underline{\text{trans}}) + \mathrm{S(C_6H_5)_2}$$

Alternatively, formation of the following intermediate of high reactivity can be offered as a mechanistic suggestion. Two ylid molecules react with each other in an electron-transfer process that would result in formation of a radical cation and the radical anion of the sulfonium ylid. The radical anion of the ylid could function



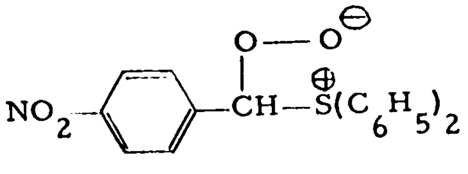
$$\begin{matrix}\mathrm{Ar\underset{\ominus}{C}H\underset{\oplus}{S}(C_6H_5)_2} \\ + \\ \mathrm{Ar\underset{\ominus}{C}H\underset{\oplus}{S}(C_6H_5)_2}\end{matrix} \longrightarrow \begin{matrix}\mathrm{Ar\dot{C}H\underset{\oplus}{S}(C_6H_5)_2} \\ + \\ \overset{\bullet}{\underset{-}{}}\mathrm{Ar\underset{\ominus}{C}H\underset{\oplus}{S}(C_6H_5)_2}\end{matrix} \longrightarrow \left[\begin{matrix}\overset{\bullet}{\underset{-}{}}\mathrm{ArCH} & \text{———} & \mathrm{CHAr}\overset{\bullet}{\underset{-}{}} \\ | & & | \\ \oplus\mathrm{S(C_6H_5)_2} & & \oplus\mathrm{S(C_6H_5)_2}\end{matrix}\right]$$

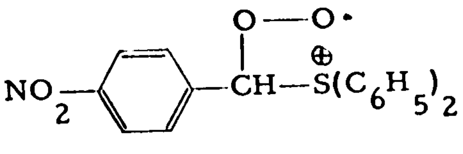
as a nucleophile in a reaction with the radical cation to form a bond between the benzylic carbon atoms of the two molecules. The depicted intermediate would be expected to be highly unstable and to collapse readily to form p,p'-dinitrostilbene without showing definite preference for the formation of the trans- isomer.

How plausible is the formation of such an intermediate which would involve electron transfer and bond formation between two ylids? Proximity of the ylids close enough for electron transfer is reasonable, since the net charge on the ylids is zero. Furthermore, the two radicals formed could be held together by electrostatic forces to allow exclusive reaction between them. The formation of a carbon-carbon bond in analogy to the reactions of nucleophiles and radicals as proposed by Kornblum (45) also appears reasonable. Thus, while the mechanistic suggestion advanced seems to be plausible, it does not offer any explanation for the observed dichotomy between the p-nitrobenzyldiphenyl- and corresponding dimethylsulfonium ions. Furthermore, the increase in reaction rate is surprising and unaccounted for, in light of the expected increase of stability of the diphenylsulfonium ylid. The variation in rate with the composition of the aqueous acetonitrile solvent mixture might be an effect of solvation of the charged intermediates envisaged in the mechanistic proposal. No interpretation for the formation of unidentified material from the reaction of the diphenylsulfonium salt with sodium hydride in acetonitrile can be offered. However, the fact that a high yield of p,p'-dinitrostilbene is obtained in the latter reaction can be considered supporting evidence for a reaction pathway involving reaction between two ylid molecules.

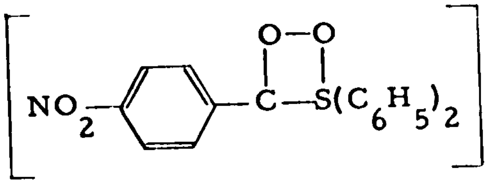
In light of the finding that the reaction of p-nitrobenzyldiphenylsulfonium ion with sodium hydroxide in aqueous acetonitrile is very fast and in view of the suggestion that reaction between sulfonium ylids might take place in anhydrous media, attempts to isolate the ylid did not seem fruitful and were abandoned.

The fact that p,p'-dinitrostilbene oxide was formed in the reaction of p-nitrobenzyldiphenylsulfonium ion with sodium hydroxide in the presence of excess oxygen indicated that molecular oxygen interfered with the course of the reaction. This behavior is reminiscent of the p-nitrobenzyldimethylsulfonium ion. With regard to the nature of the reaction between oxygen and the system consisting of the p-nitrobenzyldiphenylsulfonium ion and hydroxide ion, the possibility of formation of diphenylsulfoxide was considered. Oxygen could be visualized to react with the ylid and radicals formed from the ylid. Such an interaction would lead to the following intermediates I and II.


I


II

Addition of an electron to intermediate II would give the peroxyanion I. It is conceiveable that I then forms a four-membered intermediate or transition state involving tetravalent sulfur. Two modes of decomposition of the four-membered ring could be envisaged, forming p-nitrobenzaldehyde and diphenylsulfoxide in one case, and in a reversal of the formation reaction the ylid and molecular oxygen in the other. No studies in this regard have been reported to date.



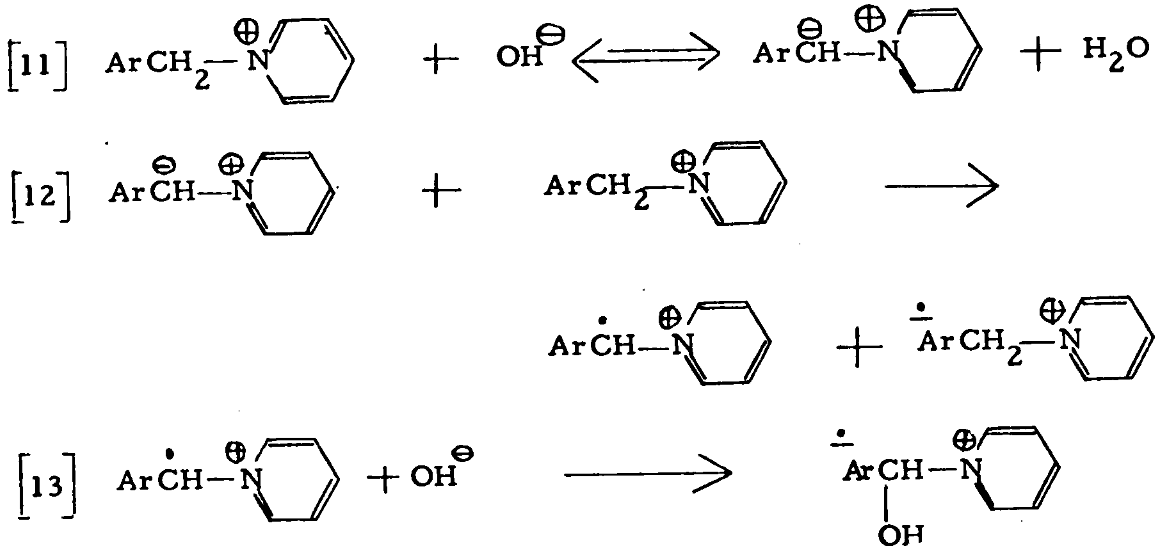
The finding that no diphenylsulfoxide is formed concurs with the well-established distinct difference between the mode of reactions of phosphonium and sulfonium ylids with carbonyl functions, giving rise to olefins and epoxides respectively. The reasons for the difference in mechanism are not fully understood at the present time. In spite of the greater ability of sulfur to stabilize an adjacent carbanion by valence shell expansion (114), sulfur apparently is more reluctant than phosphorus to form a formally bonded intermediate of higher covalency. An additional example of this behavior is provided by the reaction of p-nitrobenzyltriphenylphosphonium bromide in aqueous sodium hydroxide solution, resulting in formation of p-nitrotoluene and triphenylphosphine oxide (31). This reluctance of an oxyanion to attack tervalent sulfur may be due to the difference in the strength of the sulfur-oxygen bond (D.E. 89 kcal/mole) (115) and the phosphorus-oxygen bond (D.E. 128 kcal/mole) (116). In addition, the fact that dimethyl sulfide was found to be a better leaving group than triphenylphosphine (117), had been advanced as an explanation (118) for the difference in the mode of reaction of phosphonium and sulfonium ylids with carbonyl functions. However, in the study under discussion the mode of reaction of a peroxyanion is not influenced by leaving group ability. Moreover, conditions for formation of an intermediate of higher covalency about the sulfur atom are more favorable when two phenyl groups are attached to the sulfur in place of methyl substituents.

Reaction of p-Nitrobenzylpyridinium Bromide with Sodium Hydroxide

The analytical investigations on the reaction of p-nitrobenzylpyridinium bromide with sodium hydroxide in aqueous solution had shown that p-nitrobenzylpyridinium ion and p-nitrobenzyldimethylsulfonium ion in their respective reactions with hydroxide ion gave rise to entirely different products. The report (95) on the formation of a mixture of p-azoxybenzaldehyde and p-nitrobenzaldehyde in the reaction had been confirmed.

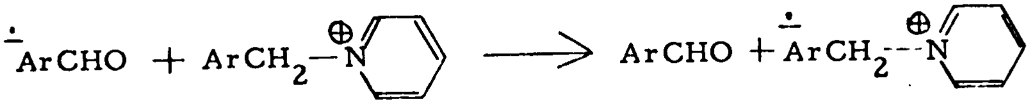
With regard to the question as to how these products arise, several features became apparent that pointed to a radical nature of the reaction. The rate of reaction was increased by light and intermediates that gave rise to e.p.r. spectra were observed. The interference from oxygen, though not understood in detail, seemed to indicate a radical process. The fact that p-nitrobenzaldehyde was formed is also suggestive of a radical mechanism as no other explanation for its formation is readily available. Theoretical considerations which will be outlined below also lend support to the view that radical intermediates are involved in the reaction. The following sequence of steps as outlined in Scheme V could account for the products observed.

