of azobenzene and 4,4'-dichloroazobenzene; these were not weighed or characterized. The next fraction (0.785 g, 28%) was 4-(fluorosulfato)azobenzene (**1**), crude mp 96–99° (mixture melting point with **1** from azoxybenzene was 97–99°). The infrared spectrum was identical with that of earlier samples of **1**.

Syntheses and Reactions of Triarylsulfonium Halides[1]

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Triarylsulfonium halides have been prepared by the reaction of diaryl sulfoxides with aromatic hydrocarbons in the presence of a large excess of aluminum halide. The structures of the salts were established by pyrolysis and subsequent glpc analysis of the pyrolysates. On the basis of product ratios produced in the pyrolysis reactions, it was possible to suggest what seemed to be the most plausible mechanism of thermal decomposition of the salts. The reaction of diphenyl-*p*-tolylsulfonium bromide with sodium *t*-butoxide was also investigated. The formation of acetone and a host of other products indicated the operation, at least in part, of a radical reaction in this instance.

In order to investigate the effects of substituents on the reactions of triarylsulfonium halides, it was first necessary to develop a reliable method of synthesis of such salts. One method that seemed potentially useful was that of Wildi, Taylor, and Potratz,[2] who prepared triphenylsulfonium bromide by treatment of diphenyl sulfoxide with phenylmagnesium bromide. However, when an attempt was made to prepare phenyl-*p*-tolyl-2,5-dimethylphenylsulfonium bromide by causing phenyl *p*-tolyl sulfoxide to react with 2,5-dimethylphenylmagnesium bromide in benzene at 75°, no reaction occurred. This was probably due in part to the sterically hindered nature of the Grignard reagent. However, it was also found that no product was obtained when *p*-anisyl- or *p*-bromophenylmagnesium bromide was used. Also, aryllithiums are known not to give appreciable quantities of sulfonium salts when caused to react with diaryl sulfoxides.[3]

Another route that appeared promising was the treatment of a diaryl sulfide with a diazonium compound, as had been developed by Horner and Hoffmann[4] in their synthesis of tetraarylphosphonium salts. However, treatment of diphenyl sulfide with benzenediazonium chloride or *p*-toluenediazonium tetrafluoroborate produced no sulfonium compounds, even when cuprous chloride was added as a catalyst.

Courtout and Tung[5] have reported the syntheses of phenyl-*p*-tolyl-2,3-dimethylphenyl- and phenyl-*p*-tolyl-2,5-dimethylphenylsulfonium chlorides by the reaction of phenyl *p*-tolyl sulfoxide with *o*- and *p*-xylene, respectively, in the presence of aluminum chloride at 40°. Our attempts to reproduce their results met with failure.

Finally, the desired sulfonium salts were prepared by using the method of Courtout and Tung[5] in a drastically modified form. Excess aluminum chloride and much higher reaction temperatures were found necessary to promote formation of the sulfonium salts. About a sixfold molar excess of aluminum chloride was found to work best, although the reason for this is not understood at this time. The most suitable reaction temperature was the reflux temperature of the aromatic hydrocarbon employed in excess as reactant and solvent. Aluminum bromide was also found suitable for use in this reaction, especially in preparation of the bromide salts. By use of this method, several asymmetric and a number of other triarylsulfonium salts were prepared in good yield and purity.

When benzene was employed as a reagent, the synthesis was unambiguous. However, because of the high reaction temperatures involved, a possible aluminum chloride induced migration of the methyl groups on the methyl-substituted benzenes was a possibility to be considered. Use of toluene or *m*-xylene also opened up possibilities of product mixtures arising from electrophilic substitution at various positions on the hydrocarbon in question. In practice, however, as demonstrated by pyrolysis studies to be described later, almost exclusive *para* substitution occurred with toluene, while *m*-xylene yielded exclusively the diaryl-2,4-dimethylphenylsulfonium salt. The results of these syntheses are summarized in Table I.

The melting point of phenyl-*p*-tolyl-2,5-dimethylphenylsulfonium chloride, as noted in Table I, also brings the results of Courtout and Tung[5] into question. The melting point of this anhydrous salt was found by us to be 122–123°, whereas the French authors reported a value of 73–74°. This latter figure is quite close to that observed for the starting material, phenyl *p*-tolyl sulfoxide, mp 75–76°. Phenyl-*p*-tolyl-2,3-dimethylphenylsulfonium chloride, as obtained by these same workers, is reported to have a melting point of 74–76°, almost the same as that for phenyl *p*-tolyl sulfoxide. In our attempts to reproduce the results of Courtout and Tung,[5] we recovered at least a significant portion of the sulfoxides unchanged.

