

of 2.30 g. (0.008 mole) of 1-methyl-1-bromo-2,2-diphenylcyclopropane in 10 ml. of THF over a 10-min. period with stirring. After stirring an additional 20 min., the reaction mixture was hydrolyzed using 99.5% D₂O. The solution was diluted with water, extracted with petroleum ether (30–60°), and dried over magnesium sulfate. Removal of the solvent gave a pale yellow oil which was distilled, b.p. 103–104° at 0.45 mm., to give 1.24 g. (74%) of the desired hydrocarbon. A peak height analysis of the n.m.r. spectra showed that 79.8 ± 1% incorporation of deuterium had occurred.

B. Grignard Reagent Prepared in Ether with Preformed Magnesium Bromide Present.—To a refluxing slurry of preformed magnesium bromide prepared from 0.50 g. (0.020 mole) of magnesium powder, 0.5 ml. of ethylene dibromide, and 4 ml. of ether was added dropwise 2.30 g. (0.0080 mole) of 1-methyl-1-bromo-2,2-diphenylcyclopropane in 10 ml. of ether over a 10-min. period. Stirring was continued for an additional 20 min. after the addition and the reaction mixture hydrolyzed using 99.5% deuterium oxide. The solution was diluted with water, extracted with petroleum ether (30–60°), and dried over magnesium sulfate. Removal of the solvent gave a yellow oil which was distilled, b.p. 100–101° at 0.32 mm., to give 11.1 g. (66%) of the hydrocarbon. A peak height analysis of the n.m.r. spectra showed that 52 ± 1% incorporation of deuterium had occurred.

N.m.r. Analysis of Deuterium Incorporated into 1-Methyl-2,2-diphenylcyclopropane on Hydrolysis of the Grignard Reagent with Deuterium Oxide.—The 60 Mc. n.m.r. spectrum of 1,1-diphenyl-2-methylcyclopropane is very complex, consisting of a broad phenyl doublet, sixteen distinguishable methylene peaks,

and a sharp methyl doublet. The components of the methyl doublet were separated by 6 c.p.s. and deuteration showed that the chemical shift between the α -H and the methyl doublet was about 40 c.p.s. Therefore it was possible to determine the extent of deuteration by comparing the relative peak heights of the α -H methyl doublet with the α -D methyl singlet.^{49,50} Analysis for deuterium was also carried out by measuring the areas under each peak after extrapolation and the results were in good agreement. The n.m.r. data was also in agreement with the results of an analysis obtained from the mass spectrum of a sample.

Thermal Stability of Grignard Reagent.—The Grignard reagent was prepared in the usual manner using 0.5 g. of magnesium, 0.5 ml. of 1,2-dibromoethane, and 4 ml. of THF. To this mixture was added a solution of 2.3 g. of (–)-1-bromo-1-methyl-2,2-diphenylcyclopropane, [α]_D²⁵ – 111°, dissolved in 10 ml. of THF. The reaction mixture was stirred for 20 min. and 25 ml. of di-*n*-butyl ether was added and the reaction flask heated to distil off the THF. After ca. 15 ml. of distillate was collected and the pot temperature reached 128–129° (15 min.) the reaction mixture was kept at reflux temperature for an additional 30 min., cooled, and poured onto Dry Ice.

The reaction products were worked up as previously described to yield 0.50 g. of (+)-1-methyl-2,2-diphenylcyclopropanecarboxylic acid, m.p. 174–181°, [α]_D²⁵ + 5.51° (*c* 3.6), 15% optical purity, and 0.65 g. of (+)-1-methyl-2,2-diphenylcyclopropane, [α]_D²⁵ + 15.0° (*c* 12.12), 11% optical purity.

(49) F. A. L. Anet, *Can. J. Chem.*, **39**, 2262 (1961).

(50) J. N. Shoolery in Varian Associates, "N.M.R. and E.P.R. Spectroscopy," Pergamon Press, New York, N. Y., 1960.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA, PHILADELPHIA 4, PA.]

Mechanisms of α -Elimination. Nitrobenzylsulfonium, -ammonium, and -phosphonium Ions Reacting with Aqueous Hydroxide¹⁻³

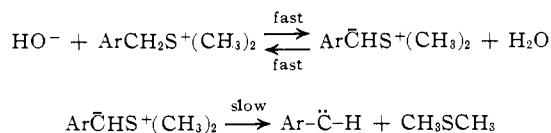
BY IRVIN ROTHBERG AND EDWARD R. THORNTON

RECEIVED MARCH 12, 1964

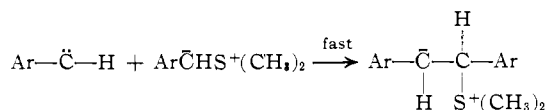
p-Nitrobenzyltrimethylsulfonium *p*-toluenesulfonate reacts with aqueous sodium hydroxide to give a quantitative yield of *p,p'*-dinitrostilbene, the methylene protons being rapidly and reversibly removed in D₂O–DO[–], according to n.m.r. *m*-Nitrobenzyltrimethylsulfonium bromide reacts with aqueous sodium hydroxide to give a 41% yield of *m,m'*-dinitrostilbene oxide and a 5% yield of *m*-nitrobenzyl alcohol, essentially the same result being obtained under nitrogen. *p*-Nitrobenzyltrimethylammonium bromide is nearly inert to refluxing aqueous sodium hydroxide. *p*-Nitrobenzyltriphenylphosphonium bromide reacts with aqueous sodium hydroxide to give largely triphenylphosphine oxide and *p*-nitrotoluene. The natures of the leaving group and the ring substituent appear to be critical for stilbene formation by α -elimination.

