

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

## Mechanisms of $\alpha$ -Elimination. *p*-Nitrobenzylsulfonium Ions Reacting with Aqueous Hydroxide<sup>1-3</sup>

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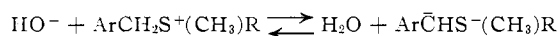
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The four sulfonium salts  $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{S}^+(\text{CH}_3)\text{RX}^-$  (where  $\text{R}, \text{X}^- = \text{C}_6\text{H}_5, \text{ClO}_4^-; p\text{-ClC}_6\text{H}_4, \text{ClO}_4^-; p\text{-CH}_3\text{C}_6\text{H}_4, \text{ClO}_4^-$ ; and  $(\text{CH}_3)_2\text{CH}, \text{Br}^-$ ) were synthesized, and a study of their decomposition in aqueous sodium hydroxide solution at 60° was made. Under nitrogen, the per cent yields of *p*-nitrobenzyl alcohol and *p,p'*-dinitrostilbene were, respectively: 19, 19; 10, 16; 12, 21; <0.5, 48. The first two salts mentioned above both gave less alcohol and substantial amounts of *p,p'*-dinitrostilbene oxide when the reaction was carried out under air. The electrical nature of the substituent on the leaving group appears to affect the yield of *p,p'*-dinitrostilbene only slightly. Rate-determining formation of *p*-nitrophenylcarbene, with a steric effect of the leaving group upon the subsequent product-determining reaction, is consistent with, but not required by, the results.

We recently reported that, although *p*-nitrobenzyl-dimethylsulfonium ion reacts with aqueous sodium hydroxide to form 100% *p,p'*-dinitrostilbene, the corresponding trimethylammonium and triphenylphosphonium ions form none of the stilbene.<sup>1</sup> Since the course of reaction was dependent on the nature of the leaving group, it seemed very important to synthesize and study the products of reaction of some other *p*-nitrobenzylsulfonium ions with aqueous sodium hydroxide.

By reaction of equimolar quantities of the phenyl methyl sulfide, *p*-nitrobenzyl alcohol, and 70% perchloric acid in nitromethane at room temperature,<sup>4</sup> *p*-nitrobenzylmethylphenylsulfonium perchlorate, *p*-nitrobenzylmethyl-*p*-chlorophenylsulfonium perchlorate, and *p*-nitrobenzylmethyl-*p*-tolylsulfonium perchlorate were prepared. By reaction of *p*-nitrobenzyl bromide with methyl isopropyl sulfide in acetonitrile at room temperature, *p*-nitrobenzylmethylisopropylsulfonium bromide was prepared.

The products of reaction of each of the four sulfonium salts with aqueous sodium hydroxide at 60° were investigated. In each case a red colored solution immediately formed on addition of hydroxide, indicative of ylid formation ( $\text{Ar} = p\text{-nitrophenyl}$ ).



In all cases mixtures of products formed and were isolated by filtration and chromatographic separation, both thin layer and column, on alumina. In addition, the aqueous filtrates were extracted with ether to isolate *p*-nitrobenzyl alcohol if formed. In each case a number of products was formed, only part of which could be identified. Some of the experiments were performed with and some without a protective cover of nitrogen. The fact that a quantitative yield of *p,p'*-dinitrostilbene was not formed from any of these salts indicates that the stilbene-forming reaction is extraordinarily sensitive to the nature of the leaving group.

(1) Previous paper: I. Rothberg and E. R. Thornton, *J. Am. Chem. Soc.*, **86**, 3296 (1964).

(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.

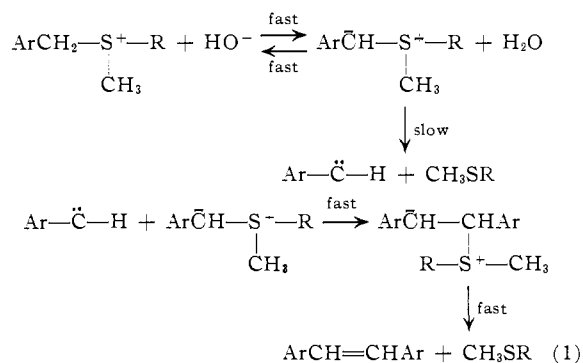
(3) For further details cf. I. Rothberg, Ph.D. dissertation in chemistry, University of Pennsylvania, 1963.

(4) C. O. Hinsberg, *Chem. Ber.*, **69**, 492 (1936); N. J. Leonard, T. W. Milligan, and T. L. Brown, *J. Am. Chem. Soc.*, **82**, 4075 (1960); T. W. Milligan and B. C. Minor, *J. Org. Chem.*, **28**, 235 (1963).

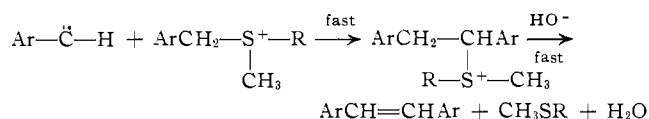
The yields of the three products which could be identified, *p*-nitrobenzyl alcohol, *p,p'*-dinitrostilbene, and *p,p'*-dinitrostilbene oxide, are given in Table I.