It is of practical value and theoretical interest that triarylsulfonium halides undergo pyrolysis at moderate temperatures to produce theoretical yields of diaryl sulfides and the corresponding aryl halides. $(R_3S^+ + X^- \rightarrow RX + R_2S)$. The practical value lies in the fact that the products of pyrolysis are easily analyzed by vapor phase chromatography, and this constitutes the most convenient method for determining

(1) A preliminary report of this work has been published: G. H. Wiegand and W. E. McEwen, *Tetrahedron Lett.*, 2639 (1965).
(2) B. S. Wildi, S. W. Taylor, and H. A. Potratz, *J. Amer. Chem. Soc.*, **73**, 1965 (1961).
(3) K. K. Anderson and S. A. Yeager, *J. Org. Chem.*, **28**, 865 (1963).
(4) L. Horner and H. Hoffmann, *Ber.*, **91**, 45 (1958).
(5) C. Courtout and T. Y. Tung, *Compt. Rend.*, **197**, 1227 (1933).

<div align="center">

TABLE I

PREPARATION OF TRIARYLSULFONIUM HALIDES

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Sulfoxide	ArH	Aluminum halide	Sulfonium cation	Anion	Mp, °C	Yield, %
Phenyl *p*-tolyl	*p*-Xylene	AlCl₃	Phenyl-*p*-tolyl-2,5-dimethylphenyl	Cl⁻	122–123	31
Phenyl *p*-tolyl	*p*-Xylene	AlCl₃	Phenyl-*p*-tolyl-2,5-dimethylphenyl	I⁻	133.5–134	38–60
Phenyl *p*-tolyl	*p*-Xylene	AlBr₃	Phenyl-*p*-tolyl-2,5-dimethylphenyl	Br⁻	124–125.5	50
Phenyl *p*-tolyl	*m*-Xylene	AlCl₃	Phenyl-*p*-tolyl-2,4-dimethylphenyl	I⁻	186–186.5	45
Phenyl *p*-tolyl	*m*-Xylene	AlBr₃	Phenyl-*p*-tolyl-2,4-dimethylphenyl	I⁻	184–186	30
Phenyl *p*-tolyl	*m*-Xylene	AlBr₃	Phenyl-*p*-tolyl-2,4-dimethylphenyl	Br⁻	170.5–171	27
Phenyl *p*-tolyl	Benzene	AlBr₃	Diphenyl-*p*-tolyl	Br⁻	246.5–248 dec	60
Diphenyl	*p*-Xylene	AlBr₃	Diphenyl-2,5-dimethylphenyl	Br⁻	158–159	61
Diphenyl	Benzene	AlBr₃	Triphenyl	Br⁻	288.5	55

the structure and purity of a given sample of a triaryl-sulfonium halide. The theoretical interest arises from the ratios of pyrolysis products obtained from triaryl-sulfonium halides in which at least two different aryl groups are present and the implications of these results with respect to the mechanism of reaction.

The results of a number of pyrolysis reactions conducted for 10–20 min at 250° are given in Table II. It

<div align="center">

TABLE II

PYROLYSES OF TRIARYLSULFONIUM HALIDES AT 250°

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Sulfonium halide	Molar ratio of aryl halides		
Phenyl-*p*-tolyl-2,5-di-methylphenylsulfonium chloride	$C_6H_5Cl:p\text{-}CH_3C_6H_4Cl:2,5\text{-}(CH_3)_2C_6H_3Cl$		
	1.63	1.00	5.00
	1.38	1.00	5.00
Phenyl-*p*-tolyl-2,5-di-methylphenylsulfonium bromide	$C_6H_5Br:p\text{-}CH_3C_6H_4Br:2,5\text{-}(CH_3)_2C_6H_3Br$		
	1.91	1.00	11.6
	1.92	1.00	11.9
Phenyl-*p*-tolyl-2,5-di-methylphenylsulfonium iodide	$C_6H_5I:p\text{-}CH_3C_6H_4I:2,5\text{-}(CH_3)_2C_6H_3I$		
	3.40	1.00	12.4
	4.00	1.00	17.2
	2.40	1.00	17.6
Phenyl-*p*-tolyl-2,4-di-methylphenylsulfonium bromide	$C_6H_5Br:p\text{-}CH_3C_6H_4Br:2,4\text{-}(CH_3)_2C_6H_3Br$		
	1.94	1.00	3.96
	1.88	1.00	4.32
Diphenyl-*p*-tolylsulfo-nium bromide	$C_6H_5Br:p\text{-}CH_3C_6H_4Br$		
	3.40	1.00	
	3.40	1.00	
Diphenyl-2,5-dimethyl-phenylsulfonium bromide	$C_6H_5Br:2,5\text{-}(CH_3)_2C_6H_3Br$		
	1.00	1.38	
	1.00	1.27	