SCHEME V

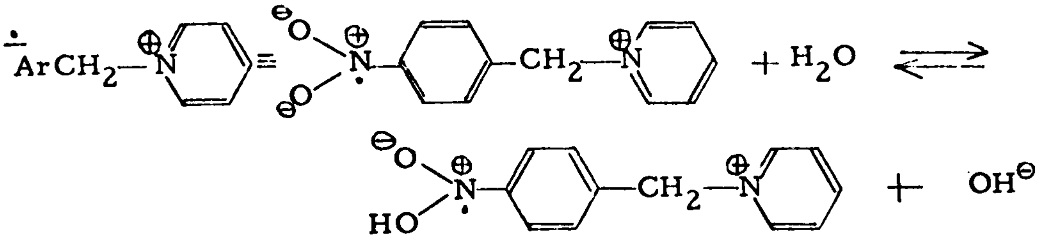


[14]

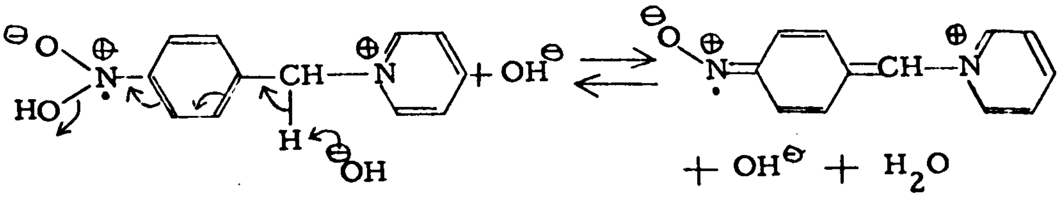
[15]



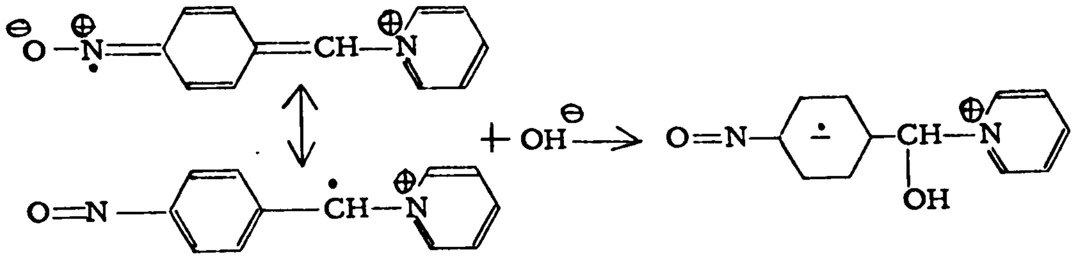
[16]



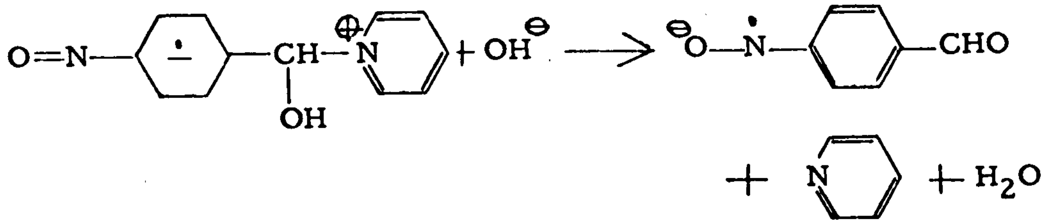
[17]



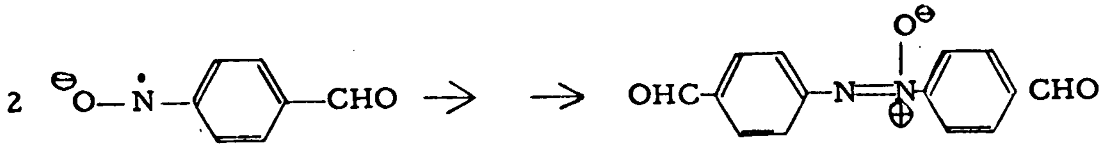
[18]



[19]



[20]

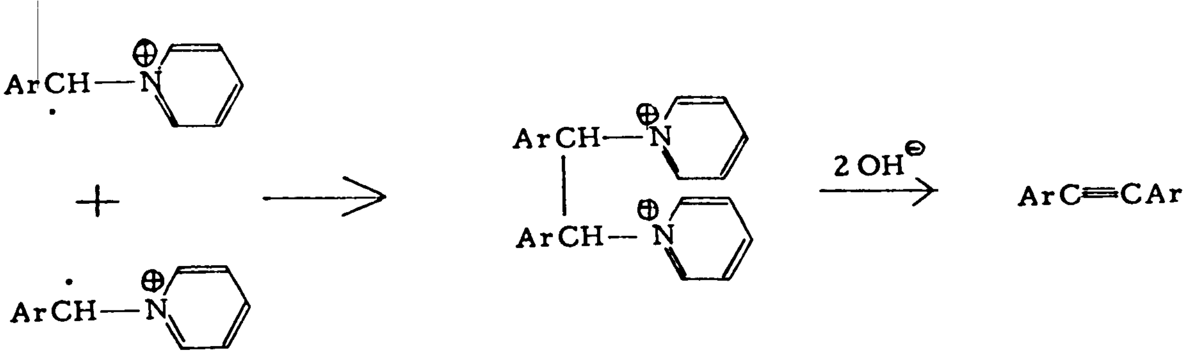


Steps 11 and 12 are in direct analogy to the proposed mechanism for the reaction of the p-nitrobenzyldimethylsulfonium ion with hydroxide ion. Step 13 is the reaction of a nucleophile with a radical as proposed by Kornblum (45) and Russell (111), followed by elimination of pyridine to give the radical anion of p-nitrobenzaldehyde. With regard to step 12, attention should be called to the report (50) that the spectrum of the radical anion of p-nitrobenzyltrimethylammonium ion was observed by electron paramagnetic resonance when p-nitrobenzyltrimethylammonium bromide was irradiated at room temperature in the presence of 2-nitro-2-propyl anion. Step 17 involves attack of hydroxide ion on the protonated form of the radical anion of p-nitrobenzylpyridinium ion to yield an intermediate radical cation which in analogy to the radical cation in step 13 undergoes reaction with hydroxide ion (step 18) to give after subsequent elimination of pyridine the radical anion of p-nitrosobenzylaldehyde. Two of these radical anions couple to give p-azoxybenzaldehyde in a process analogous to that proposed by Russell (99) to be responsible for azoxybenzene formation from nitrosobenzene and phenylhydroxylamine in base.

While the outlined separate steps seem chemically sound and justified in analogy to cited precedence, the question remains why the reaction under investigation shows this behavior. In this connection, a comparison between the reaction of p-nitrobenzyldimethylsulfonium and p-nitrobenzylpyridinium saltswith hydroxide ion is informative. Both systems readily form the respective ylids, whose similarity is apparent in their reaction with nitroso compounds. A difference between the ylids becomes evident in their reactions with carbonyl functions leading to epoxides with sulfonium ylids and in a reversible manner to pyridinium-ethanols with pyridinium ylids (102). Thus, these latter reactions point out that the difference in leaving group ability can distinctly determine the reaction course. The reaction under present investigation can be regarded as an example where both the similarity and the distinct difference between the reactions of sulfonium and pyridinium ylids become apparent. Both ylids are readily formed and capable of donating an electron to the parent compound. At this point the leaving group ability decidedly changes the course of the reaction. The fact that a *p*-nitrobenzyl radical is formed can account for the variety of products obtained from the dimethylsulfonium ion, whereas the two radical intermediates derived from the pyridinium salt undergo reactions with hydroxide ion to give two products.

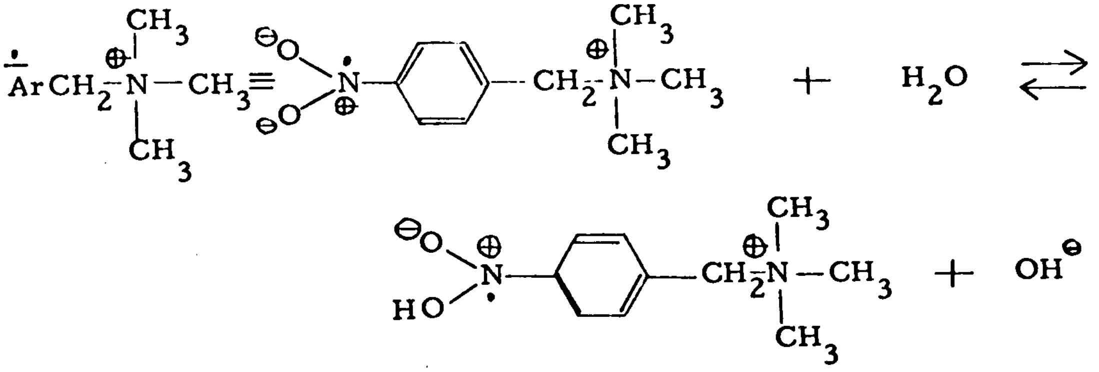
The proposed mechanism does not involve *p*-nitrosobenzaldehyde but the radical anion of *p*-nitrosobenzaldehyde which is believed to be responsible for the formation of the azoxy compound in a fast reaction (99). This is compatible with the finding that *p*-nitrosobenzaldehyde in its reaction with the ylid of the *p*-nitrobenzylpyridinium ion formed a nitrone, which however was not found among the products of the reaction under discussion. Furthermore, it has been shown that nitrosobenzene is a better electron acceptor than nitrobenzene (99), indicating that a radical anion of the *p*-nitrosobenzaldehyde is not an unlikely species in reactions involving electron transfer. The observed stoichiometry of a 1 : 1 ratio of starting materials is in agreement with the proposed mechanism.