*p,p'*-Dinitrostilbene was almost quantitatively recovered (97%) when passed through an alumina column; therefore the relatively low yields are not due to decomposition on work-up. The yield of *p,p'*-dinitrostilbene was much smaller (maximum 48%) with these four salts than with *p*-nitrobenzyl-dimethylsulfonium *p*-toluenesulfonate (100%).

Variation in the yield of *p,p'*-dinitrostilbene is 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. Therefore it seems probable that a steric factor is responsible for the differences among  $\text{R} = \text{C}_6\text{H}_5, (\text{CH}_3)_2\text{CH}$ , and  $\text{CH}_3$ . An attractive hypothesis based on a proposed<sup>1,5</sup> mechanism involving *p*-nitrophenylcarbene is that the carbene is produced and will attack the species present in solution by the pathway which requires the least energy. When  $\text{R} = \text{CH}_3$  the attack on the reversibly-formed ylid requires the least energy and is the predominant reaction



or alternatively<sup>1</sup> carbene insertion in a CH bond of the sulfonium ion occurs instead of reaction 1



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,

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

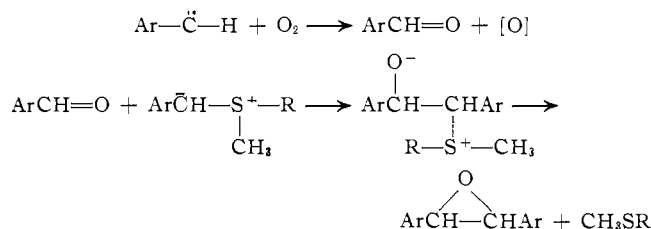
TABLE I  
PRODUCTS OF REACTION OF  $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{S}^+(\text{CH}_3)\text{RX}^-$   
WITH AQUEOUS SODIUM HYDROXIDE AT 60°

R	X <sup>-</sup>	Conditions	Yield, %		
			<i>p</i> -Nitrobenzyl alcohol	<i>p,p'</i> -Dinitrostilbene	<i>p,p'</i> -Dinitrostilbene oxide
C <sub>6</sub> H <sub>5</sub> <sup>a</sup>	ClO <sub>4</sub> <sup>-</sup>	Air	8	21	7
		Under N <sub>2</sub>	19	19	~0
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> <sup>a</sup>	ClO <sub>4</sub> <sup>-</sup>	Air	7	10	13
		Under N <sub>2</sub>	10	16	~0
<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> <sup>a</sup>	ClO <sub>4</sub> <sup>-</sup>	Under N <sub>2</sub>	12	21	~0
		(CH <sub>3</sub> ) <sub>2</sub> CH <sup>b</sup>	Br <sup>-</sup>	Under N <sub>2</sub>	<0.5

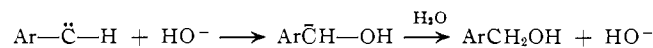
<sup>a</sup> 0.01 *M* sulfonium salt, 0.02 *M* hydroxide. <sup>b</sup> 0.1 *M* sulfonium salt, 0.2 *M* hydroxide.

and reaction with hydroxide ion or water to form *p*-nitrobenzyl alcohol).

The best explanation for the formation of *p,p'*-dinitrostilbene oxide seems to be the formation of *p*-nitrophenylcarbene which then attacks oxygen to form *p*-nitrobenzaldehyde. This type of reaction has been reported in the past.<sup>6</sup> Reaction of *p*-nitrobenzaldehyde with carbene or ylid then forms *p,p'*-dinitrostilbene oxide



When oxygen was excluded by flushing the system well with nitrogen before beginning the reaction with hydroxide, a negligible amount of *p,p'*-dinitrostilbene oxide was found, indicating that the stilbene oxide was formed from the reaction of oxygen with carbene. This is in contrast with the case of *m*-nitrobenzyl-dimethylsulfonium ion reported earlier<sup>1</sup> where oxide was formed in the same yield under nitrogen as under air. The yields of *p*-nitrobenzyl alcohol increased when air was excluded from the system indicating that at least part of the alcohol was formed by the reaction of carbene with hydroxide or water



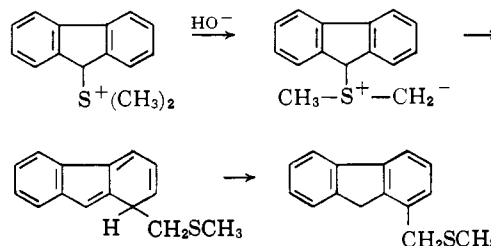
To check the possibility that the increase in alcohol yield was due to nucleophilic attack by water on the sulfonium ion during the time that the solutions were being flushed with nitrogen previous to the addition of hydroxide, the nitrogen-flushing conditions were carried out on a solution of *p*-nitrobenzylmethylphenylsulfonium perchlorate. On extraction with ether only a 0.5% yield of *p*-nitrobenzyl alcohol was obtained, so the increased *p*-nitrobenzyl alcohol could not have come from this source.