is clear that the product ratios cannot be explained on the basis of either an aromatic S$_N$1 mechanism or a bimolecular aromatic nucleophilic substitution process. For example, pyrolysis of phenyl-*p*-tolyl-2,5-dimethylphenylsulfonium iodide would be expected to give aryl iodides in the order of preference of iodobenzene > *p*-iodotoluene > 2,5-dimethyliodobenzene if a simple bimolecular nucleophilic aromatic substitution mechanism were operative. An aromatic S$_N$1 mechanism would be expected to produce aryl iodides in the order of preference of 2,5-dimethyliodobenzene > *p*-iodotoluene > iodobenzene. In a free-radical process the direction of carbon–sulfur bond cleavage might be expected to be relatively insensitive to the nature of the substituent groups present on the aromatic rings.[6] Furthermore, biaryls would probably be produced in a free-radical process, and none was found.

It is also instructive to observe the relative amounts of 2,5-dimethylhalobenzene formed by pyrolysis of the chloride, bromide, and iodide, respectively. The fact that the relative amount of 2,5-dimethyliodobenzene is greater than that of 2,5-dimethylbromobenzene, which, in turn, is distinctly greater than that of 2,5-dimethylchlorobenzene is also inexplicable in terms of any of the mechanisms cited above.

In our opinion, all of the results can best be explained in terms of the formation and subsequent intramolecular decomposition of a tetravalent sulfur compound, I. This decomposes preferentially in such a manner as to give maximum relief of steric strain; *i.e.*, the 2,5-dimethylhalobenzene and phenyl *p*-tolyl sulfide are formed in the greatest amount of the three possible pairs of products, and the effect is larger as the size of the halogen increases.

I
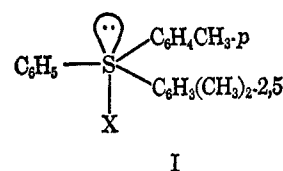
In each case the amount of the halobenzene produced exceeds that of the *p*-halotoluene. Since there are no major steric effects to consider in either of these alternative pathways of decomposition, the charge distribution in the transition state for the intramolecular decomposition of I is probably such that there is a greater electron density in the aryl groups than found in I; *i.e.*, the intramolecular decomposition has some degree of the character of a nucleophilic substitution reaction but should not be confused with an uncomplicated bimolecular aromatic nucleophilic substitution mechanism.[7]

It has recently been reported[8,9] that the reactions of triarylsulfonium halides with sodium alkoxides in alcohol solution give mixtures of aromatic hydrocarbons, diaryl sulfides, alkyl aryl ethers, and aldehydes (or ke-

(6) This has been observed in the copper-catalyzed hydrolysis of unsymmetrical diaryliodonium salts, which is known to be a free-radical process; *cf.* M. C. Caserio, D. L. Glusker, and J. D. Roberts, Theoretical Organic Chemistry, papers presented to the Kekulé Symposium, Section of Organic Chemistry, London, Sept 1958, pp 103–113.

(7) The possibility of two competing mechanisms was also considered, one involving nucleophilic attack of halide ion upon aromatic carbon to explain the halobenzene to *p*-halotoluene ratios, and the other the decomposition of the sulfonium cation to give primarily phenyl *p*-tolyl sulfide and xyleneonium ion, thus relieving the steric strain resulting from the presence of the *o*-methyl group. Since the yield of haloxylene was found to be large with respect to halobenzene and *p*-halotoluene, formation of xyleneonium ion would have to take precedence over nucleophilic attack if this argument were valid. Also, the order of nucleophilic reactivities would have to be Cl⁻ > Br⁻ > I⁻, which is the known order in aprotic solvents. An unanswered question is whether or not a molten sulfonium salt is similar in this regard to an aprotic solvent.

(8) J. W. Knapczyk, G. H. Wiegand, and W. E. McEwen, *Tetrahedron Lett.*, 2971 (1965).

(9) J. W. Knapczyk, Ph.D. Dissertation, University of Massachusetts, Amherst, Mass., 1965.

tones, depending on the structure of the alkoxide ion used). It was suggested that these products arise, at least in part, by way of radical intermediates [Ar$_3$S$^+$ + OR$^-$ $\rightleftharpoons$ Ar$_3$S–OR $\rightleftharpoons$ (Ar$_3$S· + RO·) $\rightarrow$ products]. In order to provide more direct evidence for the occurrence of radical processes, we decided to study the reaction of a triarylsulfonium halide with sodium t-butoxide in t-butyl alcohol.