Many cases of α -elimination to form divalent carbon intermediates have been reported.⁴ In most of those carried out in aqueous base a number of products form. It was therefore of considerable interest that *p*-nitrobenzyl chloride in 50% aqueous dioxane⁵ and *p*-nitrobenzyltrimethylsulfonium tosylate (*p*-toluenesulfonate) in water⁶ react with dissolved sodium hydroxide to give quantitative yields of *p,p'*-dinitrostilbene. Kinetic studies showed that these reactions are first order in *p*-nitrobenzyl compound and first order in sodium hydroxide, yet cannot involve rate-determining proton removal because infrared spectra of recovered reactant after partial reaction in D₂O–DO[–]

showed substantial replacement of C–H by C–D bonds. The only reasonable mechanism seemed to involve rate-determining formation of a divalent carbon intermediate (carbene) followed by rapid reaction of the carbene to form *p,p'*-dinitrostilbene.^{5,6} Rapid, reversible removal of the proton followed by rate-determining attack of the intermediate on another substrate molecule would require kinetics second order in *p*-nitrobenzyl compound. The scheme proposed for the *p*-nitrobenzyltrimethylsulfonium ion⁶ is (where Ar = *p*-nitrophenyl)



followed by



(1) Previous paper (preliminary communication): I. Rothberg and E. R. Thornton, *J. Am. Chem. Soc.*, **85**, 1704 (1963).

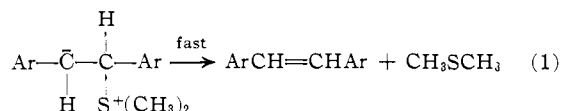
(2) Acknowledgment is made to Smith Kline and French Laboratories for a fellowship to I. R. and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

(3) For further details cf. I. Rothberg, Ph.D. dissertation in chemistry, University of Pennsylvania, 1963.

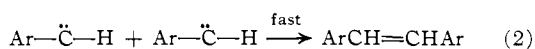
(4) For reviews, see J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, Chapter 24; E. Chinoporos, *Chem. Rev.*, **63**, 235 (1963).

(5) S. B. Hanna, Y. Iskander, and Y. Riad, *J. Chem. Soc.*, 217 (1961).

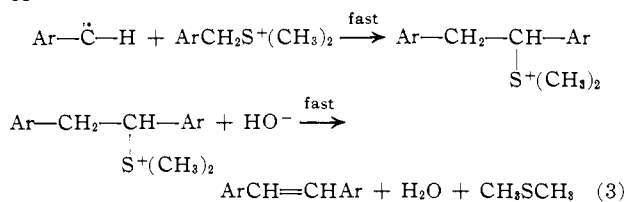
(6) C. G. Swain and E. R. Thornton, *J. Am. Chem. Soc.*, **83**, 4033 (1961):



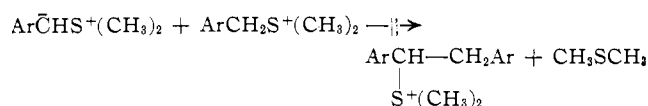
or



or

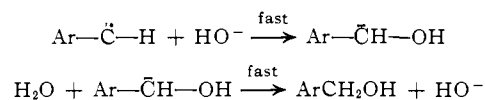


But



Reaction 1 was favored for the product-forming reaction because it seemed like a typical carbene reaction and because the kinetic sulfur isotope effect seemed to fit it better.⁶ Dimerization seems unlikely because the carbenes should be present in very low concentration. However, reaction 3 appears to be reasonable and consistent with the sulfur isotope effect also.

If these reactions do in fact proceed through a carbene intermediate, it is very surprising that the carbene does not undergo reactions with other nucleophiles, especially hydroxide ion which is present in rather high concentration.



Yet no *p*-nitrobenzyl alcohol was detected^{5,6} and it is stable under the reaction conditions.

We therefore undertook a further study of the reaction products of *p*-nitrobenzyl dimethylsulfonium ion and also of *m*-nitrobenzyl dimethylsulfonium ion, *p*-nitrobenzyl trimethylammonium ion, and *p*-nitrobenzyl triphenylphosphonium ion in aqueous sodium hydroxide solution. Our purposes were to determine what factors affect the *p,p'*-dinitrostilbene-forming reaction in order to see if the proposed carbene intermediate is reasonable, and to explore the generality of this type of reaction as a synthetic method. The results are consistent with a carbene intermediate, at least in the case of the *p*-nitrobenzyl dimethylsulfonium ion, and they show that the quantitative yield of stilbene with the latter ion is probably an exceptional case.

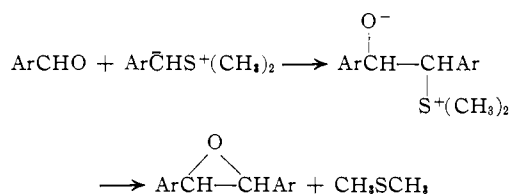
Results and Discussion

***p*-Nitrobenzyl dimethylsulfonium Ion.**—It seemed conceivable that the infrared evidence for rapid, reversible proton removal in the reaction of *p*-nitrobenzyl dimethylsulfonium tosylate with aqueous hydroxide⁶ could be misleading, because the C–D stretching vibrations in the reactant recovered after partial reaction in D₂O–DO[−] could be associated with exchange of only the *methyl* protons and not the *benzylic* protons. We therefore performed the same experiment, but analyzed the recovered reactant by n.m.r. After a short reaction time the benzylic protons were at least

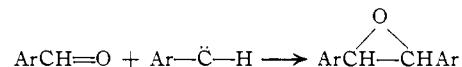
97% exchanged for deuterium while the methyl protons were approximately 50% exchanged. This eliminates the carbanion displacement mechanism.

***m*-Nitrobenzyl dimethylsulfonium Ion.**—It is known that unsubstituted, *m*-chloro-, and *p*-methylbenzyl dimethylsulfonium ions react in aqueous sodium hydroxide solution to give high yields of the corresponding benzyl alcohol.⁷ These reactions probably do not proceed through carbene intermediates but are ordinary S_N2 displacements of dimethyl sulfide by hydroxide. The nitro group appears, then, to be important for carbene formation, so it was of considerable interest to see if a resonance effect or an inductive effect dominates. The reaction of *m*-nitrobenzyl dimethylsulfonium bromide with aqueous sodium hydroxide at 100° 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 (delocalization) effect than a *p*-nitro substituent, we conclude 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. In view of the unexpected formation of the stilbene oxide, the reaction was also carried out under nitrogen; the yields of the three products were essentially unchanged.