The fact that only a little or no *p*-nitrobenzyl alcohol is formed in these reactions is unexpected. Attack of carbene on hydroxide or water would be expected to be more important than it is, because their concentrations are far greater than the concentration of ylid. Possibly *p*-nitrophenylcarbene is a very selective carbene and is simply more reactive toward ylid

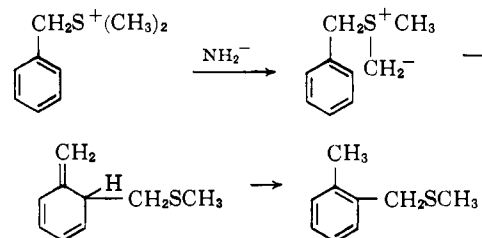
or other species present in solution than toward water or hydroxide. The fact that small amounts of alcohol are formed in some of these reactions, whereas none was formed in the reaction with *p*-nitrobenzyl-dimethylsulfonium ion,<sup>1</sup> supports this selectivity argument in the sense that, if attack of carbene on other species in solution is slowed, attack by hydroxide ion might successfully compete. We cannot rule out the possibility that some alcohol is formed through direct displacement by hydroxide on the sulfonium ion, however.

The other products of the reactions were studied, but could not be identified. When the *p*-nitrobenzylmethylarylsulfonium perchlorates reacted with hydroxide, in each case a large fraction of heavy oil which solidified to a brown tar was obtained on chromatographing the reaction products through alumina. These fractions in each case appeared to be homogeneous by thin layer chromatography, but the fact that they were tars and their complex n.m.r. spectra indicated that they were probably mixtures.

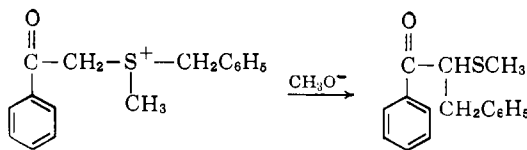
Rearrangements of sulfonium salts are known to occur. When treated with alcoholic sodium hydroxide 9-dimethylsulfoniumfluorene undergoes a Sommelet rearrangement to give fluorene-1-dimethyl sulfide<sup>7</sup>



Benzyl-dimethylsulfonium bromide undergoes Sommelet rearrangement under strongly basic conditions, with sodium amide in liquid ammonia<sup>8</sup>



The Stevens rearrangement has also been observed with sulfonium salts. When allowed to react with sodium methoxide in methanol, phenacylmethylbenzylsulfonium bromide rearranged<sup>9</sup>



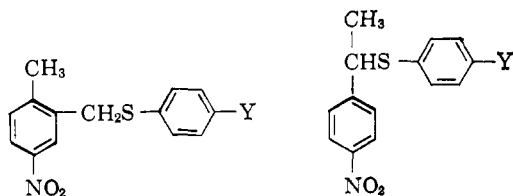
The large chromatographic fractions, of oily material might be a mixture of products resulting from Stevens and Sommelet rearrangements. The products of both of these rearrangements would be similar and

(7) A. W. Johnson and R. B. LaCount, *ibid.*, **83**, 417 (1961).

(8) C. R. Hauser, S. W. Kantor, and W. R. Brasen, *ibid.*, **75**, 2660 (1953).

(9) T. Thomson and T. S. Stevens, *J. Chem. Soc.*, 69 (1932).

perhaps not separated by either column or thin layer chromatography. However, the molecular weight and elemental analysis should be identical for the products of both rearrangements.



When  $Y = H$ , the mol. wt. should be 259; analysis of the oil gave mol. wt. 271 and an elemental analysis similar, but with considerably more N and considerably less S, to that expected (see Experimental section). When  $Y = Cl$ , the mol. wt. should be 294; analysis of the oil gave mol. wt. 320 and an elemental analysis similar, but with considerably less S, to that expected. When  $Y = CH_3$ , the mol. wt. should be 273; analysis of the oil gave mol. wt. 328 and an elemental analysis similar, but with considerably less S, to that expected. Therefore, if the rearrangement products were present they were grossly impure.

Other possible products could result from insertion of *p*-nitrophenylcarbene into CH bonds or across double bonds in the manner typical of other carbenes. Thus a very large number of products is conceivable. It appears as if most of the unidentified material is not polymeric, so it may be possible to identify further products by more extensive analytical work.

Our hypothetical mechanisms for these reactions seem to fit the experimental facts but are by no means proven. We could not find experimental evidence of carbene insertion reactions, unfortunately. Some preliminary attempts to trap the hypothetical carbene intermediate have not yet been fruitful.

### Experimental

All melting points are uncorrected except where noted. Infrared spectra were run on a Perkin-Elmer 421 spectrometer; n.m.r. spectra were run on a Varian high resolution 60 Mc. instrument.