It is known that the t-butoxyl radical decomposes into acetone and methyl radical.[10] If sodium t-butoxide were used in the decomposition of a triarylsulfonium salt and if the radical mechanism were operative, a t-butoxyl radical would be formed which would subsequently yield acetone. Also, products arising from attack of the methyl and t-butoxyl radicals upon the various species in solution would be expected. As summarized in Table III, these expectations were realized. Thus, it is evident that a free-radical mechanism is, at least in part, operative.

TABLE III

REACTION OF DIPHENYL-p-TOLYLSULFONIUM BROMIDE
WITH SODIUM t-BUTOXIDE

			% volatile products		
Run	Low mol-wt^a hydrocarbon	Acetone	Benzene^b	Toluene^b	t-Butyl phenyl ether
1	Trace	Trace	Trace	Trace	19.7
2	Trace	Trace	Trace	Trace	15.9
Average	Trace	Trace	Trace	Trace	17.8
Run	t-Butyl p-tolyl ether	Unknown^c ether	Unknown^d	Diphenyl sulfide	Phenyl p-tolyl sulfide
1	4.2	4.1	1.1	13.0	57.8
2	7.2	4.2	1.2	11.8	60.0
Average	5.7	4.2	1.2	12.4	58.9

^{a} Probably ethane, propane, or butane (not methane). ^{b} More toluene than benzene was formed. ^{c} Possibly a t-butyl, p-tolyl, or t-butyl xylyl ether. Nmr spectroscopy of a very dilute solution showed the possible presence of a t-butyl group bonded to an aromatic carbon. ^{d} Possibly a sulfide with molecular weight between unknown ether and diphenyl sulfide.

Experimental Section

General.—All melting points are uncorrected. All boiling points were obtained by use of the micro boiling point method and are also uncorrected.

The procedure of Potratz and Rosen[11] was used in the preparation of cobaltous ammonium thiocyanate solution, which was used to detect the presence of the various sulfonium ions in solution.

Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., and by Dr. Franz Pascher, Mikroanalytisches Laboratorium, Bonn, West Germany.

Phenyl-p-tolyl-2,4-dimethylphenylsulfonium Iodide.—To a solution of 3.0 g (0.014 mol) of phenyl p-tolyl sulfoxide in 100 ml of m-xylene was added 12 g (0.09 mol) of anhydrous aluminum chloride. The mixture was refluxed for 6 hr and then cooled to room temperature, whereupon it was poured into 100 ml of ice containing 20 ml of concentrated hydrochloric acid. The resulting mixture was warmed on a steam bath for a few minutes. The aqueous phase was then removed and washed twice with benzene, excess potassium iodide was added, and the resulting yellow precipitate was extracted with three 50-ml portions of chloroform. After it had been dried over anhydrous sodium sulfate, the chloroform extract was evaporated to give an oil which was dissolved in acetone and treated with an excess of anhydrous benzene. When allowed to stand, white crystals formed and

were collected by filtration to give 2.7 g (44%) of pure phenyl-p-tolyl-2,4-dimethylphenylsulfonium iodide, mp 186–186.5°. Analytical data for this and other new compounds are given in Table IV.

Phenyl-p-tolyl-2,4-dimethylphenylsulfonium Bromide.—To a solution of 2.0 g (0.009 mol) of phenyl p-tolyl sulfoxide in 50 ml of m-xylene was added 16 g (0.06 mol) of anhydrous aluminum bromide. The mixture was refluxed 24 hr, cooled, carefully poured onto a mixture of 100 ml of ice and 20 ml of concentrated hydrobromic acid, and warmed on a steam bath for a few minutes. After separation from the xylene layer, the aqueous layer was washed three times with benzene and extracted three times with 50-ml portions of chloroform. The chloroform extract was then dried over anhydrous sodium sulfate and evaporated to yield a light yellow oil. This oil was caused to crystallize by dissolving it in a minimum amount of chloroform, adding a few drops of acetone, and flooding the solution with dry benzene. This process was repeated twice to give 1.05 g (27%) of phenyl-p-tolyl-2,4-dimethylphenylsulfonium bromide, mp 170.5–171°. The infrared spectrum of this compound was identical with that of phenyl-p-tolyl-2,4-dimethylphenylsulfonium iodide.