Carbenes formed by photolysis are known to react readily with molecular oxygen to form carbonyl compounds,⁸ but our result seems to exclude molecular oxygen in the formation of *m,m'*-dinitrostilbene oxide. 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 *p*-nitrobenzaldehyde. The aldehyde could easily react with ylid to give stilbene oxide⁵



or with carbene by insertion into a C=O bond



Also *m,m'*-dinitrostilbene has been prepared⁹ and has shown no evidence of being unstable to air, so that initial formation of stilbene followed by oxidation seems unlikely.

***p*-Nitrobenzyl trimethylammonium Ion.**—Rapid, reversible exchange of protons α to the sulfur atom in sulfonium ions but very slow exchange of protons α to the nitrogen atom in ammonium ions has been observed and explained¹⁰ as being due to lowering of the energy of the transition state for ylid formation by d-orbital overlap with sulfur, which could not readily occur with nitrogen since it has no valence shell d-

(7) C. G. Swain and E. R. Thornton, *J. Org. Chem.*, **26**, 4808 (1961).

(8) W. B. DeMore, H. O. Pritchard, and N. Davidson, *J. Am. Chem. Soc.*, **81**, 5874 (1959).

(9) P. L. Ecuyer and F. Turcotte, *Can. J. Research*, **25B**, 575 (1947).

(10) W. von E. Doering and A. K. Hoffman, *J. Am. Chem. Soc.*, **77**, 521 (1955).

orbitals. It was therefore of great interest to see if a *p*-nitrobenzylammonium ion would undergo α -elimination. Carbene formation from ammonium salts has been reported.¹¹ After 72 hr. at 100° *p*-nitrobenzyltrimethylammonium bromide showed no evidence of reaction in aqueous sodium hydroxide solution, 97% being precipitated as the perchlorate by addition of sodium perchlorate to the reaction solution.

More vigorous conditions, reflux on a hot plate for 216 hr., gave some brown tar and a 1% yield of *p*-nitrotoluene. No *p*-nitrobenzyl alcohol or *p,p'*-dinitrostilbene was formed. The origin of the *p*-nitrotoluene is unclear. Formation of *p*-nitrotoluene from *p*-nitrobenzyltriphenylphosphonium bromide in 50% aqueous alcoholic sodium hydroxide solution is known¹² but is thought to proceed by initial attack of hydroxide on phosphorus to give a pentavalent intermediate, because the other product is triphenylphosphine oxide and similar reactions are third order, second order in hydroxide.¹³ Nitrogen is unlikely to form a pentavalent intermediate since it does not have valence shell d-orbitals available for bonding. Either no intermediate forms, but rather a direct displacement (on nitrogen) of *p*-nitrobenzyl anion by hydroxide occurs, or the phosphonium and ammonium mechanisms are dissimilar. Trimethylamine oxide might be expected along with the *p*-nitrotoluene, but none could be detected. However, it may have decomposed; on heating it is said to give formaldehyde and trimethylamine¹⁴ and these would have been lost under our reaction and work-up conditions. There are mechanisms which involve decomposition of the ylid formed by removal of a proton from a *methyl* group (rather than the *p*-nitrobenzyl group) which could give *p*-nitrotoluene and which would give formaldehyde and trimethylamine without the intermediacy of trimethylamine oxide.¹⁵

Trimethylamine is undoubtedly a much poorer leaving group than dimethyl sulfide¹⁶; this may be why no carbene appears to be formed by the ammonium ion. If proton removal from the benzylic carbon were very slow, no ylid, which could subsequently decompose into carbene, could form. Under the mild conditions where the benzylic protons of *p*-nitrobenzyltrimethylsulfonium ion were at least 97% exchanged with deuterium, no exchange in *p*-nitrobenzyltrimethylammonium ion could be detected by infrared or n.m.r.

We therefore conclude that the nature of the leaving group as well as the ring substituent is crucial for the stilbene-forming reaction.

***p*-Nitrobenzyltriphenylphosphonium Ion.**—Both *p*-nitrotoluene and triphenylphosphine oxide have been reported¹² as products of the reaction of *p*-nitrobenzyltriphenylphosphonium bromide in 50% aqueous alcoholic sodium hydroxide solution. However, we wished to examine the reaction of this phosphonium

ion in aqueous solution under the same conditions as we have employed for the other ions above. We also were exceedingly interested to find out if even a very small amount of *p,p'*-dinitrostilbene was formed, because this phosphonium ion has both the *p*-nitro substituent and the possibility of d-orbital stabilization through valence shell d-orbitals. It is known that phosphonium ions do undergo rapid proton exchange in aqueous base,¹⁰ presumably due to d-orbital overlap stabilizing the transition state for proton removal.

p-Nitrobenzyltriphenylphosphonium bromide reacted in aqueous sodium hydroxide solution at 100° to give a 97% crude yield (88% after purification) of triphenylphosphine oxide, a 56% yield of *p*-nitrotoluene (scraped from the reflux condenser; some was possibly lost into the air), and a 0.5% yield of *p,p'*-dinitrostilbene. The mechanism of formation of the two major products presumably proceeds by initial attack of hydroxide on phosphorus.¹³ If the reaction forming *p*-nitrotoluene is second order in hydroxide¹³ and the reaction forming *p,p'*-dinitrostilbene proceeds through a carbene intermediate and is first order in hydroxide,⁶ the yield of *p,p'*-dinitrostilbene should be increased greatly by lowering the concentration of hydroxide ion tenfold, keeping the concentration of phosphonium ion the same. In fact, such an experiment gave a negligible amount of the stilbene, even less than before. Therefore the mechanism which produces *p,p'*-dinitrostilbene from the phosphonium ion is probably not the same as the one we were looking for, the one by which *p*-nitrobenzyltrimethylsulfonium ion reacts with aqueous base. It has been reported that *p*-nitrotoluene will form *p,p'*-dinitrostilbene and *p,p'*-dinitrobenzyl when allowed to react with base in methanol.¹⁷ Under our experimental conditions, we found that *p*-nitrotoluene does indeed give small amounts of *p,p'*-dinitrostilbene. It is therefore probable that stilbene did not form by α -elimination in the reaction of *p*-nitrobenzyltriphenylphosphonium bromide in aqueous sodium hydroxide solution, but rather came from subsequent reaction of initially-formed *p*-nitrotoluene.