**Synthesis of *p*-Nitrobenzylmethylphenylsulfonium Perchlorate.**—Methyl phenyl sulfide (Aldrich, 14.4 g., 0.116 mole) and *p*-nitrobenzyl alcohol (Eastman, 18.0 g., 0.116 mole) were dissolved in 150 ml. of nitromethane and to the solution 16.8 g. (0.116 mole) of 70% perchloric acid was added. After 72 hr. at *ca.* 25° the solvent was evaporated to *ca.* 50 ml. at reduced pressure on a rotary evaporator. Upon addition of excess ether an oil came out of solution and solidified upon standing at 5° for 10 hr.; yield 15.0 g. (0.0418 mole, 36%) of crude *p*-nitrobenzylmethylphenylsulfonium perchlorate, m.p. 132–136°. The solid was purified by dissolving it in acetone and precipitating it with excess ether; recovery 14.3 g. (0.0397 mole, 34%) of brownish white solid, m.p. 133–136°. Purification was repeated eight times giving 10.3 g. (0.0287 mole, 25%) of white solid, m.p. 135–137°. The infrared spectrum (KBr) showed bands at: 3100 (vw), 3070 (m), 3000 (vw), 2920 (w), 2850 (m), 1600 (m), 1570 (w), 1510 (vs), 1480 (m), 1440 (m), 1390 (w), 1340 (s), 1320 (m), 1290 (w), 1220 (m), 1200 (w), 1100 (vs), 1010 doublet (w), 950 (w), 850 (m), 800 (m), 730 (m), 690 (m), 630 doublet (m)  $cm^{-1}$ . Thin layer chromatography on alumina with 1:1 chloroform-acetonitrile for elution showed a single spot with  $R_f$  0.63.

*Anal.* Calcd. for  $C_{14}H_{13}ClNO_2S$ : C, 46.74; H, 3.92; S, 8.91. Found: C, 46.80; H, 4.26; S, 8.90.

**Synthesis of *p*-Nitrobenzylmethyl-*p*-tolylsulfonium Perchlorate.**—To prepare *p*-tolyl methyl sulfide, *p*-methylphenyl mercaptan (K and K Laboratories, 50 g., 0.40 mole) was dissolved in 118 ml. of a 20% aqueous sodium hydroxide solution (0.59 mole of base) and to the solution was slowly added 58 g. (0.47 mole) of methyl sulfate with stirring. After refluxing for 2 hr., the oily

top layer was separated, dissolved in 100 ml. of ethyl ether, and the ether solution washed twice with 25 ml. portions of water. The ether solution was dried over anhydrous magnesium sulfate for 24 hr. and the ether removed at reduced pressure on a rotary evaporator. Distillation of the oily residue gave 43 g. (0.312 mole, 78%) of *p*-tolyl methyl sulfide as a colorless oil, b.p. 104–105° (20 mm.) (lit.<sup>10</sup> 104–105° (20 mm.)).

*p*-Tolyl methyl sulfide (16.1 g., 0.116 mole) and *p*-nitrobenzyl alcohol (18.0 g., 0.116 mole) were dissolved in 150 ml. of nitromethane and to the solution 16.8 g. (0.116 mole) of 70% perchloric acid was added. After 72 hr. at *ca.* 25° the solvent was evaporated to *ca.* 75 ml. at reduced pressure on a rotary evaporator. Upon addition of excess ether an oil came out of solution and upon standing at 5° for 12 hr. crystallized; yield 19.0 g. (0.0507 mole, 44%) of crude *p*-nitrobenzylmethyl-*p*-tolylsulfonium perchlorate, m.p. 140–143°. The solid was purified by dissolving it in acetone and precipitating it with excess ether. Purification was repeated four times giving 16.0 g. (0.0427 mole, 37%) of white solid, m.p. 141.5–143°. The infrared spectrum (KBr) showed bands at: 3100 (w), 3070 (m), 3010 (m), 2980 (vw), 2910 (m), 2850 (m), 1600 (m), 1510 (s), 1490 (s), 1430 (m), 1390 (m), 1340 (s), 1320 (m), 1300 (vw), 1220 (m), 1200 (w), 1100 (vs), 1000 (w), 950 (w), 850 (m), 800 (s), 750 (w), 690 (s), 630 doublet (s), 600 (m)  $cm^{-1}$ . Thin layer chromatography on alumina with 1:1 chloroform-methanol for elution showed a single spot with  $R_f$  0.58.

*Anal.* Calcd. for  $C_{15}H_{16}ClNO_2S$ : C, 48.19; H, 4.32; S, 8.58. Found: C, 47.76; H, 4.24; S, 8.39.

**Synthesis of *p*-Nitrobenzylmethyl-*p*-chlorophenylsulfonium Perchlorate.**—To prepare *p*-chlorophenyl methyl sulfide, sodium (8 g., 0.35 g.-atom) was added to 150 ml. of ethanol and to the solution was added 43.2 g. (0.30 mole) of *p*-chlorophenyl mercaptan. Methyl iodide (60 g., an excess) was added slowly with vigorous stirring and the mixture was refluxed for 2 hr. After the ethanol had been removed by distillation, the oily residue was mixed with 150 ml. of ethyl ether and the ether solution washed twice with 50-ml. portions of water. The ether solution was dried over anhydrous magnesium sulfate for 10 hr. and the ether removed at reduced pressure. Distillation of the oily residue gave 40.0 g. (0.254 mole, 84%) of *p*-chlorophenyl methyl sulfide, b.p. 112–113° (18 mm.) (lit.<sup>11</sup> b.p. 112° (18 mm.)).