Phenyl-p-tolyl-2,4-dimethylphenylsulfonium Chloride.—A solution containing 5.0 g (0.025 mol) of phenyl p-tolyl sulfoxide in 100 ml of p-xylene was treated with 16.2 g (0.12 mol) of anhydrous aluminum chloride, and the mixture was refluxed for 18 hr. After it has been cooled to room temperature, the mixture was poured slowly over 200 ml of ice containing 25 ml of concentrated hydrochloric acid; the resulting mixture was allowed to warm to room temperature. The aqueous layer was removed, washed once with benzene, and extracted four times with 50-ml portions of chloroform; the chloroform extract was dried over anhydrous sodium sulfate. After evaporation of the chloroform, a yellow viscous oil remained which was suspended in 100 ml of boiling benzene. Absolute ethanol was added to the boiling mixture until the oil just dissolved, and the resulting solution was added dropwise from a separatory funnel to 450 ml of rapidly stirred benzene at room temperature. Stirring was continued for 1 hr, whereupon 2.13 g (31%) of phenyl-p-tolyl-2,5-dimethylphenylsulfonium chloride, a white solid, formed, mp 122–123°. The infrared spectrum of this compound was found to be almost identical with that of phenyl-p-tolyl-2,5-dimethylphenylsulfonium iodide.

Other Triarylsulfonium Halides.—The other triarylsulfonium halides listed in Tables I and IV were prepared in essentially the same manner as described above, with the exception of periods of reflux and solvents used for recrystallizations. These differences are summarized in Table IV. It was found possible to convert the triarylsulfonium chlorides and bromides into the respective iodides by metathesis. For example, treatment of an aqueous solution of phenyl-p-tolyl-2,5-dimethylphenylsulfonium bromide with an excess of potassium iodide, subsequent extraction with chloroform, drying of the chloroform extract with anhydrous sodium sulfate, and evaporation of the chloroform left an oil which, when crystallized from hot water, gave white needle-like crystals, mp 135.5–136°. That this substance was phenyl-p-tolyl-2,5-dimethylphenylsulfonium iodide was shown by a mixture melting point test with an authentic sample. No depression was observed.

p-Tolyl 2,5-Dimethylphenyl Sulfide.—To a solution of 135 ml of concentrated hydrochloric acid in 250 ml water was added 86 g of 2,5-xylidine (Technical, Matheson Coleman and Bell) with vigorous swirling to prevent the formation of lumps. Diazotization was carried out at 0–5° by use of a solution of 37 g of sodium nitrite in 150 ml of cold water, and the resulting solution was added slowly to a solution containing 65 g of p-toluenethiol and 82.5 g of sodium hydroxide in 750 ml of water maintained at 50°. After completion of the addition, the resulting mixture was stirred at 50° for 1 hr, and the oily layer was allowed to settle. The oily layer was collected, acidified, steam distilled, separated from the aqueous distillate, and distilled to yield 42 g (35%) of p-tolyl 2,5-dimethylphenyl sulfide, bp 147–150° (0.2 mm).

Anal. Calcd for C$_{15}$H$_{16}$S: C, 79.4; H, 7.1. Found: C, 79.1; H, 7.1.

Phenyl 2,5-Dimethylphenyl Sulfide.—The procedure used was the same as that for p-tolyl 2,5-dimethylphenyl sulfide, 59.0 g of benzenethiol being used in the preparation. The yield of phenyl 2,5-dimethylphenyl sulfide was 54 g (47%), bp 130–135° (0.2 mm).

Anal. Calcd for C$_{14}$H$_{14}$S: C, 78.6; H, 6.6; S, 15.0. Found: C, 78.5; H, 6.9; S, 15.2.

(10) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p 470.

(11) H. A. Potratz and J. M. Rosen, *Anal. Chem.*, **21**, 1276 (1949).

TABLE IV

REACTION CONDITIONS AND ANALYTICAL DATA FOR TRIARYLSULFONIUM HALIDES

Ar₃S⁺ X⁻	Time of reflux, hr	Recrystallization Solvent	Anal, %							
			Calcd				Found			
			C	H	S	X	C	H	S	X
Phenyl-p-tolyl-2,4-dimethyl-phenylsulfonium iodide	6	Acetone–benzene	58.3	4.9	7.4	29.4	58.3	5.0	7.5	29.2
Phenyl-p-tolyl-2,4-dimethyl-phenylsulfonium bromide	24	Chloroform–acetone–benzene	...	...	...	...	...	...	...	...
Phenyl-p-tolyl-2,5-dimethyl-phenylsulfonium iodide	28	Water	...	...	7.4	29.4	...	...	7.3	29.3
Phenyl-p-tolyl-2,5-dimethyl-phenylsulfonium bromide	22	Chloroform–benzene or absolute ethanol–ethyl acetate	...	...	...	...	...	...	...	...
Phenyl-p-tolyl-2,5-dimethyl-phenylsulfonium chloride	18	Absolute ethanol–benzene	...	...	...	...	...	...	...	...
Diphenyl-p-tolylsulfonium bromide	23	Chloroform–benzene	64.0	4.8	9.0	22.2	63.9	4.8	9.1	22.2
Diphenyl-2,5-dimethylphenyl-sulfonium bromide	22	Absolute ethanol–ethyl acetate	64.7	5.2	8.6	21.5	64.4	5.5	8.5	21.3
Triphenylsulfonium bromide[a]	24	Absolute ethanol–benzene	...	...	...	...	...	...	...	...

