Table VI. Competitive Reactions of Substituted Benzenes

A	B	A_0/Std	A/Std	B_0/Std	B/Std	Std	k_B/k_A
C_6H_6	C_6H_5Br	1.62	1.39	1.55	1.33	20 μl of toluene	1.00
C_6H_6	C_6H_5Cl	1.62	1.34	1.51	1.24	20 μl of toluene	1.04
C_6H_5Cl	C_6H_5Br	1.25	1.01	1.24	1.00	20 μl of cumene	1.01
C_6H_5-tBu	C_6H_5Cl	2.06	1.72	1.19	0.98	20 μl of cumene	1.07
C_6H_5Br	$C_6H_5COOCH_3$	1.49	1.23	1.66	1.29	20 μl of *o*-dichlorobenzene	1.32
C_6H_5Br	$C_6H_5NO_2$	1.15	1.02	1.05	0.88	25 μl of *o*-dichlorobenzene	1.47
C_6H_5Cl	$C_6H_5OCH_3$	1.55	1.29	1.63	0.95	15 μl of *o*-xylene	2.93

$Mn(OAc)_3 \cdot 2H_2O$ in acetic acid, also 1 *M*, in potassium acetate. The reaction mixture was placed in a tube, flushed with nitrogen and sealed. The reactions were run in a constant temperature bath maintained at 130 ± 1° for a period of 2 hr by which time the brown manganic color had disappeared. When the reaction was over, the tube was cooled and the reaction mixture diluted with 500 ml of ether. The ether solution was extracted twice with ice water and three more times with cold saturated sodium bicarbonate solution. The ether extract was then dried over sodium sulfate and after filtration, the ether was removed on a rotary evaporator. The resulting reaction residue was then analyzed by vapor phase chromatography.

The relative amounts of the two benzyl acetates formed were determined by the areas of the corresponding peaks in the gas chromatogram, corrected for differences in response for the two compounds. This correction factor was obtained from a known mixture of authentic samples prepared by conventional methods from the corresponding benzyl alcohols or halides. Vpc analyses were conducted on an F & M Model 810 gas chromatograph with dual thermal conductivity detectors using 2–12-ft 10% Silicone SE-30 columns and temperature programming. Peak areas were obtained by a Varian Aerograph Model 475 automatic integrator. In general, each reaction was run in duplicate and analyzed twice by vpc. Average deviations were usually less than 2%.

In the reactions run under anhydrous conditions, 200 ml of glacial acetic acid, 60 g of potassium acetate, and 20 ml of acetic anhydride were heated at 130° under a stream of nitrogen. After 6 hr, 25 mmol each of the two hydrocarbons of interest were added along with 12.4 mmol of anhydrous $Mn(OAc)_3$. When the reaction was over, the reaction mixture was worked up and analyzed in the usual manner.

Relative Reactivity of Substituted Benzenes. Competitive Procedure. Each substituted benzene was dissolved in glacial acetic acid to give a 0.14 *M* solution of hydrocarbon. Twenty milliliters of each of two hydrocarbon solutions were then mixed, and 4-ml aliquots of the resulting mixture were then added to six ampoules, three of which contained 700 mg of $Mn(OAc)_3 \cdot 2H_4O$. The ampoules were then purged with nitrogen and sealed. The sealed ampoules were placed in a constant-temperature bath maintained at 130 ± 1° until the reaction mixtures containing manganic acetate turned clear, usually about 5 hr. The ampoules were then cooled in ice–water and opened. A specific amount of standard (usually 15–25 μl) was then added to each tube. The standard used varied with the two hydrocarbons under study as shown in Table VI. Analyses were performed on an F & M Model 5750 gas chromatograph with dual flame detectors using $^1/_8$ in. 3- or 6-ft Polypak No. 1 columns and temperature programming. Pea kareas were determined with a planimeter, and each reaction and control was analyzed at least twice. The average area ratios are shown in Table VI. The relative reactivities of the substituted benzenes were calculated from the equation

$$k_A/k_B = \log (A_0/A)/\log (B_0/B)$$

where A_0 and B_0 are the relative areas obtained from the control runs (*i.e.*, before reaction), and A and B are the relative areas of the completed reactions.