*p*-Chlorophenyl methyl sulfide (15.9 g., 0.10 mole) and *p*-nitrobenzyl alcohol (15.3 g., 0.10 mole) were dissolved in 150 ml. of nitromethane and to the solution 14.3 g. (0.10 mole) of 70% perchloric acid was added. After 72 hr. at *ca.* 25° the solvent was evaporated to *ca.* 75 ml. at reduced pressure. Upon addition of excess ether an oil came out of solution and soon crystallized; yield 12.0 g. (0.0305 mole, 31%) of yellow solid, crude *p*-nitrobenzylmethyl-*p*-chlorophenylsulfonium perchlorate, m.p. 160–165°. The solid was purified by dissolving it in acetone and precipitating it with excess ether. Purification was repeated five times giving 9.3 g. (0.0236 mole, 24%) of white solid, m.p. 170–171°. The infrared spectrum (KBr) showed bands at: 3100 (w), 3080 (w), 2920 (m), 2850 (w), 1600 (m), 1520 (s), 1470 (s), 1440 (m), 1390 (m), 1350 (s), 1320 (m), 1300 (vw), 1220 (m), 1200 (m), 1100 (vs), 1000 (m), 950 doublet (m), 850 (m), 800 doublet (s), 750 (m), 690 (m), 630 doublet (s), 590 (m)  $cm^{-1}$ . Thin layer chromatography on alumina with 1:1 chloroform-acetonitrile for elution gave a single band of  $R_f$  0.52.

*Anal.* Calcd. for  $C_{14}H_{13}Cl_2NO_2S$ : C, 42.65; H, 3.32; S, 8.13. Found: C, 42.71; H, 3.31; S, 8.10.

**Synthesis of *p*-Nitrobenzylmethylisopropylsulfonium Bromide.**—Methyl isopropyl sulfide (Aldrich, 20 g., an excess) and *p*-nitrobenzyl bromide (Matheson Coleman and Bell; 15.0 g., 0.0695 mole) were dissolved in 20 ml. of acetonitrile and allowed to stand at *ca.* 25° for 24 hr. Addition of an excess of ethyl ether gave a yellowish white solid, crude *p*-nitrobenzylmethylisopropylsulfonium bromide (16.1 g., 0.0526 mole, 76%), m.p. 101–103°. The compound was purified by dissolving it in methanol and precipitating it with excess ether. Purification was repeated four times giving 9.0 g. (0.0294 mole, 43%) of white solid, m.p. 101–102°. The infrared spectrum (KBr) showed bands at: 3100 (vw), 3070 (vw), 3040 (vw), 2970 (s), 2950 (s), 2900 (s), 1600 (m), 1520 (s), 1490 (m), 1450 doublet (m), 1400 triplet (m), 1375 (m), 1350 (s), 1300 triplet (m), 1260 (m), 1200 (w), 1180 (vw), 1160 (m), 1100 doublet (m), 1070 (s), 1010 (w),

(10) H. Gilman and N. J. Beaber, *J. Am. Chem. Soc.*, **47**, 449 (1925).

(11) H. Lumbruso and G. Dumas, *Bull. soc. chim. France*, 651 (1955); G. Leandri and A. Mangini, *Gazz. chim. ital.*, **84**, 1 (1954).

980 (m), 880 (w), 860 (s), 850 (m), 830 (w), 800 (m), 750 (w), 700 (s), 630 (w)  $\text{cm}^{-1}$ .

*Anal.* Calcd. for  $\text{C}_{11}\text{H}_{15}\text{BrNO}_2\text{S}$ : C, 43.14; H, 5.27; S, 10.47. Found: C, 43.55; H, 5.40; S, 10.63.

**Preparation of *p,p'*-Dinitrostilbene Oxide.**—Both *cis*- and *trans-p,p'*-dinitrostilbene oxide were prepared by the reaction of *p*-nitrobenzyl chloride with *p*-nitrobenzaldehyde in methanol containing potassium carbonate<sup>12</sup>; for the *trans* form, m.p. 200–201° (lit.<sup>12</sup> 200–201°); for the *cis* form, m.p. 152–154° (lit.<sup>12</sup> 153–154°). Thin layer chromatography on alumina with toluene for elution showed a single band for both isomers with the same  $R_f$  0.60, for both. These compounds were used as the standards for comparisons of infrared spectra and chromatographic behavior.

**Other Compounds.**—*p,p'*-Dinitrostilbene, available from previous work,<sup>1</sup> and *p*-nitrobenzyl alcohol (Eastman) were examined, found to be essentially pure by thin layer chromatography, and used as the standards for comparisons of infrared spectra and chromatographic behavior.

**Analytical Methods.**—The combination of column and thin layer chromatography described in more detail previously<sup>1</sup> was used for the analysis of products of the reactions of the sulfonium salts with aqueous sodium hydroxide. Thin layer chromatograms were run on each fraction from the column.