[a] Mp 288–289° (lit.[6] mp 285–286°).

p-Tolyl 2,4-Dimethylphenyl Sulfide.—This compound was prepared in the same manner as described above for p-tolyl 2,5-dimethylphenyl sulfide; 86.0 g of 2,4-xylidine (Technical, Matheson Coleman and Bell) was used in the reaction. The yield of p-tolyl 2,4-dimethylphenyl sulfide was 60 g (46%), bp 158° (0.3 mm). Vpc analysis, by use of an F & M Model 500 gas chromatograph equipped with a 2-ft silicone rubber column at 160°, showed the presence of an impurity, amounting to about 10–20%, which was probably isomeric material.

Anal. Calcd for $C_{15}H_{16}S$: C, 79.4; H, 7.1. Found: C, 79.4; H, 7.0.

Phenyl 2,4-Dimethylphenyl Sulfide.—This compound was prepared in the same manner as that described for p-tolyl 2,4-dimethylphenyl sulfide, 59.0 g of benzenethiol being used in the synthesis. The yield of phenyl 2,4-dimethylphenyl sulfide was 52 g (45%), bp 126° (0.3 mm). Vpc analysis, by use of an F & M Model 500 gas chromatograph equipped with a 2-ft silicone rubber column at 160°, showed the presence of an impurity, amounting to about 10–20%, which was probably isomeric material.

Anal. Calcd for $C_{14}H_{14}S$: C, 78.6; H, 6.6; S, 15.0. Found: C, 78.1; H, 6.6; S, 14.5.

p-Tolyl 2,5-Dimethylphenyl Sulfoxide.—To 25 ml of glacial acetic acid was added 2.28 g (0.01 mol) of p-tolyl 2,5-dimethylphenyl sulfide, and the resulting mixture was treated with 1.07 g (1 equiv) of 30% hydrogen peroxide solution and heated overnight on a steam bath. The mixture was then added to an excess of water, the aqueous solution was extracted with chloroform, and the chloroform extract was dried over anhydrous magnesium sulfate. Evaporation of the chloroform left an oil which was crystallized from a minimum amount of Skellysolve F solvent to give large, tan crystals. After four more recrystallizations from Skellysolve F solvent, a yield of 0.98 g (40%) of tan, crystalline p-tolyl 2,5-dimethylphenyl sulfoxide, mp 74–75°, was obtained. A fifth recrystallization from Skellysolve F solvent (Norit) gave the product as white needles, mp 79–80°.

Anal. Calcd for $C_{15}H_{16}SO$: C, 73.8; H, 6.6; S, 13.1. Found: C, 73.9; H, 6.6; S, 13.0.

Phenyl 2,5-Dimethylphenyl Sulfoxide.—This compound was prepared in the same manner as was p-tolyl 2,5-dimethylphenyl sulfoxide, 2.14 g (0.01 mol) of phenyl 2,5-dimethylphenyl sulfide being used as starting material. The yield was 0.90 g (39%) of pure phenyl 2,5-dimethylphenyl sulfoxide as white prisms, mp 65.5–66.5°.

Anal. Calcd for $C_{14}H_{14}SO$: C, 73.0; H, 6.1; S, 13.9. Found: C, 72.9; H, 6.6; S, 13.9.

Pyrolysis of Sulfonium Salts for Proof of Structure.—Each of the sulfonium salts listed in Table I, except triphenylsulfonium bromide, was pyrolyzed in a 4-mm Pyrex tube about 30 cm long, sealed at one end, at 250 ± 5° for 10–20 min until reaction was complete. Only about 2 cm of the sealed end of the tube was immersed in the oil bath used, the remainder of the tube being used as an air condenser. In all cases the compositions of the pyrolysates were determined by use of either an F & M Model 500 or an F & M Model 609 gas chromatograph, a 2-ft silicone rubber column being used. Identification of the products was

accomplished by use of retention times. Where applicable, a small amount of the suspected material was added to the pyrolysate and an increase in peak height observed. It was found possible to separate the isomeric aromatic sulfides from one another by use of these conditions. The isomeric aromatic halides were also found separable, except for the 4- and 5-bromo-m-xylenes, which were separated by use of a 2-ft Apiezon L column.

In no case was any significant amount of unexpected product found, and all of the sulfonium salts, when pyrolyzed, gave the products expected from their thermal decomposition. Thus, the sulfonium salts listed in Table I, with the exception of triphenylsulfonium bromide, were found by pyrolysis and subsequent vpc analysis to have the structures given.