Triphenylphosphine is probably a poor leaving group relative to dimethyl sulfide.¹⁸ Thus the combination of relatively facile phosphine oxide formation and poor leaving group ability of triphenylphosphine appear to prevent carbene formation.

Conclusions.—We conclude 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 the α -elimination in aqueous sodium hydroxide. Apparently a delicate balance of electrical, and possibly other, effects is necessary. It may be simply a matter of having a reactant which can form an ylid reasonably easily and which can then lose its leaving group reasonably easily to form the carbene.

The question of why *p*-nitrophenylcarbene (if formed) should react as it seems to, rather than with other

(11) V. Franzen, *Chem. Ber.*, **93**, 557 (1960); V. Franzen and G. Wittig, *Angew. Chem.*, **72**, 417 (1960); C. K. Ingold and J. A. Jessop, *J. Chem. Soc.*, 2357 (1929).

(12) F. Krohnke, *Chem. Ber.*, **83**, 291 (1950).

(13) M. Zanger, C. A. VanderWerf, and W. A. McEwen, *J. Am. Chem. Soc.*, **81**, 3806 (1959); R. F. Kumli, W. F. McEwen, and C. A. VanderWerf, *ibid.*, **81**, 3805 (1959).

(14) W. R. Dunstan and E. Goulding, *J. Chem. Soc.*, **75**, 792 (1899).

(15) See, for example, C. R. Hauser and D. N. Van Eenam, *J. Am. Chem. Soc.*, **78**, 5698 (1956); **79**, 5512, 6274, 6277, 6280 (1957); T. S. Stevens, W. W. Sneeden, F. T. Stillier, and T. Thompson, *J. Chem. Soc.*, 2119 (1930).

(16) J. Hine, ref. 4, p. 184.

(17) A. G. Green, A. H. Davies, and R. S. Horsfall, *J. Chem. Soc.*, **91**, 2076 (1907); O. Fischer and E. Hepp, *Chem. Ber.*, **26**, 2231 (1893); T. Tsuruta, R. Nagatomi, and J. Furukawa, *J. Bull. Inst. Chem. Res., Kyoto Univ.*, **30**, 46 (1952) [*Chem. Abstr.*, **48**, 11369i (1954)]; R. Oda and T. Tsuruta, *Rept. Chem. Res. Inst. Kyoto Univ.*, **16**, 6 (1947) [*Chem. Abstr.*, **46**, 950g (1952)].

(18) A. W. Johnson and R. B. LaCount, *J. Am. Chem. Soc.*, **83**, 417 (1961).

nucleophiles such as hydroxide, is not answered. A possible explanation is investigated in the next paper.¹⁹

Experimental

All melting points are uncorrected except where noted. Nuclear magnetic resonance spectra were run on a Varian high resolution 60 Mc. instrument; measurements are expressed in p.p.m. downfield from tetramethylsilane used as an internal standard. Infrared spectra were taken on a Perkin-Elmer 421 spectrometer.

p-Nitrobenzyl dimethylsulfonium *p*-toluenesulfonate was available from a previous investigation.⁶ It was dissolved in methanol and precipitated by addition of ether; m.p. 138–139°, unchanged after an additional reprecipitation (lit.⁶ m.p. 138–139°).

m-Nitrobenzyl dimethylsulfonium bromide was prepared by reaction of *m*-nitrobenzyl bromide with excess dimethyl sulfide. *m*-Nitrobenzyl bromide (K and K Laboratories, 10 g., 0.05 mole) was dissolved in dimethyl sulfide (Matheson Coleman and Bell, 10 g.). After 72 hr. at ca. 25° the white precipitate which formed was isolated by filtration and dried at ca. 25° at 2 mm. pressure; yield 12.5 g. (97%) of white solid, m.p. 132–134°. It was dissolved in methanol and precipitated by addition of ether; yield 11.0 g., m.p. 135–136°. After repetition of the purification procedure, 10.0 g. (78%) was recovered, m.p. 135–136°. The infrared spectrum (KBr) showed peaks at: 3090 (w), 3030 (w), 3010 (w), 2980 (w), 2960 (m), 2900 (m), 2000 (vw), 2170 (vw), 1570 (w), 1525 (vs), 1480 (m), 1430 triplet (s), 1350 (vs), 1320 (m), 1300 (w), 1270 (m), 1210 (m), 1175 (m), 1100 (m), 1090 (m), 1055 (m), 1020 (s), 980 (w), 940 (w), 920 (m), 875 (m), 810 doublet (s), 730 (s), 700 (s), 680 (s), 670 (s) cm.⁻¹.

Anal. Calcd. for C₉H₁₂BrO₂S: C, 38.86; H, 4.34; S, 11.53. Found: C, 38.69; H, 4.35; S, 11.41.

p-Nitrobenzyl trimethylammonium bromide was prepared by the reaction of *p*-nitrobenzyl bromide with excess trimethylamine. *p*-Nitrobenzyl bromide (10 g., 0.05 mole) was dissolved in 35 ml. of a 25% solution of trimethylamine in methanol (Eastman) and allowed to stand for 2 weeks at ca. 25°. Addition of an excess of ethyl ether brought out an oil which crystallized after standing for 24 hr. The crystals were isolated by filtration and washing with ether; yield 12.7 g. (99.5%) of tan solid, m.p. 208–215°. The solid was purified by dissolving in methanol and precipitating out slowly by addition of ether; yield 11.0 g., m.p. 216–217°. After repetition of the purification procedure, 10.0 g. (79%) of white crystals was obtained, m.p. 216–217°. The infrared spectrum (KBr) showed peaks at: 3050 (m), 3000 (m), 2960 (m), 1600 (m), 1520 (vs), 1470 (s), 1410 (m), 1380 (vw), 1350 (vs), 1320 (m), 1290 (m), 1210 (w), 1180 (w), 1100 (m), 990 (vw), 960 (w), 920 (w), 890 (m), 870 (m), 850 (s), 810 (w), 720 (s), 690 (m) cm.⁻¹.