**Reaction of *p*-Nitrobenzylmethylphenylsulfonium Perchlorate with Sodium Hydroxide.** *p*-Nitrobenzylmethylphenylsulfonium perchlorate (1.8033 g.,  $5.00 \times 10^{-3}$  mole) was dissolved in 545 ml. of water and 5.0 ml. of 2 *M* aqueous sodium hydroxide added, then allowed to react in a constant temperature bath at 60° for 22 hr. The solution immediately became red on addition of hydroxide ion. After neutralization to pH 7 the brown, semisolid precipitate (0.6947 g.) was removed by filtration, and the filtrate was extracted with three 100-ml. portions of ethyl ether. The combined ether extracts were dried for 12 hr. over anhydrous magnesium sulfate; after filtration, the ether was evaporated at reduced pressure. The residue, a white solid (61.3 mg.), m.p. 89–93°, showed essentially a single band of  $R_f$  0.15, identical with that of authentic *p*-nitrobenzyl alcohol, on thin layer chromatography on alumina with toluene for elution. The infrared spectrum of the solid was identical with that of authentic *p*-nitrobenzyl alcohol. After recrystallization from water a white solid, *p*-nitrobenzyl alcohol, was obtained, m.p. 92–93° (lit.<sup>13</sup> m.p. 92°).

The brown semisolid filtered from the reaction mixture gave the results listed in Table II upon thin layer chromatography on alumina with toluene for elution.

TABLE II

$R_f$	Estimated amount <sup>a</sup>	Ultraviolet color
0.00	Significant	Black
.50	Small	Yellow fluorescent
.62	Trace	Brown
.70	Small	Black
.75	Significant	Yellow fluorescent
.80	Major	Black
.89	Small	Black
.95	Trace	Black
<i>p,p'</i> -Dinitrostilbene		
0.75	Major	Yellow fluorescent
<i>p,p'</i> -Dinitrostilbene oxide		
0.70	Major	Black

<sup>a</sup> Key: major > large > significant > small > trace.

Column chromatography was used to purify the brown solid, using a 0.6942-g. sample, on alumina and taking 50-ml. fractions. With increasingly polar solvents and mixtures (petroleum ether, benzene, acetone, methanol) up to 4:1 acetone-methanol, 14 fractions were collected with 94% recovery from the column. Thin layer chromatography on each fraction indicated that fraction 9 contained essentially all of the *p,p'*-dinitrostilbene oxide, fractions 10–11 contained essentially all of the *p,p'*-dinitrostilbene, and fractions 5–6 might possibly contain small amounts of methyl phenyl sulfide. The infrared spectrum (KBr) of fraction 9 was identical with that of *p,p'*-dinitrostilbene oxide. After recrystallization from dioxane, the compound had a m.p. and mixture m.p. with authentic *trans-p,p'*-dinitrostilbene oxide of 200–201°; yield 48 mg. ( $0.168 \times 10^{-3}$  mole, 7%). Fractions

10–11 were combined and the infrared spectrum (KBr) was identical with that of authentic *p,p'*-dinitrostilbene. A small amount refluxed with a crystal of iodine in nitrobenzene gave on cooling a yellow solid, m.p. 288–290° (uncor.), 300–302° (cor.) (lit.<sup>5</sup> 288° (uncor.), 304–306° (cor.)); yield from reaction, 142.8 mg. ( $0.530 \times 10^{-3}$  mole, 21%). The yield of *p*-nitrobenzyl alcohol was 61.3 mg. ( $0.400 \times 10^{-3}$  mole, 8%).

In view of the formation of *p,p'*-dinitrostilbene oxide in this reaction, it was repeated under nitrogen. *p*-Nitrobenzylmethylphenylsulfonium perchlorate (1.8030 g.,  $5.00 \times 10^{-3}$  mole) was added to 495 ml. of water and flushed with nitrogen (99.996% pure and passed through Fieser<sup>14</sup> solution) for 19 hr., then warmed at 60° for 10 min. to dissolve the sulfonium salt. Sodium hydroxide (5.0 ml. of 2.0 *M* aqueous solution) was then added. The solution was allowed to react for 24 hr. under nitrogen, cooled to ca. 25°, and neutralized to pH 7 with concentrated hydrochloric acid. A brown semisolid (0.7641 g.) was removed by filtration. The filtrate was examined by thin layer chromatography with 1:1 chloroform-acetonitrile for elution. Authentic *p*-nitrobenzylmethylphenylsulfonium perchlorate ( $R_f$  0.20) was easily visible under these conditions and was not visible from the filtrate; less than 2% of this reactant was present.

The filtrate and the brown solid were analyzed just as in the run under air, and the results were: *p*-nitrobenzyl alcohol yield, 19%; *p,p'*-dinitrostilbene yield, 19%; *p,p'*-dinitrostilbene oxide yield, no more than a trace.

Also, fraction 6, which showed essentially a single band on thin layer chromatography, was examined further. The microanalysis was compared with that calculated for the Stevens or Sommet rearrangement products (isomers), calling for a molecular formula  $\text{C}_{14}\text{H}_{18}\text{NO}_2\text{S}$ , mol. wt. 259, and elemental composition C, 64.84; H, 5.05; N, 5.04; O, 12.34; S, 12.37.