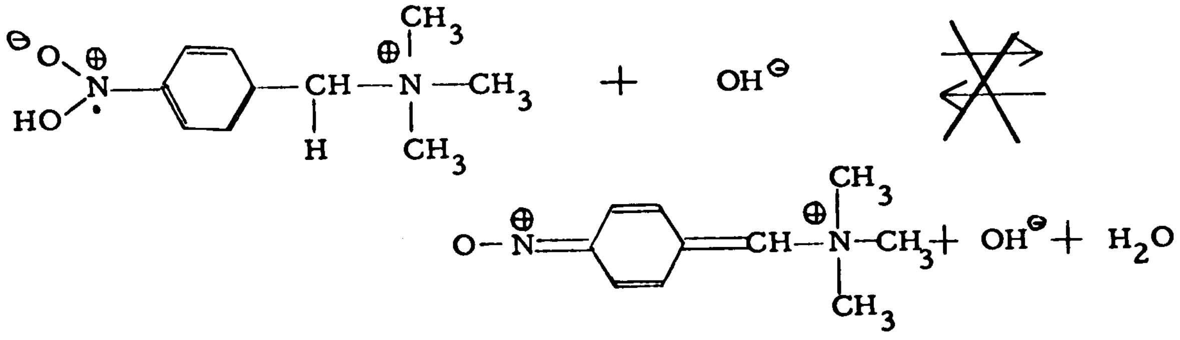
Symmetrical coupling of two molecules of the radical cation



derived from the p-nitrobenzylpyridinium system could upon further action of base give rise to p,p'-dinitrotolane formation. A steric factor might be responsible for the fact that no p,p'-dinitrotolane was formed. This, however, does not offer an explicit answer with regard to the observed p,p'-dinitrotolane formation in the p-nitrobenzyldimethylsulfonium system. Alternatively, it could be suggested that the p-nitrobenzylpyridinium radical cation exhibits a higher degree of reactivity towards hydroxide ion than the corresponding sulfonium radical cation.

With regard to the inertness of the p-nitrobenzyltrimethylammonium ion in an aqueous solution containing p-nitrobenzylpyridinium ion and hydroxide ion, two explanations can be advanced. In the trimethylammonium system the benzylic hydrogens in the ion and the possibly present radical anion are sterically hindered and less activated. Secondly, the formation of a quinoid radical intermediate is less favorable compared to the p-nitrobenzylpyridinium system for lack of resonance through the whole system. Thus, an electron transfer from the p-nitrobenzylpyridinium ylid to the p-nitrobenzyltrimethylammonium ion might have taken place without being made apparent by further reaction of the radical anion of the p-nitrobenzyltrimethylammonium ion with aqueous hydroxide solution. Electron transfer from the radical anion of the p-nitrobenzyltrimethylammonium ion to another electron acceptor in the solution would account for recovery of starting material.





Since no proof was obtained for the formation of the radical anion of the p-nitrobenzyltrimethylammonium ion, these interpretations are not conclusive, but are compatible with the proposed mechanism for the reaction of p-nitrobenzylpyridinium bromide with sodium hydroxide.

Reaction of 3,5-Dimethyl-4-nitrobenzyl 'Onium Salts with Sodium Hydroxide

The experiments described indicate that the p-nitrobenzylpyridinium ion carrying two methyl groups in positions ortho to the nitro group was not consumed in aqueous sodium hydroxide solution, a behavior in marked contrast to that of the p-nitrobenzylpyridinium ion. This difference in reactivity could be accounted for in one of two ways. Firstly, the introduction of two ortho methyl groups deprives the p-nitrobenzyl system of its unique ability among para-substituted benzyl systems to enter into radical processes. Secondly, electron transfer between the ylid and the salt could take place but would not lead to any further reaction. Reversibility of the electron transfer would account for recovery of starting material. A decision between these possibilities would involve the intricate nature of the electron-transfer processes and the reactions of radicals with nucleophiles. Elucidation of the above mentioned possibilities is beyond the scope of this thesis.

The complexity of these processes is indicated by the fact that 3,3',5,5'-tetramethyl-4,4'-dinitrostilbene oxide is formed in the reaction of the 3,5-dimethyl-4-nitrobenzyldimethylsulfonium ion in aqueous base. Formation of the epoxide shows that the 3,5-dimethyl-4-nitrobenzyldimethylsulfonium ion in its reaction with hydroxide ion behaves in no direct analogy to ordinary benzyldimethylsulfonium ions, as 3,5-dimethyl-4-nitrobenzyl alcohol would be expected as sole product; nor is the behavior in direct analogy to the p-nitrobenzyldimethylsulfonium ion, as no correspondingly substituted stilbene is obtained. Failure to detect the dimeric olefin argues against an electron transfer between the 3,5-dimethyl-4-nitrobenzyldimethylsulfonium ylid and the corresponding salt. Lack of coplanarity of the nitro group and the phenyl system is thought to be responsible for this difference in reactivity as no other factors seem to be changed in a comparison of the p-nitrobenzylsulfonium ion and its analogue carrying two methyl groups in positions ortho to the nitro group. The epoxide is believed to be formed by reaction of 3,5-dimethyl-4-nitrobenzaldehyde and the sulfonium ylid. The nature of the formation of the aldehyde, however, is not clear. Possibly the ylid functions as an electron donor in a reaction with oxygen. This would indicate a limited ability of the 3,5-dimethyl-4-nitrobenzyl system to enter into radical processes in basic solutions.

The analytical investigations of the reactions of the various p-nitrobenzyl 'onium ions with aqueous sodium hydroxide revealed that a wide variety of products are formed. While it becomes apparent from the studies in this work and from literature reports (43, 50) that the p-nitrobenzyl system is capable of entering into radical processes characterized by electron transfer, it is also evident that slight variations in the nature of the various p-nitrobenzyl systems can change the course of reactions considerably. Thus, Kornblum (43) had found that reaction of the 2-nitro-2-propyl anion with p-nitrobenzyl chloride afforded almost exclusively carbon alkylation, whereas the reaction with p-nitrobenzyl iodide afforded predominantly oxygen alkylation. The p-nitrobenzyl bromide gave rise to formation of substantial amounts of both carbon and oxygen alkylation products, via pathways involving electron-transfer processes and nucleophilic displacements respectively.

The difference in the reactivity and mode of reactions of the various p-nitrobenzyl 'onium ions are found to be very drastic and more varied than in the p-nitrobenzyl halide series. Even within the category of electron-transfer processes between ylids and 'onium ions a wide variety of products are obtained, the variation depending largely on the leaving group ability. In cases where the radical anions of the p-nitrobenzyl 'onium ions contain a good leaving group as exemplified in the sulfonium ions, products are obtained that originate from carbon-carbon bond formation. When the radical anions are derived from 'onium salts with a poor leaving group, like pyridine, dimeric material is obtained with bond formation between nitrogen atoms of the original nitro groups. Finally, when electron transfer from the ylid to the 'onium ion is inhibited by lack of coplanarity of the nitro group and the phenyl system, a limited ability to enter into radical processes might still prevail. The ylid could function as an electron donor in a reaction with oxygen, judging from the formation of the corresponding stilbene oxide.

EXPERIMENTAL

Reaction of p-Nitrobenzyldimethylsulfonium Tosylate with Sodium Hydroxide

p,p'-Dinitrotolane (86):

This material was prepared by light-catalyzed addition of bromine to p,p'-dinitrostilbene (12) and subsequent debromination of the product with potassium hydroxide, overall yield 56%. Recrystallization from glacial acetic acid afforded yellow crystals, m.p. 211-212° (lit. (86) 210-212°). The infrared spectrum (Nujol) showed bands at 3100, 3080, 1590, 1530, 1500, 1400, 1340, 1300, 1280, 1165, 1105, 1100, 1005, 955, 860, 845, 820, 740, 680 and 630 cm^{-1}. No characteristic C≡C bond stretching could be observed. The n.m.r. spectrum (dimethylsulfoxide) at 100° showed an A_2B_2 pattern centered at τ 2.0 (J = 9 cps).

cis-p,p'-Dinitrostilbene (86):

This compound was obtained from reaction of p-nitrophenylacetic acid and p-nitrobenzaldehyde in the presence of acetic anhydride and zinc chloride and subsequent decarboxylation in quinoline solution containing small amounts of copper powder, 25% yield. Recrystallization from aqueous acetic acid gave yellow crystals, m.p. 185-187° (lit. (86) 185-186°). The infrared spectrum (Nujol) showed bands at 3100, 1590, 1505, 1345, 1330, 1175, 1100, 970, 890, 855, 825, 770, 750, 710, 690, and 665 cm^{-1}. The n.m.r. spectrum (dimethylsulfoxide) at 130° exhibited an A_2B_2 pattern centered at τ 2.0 (J = 9 cps) and a singlet at τ 2.5, ratio 7.82 : 2.06, required 8 : 2.

trans-*p*,*p*'-Dinitrostilbene (86):

cis-*p*,*p*'-Dinitrostilbene (1 g) was heated in nitrobenzene at 200° for 10 min. in the presence of catalytic amounts of iodine. Filtration of the cooled solution afforded 970 mg of *trans*-*p*,*p*'-dinitrostilbene, m.p. 300-302° (lit. (12) 304-306°); the infrared spectrum was confirmatory.