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Reactions of Triarylsulfonium Salts with Bases[1]

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Contribution from the Chemistry Departments of the University of Massachusetts, Amherst, Massachusetts 01002, and Johnson State College, Johnson, Vermont 05656. Received August 7, 1968

Abstract: Triphenylsulfonium and tri-*p*-tolylsulfonium fluoroborate, iodide, bromide, and chloride salts have been prepared and subjected to reaction with sodium methoxide in methanol solution. In all cases, a mixture of aromatic hydrocarbons, biaryls, methyl aryl ethers, diaryl sulfides, and products of relatively high molecular weight were obtained. However, the molar ratios of these products differed markedly from one system to another. An interpretation of these results and of those of the reactions of some of the same triarylsulfonium salts with other sodium alkoxides is offered in terms of competing free-radical and aromatic bimolecular nucleophilic substitution reactions. Preliminary examinations of the thermal decomposition of triphenylsulfonium hydroxide and of the photolysis of triphenylsulfonium salts have also been made.

Reactions of triphenylsulfonium and tri-*p*-tolylsulfonium fluoroborate, iodide, bromide, and chloride salts with sodium methoxide in methanol solution have been carried out at 72° for 60 hr. The results are summarized in Table I. Similar reactions have also been carried out with triphenylsulfonium iodide, triphenylsulfonium bromide, and tri-*p*-tolylsulfonium bromide and sodium ethoxide, sodium *n*-butoxide, and sodium isopropoxide, respectively, the corresponding alcohols being used as solvents. The results of these reactions are summarized in Table II.

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(1) A preliminary report of some of this work has been published: J. W. Knapczyk, G. H. Wiegand, and W. E. McEwen, *Tetrahedron Letters*, 2971 (1965).

Table I. Reactions of Triarylsulfonium Salts with Sodium Methoxide in Methanol Solution at 72° for 60 Hr

$Ar_3S^+X^-$		Products, % yield			
Ar	X	Ar–H	ArOMe	Ar–Ar	Ar–S–Ar
C_6H_5	BF_4	4	85	0.1	100
	Cl	2	85	0.1	100
	Br	3	85	0.1	100
	I	6	60	0.3	90
	Cl[a]	10	68	0.6	100
p-$CH_3C_6H_4$	BF_4	15	26	4	70
	Cl	17	28	7	74
	Br	18	27	7	77
	I	6	5	10	28[b]
	Cl[a]	19	25	3.2	77

[a] 2.5×10^{-5} mol of $CuCl_2$ 0.0005 mol of $Ar_3S^+Cl^-$ present. [b] 66% of tri-*p*-tolylsulfonium iodide recovered unchanged.

Table II.[a] Reactions of Triarylsulfonium Halides with Alkoxide Ions

Triarylsulfonium halide	RO^-, in solvent ROH	Temp, °C	Time, hr	Products, %			
				Hydrocarbon	Ether	Sulfide	Carbonyl compound
$(C_6H_5)_3S^+$, I^-	$C_2H_5O^-$	78	24	19	46	95	Aldol resins
	n-$C_4H_9O^-$	116	24	9	86	98	Aldol resins
	$(CH_3)_2CHO^-$	80	39	25	52	100	Acetone, 29
$(C_6H_5)_3S^+$, Br^-	$C_2H_5O^-$	78	24	<7	69	95	Aldol resins
	n-$C_4H_9O^-$	116	24	1	98	98	Aldol resins
	$(CH_3)_2CHO^-$	80	39	2	97	98	Acetone, trace
(*p*-$CH_3C_6H_4)_3S^+$, Br^-	$C_2H_5O^-$	78	24	48	9	85	Aldol resins
	n-$C_4H_9O^-$	116	24	21	73	96	Aldol resins
	$(CH_3)_2CHO^-$	80	39	77	15	99	Acetone, 70
$(C_6H_5)_3S^+$, I^-	*n*-$C_4H_9S^-$ in *n*-C_4H_9OH	116	24	1	77[b]	97	

[a] No attempt was made to detect biaryls in these reactions. [b] *n*-Butyl phenyl sulfide.