Anal. Calcd. for C₁₀H₁₅BrN₂O₂: C, 43.65; H, 5.49. Found: C, 43.45; H, 5.40.

p-Nitrobenzyl trimethylammonium perchlorate was prepared by addition of 5 ml. of a saturated aqueous solution of sodium perchlorate to a solution of *p*-nitrobenzyl trimethylammonium bromide in 50 ml. of water. The white solid which precipitated was isolated by filtration, washed with water, and dried at ca. 25° at 2 mm. pressure; yield 1.381 g. (4.69 × 10⁻³ mole, 93%) of white crystals, m.p. 196.5–197.5°. The crystals were dissolved in methanol and precipitated by adding ether; m.p. 196.5–197.5°. The infrared spectrum of the perchlorate was similar to that of the bromide.

Anal. Calcd. for C₁₀H₁₅ClN₂O₄: C, 40.76; H, 5.13. Found: C, 41.05; H, 5.31.

p-Nitrobenzyl triphenylphosphonium bromide was prepared by the reaction of *p*-nitrobenzyl bromide with triphenylphosphine. A mixture of 12.5 g. (0.058 mole) of *p*-nitrobenzyl bromide and 16.5 g. (0.065 mole) of triphenylphosphine (Eastman) in 150 ml. of xylene was refluxed with stirring for 26 hr. after which the light tan solid obtained was isolated by filtration. The solid was dried for 24 hr. at ca. 25° at 2 mm. pressure; yield 27.0 g. (97%), m.p. 256–257° (lit.¹² 261°). After recrystallization from ethanol 20.0 g. (72%) was obtained, m.p. 262–263°.

m-Nitrobenzyl alcohol (Eastman practical) was purified by column chromatography on alumina followed by fractional distillation; b.p. 155–156° (3 mm.) (lit.²⁰ 175–180° (3 mm.)).

A thin layer chromatogram of this material showed only a trace impurity. This sample was used as the standard for comparisons of infrared spectra and chromatographic behavior.

p,p'-Dinitrostilbene was prepared by reaction of *p*-nitrobenzyl dimethylsulfonium *p*-toluenesulfonate (3.699 g., 1.00 × 10⁻² mole) dissolved in 100 ml. of 0.2 *M* aqueous sodium hydroxide at ca. 100° for 1 hr. The yellow precipitate which formed was isolated by filtration, washed with water, and dried at 50° at 2 mm. pressure for 24 hr.; yield 1.350 g. (5.00 × 10⁻³ mole, 100%) of *cis*- and *trans*-*p,p'*-dinitrostilbene, m.p. 185–240°. A thin layer chromatogram showed essentially a single band. A small amount of the solid was refluxed for 10 min. with a crystal of iodine in nitrobenzene. *trans*-*p,p'*-Dinitrostilbene was recovered, m.p. 288–290° (uncor.), 300–302° (cor.) (lit.⁶ 304–306° (cor.)). This sample of *cis*- and *trans*-*p,p'*-dinitrostilbene was used as the standard for comparisons of infrared spectra and chromatographic behavior.

Miscellaneous.—*p*-Nitrobenzyl alcohol (Eastman), *p*-nitrotoluene (Eastman), trimethylamine oxide (K and K Laboratories), and triphenylphosphine oxide (Aldrich Chemical Co.) were examined, found to be essentially pure by thin layer chromatography, and used as the standards for comparisons of infrared spectra and chromatographic behavior.

A solution of sodium deuterioxide in deuterium oxide was prepared by reaction of freshly cut sodium with a small amount of D₂O (Liquid Carbonic 99.6%) in a drybox flushed with nitrogen and dried with phosphorus pentoxide for 24 hr. previously. The solution was then diluted to volume with more D₂O.

Analytical Techniques.—Nitrobenzyl alcohols were extracted from the aqueous filtrate after the water-insoluble products had been removed. The water-insoluble products were normally analyzed by a combination of chromatography on alumina and thin layer chromatography on either alumina or silica gel (calcium sulfate binder) with ca. 250 μ films. The column chromatography fractions were isolated by evaporation of solvent with a stream of air across the surface. Thin layer chromatograms were then run on each fraction from the column. Based on the thin layer analysis, several column fractions were sometimes combined and run through the column again. The thin layer chromatograms were usually examined in ultraviolet light, and were usually run with 100-μg. samples.

Deuterium Exchange of *p*-Nitrobenzyl dimethylsulfonium Ion.—*p*-Nitrobenzyl dimethylsulfonium *p*-toluenesulfonate (0.7427 g.) was dissolved in a small amount of D₂O, 1.50 ml. of 2.70 *M* sodium deuterioxide solution was added, and the solution was diluted to 10.00 ml. with D₂O in a drybox. The solution reacted for 3 min. at 25.2°, and was then neutralized with concentrated hydrochloric acid and filtered. Because protons in water happen to have the same n.m.r. absorption (5.2 δ) as the methylene (benzylic) protons of the sulfonium ion, it was not possible to analyze the filtrate directly. To a portion of the filtrate 5 ml. of a saturated solution of sodium perchlorate in D₂O was added. A white precipitate, the sulfonium perchlorate, formed and was collected and dried at ca. 25° for 24 hr. at 2 mm. pressure. To a solution of 0.7382 g. (2.0 × 10⁻³ mole) of *p*-nitrobenzyl dimethylsulfonium *p*-toluenesulfonate dissolved in 20 ml. of water was added 5 ml. of a saturated aqueous solution of sodium perchlorate. The sulfonium perchlorate precipitated, was isolated by filtration, and was dried at ca. 25° at 2 mm. pressure; yield 0.5549 g. of the perchlorate (1.87 × 10⁻³ mole, 93%).