Product Indentification by Thin Layer Chromatography

TABLE III

	Methods of Detection	
Compound	Color under ultraviolet light	Appearance after spraying with 25% sulfuric acid and heating
suspected polymer	yellow-brown	dark brown
 *trans*-$\mathrm{ArCH\underset{O}{-}CHAr}$	black	black
cis- and *trans*-$\mathrm{ArCH{=}CHAr}$	yellow flurorescent	brown
$\mathrm{ArCH_2{-}CH_2Ar}$	black	black
$\mathrm{Ar\,C{\equiv}CAr}$	black	black

TABLE IVa

Absorbent: Aluminum Oxide G

Eluent: benzene-ether (5 : 1)

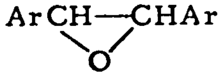
R_f	Compounds
0.0	suspected polymer
0.41	point to where unknown material advances
0.73	*trans*- 
0.76	*cis*- and *trans*-$ArCH{=}CHAr$
0.79	$ArCH_2{-}CH_2Ar$
0.90	$ArC{\equiv}CAr$

TABLE IVb

Absorbent: Silica Gel GF$_{254}$

Eluent: benzene

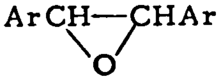
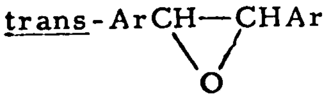
R_f	Compounds
0.0	suspected polymer
0.3	point to where unknown material advances
0.64	*trans*- 
0.69	$ArCH_2{-}CH_2Ar$
0.71	*cis*- and *trans*-$ArCH{=}CHAr$
0.83	$ArC{\equiv}CAr$

TABLE IVc

Absorbent: Aluminum Oxide G

Eluent: benzene-carbon tetrachloride (2 : 1)

R_f	Compounds
0.0	suspected polymer
0.33	 <u>trans</u>-$\mathrm{ArCH{-}CHAr}$ (O bridging)
0.38	<u>trans</u>-$\mathrm{ArCH{=}CHAr}$
0.42	$\mathrm{ArCH_2{-}CH_2Ar}$
0.58	<u>cis</u>-$\mathrm{ArCH{=}CHAr}$
0.64	$\mathrm{ArC{\equiv}CAr}$

<u>Gas-Liquid Chromatography:</u>

All samples were injected as hot nitrobenze solutions, unless otherwise stated. Two 20% SF-96 columns of different lengths (18 in and 5 ft) were used at two different temperatures (160° and 245°). In preparative chromatography runs the material was collected in capillary tubes inserted into the gas outlet. Quantitative evaluation was based on molar response factors which were determined using authentic materials. It was found that <u>p</u>-nitrostilbene, <u>p</u>,<u>p</u>'-dinitrotolane and <u>trans</u>-<u>p</u>,<u>p</u>'-dinitrostilbene had molar response factors within 10% of each other. This was considered sufficiently accurate in the present study so that the molar response factors were considered to be the same for these compounds. Quantitative evaluation of amounts of p-nitrotoluene, p-nitrobenzaldehyde, p-nitrobenzyl alcohol and p-nitrobenzoic acid using benzophenone as internal standard are only approximate, since the first two compounds showed peaks very close to the solvent peak, whereas the latter two compounds had broad trailing peaks with similar retention times. Determination of the amount of p,p'-dinitrostilbene was done on the shorter column using p,p'-dinitrotolane and p-nitrostilbene as internal standards. Quantitative evaluations of the amount of cis-p,p'-dinitrostilbene and the sum of p,p'-dinitrotolane and p,p'-dinitrobibenzyl were carried out on the longer column. Yields were calculated in comparison to the amount of trans-p,p'-dinitrostilbene present in the reaction product.

Experimental Conditions for Gas-Liquid Chromatography on SF-96 Columns

TABLE Va

Column length: 18 in

Temperature: 160°

Compound	Retention time (min.)	Flow rate (ml/min.)
$ArCH_3$	1	70
ArCHO	1.5	70
$ArCH_2OH$	4	70
ArCOOH	5	70

TABLE Vb

Column length: 5 ft

Temperature: 245°

Compound	Retention time (min.)	Flow rate (ml/min.)
cis-$\text{ArCH}{=}\text{CHAr}$	12	100
$\text{ArCH}_2\text{—CH}_2\text{Ar}$	14	100
$\text{ArC}{\equiv}\text{CAr}$	14	100
trans-$\text{ArCH}{=}\text{CHAr}$	20	100

TABLE Vc

Column length: 18 in

Temperature: 245°

Compound	Retention time (min.)	Flow rate (ml/min.)
ArCOOH	2	20
cis-$\text{ArCH}{=}\text{CHAr}$	5	70
$\text{ArCH}_2\text{—CH}_2\text{Ar}$	6	70
$\text{ArC}{\equiv}\text{CAr}$	6	70
trans-$\text{ArCH}{=}\text{CHAr}$	8	70

Reaction of *p*-Nitrobenzyldimethylsulfonium Tosylate with Aqueous Sodium Hydroxide:

p-Nitrobenzyldimethylsulfonium tosylate (3.7 g) was dissolved in

90 ml of hot water and 10 ml of a 2N sodium hydroxide solution was added. The reaction mixture was heated on a steam bath for 1 hr and after cooling was acidified with concentrated hydrochloric acid. The precipitate was filtered off, its weight (1.385 g) corresponding to 102% yield based on p,p'-dinitrostilbene. The infrared spectrum (KBr) showed the features of a poorly resolved spectrum of trans-p,p'-dinitrostilbene, with the bands for the nitro group at 1510 and 1340 cm^{-1} definitely predominant. The n.m.r. spectrum (pyridine-d_5) of the raw product showed broad multiplets at τ6.25 and τ6.85 and singlets at τ5.8 and τ8.0. No integration could be obtained. The two singlets were assigned to trans-p,p'-dinitrostilbene oxide and dimethyl sulfide which was trapped in the precipitate as indicated by comparison with authentic materials. The peak due to dimethyl sulfide disappeared on dissolving the precipitate in hot nitrobenzene. Gas-liquid chromatgraphic analysis showed that the product contained 30-35% of trans-p,p'-dinitrostilbene, traces ($<$1%) of cis-p,p'-dinitrostilbene, 1-2% of p,p'-dinitrotolane and p,p-dinitrobibenzyl combined, 2% of p-nitrobenzaldehyde and 0.5% of p-nitrotoluene. The amount of trans-p,p'-dinitrostilbene oxide present in the raw product was determined as about 10% by n.m.r. spectroscopy (nitrobenzene) using p-nitrotoluene as internal standard. The ether extract of the aqueous phase after drying over magnesium sulfate yielded 80 mg of material. G.l.c. analysis (dissolved in acetone) showed a mixture of p-nitrobenzyl alcohol, p-nitrobenzaldehyde, p-nitrobenzoic acid and p-nitrotoluene; yields based on starting material are 2%, 0.5%,

2%, and 0.5% respectively. Thus, 50% of the material had been identified.

Determination of Yield of *trans*-*p*,*p*'-Dinitrostilbene:

A simple test for the approximate amount of *trans*-*p*,*p*'-dinitrostilbene present in the raw product is based on its insolubility in nitrobenzene at room temperature and its solubility in hot nitrobenzene. Crude product (1 g) was dissolved in the minimum amount of hot nitrobenzene. On cooling a yellow voluminous precipitate appeared; filtration yielded 320 mg (32%) of pure *trans*-*p*,*p*'-dinitrostilbene as indicated by the infrared spectrum and the melting point, 302-303°. On addition of carbon tetrachloride to the filtered solution no further precipitation occurred. Concentration of the solution under vacuum afforded 695 mg of material. The infrared spectrum of the concentrate showed features similar to those of the spectrum obtained for the crude product. Thin layer chromatography showed that *trans*-*p*,*p*'-dinitrostilbene was present only in traces. The n.m.r. spectrum (nitrobenzene) showed a singlet at τ6.2, assigned to *trans*-*p*,*p*'-dinitrostilbene oxide and a broad signal at τ6.5-7 believed to be due to benzylic hydrogens. G.l.c. did not reveal any peaks.