It is clear that the complex mixture of products produced in each case precludes a rationalization based on the operation of a simple and exclusive aromatic SN1 mechanism or bimolecular aromatic nucleophilic substitution process. In fact, the only single mechanism able to account for all of the products is a radical process analogous to that suggested for the decomposition of various diaryliodonium salts.[2-11]

The gross features of the mechanism, as applied to triarylsulfonium alkoxides, are

$$Ar_3S^+,\ OCHR_2^- \rightleftharpoons Ar_3SOCHR_2 \rightleftharpoons (Ar_3\dot{S},\ R_2CH\dot{O}) \tag{a}$$

$$(Ar_3\dot{S},\ R_2CH\dot{O}) \longrightarrow Ar_2S + ArOCHR_2 \tag{b}$$

$$(Ar_3\dot{S},\ R_2CH\dot{O}) \longrightarrow Ar_3S\cdot + R_2CHO\cdot \tag{c}$$

$$Ar_3S\cdot \longrightarrow Ar_2S + Ar\cdot \tag{d}$$

$$Ar\cdot + R_2CHOH \longrightarrow ArH + R_2\dot{C}OH \tag{e}$$

$$R_2CHO\cdot + R_2CHOH \longrightarrow R_2CHOH + R_2\dot{C}OH \tag{f}$$

$$2R_2\dot{C}OH \longrightarrow RCOR + R_2CHOH \tag{g}$$

Most of the outstanding features of the data presented in Tables I and II and in previous papers[1,12] are readily understood in terms of this mechanism. (1) The major products of the decomposition reactions are alkyl aryl ethers, diaryl sulfides, aromatic hydrocarbons, ketones (or aldol resins derived from aldehydes), and biaryls. (2) In the reaction of diphenyl-*p*-tolylsulfonium bromide with sodium *t*-butoxide, trace amounts of acetone and an alkane of low molecular weight were detected.[12] These could only have arisen by the decomposition of the *t*-butoxyl radical. Also, a host of unidentified products were formed, these probably arising by attack of various reactive radicals on the primary products. The nmr spectra of some of these products suggested the presence of *t*-butoxyl and aromatic methyl groups. (3) In the reaction of triphenylsulfonium iodide with sodium isopropoxide in isopropyl alcohol solution, the ratio of isopropyl phenyl ether to benzene produced was about 2:1. In the identical reaction with triphenylsulfonium bromide, the ratio was about 49:1. Similar results were obtained with other alkoxides. A possible explanation of this effect will be offered later, but, for the present, it is sufficient to point out that the sensitivity of product ratios to the halide ion present in solution is a phenomenon which has been observed for other radical processes.[13] (4) It is striking that decomposition of triphenylsulfonium bromide by the action of sodium isopropoxide gives but a 2% yield of benzene (and acetone), whereas the similar reaction of tri-*p*-tolylsulfonium bromide with sodium isopropoxide affords a 77% yield of toluene (and acetone). A possible explanation for this observation is as follows: the more reactive the radicals in the radical pair ($Ar_3\dot{S}$, $R_2CH\dot{O}$), the greater will be the yield of alkyl aryl ether and diaryl sulfide. The more stable the radicals that make up the radical pair, the greater is the likelihood of the radicals becoming free from one another and reacting with the solvent, this giving rise to the sequence of reactions that produces the aromatic hydrocarbons plus the carbonyl compounds. The larger yield of toluene in the reactions of tri-*p*-tolylsulfonium bromide with sodium alkoxides than that of benzene in the corresponding reactions of triphenyl-

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(2) R. B. Sandin, F. T. McClure, and F. Irwin, *J. Am. Chem. Soc.*, **61**, 2944 (1939).

(3) R. B. Sandin, R. G. Christiansen, R. K. Brown, and S. Kirkwood, *ibid.*, **69**, 1550 (1947).

(4) R. B. Sandin and R. K. Brown, *ibid.*, **69**, 2253 (1947).