The partially reacted sulfonium salt showed infrared peaks at 2150 and 2250 cm.⁻¹ which were not present in the sample not treated with sodium deuterioxide. These bands must be due to C–D stretching vibrations.

The n.m.r. spectrum of the undeuterated sulfonium perchlorate showed methyl protons at 2.8, methylene protons at 4.7, and aromatic protons at 8.0 δ, in the expected ratio of 3:1:2. The n.m.r. spectrum of the deuterioxide-treated salt, using the aromatic protons as the reference, showed that at least 50% of the methyl protons were replaced and at least 97% of the methylene protons were replaced.

Reaction of *m*-Nitrobenzyl dimethylsulfonium Bromide with Sodium Hydroxide.—*m*-Nitrobenzyl dimethylsulfonium bromide (1.3909 g., 5.00 × 10⁻³ mole) was dissolved in 50 ml. of 0.2 *M* aqueous sodium hydroxide, and allowed to react on a steam bath (100°) for 20 hr. A brown amorphous precipitate was removed by filtration, and the filtrate was extracted with four 50-ml. portions of ether. The combined ether extracts were dried for 24 hr. over anhydrous magnesium sulfate; after filtration the ether was evaporated at reduced pressure. The residue was an

(19) I. Rothberg and E. R. Thornton, *J. Am. Chem. Soc.*, **86**, 3302 (1964).

(20) E. Grimaux, *Z. Chem.*, 562 (1867).

oil mixed with tar (74.5 mg.). This material was dissolved in 1:1 petroleum ether-ethyl ether and put onto an alumina column. The material was fractionated using 25-ml. portions of successively more polar solvents, ranging up to 2:3 chloroform-methanol, eight fractions being taken with 59% recovery from the column. *m*-Nitrobenzyl alcohol had a R_f 0.40 on thin layer chromatography on alumina with 4:1 chloroform-petroleum ether. Column fractions 1-4 had as major components a material of R_f 0.40 along with minor amounts of about four other materials, so they were combined and the infrared spectrum of a chloroform solution was compared with that of authentic *m*-nitrobenzyl alcohol; the spectra were identical; yield 36.0 mg. (0.235×10^{-3} mole, 5%).

The brown amorphous solid filtered from the reaction mixture had m.p. 110-125°. The results of a thin layer chromatogram on alumina with 6.5:3.5 petroleum ether-chloroform are listed in Table I.

TABLE I

R_f	Estimated amount ^a	Ultraviolet color	R_f	Estimated amount ^a	Ultraviolet color
0.00	Major	Brown	0.40	Small	Black
.10	Trace	Black	.68	Major	Black
.20	Trace	Black	.80	Small	Black
.27	Trace	Black	.92	Small	Black

Key: major > large > significant > small > trace.

Column chromatography was used to purify the brown solid, using a 0.2465-g. sample, on alumina and taking 75-ml. fractions. With increasingly polar solvents and mixtures (petroleum ether, ethyl ether, acetonitrile, chloroform, methanol) up to 7:1 chloroform-methanol, 12 fractions were collected with 100% recovery from the column. Thin layer chromatography on each fraction indicated that a component of R_f 0.68 was the major compound in fractions 2-4. Fractions 2-4 were therefore combined (142.6 mg.) and rechromatographed using 7:3 chloroform-petroleum ether for elution and taking 13 fractions, each 5 ml. Fractions 5'-8' contained a major component with thin layer R_f 0.60, so they were combined (116.4 mg.) and recrystallized from acetone-water; m.p. 154-155°, essentially unchanged. Since *m,m'*-dinitrostilbene has m.p. 240-242°,⁹ this product is not the stilbene. The analysis is in agreement with *m,m'*-dinitrostilbene oxide.

Anal. Calcd. for $C_{14}H_{10}N_2O_3$: C, 58.74; H, 3.52; N, 9.79. Found: C, 58.50; H, 3.62; N, 9.33; mol. wt. (osmometer), 276.

The infrared spectrum (KBr) showed peaks at: 3100 (w), 3070 (m), 2920 (vw), 2450 (vw), 1700 (vw), 1580 (w), 1520 (vs), 1470 (m), 1440 (w), 1420 (w), 1340 (vs), 1260 (m), 1220 (vw), 1160 (w), 1090 (s), 1070 (s), 930 doublet (m), 900 (m), 850 (s), 830 (m), 795 (s), 725 (s), 680 (s), 670 (s), 610 (m) cm^{-1} . The peaks at 1260 and 920 cm^{-1} are characteristic of epoxides, and the peaks at 1520 and 1340 cm^{-1} are characteristic of nitro groups.²¹

The n.m.r. spectrum in deuterated chloroform showed aromatic protons at 7.9 δ and a single sharp peak at 4.0 δ with areas in the ratio 4:1.

Recently, *trans-m,m'*-dinitrostilbene oxide has been reported²² to have a m.p. of 156-158° and n.m.r. absorption of the ethylene protons at 4.08 δ ; the *cis* form absorbs at 4.5 δ .

The yield of *m,m'*-dinitrostilbene oxide was 116.4 mg., equivalent to 290 mg. (1.01×10^{-3} mole, 41%) if the entire reaction product had been chromatographed.

Most of the remainder of the reaction product was a brown tar with R_f 0.00 on thin layer chromatography.