Determination of the Yield of Dimethyl Sulfide (89):

The determination of the amount of dimethyl sulfide produced in the reaction of *p*-nitrobenzyldimethylsulfonium tosylate with hydroxide ion was carried out in the following manner. The salt (3.7 g) was dissolved in 100 ml of water in a 250 ml flask surmounted by a Claisen still-head to which a dropping funnel and a downward condenser were connected. A series of three 50 ml flasks with inlet tubes reaching deep into the flasks was connected to the condenser. The flasks were slightly more than half filled with an aqueous solution of mercuric chloride and were immersed into an ice bath. The dropping funnel contained 100 ml of 0.2 N sodium hydroxide solution. A nitrogen inlet tube was connected to the top of the dropping funnel so that a gentle flow of nitrogen prevailed. The aqueous solution was heated on a steam bath and the basic solution was added dropwise. After 1 hr the dropping funnel was quickly removed and the nitrogen inlet was put in its place so that the end of the tube reached into the solution. After 1 additional hr the white precipitate in the first two receiving flasks was filtered off, thoroughly air dried, and weighed, 4.04 g corresponding to a yield of 86%. A second run gave 3.84 g, 82%. Two test runs with authentic dimethyl sulfide using the same apparatus were carried out. The thioether was introduced into the dropping funnel containing ice water by means of a 1 ml automatic pipette. The resulting mixture was added dropwise to 100 ml of water at room temperature. The amounts of dimethyl sulfide recovered corresponded to yields of 85% and 88% respectively. Calculations were based on a compound of the composition $2(CH_3)_2S \cdot 3HgCl_2$ (89).

Reaction of p-Nitrobenzyldimethylsulfonium Tosylate with Hydroxide Ion in a Stream of Air:

p-Nitrobenzyldimethylsulfonium tosylate (3.7 g) was dissolved in 1 l of hot water in a suction flask on the steam bath. A 2 N sodium hydroxide solution (10 ml) was added and a rapid stream of air was passed through the solution by applying a slight vacuum. The yellow solution slowly turned opaque due to precipitation. After 5 hr the mixture was cooled, filtered, and the precipitate was air dried (900 mg). The aqueous layer was acidified with concentrated hydrochloric acid and extracted with ether. The organic phase was dried over magnesium sulfate and concentrated under vacuum (360 mg). The infrared spectrum indicated a mixture of p-nitrobenzyl alcohol, p-nitrobenzaldehyde and p-nitrobenzoic acid. Gas-liquid chromatography confirmed the presence of these compounds and in addition showed a trace of p-nitrotoluene. The combined yield of these materials amounted to 26%. The filtered precipitate was shown to contain trans-p,p'-dinitrostilbene oxide, trans-p,p'-dinitrostilbene and material of R_f 0.0 by thin layer chromatography. Analysis by n.m.r. spectroscopy (deuterated dimethylsulfoxide) at 130° with trans-dimethystilbene as internal standard showed the material to contain 54% of trans-p,p'-dinitrostilbene oxide. A sample of trans-dimethylstilbene was kindly donated by Mr. J. H. van de Sande. Gas-liquid chromatgraphy demonstrated 21-24% of trans-p,p'-dinitrostilbene, 2% of p-nitrobenzaldehyde and a trace of p-nitrotoluene. The yields of trans-p,p'-dinitrostilbene oxide and trans-p,p'-dinitrostilbene based on starting material are 34% and 15%. Thus, 75% of the material had been accounted for.

Reaction of p-Nitrobenzyldimethylsulfonium Tosylate with Hydroxide Ion in an Atmosphere of Oxygen:

p-Nitrobenzyldimethylsulfonium tosylate (1.85 g) was dissolved in 50 ml of water in a 300 ml three-necked creased flask equipped with a high speed Morton stirrer. The solution was stirred rapidly and heated on a steam bath, while a rapid stream of oxygen was conducted into the solution. An 0.2 N solution of sodium hydroxide (50 ml) was added over a period of 3 min. and after 1 hr the reaction mixture was cooled and a greyish precipitate was filtered off (510 mg, 71%). The infrared spectrum showed the material to be trans-p,p'-dinitrostilbene oxide. Thin layer chromatography was confirmatory and simultaneously indicated the absence of trans-p,p'-dinitrostilbene and any material of R_f 0.0. The aqueous phase was acidified with concentrated hydrochloric acid and extracted with ether. The ether solution was dried over magnesium sulfate and on concentration yieled 179 mg of material. The infrared spectrum showed it to be mainly p-nitrobenzoic acid contaminated by p-nitrobenzaldehyde and p-nitrobenzyl alcohol. The total yield of these materials amounted to approximately 24%.

Reaction of p-Nitrobenzyldimethylsulfonium Tosylate with Hydroxide Ion under Nitrogen:

p-Nitrobenzyldimethylsulfonium tosylate (3.7 g) was dissolved in 90 ml of water in a 250 ml three-necked flask equipped with a dropping funnel, a nitrogen inlet tube and a reflux condenser. This system and a 2 N solution of sodium hydroxide (10 ml) were thoroughly flushed with nitrogen for 5 hr. The basic solution was poured into the dropping funnel and the flask was heated on the steam bath. The base was added rapidly and the mixture was kept on the steam bath under a protective cover of nitrogen for 1 hr. The cooled mixture was acidified with concentrated hydrochloric acid and the precipitate was filtered off (1.322 g). Analysis by n.m.r. spectroscopy (deuterated dimethylsulfoxide) at 130° using trans-dimethylstilbene as internal standard showed trans-p,p'-dinitrostilbene oxide to be present in an amount of 10%; the n.m.r. spectrum also indicated a broad signal in the region of τ 6.1-6.9. G.l.c. analysis indicated 30-35% of trans-p,p'-dinitrostilbene, 1-2% of p,p'-dinitrotolane and p,p'-dinitrobibenzyl, 2% of p-nitrobenzaldehyde and 0.5% of p-nitrotoluene. An ether extract of the aqueous phase after drying over magnesium sulfate yielded 72 mg of material after concentration under vacuum. G.l.c. analysis (dissolved in acetone) showed it to be a mixture of p-nitrobenzyl alcohol (2%), p-nitrobenzaldehyde (0.5%), p-nitrobenzoic acid (2%), and p-nitrotoluene (0.5%).

To ascertain that no oxygen could have been introduced into the system with the nitrogen stream during the reaction, a test run was conducted at room temperature. At this temperature the flask could be stoppered for the period of reaction. The reactants (3 mmole) were thoroughly flushed with nitrogen and allowed to react for 24 hr. Filtration yielded material (340 mg, 84%) which by thin layer chromatography was shown to contain significant amounts of trans-p,p'-dinitrostilbene oxide, in addition to trans-p,p'-dinitrostilbene and material of R_f 0.0.

Reaction of p-Nitrobenzyldimethylsulfonium Tosylate with Water at 100°:

To 50 ml of water was added 500 mg of p-nitrobenzyldimethylsulfonium tosylate and the clear solution was heated at reflux for 7 hr. The cooled solution was extracted with ether. The ether phase, dried over magnesium sulfate, did not produce any material on concentration. The aqueous layer after concentration under vacuum on a steam bath yielded 485 mg of starting material (97%), which was identified by its n.m.r. spectrum (D_2O).

Behavior of cis-p,p'-Dinitrostilbene under Reaction Conditions:

cis-p,p'-Dinitrostilbene (100 mg) was stirred in 50 ml of 0.2 N sodium hydroxide solution at 100° for 1 hr. After the solution had been cooled the precipitate (96 mg) was filtered off and identified as pure cis-p,p'-dinitrostilbene by its infrared spectrum.

Reactions of p-Nitrobenzyldiphenylsulfonium Fluoroborate with Base

p-Nitrobenzyldiphenylsulfonium Fluoroborate:

A mixture of 16 g (0.74 mole) of p-nitrobenzyl bromide and 70 g of diphenyl sulfide was placed into a 500 ml flask which was surmounted by a drying tube. The mixture was stirred magnetically and heated in a water bath until a clear solution was obtained. The water bath was removed and 6.5 g (0.33 mole) of silver tetrafluoroborate was added to the solution in small portions over a period of 0.5 hr. The resulting slurry was stirred for another 0.5 hr and was filtered through a Buchner funnel. The product was dissolved in acetonitrile and freed of silver bromide by filtration. Addition of ether to the solution with cooling in an ice bath yielded white crystals 11.9 g, 88% yield, m.p. 166-167°. The infrared spectrum (Nujol) exhibited bands at 3080, 3070, 1605, 1595, 1575, 1525, 1345, 1180, 1160, 1150 (broad), 990, 900, 870, 855, 800, 750, 740 and 680 cm^{-1}. The n.m.r. spectrum (deuterated acetone) showed a multiplet at τ 2.1 and a singlet at τ 4.18, ratio 14.15:1.98, required 14:2.

Anal. Calcd. for $C_{19}H_{16}BF_4NO_2S$: C, 55.76; H, 3.94; N, 3.42. Found: C, 55.72; H, 4.03; N, 3.42.

Hydrolysis of p-Nitrobenzyldiphenylsulfonium Fluoroborate:

The salt (100 mg) when added to 20 ml of water did not dissolve, but floated on the surface of the liquid. After magnetic stirring for 2 hr the precipitate (91 mg) was filtered off and identified as starting material by its infrared spectrum and melting point (165-166°). When identical quantities of salt and water were used and the mixture was heated on a steam bath, the precipitate gradually disappeared and the mixture turned cloudy. After 15 min. the mixture was rapidly cooled and extracted with ether. When excess sodium hydroxide was added to the aqueous phase, no red color nor yellow precipitate formed indicating the salt had hydrolyzed quantitatively. The dry ether phase contained diphenyl sulfide and p-nitrobenzyl alcohol in equivalent amounts as indicated by the n.m.r. spectrum ($CDCl_3$).

Reactivity of p-Nitrobenzyldiphenylsulfonium Ion towards Pyridine:

A solution of the salt in pyridine was colorless. A solution of the salt in acetonitrile after addition of a few drops of pyridine showed a signal for diphenyl sulfide at τ 3.1 and no signal for the diphenylsulfonium group.