(5) L. G. Markarova and A. N. Nesmeyanov, *Bull. Acad. Sci. USSR, Classe Sci. Chim.*, 617 (1945).

(6) M. C. Caserio, D. L. Glusker, and J. D. Roberts, *J. Am. Chem. Soc.*, **81**, 336 (1959).

(7) F. M. Beringer, E. M. Gindler, M. Rapoport, and R. J. Taylor, *ibid.*, **81**, 351 (1959).

(8) F. M. Beringer, J. W. Dehn, Jr., and M. Winicov, Jr., *ibid.*, **82**, 2948 (1960).

(9) F. M. Beringer, P. S. Forgione, and M. D. Yudis, *Tetrahedron*, **8**, 49 (1960).

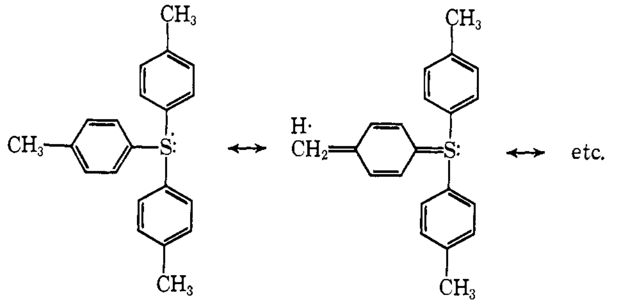
(10) F. M. Beringer, S. A. Galton, and S. J. Huang, *J. Am. Chem. Soc.*, **84**, 2819 (1962).

(11) F. M. Beringer and P. S. Forgione, *Tetrahedron*, **19**, 739 (1963).

(12) G. H. Wiegand and W. E. McEwen, *J. Org. Chem.*, **33**, 2671 (1968).

(13) A. N. Nesmeyanov, L. G. Makarova, and T. P. Tolstaya, *Tetrahedron*, **1**, 145 (1957).

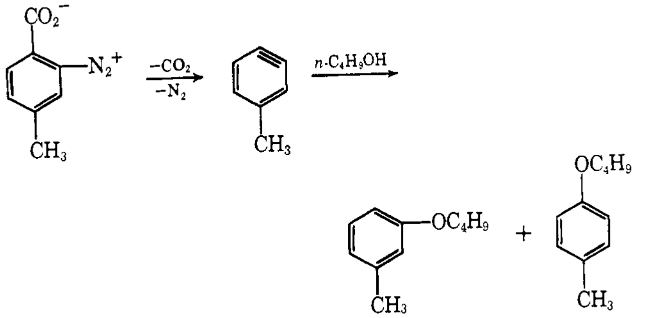
sulfonium bromide may be attributable to the greater stability of the tri-*p*-tolylsulfur radical over the triphenylsulfur radical.[14] The enhanced stability of the tri-*p*-tolylsulfur radical can be attributed to a type of hyperconjugation involving use of the d orbitals of the sulfur atom. (5) The formation of significant quantities of biaryls, particularly in the reactions of the tri-*p*-tolylsulfonium salts, constitutes strong evidence in favor of a radical mechanism and for the idea that the tri-*p*-tolylsulfur radical is better able than the triphenylsulfur radical to become free of the alkoxyl radical and undergo reaction independent of the latter radical.



It should be emphasized, however, that none of the facts in support of a free-radical mechanism, cited above, exclude the possibility of a concomitant aromatic bimolecular nucleophilic displacement reaction. In fact, the results of the reaction of triphenylsulfonium iodide with sodium *n*-butylmercaptide, in which *n*-butyl phenyl sulfide and diphenyl sulfide are formed in high yields, strongly suggest that an aromatic bimolecular substitution reaction can occur in competition with the radical reaction.

An argument could be made that the diaryl sulfides plus the corresponding aryl alkyl ethers arise by a bimolecular aromatic nucleophilic substitution process, while the aromatic hydrocarbons plus ketones (or aldehydes) result from a competing reaction analogous to the Meerwein–Ponndorf–Verley reaction. This possibility can be ruled out on the basis that the combination of these reactions cannot be used to explain the formation of acetone and the large number of byproducts in the diphenyl-*p*-tolylsulfonium *t*-butoxide decomposition reaction,[12] the formation of biaryls in the various reactions, and the sharply divergent ratios produced in the various reactions.