*Anal.* Found: C, 63.72; H, 4.57; N, 7.32; S, 7.05; mol. wt. (Rast) 271.

Indications that fraction 6 was not a pure compound, even though homogeneous by thin layer chromatography, include the fact that it was a heavy yellow oil which eventually solidified into a brown tar and its very complex n.m.r. spectrum.

**Hydrolysis of *p*-Nitrobenzylmethylphenylsulfonium Perchlorate.**—To check the possibility that a significant amount of *p*-nitrobenzyl alcohol might have formed by hydrolysis before addition of hydroxide in the reaction run under nitrogen, *p*-nitrobenzylmethylphenylsulfonium perchlorate (1.803 g.,  $5.00 \times 10^{-3}$  mole) was added to 500 ml. of water and flushed with nitrogen for 24 hr., and warmed at 60° for 15 min. to dissolve the salt. The solution was then cooled to room temperature and extracted with three 150-ml. portions of ether. The ether solution was dried for 12 hr. over anhydrous magnesium sulfate, and after filtration the ether was evaporated at reduced pressure. The residue was 4.0 mg. ( $2.62 \times 10^{-5}$  mole, 0.5%) of *p*-nitrobenzyl alcohol, with  $R_f$  0.45, identical with that of authentic *p*-nitrobenzyl alcohol, by thin layer chromatography on alumina with chloroform for elution.

**Reaction of *p*-Nitrobenzylmethyl-*p*-chlorophenylsulfonium Perchlorate with Sodium Hydroxide.**—*p*-Nitrobenzylmethyl-*p*-chlorophenylsulfonium perchlorate (1.9771 g.,  $5.03 \times 10^{-3}$  mole) was dissolved in 495 ml. of water at 60° and 5.0 ml. of 2 *M* aqueous sodium hydroxide added, then allowed to react in a constant temperature bath at 60° for 22 hr. The solution immediately became red on addition of hydroxide ion. After neutralization of the cooled solution to pH 7 with concentrated hydrochloric acid, the brown semisolid precipitate (0.9715 g.) was removed by filtration. The filtrate was analyzed by thin layer chromatography on alumina with 1:1 chloroform-acetonitrile for elution. Authentic *p*-nitrobenzylmethyl-*p*-chlorophenylsulfonium perchlorate ( $R_f$  0.32) was easily visible under these conditions and was not visible from the filtrate; less than 3% of this reactant was present. The filtrate was extracted with ether, as in the previous experiments. The residue after evaporation of ether, a white solid (55.7 mg.), m.p. 90–92° (lit.<sup>13</sup> m.p. 92° for *p*-nitrobenzyl alcohol), showed essentially a single band of  $R_f$  0.55, identical with that of *p*-nitrobenzyl alcohol, on thin layer chromatography on alumina with chloroform for elution. The infrared spectrum was identical with that of authentic *p*-nitrobenzyl alcohol.

Column chromatography was used to purify the brown solid, using a 0.9715-g. sample on alumina and taking 25-ml. fractions,

(12) E. Bergmann and J. Hervey, *Chem. Ber.*, **62**, 893 (1929).

(13) A. Basler, *ibid.*, **16**, 2714 (1883).

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

in almost exactly the same way as described for the previous reactions (above) with similar results: *p,p'*-dinitrostilbene oxide, yield 91.8 mg. ( $0.320 \times 10^{-3}$  mole, 13%); *p,p'*-dinitrostilbene, yield 69.1 mg. ( $0.256 \times 10^{-3}$  mole, 10%); *p*-nitrobenzyl alcohol, yield 55.7 mg. ( $0.364 \times 10^{-3}$  mole, 7%); possibly very small amounts of *p*-chlorophenyl methyl sulfide.

This reaction, as the previous one, was repeated under nitrogen under conditions essentially identical with those described above. Less than 3% of starting sulfonium salt remained after the reaction. Column chromatography was used to purify the brown semisolid (0.9340 g.) which was isolated from the reaction mixture by filtration. The results were: *p*-nitrobenzyl alcohol, yield 10%; *p,p'*-dinitrostilbene, yield 16%; *p,p'*-dinitrostilbene oxide, yield, none detected.

Also, fraction 7, which showed essentially a single band on thin layer chromatography, was examined further. The microanalysis was compared with that calculated for the Stevens or Sommelet rearrangement products, calling for a molecular formula  $C_{14}H_{12}ClNO_2S$ , mol. wt. 294, and elemental composition C, 57.24; H, 4.12; Cl, 12.07; N, 4.77; O, 10.89; S, 10.91.

*Anal.* Found: C, 58.61; H, 4.53; Cl, 12.76; N, 6.40; S, 6.49; mol. wt. (Rast) 320.

Fraction 7 was a heavy oil which solidified to a brown tar and had a very complex n.m.r. spectrum, indicating it was not a pure compound.