Reaction of p-Nitrobenzyldiphenylsulfonium Fluoroborate with Sodium Hydroxide in Aqueous Acetonitrile:

The salt (409 mg, 1 mmole) was dissolved in 10 ml of acetonitrile and 50 ml of water and 10 ml of 0.2 N sodium hydroxide solution were added. A deep red color developed immediately, followed by appearance of yellow precipitate. After 5 min. the solution was acidified with hydrofluoroboric acid and the precipitate (129 mg) was filtered off, corresponding to a yield of 96%. Thin layer and gas-liquid chromatography and infrared spectroscopy showed it to be a mixture of cis- and trans-p,p'-dinitrostilbene in approximately equal amounts.

A reaction between the salt (409 mg) and base (10 ml of 0.2 N sodium hydroxide solution) in a mixture of 10 ml of water and 50 ml of acetonitrile gave 55 mg of precipitate after 5 min., the material being p,p'-dinitrostilbene (41% yield) with the trans- isomer being present in larger proportion. Addition of excess base to the acidified filtrate yielded a second crop of p,p'-dinitrostilbene (47 mg), indicating that the reaction had not gone to completion after 5 min. reaction time.

Reaction of p-Nitrobenzyldiphenylsulfonium Fluoroborate with Sodium Hydride in Acetonitrile:

Into a 250 ml three-necked flask, equipped with a drying tube, an addition funnel and a nitrogen inlet tube was placed 20 ml of acetonitrile. The system was thoroughly flushed with nitrogen and 41 mg (1.04 mmole) of sodium hydride was added. The resulting slurry was stirred magnetically. A solution of 409 mg (1 mmole) of the salt in 10 ml of acetonitrile was placed into the addition funnel and light was excluded by wrapping the flask with aluminum foil. The salt solution was added slowly over a period of 10 min. and after 45 min. the deep red solution was poured into 100 ml of an aqueous solution of excess fluoroboric acid. A yellow precipitate was obtained by filtration and identified as trans-p,p'-dinitrostilbene by infrared spectroscopy and thin layer and gas-liquid chromatography. The weight of 85 mg corresponded to a yield of 63%. On standing a yellow syrup-like material separated from the filtrate. Thin layer chromatography using benzene-carbon tetrachloride (2 : 1) as eluent showed the material to be a mixture of components of R_f 0.0 and components of trailing appearance in the low R_f value region. Small amounts of cis- and trans-p,p'-dinitrostilbene were also detected by thin layer and gas-liquid chromatography. The infrared spectrum of the syrup-like material showed pronounced absorption due to the nitro group, but did not allow identification of the material. An ether extract of the aqueous phase which had been decanted from the syrup-like material was on concentration shown to be void of material. In an alternate mode of work-up the aqueous phase was extracted with ether immediately after filtration of the reaction mixture. The organic phase was dried over magnesium sulfate and on concentration yielded the above mixture of material in the form of a yellow solid, 48 mg, 35%. Addition of excess sodium hydroxide to the aqueous solution did not result in appearance of red color nor yellow precipitate.

Monitoring of the Reaction of p-Nitrobenzyldiphenylsulfonium Ion with Sodium Hydride by N.M.R. Spectroscopy:

The reaction of p-nitrobenzyldiphenylsulfonium fluoroborate and sodium hydride in acetonitrile was carried out in an n.m.r. tube by adding a solution of the salt in acetonitrile to a slurry of sodium hydride in acetonitrile. A deep red color accompanied by evolution of gas developed immediately after mixing of the reagents. The n.m.r. spectrum showed two singlets at τ 2.86 and τ 3.03 in a ratio of 1 : 5. The signal at τ 2.86 slowly decayed and had disappeared after 12 min. Evolution of gas had almost ceased at that time and ample precipitate had formed in the reaction mixture.

Reaction of p-Nitrobenzyldiphenylsulfonium Ion with Sodium Hydroxide in the Presence of Excess Oxygen:

The salt (200 mg, 0.49 mmole) was dissolved in 10 ml of acetonitrile and added to 250 ml of water. The mixture was placed in a suction flask and after addition of 250 ml of aqueous solution containing 40 mg of sodium hydroxide, a rapid stream of air was passed through the solution. After 3 hr, the solution was acidified with concentrated hydrochloric acid and the precipitate was filtered off (65 mg). The aqueous layer was extracted with ether, dried over magnesium sulfate and concentrated. An oily residue was obtained which by infrared spectrscopy and g.l.c. was shown to be diphenyl sulfide. No diphenylsulfoixde could be detected. Thin layer chromatography on aluminum oxide G with benzene-ether (5 : 1) as eluent did not show any diphenylsulfoxide in the oily residue nor in the precipitate, the R_f for authentic material being 0.4. The precipitate was shown by thin layer chromatography to be a mixture of cis- and trans-p,p'-dinitrostilbene and trans-p,p'-dinitrostilbene oxide. Analysis by n.m.r. spectroscopy (nitrobenzene) using p-nitrotoluene as internal standard indicated 29% of p,p'-dinitrostilbene oxide. G.l.c. analysis showed cis- and trans-p,p'-dinitrostilbene to be present in 6% and 61% respectively.

Reaction of p-Nitrobenzylpyridinium Bromide with Sodium Hydroxide

p-Azoxybenzaldehyde (104):

p-Azoxybenzaldehyde was obtained as a side-product (28% yield) from the reaction of p-nitrobenzaldehyde with zinc in glacial acetic acid followed by oxidation of the intermediate p-hydroxyaminobenzaldehyde with potassium dichromate in dilute sulfuric acid, m.p. 193-194° (lit. (51) 193-194°). The infrared spectrum (Nujol) exhibited a strong band at 1690 cm^{-1} and a weak band at 1560 cm^{-1}, typical of the azoxy group. The n.m.r. spectrum (nitrobenzene) at 100° showed two singlets at τ 0.07 and τ 0.14 of equal intensity.

p-Nitrosobenzaldehyde (104):

This material was prepared in the above reaction (104) in 51% yield, m.p. 138-139° (lit. (119) 137-138°). The infrared spectrum (Nujol) showed strong bands at 1700, 1535, and 1255 cm^{-1}. The n.m.r. spectrum (acetonitrile) was characterized by a singlet at τ-0.2 and a multiplet centered at τ 1.85, ratio 0.98:4, required 1:4.

p-Azobenzaldehyde (103):

This compound was prepared from reaction of p-nitrobenzyl alcohol with arsenic oxide in aqueous potassium hydroxide solution, 36% yield, m.p. 235-237° (lit. (103) 236-238°). The infrared spectrum (Nujol) showed bands at 1700 and 1575 cm^{-1}.

Reaction of p-Nitrobenzylpyridinium Bromide with Sodium Hydroxide:

An 0.1 molar aqueous solution (250 ml) of p-nitrobenzylpyridinium bromide was mixed with an 0.1 N sodium hydroxide solution (250 ml) and the mixture was stirred magnetically at room temperature. The solution turned slightly red; the color gradually deepened and after 2 hr precipitate formed accompanied by the odor of pyridine. After 24 hr the reaction mixture was acidified with hydrochloric acid and the precipitate was filtered off, 2.525 g. G.l.c. analysis showed the product to contain p-azoxybenzaldehyde and p-nitrobenzaldehyde. In addition a third peak was observed which by preparative and analytical g.l.c. was identified as p-azobenzaldehyde in comparison with an authentic sample. Thin layer chromatography and mass spectrometry on the material obtained on a preparative scale were confirmatory. *p*-Azoxybenzaldehyde could also be collected and was identified by the mass spectrum, the melting point of 194° and the infrared spectrum. Injecting a pure sample of *p*-azoxybenzaldehyde into the g.l.c. column resulted in peaks of *p*-azo- and *p*-azoxybenzaldehyde in a ratio similar to that in the raw reaction product. Thin layer chromatography using authentic *p*-azobenzaldehyde (R_f 0.45) for comparison showed the crude reaction product to be free of *p*-azobenzaldehyde. It was thereby established that part of the *p*-azoxybenzaldehyde was transformed into *p*-azobenzaldehyde on the g.l.c. column at 210°. Since the nature of the formation of *p*-azobenzaldehyde on the g.l.c. column is not known, quantitative determination of the *p*-azoxybenzaldehyde was not attempted by g.l.c. Instead, the amount of *p*-nitrobenzaldehyde present in the crude reaction product was determined by g.l.c. analysis at 160° using acetone as solvent and benzophenone as internal standard. The ratio of the molar response factors of *p*-nitrobenzaldehyde and benzophenone was found to be 1.2 : 1. The crude reaction product was found to contain 17% of *p*-nitrobenzaldehyde. The aqueous filtrate was extracted with ether and the dried ether layer on concentration afforded 0.806 g of material which by g.l.c. and infrared spectroscopy was shown to be *p*-nitrobenzaldehyde containing traces of *p*-nitrobenzoic acid and *p*-nitrobenzyl alcohol. The total amounts of *p*-nitrobenzaldehyde corresponded to 8.27 mmoles and the amount of *p*-azoxybenzaldehyde to 8 mmoles. It was established by g.l.c. and thin layer chromatography by comparison with authentic materials that neither of the two product portions contained any of these compounds: p,p'-dinitrostilbene, p,p'-dinitrotolane, p,p'-dinitrobibenzyl, p,p'-dinitrostilbene oxide and p-nitrotoluene.