Another possibility worthy of consideration is that the diaryl sulfides and alkyl aryl ethers arise by a mechanism in which a benzyne type of intermediate is generated by attack of the alkoxide ion on the triarylsulfonium cation. Benzynes have been postulated to be intermediates in other reactions between triarylsulfonium cations and bases.[15,16] This possibility was ruled out for the triarylsulfonium alkoxide decomposition reactions on the basis of the following experimental observations. (a) The reaction of tri-*p*-tolylsulfonium bromide with sodium *n*-butoxide gave *n*-butyl *p*-tolyl ether as the sole alkyl aryl ether. (b) Decomposition of the dipolar ion derived by diazotization of 2-amino-4-methylbenzoic acid, a type of reaction known[17] to give a benzyne type of intermediate, in *n*-butyl alcohol afforded *n*-butyl *m*-tolyl ether and *n*-butyl *p*-tolyl ether in a 65:35 ratio.



The ultraviolet and infrared spectra of the various triarylsulfonium salts were taken, and the results are pertinent to the discussion of the mechanisms of their reactions with sodium alkoxides. The ultraviolet spectra of the fluoroborate, chloride, and bromide salts of the triphenylsulfonium ion, taken in methanol, all showed maxima at 234 (17,000), 268 (4000), and 276 mμ (ϵ 2950). However, triphenylsulfonium iodide, while exhibiting the maxima at 268 and 276 mμ, lacked the absorption peak at 234 mμ. Since sodium iodide itself exhibits an intense absorption peak at 222 mμ in methanol solution which is absent in the spectrum of the sulfonium iodide,[18] it is clear that the iodide and triphenylsulfonium ions interact strongly with each other, and this probably means that tight ion pairs predominate even in very dilute solution.[19]

The major differences between the triarylsulfonium iodides and the corresponding chlorides, bromides, and fluoroborates in their reactions with sodium alkoxides are (1) that the reactions of the iodides are slower and (2) that the ratios of aromatic hydrocarbon to aryl alkyl ether produced in the iodide reactions are much greater than the corresponding ratios produced in the reactions of the other salts. Attack of alkoxide ion at either the sulfur atom or one of the aromatic carbon atoms bonded to the sulfur atom would be inhibited by the close association of iodide ion with the sulfonium cation in the tight ion pair; thus, the sulfonium iodides would undergo reaction with sodium alkoxides more slowly than would the corresponding chlorides, bromides, or fluoroborates. Also, if most of the aryl alkyl ether produced in each reaction arises by an aromatic bimolecular nucleophilic substitution reaction at carbon, while all of the aromatic hydrocarbon produced in each reaction arises by addition of the alkoxide ion to the sulfur atom and the subsequent radical reactions cited above, it is at least a reasonable possibility that the presence of the iodide ion in the tight ion pair would inhibit the former reaction more than the latter. The greater ratio of aromatic hydrocarbon to aryl alkyl ether produced in the reactions of tri-*p*-tolylsulfonium iodide with sodium alkoxides as against those of triphenylsulfonium iodide can be attributed both to the greater stability of the tri-*p*-tolyl-

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[14] There is electrochemical evidence for the existence of the triphenylsulfur radical: M. Finkelstein, R. C. Peterson, and S. D. Ross, *J. Electrochem. Soc.*, **110**, 422 (1963); M. Shinagawa, H. Matsuo, and N. Maki, *Japan Analyst*, **5**, 80 (1956); *Chem. Abstr.*, **51**, 3356 (1957); H. Matsuo, *J. Sci. Hiroshima Univ., Ser. A.*, **22**, 281 (1960); *Chem. Abstr.*, **54**, 4206 (1958).

[15] K. K. Anderson and S. A. Yeager, *J. Org. Chem.*, **28**, 865 (1963).

[16] V. Franzen, H. I. Joschek, and C. Merta, *Ann.*, **554**, 82 (1962).