Pyrolysis of Sulfonium Salts. Product Ratios.—Resolution and appropriate shape of the halide peaks obtained in the chromatograms of the pyrolysates used for structure determinations were sufficient to permit determination of the relative ratios of the halides formed in each pyrolysate. In each experiment on an individual pyrolysate, the approximate relative amounts of the halides formed were determined by finding the approximate relative areas of the halide peaks obtained. Approximate peak areas were obtained by multiplying the peak height by the peak width at half-height. At least three standard solutions were then prepared having various compositions near the approximate values obtained. Vpc analysis was then performed on these standards; the approximate area ratios were obtained and plotted graphically with respect to composition. The actual product ratios of the halides in the pyrolysate were then obtained directly from the graphs.

The total aromatic halide to total aromatic sulfide ratio in the case of the pyrolysis of phenyl-p-tolyl-2,5-dimethylphenyl-sulfonium bromide was obtained in the following manner. The column temperature was raised until the halide peaks coalesced into one peak and the sulfide peaks did likewise, the resulting two peaks being sharp and cleanly resolved. Standard mixtures were again prepared and subjected to vpc analysis. From this analysis, the ratio of total aromatic halide to total aromatic sulfide was found to be approximately 1:1.

t-Butyl Phenyl Ether.—The method of Baddeley, *et al.,*[12] was used in the preparation of this compound. A 15% yield of t-butyl phenyl ether, a colorless oil, bp 27° (0.15 mm), was obtained [lit.[13] bp 70–71° (11 mm)]. The nmr spectrum (neat) of this compound was in agreement with the structure given.

t-Butyl p-Tolyl Ether.—This compound was prepared in low yield by the same method as described above. It was obtained as a colorless oil, bp 38–40° (0.2 mm) [lit.[13] bp 79–81° (9 mm)]. Nmr and ir spectra (both neat) were consistent with the structure given.

p-Methylphenetole (Ethyl p-Tolyl Ether).—A sample of p-methylphenetole was vacuum distilled from a small amount of ferrous sulfate to give a colorless liquid, bp 51° (1 mm). A

(12) G. Baddeley, N. H. P. Smith, and M. A. Vickars, *J. Chem. Soc.*, 2455 (1956).

(13) S. O. Lawesson and N. C. Yang, *J. Amer. Chem. Soc.*, **81**, 4230 (1959).

micro boiling point at atmospheric pressure gave a value of 190.5–191° (lit.[14] 189–191°).

5-Bromo-*m*-Xylene.—This compound was prepared by the method of Buehler, *et al.*,[15] in 27.6% yield, bp 33° (0.1 mm) [lit.[15] bp 70° (6 mm)].

Reaction of Diphenyl-*p*-Tolylsulfonium Bromide with Sodium *t*-Butoxide.—A sample of 0.357 g (0.001 mol) of diphenyl-*p*-tolylsulfonium bromide was mixed with 6 ml of an approximately 0.16 *M* (1 equiv) slurry of sodium *t*-butoxide in anhydrous *t*-butyl alcohol, and the mixture was refluxed under an efficient condenser for 24 hr. During this time a precipitate of sodium bromide formed. The reaction mixture was then subjected to vpc analysis. Quantitative determinations were carried out by use of an F & M Model 609 gas chromatograph equipped with a 2-ft Apiezon L column; a time–temperature program from 25 to 200° at 4.6°/min was employed. Standards were prepared as in the analyses of the pyrolysates, and the product percentages were determined graphically. Quantities of the unknown materials were estimated by measurement of their peak areas. The results of this analysis are listed in Table III.

Trace amounts of materials in the reaction mixture were identified by use of an Aerograph Autoprep Model A-700 gas chromatograph equipped with a 20-ft silicone rubber column. The minor products were identified by retention times. Where possible, a small amount of an authentic sample of the suspected material was added to a small quantity of the mixture and an increase in peak height was observed. An attempt was made to collect a sample of the unknown ether by preparative gas chromatography, the Autoprep being used. A very small amount of the material was collected and subjected to nmr analysis. A

(14) J. Pinette, *Ann.*, **243**, 32 (1888).

(15) C. A. Buehler, T. A. Magee, K. V. Nyak, and D. M. Glenn, *J. Org. Chem.*, **24**, 1307 (1959).

carbon tetrachloride solution of the substance gave a weak signal; however, the presence of *t*-butyl and aromatic methyl groups was indicated. The retention time was about that expected for a tolyl or xylyl *t*-butyl ether other than *t*-butyl *p*-tolyl ether, and the substance had the odor of an ether.