In view of the formation of *m,m'*-dinitrostilbene oxide in this reaction, it was repeated under nitrogen. *m*-Nitrobenzyltrimethylsulfonium bromide (1.3890 g., 5.00×10^{-3} mole) was dissolved in 25 ml. of water in a three-neck flask with a reflux condenser, nitrogen inlet, and a pressure-equalizing dropping funnel containing another nitrogen inlet tube. A mineral oil bubbler attached to the exit of the condenser prevented back diffusion of air into the system. In the dropping funnel was placed 25 ml. of 0.4 *M* sodium hydroxide solution. Nitrogen (99.996% and passed through Fieser solution²³ to remove oxygen) was passed through the aqueous sodium hydroxide solution and through the

sulfonium salt solution for 48 hr. Then the sodium hydroxide solution was added to the sulfonium salt solution, and the solution was heated under nitrogen for 5 hr. at 100°. The cooled reaction mixture was filtered under a nitrogen atmosphere to isolate the brown solid which had precipitated. A thin layer chromatogram was immediately run on this solid, using alumina with 6.5:3.5 petroleum ether-chloroform for elution. A sample of impure *m,m'*-dinitrostilbene oxide from the previous reaction (under air) was run at the same time; the chromatograms were identical. The two materials were also compared on silica gel with toluene for elution and were once again identical. In both the silica gel and alumina systems the bands were sharp and well defined, showing no indication of decomposition as development occurred.

The filtrate and the brown solid were analyzed just as in the run under air, and the results were essentially identical: *m*-nitrobenzyl alcohol, yield 5%; *m,m'*-dinitrostilbene oxide, yield 43%. No *m,m'*-dinitrostilbene appeared to be formed in either reaction.

Reaction of *p*-Nitrobenzyltrimethylammonium Bromide with Sodium Hydroxide.—*p*-Nitrobenzyltrimethylammonium bromide (1.376 g., 5.02×10^{-3} mole) was dissolved in 50 ml. of aqueous 0.2 *M* sodium hydroxide, and heated at 100° for 72 hr. The solution was then cooled to ca. 25°, neutralized to pH 7 with concentrated hydrochloric acid, and mixed with 5 ml. of a saturated aqueous solution of sodium perchlorate. After cooling to 5°, the reaction mixture was filtered, a white solid (1.4280 g.) being collected, m.p. 196.5-197.5°, which had an infrared spectrum (KBr) identical with that of *p*-nitrobenzyltrimethylammonium perchlorate; yield of perchlorate 1.428 g. (4.85×10^{-3} mole, 97%). The product also had the same R_f as the authentic perchlorate in thin layer chromatography. Thus essentially no reaction occurred. Under identical conditions, a 100% yield of *p,p'*-dinitrostilbene was isolated from *p*-nitrobenzyltrimethylsulfonium *p*-toluenesulfonate.

The ammonium salt was subjected to more vigorous conditions. *p*-Nitrobenzyltrimethylammonium bromide (1.374 g., 4.97×10^{-3} mole) was dissolved in 50 ml. of 0.2 *M* aqueous sodium hydroxide, and heated at reflux for 216 hr. on a hot plate. A brown solid precipitated out, and a white solid sublimed onto the condenser. The reaction mixture was cooled to ca. 25° and filtered. The precipitate and condenser were washed with petroleum ether, and the filtrate was extracted with petroleum ether. Evaporation of the petroleum ether from the combined extracts with a stream of air gave 25.4 mg. of a brown solid, which was analyzed by thin layer chromatography on alumina with 4:1 petroleum ether-ethyl ether as eluting solvent, giving a major spot at R_f 0.77. Authentic *p*-nitrotoluene had R_f 0.77 under these conditions. By comparison with the chromatographic spots of known amounts of *p*-nitrotoluene, the amount of *p*-nitrotoluene present on the chromatogram of the reaction mixture was estimated as between 25 and 50 $\mu g.$, corresponding to a total yield of 10 mg. (7.3×10^{-5} mole, 1%). For further evidence of the identity of the *p*-nitrotoluene, the brown product from the petroleum ether extractions was heated in a flask on a hot plate. The white solid which sublimed on the sides was scraped out; its infrared spectrum (KBr) was identical with that of authentic *p*-nitrotoluene.

The brown solid isolated by filtration from the original reaction mixture, 110.3 mg., not completely melted at 360°, showed no signs of a hydroxyl group in its infrared spectrum. The spectrum in KBr showed peaks at: 3030 (vw), 2930 (w), 1600 very broad (vs), 1520 (s), 1460 (s), 1400 (s), 1350 (s), 1310 (vw), 1280 (w), 1050 very broad (s), 890 shoulder (w), 850 (m), 780 (m), 700 (w) cm^{-1} . A thin layer chromatogram on alumina with 6:4 petroleum ether-chloroform for elution showed no signs of *p,p'*-dinitrostilbene (R_f 0.57). The material was essentially insoluble in acetonitrile, ethyl ether, methanol, and chloroform; it was not investigated further.

The aqueous filtrate was evaporated to dryness at reduced pressure. Thin layer chromatography on alumina with 49:1 chloroform-methanol for elution gave a major spot at R_f 0.00. The starting material, *p*-nitrobenzyltrimethylammonium bromide, has R_f 0.00 under these conditions.

Alumina column chromatography was used to analyze the brown solid, taking 100-ml. fractions. With increasingly polar solvents and mixtures (petroleum ether, ethyl ether, chloroform, methanol) up to 2:3 chloroform-methanol, 12 fractions were collected. Thin layer chromatography on each fraction using alumina with 97:3 chloroform-methanol for elution indicated that fractions 6-10 contained a compound of R_f 0.05 as their major

(21) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 118, 298.

(22) V. J. Mark, *J. Am. Chem. Soc.*, **85**, 1884 (1963).

(23) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1957, p. 299.

component. The starting material had R_f 0.05 under these conditions. Fractions 6-10 were dissolved in water and combined, then mixed with 5 ml. of a saturated aqueous solution of sodium perchlorate. The precipitate collected by filtration after cooling to 5° was dried for 24 hr. at ca. 25° and 2 mm. pressure, m.p. 196-197.5°, identical with authentic *p*-nitrobenzyltrimethylammonium perchlorate, as was the infrared spectrum. Unreacted ammonium ion therefore amounted to 580.0 mg. (1.97×10^{-3} mole, 40%), as the perchlorate.