**Reaction of *p*-Nitrobenzylmethyl-*p*-tolylsulfonium Perchlorate with Sodium Hydroxide.**—In view of the results with the two compounds above, this reaction was run only under nitrogen. *p*-Nitrobenzylmethyl-*p*-tolylsulfonium perchlorate (1.8812 g.,  $5.03 \times 10^{-3}$  mole) was added to 495 ml. of water and the system flushed with nitrogen for 19 hr. just as described above. After warming at 60° for 15 min. to dissolve the salt, 5.0 ml. of 2 *M* aqueous sodium hydroxide was added. The solution, which immediately became red upon addition of hydroxide, was heated at 60° for 22 hr., cooled to ca. 25°, and neutralized to pH 7 with concentrated hydrochloric acid. The brown semisolid precipitate (0.8636 g.) was removed by filtration.

Column chromatography was used to purify the brown solid, using a 0.8636-g. sample on alumina and taking 25-ml. fractions, in almost exactly the same way described for the previous reactions (above) with similar results: *p*-nitrobenzyl alcohol, yield 92.0 mg. ( $0.600 \times 10^{-3}$  mole, 12%); *p,p'*-dinitrostilbene, yield 144.5 mg. ( $0.534 \times 10^{-3}$  mole, 21%); *p,p'*-dinitrostilbene oxide, yield, no more than a trace.

Also, fractions 5-6, which showed essentially a single band on thin layer chromatography, were examined further. The microanalysis was compared with that calculated for the Stevens or Sommelet rearrangement products, calling for a molecular formula  $C_{16}H_{13}NO_2S$ , mol. wt. 273, and elemental composition C, 65.91; H, 5.53; N, 5.12; O, 11.71; S, 11.73.

*Anal.* Found: C, 64.00; H, 4.94; N, 6.53; S, 6.73; mol. wt. (Rast), 328.

Fractions 5-6 were a heavy oil which solidified to a brown tar and had a very complex n.m.r. spectrum, indicating it was not a pure compound.

**Reaction of *p*-Nitrobenzylmethylisopropylsulfonium Bromide with Sodium Hydroxide.**—*p*-Nitrobenzylmethylisopropylsulfonium bromide (1.5306 g.,  $5.00 \times 10^{-3}$  mole) was dissolved in 45 ml. of water, the solution flushed with nitrogen (99.996% and passed through Fieser<sup>14</sup> solution) for 21 hr., and 5.0 ml. of 2 *M* aqueous sodium hydroxide added. The solution, which im-

mediately became red on addition of hydroxide, was allowed to react at 60° for 19 hr., cooled to ca. 25°, and neutralized to pH 7 with concentrated hydrochloric acid. The brown solid (0.7074 g.) was removed by filtration, and the filtrate was extracted with ether, as in the previous experiments. The residue after evaporation of ether (3.2 mg.), if entirely *p*-nitrobenzyl alcohol, would correspond to a yield of less than 0.5%.

The brown solid filtered from the reaction mixture gave the results listed in Table III upon thin layer chromatography on alumina with toluene for elution.

TABLE III

$R_f$	Estimated amount	Ultraviolet color
0.00	Major	Black
.23	Significant	Black
.34	Small	Black
.55	Small	Black
.60	Major	Yellow fluorescent
.70	Small	Black
.80	Small	Black
.98	Trace	Black
<i>p</i> -Nitrobenzyl alcohol		
0.15	Major	Black
<i>p,p'</i> -Dinitrostilbene		
0.60	Major	Yellow fluorescent
<i>p,p'</i> -Dinitrostilbene oxide		
0.55	Major	Black

Column chromatography was used to purify the brown solid, using a 0.6602-g. sample, on alumina and taking 25-ml. fractions. With increasingly polar solvents and mixtures (petroleum ether, benzene, acetone, methanol) up to 2:1 acetone-methanol, 13 fractions were collected with 99% recovery from the column. Thin layer chromatography on each fraction indicated that fractions 7-12 contained *p,p'*-dinitrostilbene. All of these contained essentially pure *p,p'*-dinitrostilbene except fraction 8, which was rechromatographed, fractions 5' and 6' being essentially pure stilbene. Fractions 7, 9-12, 5'-6' were combined and gave an infrared spectrum identical with that of authentic *p,p'*-dinitrostilbene. Refluxing with a crystal of iodine in nitrobenzene gave *trans-p,p'*-dinitrostilbene, m.p. 288-290° (uncor.), 300-302° (cor.) (lit.<sup>5</sup> 288° (uncor.), 304-306° (cor.); yield 307 mg., equivalent to 327 mg. ( $1.21 \times 10^{-3}$  mole, 48%) if all the reaction product had been chromatographed. Also fraction 11', 210.8 mg., on thin layer chromatography on alumina with 4:1 toluene-acetone for elution, gave the results in Table IV. Since it was obviously a complex mixture, this material was not examined further.

TABLE IV

$R_f$	Estimated amount	Ultraviolet color
0.40	Significant	Black
.52	Major	Black
.60	Significant	Black
.70	Major	Black
.75	Large	Black
.85	Trace	Yellow fluorescent