Determination of Consumption of Base in the Reaction of p-Nitrobenzylpyridinium Bromide with Sodium Hydroxide:

The consumption of base in the reaction between p-nitrobenzylpyridinium bromide and sodium hydroxide was determined by allowing a mixture containing one equivalent of the salt and two equivalents of the base to stand at room temperature for 24 hr in a stoppered flask which had been flushed with nitrogen. The precipitate was filtered off and the filtrate was titrated with 0.10 N hydrochloric acid against Thymol Blue, indicating a consumption of base that corresponded to 1.05 equivalents per equivalent of salt. Duplicate runs were confirmatory.

Reaction of p-Nitrobenzylpyridinium Bromide with Sodium Hydroxide under Nitrogen:

An 0.1 molar aqueous solution (125 ml) of p-nitrobenzylpyridinium bromide and an 0.1 N sodium hydroxide solution (125 ml) were flushed with nitrogen and then mixed under a protective cover of nitrogen. After a reaction period of 24 hr at room temperature in a stoppered flask the reaction mixture was acidified with concentrated hydrochloric acid. The filtered precipitate weighed 1.24 g and contained 20% of p-nitrobenzaldehyde (g.l.c.). The other portion of the precipitate was p-azoxybenzaldehyde as indicated by g.l.c. and infrared spectroscopy. The yield of p-azoxybenzaldehyde corresponded to 31.5%. Ether extraction of the aqueous layer and subsequent concentration of the dried organic phase yielded 0.34 g of p-nitrobenzaldehyde which was identified by the infrared spectrum. The total yield of p-nitrobenzaldehyde amounted to 31.5%.

Reaction of p-Nitrobenzylpyridinium Bromide with Sodium Hydroxide in the Presence of Excess Oxygen:

p-Nitrobenzylpyridinium bromide (4.15 mmole) was dissolved in 41.5 ml of water in a suction flask and 41.5 ml of 0.1N sodium hydroxide solution was added. A rapid stream of oxygen was conducted through the solution. No precipitate formed and after 6 hr the solution was acidified with concentrated hydrochloric acid and concentrated by rotary evaporation. Recrystallization from hot acetonitrile separated the organic salt from sodium chloride. The organic material melted at 219° and weighed 115 mg, 94% recovery. The infrared and n.m.r. spectra showed it to be starting material.

When a similar experiment was conducted for 24 hr, a dark, very hard precipitate formed slowly which was only sparingly soluble in organic solvents. The infrared spectrum (Nujol) showed very strong nitro bands.

Reaction of p-Nitrobenzylpyridinium Bromide with Sodium Hydroxide under Irradiation:

p-Nitrobenzylpyridinium bromide (5 mmole) was dissolved in 50 ml of water and 50 ml of 0.1 N sodium hydroxide solution was added. The mixture was kept at room temperature by means of a water bath and irradiated with a sun lamp. The precipitation set in after 10 min. and after 40 min. the reaction mixture was worked up, yielding 460 mg of a mixture of p-azobenzaldehyde and p-nitrobenzaldehyde by filtration. G.l.c. analysis showed the mixture to contain 15% of p-nitrobenzaldehyde. The aqueous filtrate was extracted with ether and the organic phase was dried over magnesium sulfate. After concentration by rotary evaporation 170 mg of p-nitrobenzaldehyde (infrared spectrum) were obtained. The yield of p-azoxybenzaldehyde amounted to 1.54 mmoles and the yield of p-nitrobenzaldehyde to 1.59 mmoles.

Reaction of p-Nitrobenzylpyridinium Ion and Hydroxide Ion in the E.P.R. Cell of a Flow System:

The reaction between 0.1 molar solutions of p-nitrobenzylpyridinium bromide and sodium hydroxide was carried out in the e.p.r. cell of a flow system. At a flow rate of approximately 1.5 ml/min. a complex spectrum at a g-value of approximately 2.006 was observed. The spectrum decayed when the flow of reactants was stopped. When the reactants were mixed in 2 molar solutions and when the flow of reactants was stopped after mixing, a spectrum consisting of three identical and equally intense complex multiplets with a spacing of 13.0 gauss centered at g = 2.0050 was obtained showing at least 81 lines. The spectrum decayed within a few minutes.

Deuterium Exchange of p-Nitrobenzylpyridinium Ion:

p-Nitrobenzylpyridinium bromide was dissolved in a solution of sodium deuteroxide in deuterated water. The solution was allowed to stand for 3 min. and was then acidified by adding heavy water containing phosphorus pentoxide. The solution was concentrated by rotary evaporation and the n.m.r. spectrum of the concentrate showed identical features to those of authentic material except for complete absence of a signal at τ 4.0. Another sample of a mixture of p-nitrobenzylpyridinium bromide and sodium deuteroxide in heavy water was poured into a solution of p-toluenesulfonic acid in heavy water. The mixture was concentrated to dryness and then treated with a small amount of acetonitrile to dissolve excess p-toluenesulfonic acid. The filtered precipitate was heated to boiling in acetonitrile and the insoluble sodium tosylate was filtered off. On cooling crystals formed, m.p. 221-222°; the infrared spectrum (Nujol) showed in addition to bands assigned to the starting material stretchings at 2070, 2155, 2220 and 2280 cm^{-1}. The bands at 2220 and 22280 cm^{-1} were attributed to hydrogen exchange in the pyridinium ring, a phenomenon also reported in the literature (120).

Preparation of N-(p-Formylphenyl)isoxime of p-Nitrobenzaldehyde:

This compound was prepared following the general procedure by Kröhnke (81). p-Nitrosobenzyldehyde (75 mg) was dissolved in a mixture of 10 ml of 98% ethanol and 10 ml acetonitrile. p-Nitrobenzylpyridinium bromide (150 mg) was dissolved in 10 ml of 95% ethanol and 10 ml of acetonitrile. The solutions were mixed and 0.8 ml of 1 N sodium hydroxide solution was added and the solution was allowed to stand for 24 hr. The deeply colored mixture was poured onto ice water and after 3 days a precipitate had settled and was filtered off.

The material was recrystallized from hot pyridine, yielding 99 mg of a yellow-brown precipitate, 66%, m.p. 224-225° (dec.) (lit. (104) 224°). The infrared spectrum (Nujol) showed bands at 3100, 1685, 1595, 1585, 1540, 1500, 1400, 1335, 1200, 1190, 1160, 1100, 1075, 890, 855, 835, 800 and 740 cm^{-1}. No p-azoxybenzaldehyde was formed as shown by g.l.c. at 210°.

p-Nitrobenzyltrimethylammonium Bromide:

p-Nitrobenzyl bromide (21.6 g) was dissolved in 500 ml of anhydrous ether in a 1 l three-necked flask equipped with a Dry-Ice condenser surmounted by a drying tube and a gas inlet tube connected to a bottle of trimethylamine. The inlet tube did not extend into the liquid. The solution was stirred magnetically at room temperature and a stream of the amine was passed into the reaction vessel. Precipitation occurred immediately and the precipitate was filtered off after 2 hr and washed with ether. Recrystallization from hot acetonitrile yielded 22.5 g of white crystals, m.p. 218-219° (lit. (31) 216-217°), 82%. The n.m.r. spectrum (D_2O) showed an A_2B_2 pattern centered at τ 2.1 and singlets at τ 5.4 and τ 6.9, ratio 4.1 : 9, required 4 : 9 for peaks at τ 2.1 and τ 6.9. Due to interference from the solvent peak no integration could be obtained for the signal at τ 5.4.

Reaction of a Mixture of p-Nitrobenzylpyridinium Ion and p-Nitrobenzyltrimethylammonium Ion in Aqueous Sodium Hydroxide Solution:

A solution of 295 mg (1 mmole) of p-nitrobenzylpyridinium bromide and 1.375 g (5 mmole) of p-nitrobenzyltrimethylammonium bromide in 100 ml of water and 100 ml of a solution of 0.2 N sodium hydroxide were mixed under nitrogen cover in a stoppered flask. The flask was immersed into a water bath of room temperature while the reaction mixture was irradiated for 2 hr. After acidification with concentrated hydrochloric acid a precipitate was filtered off, 79 mg, and the aqueous solution was extracted with ether. The infrared spectrum and g.l.c. showed the precipitate to be p-azoxybenzaldehyde, 0.31 mmole. The ether phase was dried over magnesium sulfate and concentrated under vacuum, yielding 51 mg of p-nitrobenzaldehyde (infrared spectrum) 0.33 mmole. The aqueous phase was concentrated to dryness under vacuum. The n.m.r. spectrum (D_2O) of the residue was identical to that of p-nitrobenzyltrimethylammonium ion except for the signals due to the pyridinium ion.

Reaction of 3,5-Dimethyl-4-nitrobenzyl 'Onium Salts with Sodium Hydroxide

3,5-Dimethyl-4-nitrobenzaldehyde (108):

Nitromesitylene (4 g) was dissolved in a mixture of glacial acetic acid (38 g) and acetic anhydride (41 g). To the vigorously stirred solution concentrated sulfuric acid (5.6 ml) was added slowly and over a period of 1 hr chromium trioxide (6.5 g) was added in small portions while the temperature was kept at -5 to 0°. The mixture was poured onto ice water and the solid material was filtered off. After washing with cold water the material was suspended in a 5% solution of sodium bicarbonate and the resulting mixture was stirred. The solid was collected on a filter and allowed to hydrolyze for 2.5 hr in a refluxing mixture of 9 ml of water containing 0.6 ml of concentrated sulfuric acid and 9 ml of 95% ethanol. The mixture was cooled and extracted with ether. After drying over magnesium sulfate the ether layer was concentrated and yielded 1.8 g of a viscous oil corresponding to an overall yield of 41.5%. The infrared spectrum (Nujol) showed significant bands at 2740 and 1700 cm^{-1}. The n.m.r. spectrum ($CDCl_3$) showed singlets at τ0.0, τ2.4 and τ7.67, ratio 1 : 1.9 : 6, required 1 : 2 : 6.