Most of the rest of the fractions contained tars or high-melting materials. None of the fractions contained trimethylamine oxide (R_f 0.40, visible when sprayed with 95% sulfuric-5% nitric acid and heated) or *p*-nitrobenzyl alcohol (R_f 0.77) upon thin layer chromatography.

Deuterium Exchange of *p*-Nitrobenzyltrimethylammonium Ion.—A sample of *p*-nitrobenzyltrimethylammonium bromide was subjected to the same conditions for the same time as described above for *p*-nitrobenzyltrimethylsulfonium *p*-toluenesulfonate. The ammonium perchlorate was isolated and dried. The infrared spectrum (KBr) was identical with that of untreated *p*-nitrobenzyltrimethylammonium perchlorate and showed no signs of C-D bonds. The n.m.r. spectra in acetonitrile of treated and untreated perchlorate were identical also, with absorption for aromatic protons at 8.0, methylene protons at 4.5, and methyl protons at 3.1 δ . Neither the methyl nor the methylene peaks showed any diminution in the spectrum of the treated sample, using the aromatic peaks as the standard; apparently no exchange took place.

Reaction of *p*-Nitrobenzyltriphenylphosphonium Bromide with Sodium Hydroxide.—*p*-Nitrobenzyltriphenylphosphonium bromide (1.1935 g., 2.48×10^{-3} mole) was dissolved in 25 ml. of water and 25 ml. of a 0.2 *M* aqueous sodium hydroxide solution was added. The solution was heated at 100° for 72 hr.: a light brown solid precipitated and a white solid sublimed into the reflux condenser. The white solid was scraped out; yield 190.0 mg., m.p. 51-52° (lit.²⁴ m.p. for *p*-nitrotoluene 51.5°). The infrared spectrum (KBr) was identical with that of an authentic sample of *p*-nitrotoluene. Thin layer chromatography on silica gel with 4:1 petroleum ether-ethyl ether showed a single band (R_f 0.20) identical with that of *p*-nitrotoluene. The yield (0.1900 g., 1.39×10^{-3} mole) of *p*-nitrotoluene was therefore 56%.

The light brown solid (yield 0.6680 g.) was analyzed by thin layer chromatography on alumina with 1:1 chloroform-petroleum ether for elution (Table II).

TABLE II

R_f	Estimated amount	Ultraviolet color
0.35	Major	Black
.88	0.5%	Yellow
.88	Trace	Black
.95	Trace	Pink

(24) W. H. Gibson, R. Duckham, and R. Fairbairn, *J. Chem. Soc.*, **121**, 270 (1922).

Under these conditions triphenylphosphine oxide has R_f 0.35. The material is therefore probably slightly impure triphenylphosphine oxide; yield 0.6680 g. (2.41×10^{-3} mole, 97%). *p*-Nitrobenzyl alcohol (R_f 0.25) was apparently not formed, and *p,p'*-dinitrostilbene (R_f 0.88) was apparently formed. By comparison with spots for known amounts of the stilbene, its yield in this reaction was estimated as 0.5%.

Column chromatography of 0.3143 g. of the solid on alumina taking 50-ml. fractions gave 10 fractions (95% recovery from column). Increasingly polar solvents (petroleum ether, ethyl ether, ethyl acetate, chloroform, methanol) and mixtures up to 1:1 chloroform-methanol were used. Thin layer chromatography indicated that small amounts of *p,p'*-dinitrostilbene were present in fractions 3 and 4, and that triphenylphosphine oxide was a major component of fractions 4-7. Rechromatography of fractions 4 and 7 and combination of the triphenylphosphine oxide from these with original fractions 5 and 6 gave a solid, m.p. 155-156° (lit.²⁵ m.p. for triphenylphosphine oxide 156°). The infrared spectrum (KBr) was identical with that of authentic triphenylphosphine oxide, and the microanalysis agreed well with the proposed formula.

Anal. Calcd. for $C_{18}H_{15}OP$: C, 77.68; H, 5.43. Found: C, 77.67; H, 5.51.

The yield of analytically pure triphenylphosphine oxide was 0.2843 g., equivalent to 0.606 g. (2.18×10^{-3} mole, 88%) if the entire sample had been chromatographed.

To check a possible source of the *p,p'*-dinitrostilbene, *p*-nitrotoluene (0.3485 g., 2.52×10^{-3} mole) was added to 50 ml. of 0.1 *M* aqueous sodium hydroxide and the solution heated on the steam bath for 24 hr. A yellow solid (2 mg.) was isolated by filtration. Thin layer chromatography of the yellow solid on silica gel with toluene for elution gave a major spot at R_f 0.43; *p,p'*-dinitrostilbene has R_f 0.43 under the same conditions and is yellow under ultraviolet light (Table III).

TABLE III

R_f	Estimated amount	Ultraviolet color
0.25	Large	Pink
.35	Significant	Yellow
.43	Major	Yellow
.50	Small	Yellow

p-Nitrobenzyltriphenylphosphonium bromide (1.1955 g., 2.48×10^{-3} mole) was dissolved in 47.50 ml. of water and 2.50 ml. of 0.197 *M* aqueous sodium hydroxide was added, giving final concentrations of 0.05 *M* phosphonium salt and 0.01 *M* hydroxide. The phosphonium salt concentration was the same as in the previous experiment, but the hydroxide concentration was one-tenth as great. The solution was heated at 100° for 3 hr. and then cooled and filtered. The precipitate recovered showed essentially no sign of *p,p'*-dinitrostilbene by thin layer chromatography on silica gel with toluene for elution. Authentic *p,p'*-dinitrostilbene had R_f 0.43 under the same conditions.

(25) H. Staudinger and J. Meyer, *Helv. Chim. Acta*, **2**, 635 (1919).