Although both were formed in small amounts, it was possible to see that toluene was formed in greater quantity than benzene. The presence of a polymeric material was also indicated by a very broad "peak" which was observed at long retention times.

Ozonation of Amines. II. The Competition between Amine Oxide Formation and Side-Chain Oxidation

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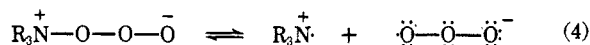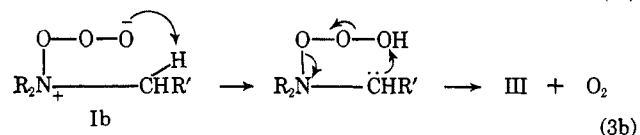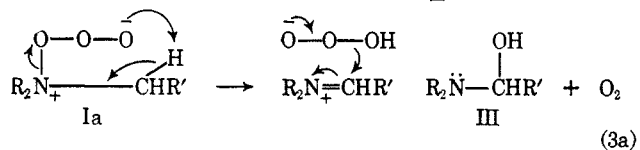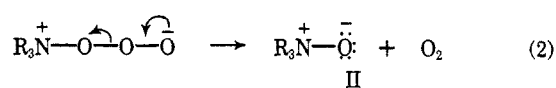
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The competition between amine oxide formation and side-chain oxidation during ozonation of tri-*n*-butylamine in several different solvents has been studied, using ozone–nitrogen mixtures. To obtain a better understanding of the side-chain oxidation, 1-di-*n*-butylamino-2-butanone (XV) was synthesized and ozonized. A preference for attack at the methylene group between the amino and carbonyl groups was observed. The results, including solvent effects, are explained on the basis of competitive fates of an initial amine–ozone adduct.

In the first paper of this series[1] the hypothesis was presented that all known reactions between ozone (an electrophile) and amines (nucleophiles) can be explained on the basis of the initial formation of an adduct (I, eq 1) for which there are at least three major fates: (1) loss of molecular oxygen to give an amine oxide (II, eq 2) or further reaction products thereof; (2) an intramolecular side-chain oxidation (eq 3a or b) to give molecular oxygen and further reaction products of III; (3) dissociation to cation and anion radicals (eq 4), followed by stabilizing reactions thereof.

Equation 3a is based on a recent suggestion of Kolsaker and Meth-Cohn[2a] and is analogous to the accepted mechanism of the Polonovski reaction.[2b]

(1) P. S. Bailey, J. E. Keller, D. A. Mitchard, and H. M. White, paper presented at the International Oxidation Symposium, San Francisco, Calif., Aug 1967; Advances in Chemistry Series, American Chemical Society, Washington, D. C., in press.

(2) (a) P. Kolsaker and O. Meth-Cohn, *Chem. Commun.*, **18**, 423 (1965); (b) R. Huisgen, F. Bayerlein, and W. Heydkamp, *Chem. Ber.*, **92**, 3223 (1959); (c) C. R. Hauser and S. W. Kantor, *J. Amer. Chem. Soc.*, **73**, 1437 (1951).

$$R_3N: \ + \ \overset{..}{O}{=}\overset{..}{O}{-}\overset{..}{O}:^- \ \longrightarrow \ R_3\overset{+}{N}{-}\overset{..}{O}{-}\overset{..}{O}{-}\overset{..}{O}:^- \quad (1)$$
$$\text{I}$$

$$R_3\overset{+}{N}{-}O{-}O{-}O \ \longrightarrow \ R_3\overset{+}{N}{-}\overset{..}{O}:^- \ + \ O_2 \quad (2)$$
$$\text{II}$$

$$\underset{\text{Ia}}{\overset{O-O-O}{\underset{R_2\overset{+}{N}{-}{-}{-}CHR'}{|}}} \overset{H}{\longrightarrow} R_2\overset{+}{N}{=}CHR' \quad R_2\overset{..}{N}{-}CHR' \ + \ O_2 \quad (3a)$$
$$\qquad\qquad\qquad\qquad \text{III}$$

$$\underset{\text{Ib}}{\overset{O-O-O}{\underset{R_2\overset{+}{N}{-}{-}{-}CHR'}{|}}} \overset{H}{\longrightarrow} R_2N{-}{-}\overset{.}{C}HR' \ \longrightarrow \ \text{III} \ + \ O_2 \quad (3b)$$

$$R_3\overset{+}{N}{-}O{-}O{-}\overset{-}{O} \ \rightleftharpoons \ R_3\overset{+}{N}\cdot \ + \ \overset{..}{O}{-}\overset{..}{O}{-}\overset{..}{O}:^- \quad (4)$$

Equation 3b bears an analogy to the accepted mechanism of the Steven's rearrangement.[2c]

The conversion of tertiary amines into amine oxides