3,5-Dimethyl-4-nitrobenzylpyridinium Bromide:

3,5-Dimethyl-4-nitrobenzaldehyde (20 mmole) was dissolved in a mixture of 60ml of 95% ethanol and 2 ml of tetrahydrofuran in a 250 ml beaker. The solution was stirred magnetically and the beaker was immersed in a water bath at room temperature. Sodium borohydride (10 mmole) was added in small portions over a period of 15 min. The solution turned yellow and white lumps formed. After an additional reaction period of 30 min. at room temperature, the mixture was poured onto ice water. The solution was extracted with ether; the ether layer was dried over magnesium sulfate and concentrated by rotary evaporation, yielding a viscous liquid. The formation of the 3,5-dimethyl-4-nitrobenzyl alcohol was indicated by a broad absorption at 3350 cm^{-1} and disappearance of the absorption due to the C=O bond. The n.m.r. spectrum ($CDCl_3$) showed singlets at τ2.97, τ5.4 (broad), τ7.4 (broad) and τ7.75, ratio 2 : 2.06 : 1 : 6.2, required 2 : 2 :1 :6.

The alcohol was transformed into the corresponding bromide following a general procedure (121). The crude alcohol was added to 10 g of concentrated hydrobromic acid (d = 1.49) in a 50 ml flask equipped with a reflux condenser which was surmounted by a drying tube containing calcium chloride. The resulting emulsion was heated on a steam bath for 30 min. while occasionally shaken by hand. The mixture was cooled and the organic layer was separated in a separatory funnel and dried over calcium chloride. The conversion of the alcohol to the bromide was indicated by the absence of the OH absorption in the infrared spectrum. The n.m.r. spectrum ($CDCl_3$) showed singlets at τ 2.9, τ 5.65 and τ 7.75, ratio 1.85 : 1.85 : 6.15, required 2 : 2 : 6.

The crude bromide was dissolved in 8 ml of pyridine and the solution was gently heated on a hot plate for 10 min. and was then allowed to cool. White crystals formed which were collected by filtration, 4 g, 62% yield. The material was recrystallized from acetonitrile and a melting point of 251-253° was obtained for the purified solid. The infrared spectrum (Nujol) showed significant bands at 3020, 1630, 1600, 1520, 1480, 1365, 1300, 1215, 1160, 890, 835, 810, 775, 715, 695 and 665 cm^{-1}. The n.m.r. spectrum (D_2O) showed a multiplet in the region of τ 1.0-2.2 and singlets at τ 2.63, τ 4.1 and τ 8.0, ratio 5.07 : 2 : 2 : 6, required 5 : 2 : 2 : 6.

Anal. Calcd. for $C_{14}H_{15}N_2O_2Br$: C, 52.02; H, 4.68; N, 8.67. Found: C, 52.11; H, 4.89; N, 8.65.

Deuterium Exchange of 3,5-Dimethyl-4-nitrobenzylpyridinium Ion:

A solution of 3,5-dimethyl-4-nitrobenzylpyridinium bromide in heavy water was added to a solution of sodium deuteroxide in heavy water. After 3 min. the reaction mixture was acidfied by addition of a solution of phosphorus pentoxide in heavy water. The resulting mixture was concentrated under vacuum to a volume suitable for n.m.r. analysis which showed that 63% of the benzylic hydrogens at τ4.15 had been exchanged.

Reaction of 3,5-Dimethyl-4-nitrobenzylpyridinium Bromide with Sodium Hydroxide:

3,5-Dimethyl-4-nitrobenzylpyridinium bromide (100 mg) was dissolved in 10 ml of water and 10 ml of 0.2 N sodium hydroxide solution was added. The reaction mixture was allowed to stand at room temperature for 60 hr. After acidification with concentrated hydrochloric acid 2 mg of a greyish precipitate was collected by filtration. The infrared spectrum of this material showed very prominent bands due to absorption by the nitro group. The aqueous solution was extracted with ether and was then concentrated on a steam bath under vacuum. The n.m.r. spectrum (D_2O) of the residue showed only starting material which was shown to be recovered in 83% yield by quantitative analysis using p-nitrobenzyltrimethylammonium bromide as internal standard. The ether phase was dried over magnesium sulfate and concentrated by rotary evaporation; no organic material was obtained.

Reaction of 3,5-Dimethyl-4-nitrobenzylpyridinium Bromide with Sodium Hydroxide under Irradiation:

A solution of 50 mg of 3,5-dimethyl-4-nitrobenzylpyridinium bromide in 5 ml of water was thoroughly flushed with nitrogen and

5 ml of 0.2 N sodium hydroxide solution which had also been flushed with nitrogen was added. The flask was closed and placed in a water bath while being exposed to a sun lamp for 2 hr. After acidification with concentrated hydrochloric acid the solution was concentrated to dryness by rotary evaporation. Quantitative analysis of the residue by n.m.r. spectroscopy (D_2O) using p-nitrobenzyltrimethylammonium bromide as internal standard indicated 93% recovery of 3,5-dimethyl-4-nitrobenzylpyridinium bromide.

3,5-Dimethyl-4-nitrobenzyldimethylsulfonium Tosylate:

3,5-Dimethyl-4-nitrobenzyl bromide (2 g) was dissolved in a mixture of 15 ml of dimethyl sulfide and 5 ml of acetonitrile. The flask was stoppered and allowed to stand at room temperature for 48 hr. The precipitate was filtered off and treated with anhydrous ether yielding 1.85 g, 74% yield, of 3,5-dimethyl-4-nitrobenzyldimethylsulfonium bromide which was identified by n.m.r. spectroscopy. The n.m.r. spectrum (D_2O) showed singlets at τ2.72, τ5.45, τ7.2 and τ7.8, ratio 1.95 : 6.1 : 6.95 for the signals at τ2.72, τ7.2 and τ7.8, required 2 : 6 : 6. Interference from the solvent signal rendered the integration for the signal at τ5.45 unreliable.

The bromide (1.53 g, 5 mmole) was dissolved in a mixture of 15 ml of water and 15 ml of acetonitrile. A solution of one equivalent of silver tosylate in 30 ml of acetonitrile was added slowly under exclusion of light. The formed precipitate of silver bromide was collected on a fluted filter paper and the filtrate was concentrated by rotary evaporation. The residue was recrystallized from hot acetonitrile yielding 1.45 g, 73% of white crystals, m.p. 172-174°. The salt was insoluble in cold water, but dissolved in hot water. The infrared spectrum (Nujol) showed significant bands at 3030, 3010, 1600, 1530, 1520, 1360, 1200, 1175, 1120, 1030, 10'0, 1000, 890, 830, 820, and 680 cm^{-1}. The n.m.r. spectrum in a solvent mixture of heavy water and acetone-$\underline{d}_6$ showed a multiplet at τ 2.9 and singlets at τ 5.65, τ 7.4 and τ 8.05, ratio 6.1 : 2.1 : 6 : 8.9, required 6 : 2 : 6 : 9.

Anal. Calcd. for $C_{18}H_{23}NO_5S_2$: C, 54.40; H, 5.83; N, 3.53. Found: C, 54.47; H, 5.79; N, 3.82.

Reaction of 3,5-Dimethyl-4-nitrobenzyldimethylsulfonium Tosylate with Sodium Hydroxide:

3,5-Dimethyl-4-nitrobenzyldimethylsulfonium tosylate (100 mg) was dissolved in 10 ml of water. After addition of 2.5 ml of 0.2 N sodium hydroxide solution the reaction mixture was heated on a steam bath for 36 hr. The mixture was cooled and acidified with concentrated hydrochloric acid. A yellowish precipitate was filtered off, m.p. 215-217°, 27 mg, 66% yield. The infrared spectrum (Nujol) showed significant peaks at 3040, 3010, 1600, 1520, 1360, 1100, 1030, 880, 850, 840, 835 and 710 cm^{-1}. The mass spectrum showed a molecular ion peak at m/e 342. Other significant peaks were at m/e 327, 325, 313, 296, 295, 281, 178, 163, 162, 134, 133, 115, 91 and 77. The peak at m/e 327 could not be assigned. The aqueous solution was extracted with ether. The organic layer was dried over magnesium sulfate and concentrated by rotary evaporation. A small amount of a yellowish liquid was left which by its infrared spectrum was identified as 3,5-dimethyl-4-nitrobenzyl alcohol by comparison with the infrared spectrum of authentic material. No n.m.r. spectra of the products were obtained due to lack of materials.

In another experiment 3,5-dimethyl-4-nitrobenzyldimethylsulfonium tosylate (99 mg, 0.25 mmole) was dissolved in 2 ml of hot water and 0.5 ml of 1 N sodium hydroxide solution were added. The solution was heated on a steam bath for 7 hr and after rapid cooling was acidified by addition of concentrated hydrochloric acid. The filtered solution was concentrated by rotary evaporation on a steam bath. The n.m.r. spectrum (D_2O) of the residue indicated 45% recovery of starting material by quantitative comparison of the signals due to the dimethylsulfonium group and the methyl group of the tosylate ion.

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