[17] M. Stiles, R. G. Miller, and U. Burckhardt, *J. Am. Chem. Soc.*, **85**, 1792 (1963).

[18] The ultraviolet spectrum of sodium iodide in aqueous solutions shows a maximum at 232 mμ: R. U. Marcus, *Science*, **123**, 399 (1956).

[19] The triarylsulfonium iodides are very insoluble in water.

sulfur radical over the triphenylsulfur radical, and to the fact that the mildly electron-donating *p*-methyl groups would decrease the rate of aromatic bimolecular nucleophilic substitution at carbon in the case of the tri-*p*-tolylsulfonium cation.

The infrared spectra of the various sulfonium salts are also of interest. Both triphenylsulfonium fluoroborate and tri-*p*-tolylsulfonium fluoroborate exhibit an aromatic C–H stretching absorption peak at 3040 cm^{-1} in chloroform solution, whereas the corresponding chloride, bromide and iodide salts exhibit the aromatic C–H stretching absorption peak at 2930 cm^{-1}, with only very weak absorption in the 3020–3040-cm^{-1} region. The absorption at longer wavelengths for the chloride, bromide, and iodide salts indicates a significant drain of electron density from the aromatic rings toward the sulfur atom owing to inductive and resonance effects.[20] This constitutes evidence that these compounds are essentially ionic and that covalent species, Ar_3S–X, are not present in any significant concentrations. In the case of the fluoroborate salts, it can be assumed that ion pairs predominate in the fairly concentrated chloroform solutions used for the infrared spectral determinations (5% solutions), and that the fluorine atoms of the fluoroborate anion are sufficiently close to the aromatic rings of the triarylsulfonium cations to increase the over-all electron density in the neighborhood of these rings.

Some consideration should be given to the question of whether or not a halide ion can function as an electron transfer agent in the reactions of triarylsulfonium halides with sodium alkoxides.[21] Since products, yields, and apparent rates of reaction are nearly identical in the reactions of each of the triarylsulfonium chlorides, bromides, and fluoroborates with sodium methoxide, it is doubtful that any of the anions are functioning as electron-transfer agents. The fluoroborate anion, in particular, would not be able to function in this manner.

The addition of a small amount of cupric chloride to each triarylsulfonium chloride–sodium methoxide reaction mixture seemed to increase the ratio of aromatic hydrocarbon to aryl methyl ether produced. However, the effect was a small one and should not be overly emphasized as an indication of catalysis of the radical reaction at the expense of the aromatic bimolecular nucleophilic substitution reaction.

An attempt was made to carry out an epr study of the reactions of triarylsulfonium halides with sodium methoxide. However, no signals were observed for the reaction mixtures of either tri-*p*-tolylsulfonium iodide or triphenylsulfonium iodide with sodium methoxide in methanol solution at room temperature. This is not surprising in view of the small concentration of radicals that would be present at any given time. In the reaction of tri-*p*-tolylsulfonium iodide with sodium methoxide, for example, the reaction is far from complete even after 60 hr at 72°.

A preliminary study was made of the pyrolysis of triphenylsulfonium hydroxide. When a sample of the crystalline compound was heated at 190° for a few minutes and the volatile products analyzed by vapor phase chromatography, diphenyl sulfide was found to have been produced in 70% yield, biphenyl in 18% yield, and benzene in 2% yield. Although additional work will have to be carried out before any extensive discussion of mechanism of reaction is warranted, it is apparent from the significant amount of biphenyl formed that a free-radical mechanism is operative, at least in part. The mechanism is probably similar to that specified above for the radical component of the reaction of triarylsulfonium salts with sodium alkoxides.

A preliminary study was also made of the photolysis of the triphenylsufonium chloride, bromide, iodide, and nitrate salts in ethanol solutions. The results, which are summarized in Table III, are closely parallel to those observed for the photolysis of quaternary anilinium salts.[22] If the mechanism of the formation of benzene is similar to that proposed by Walsh and Long[22] for their system, the order of yields of benzene and the halobenzenes, and the extent of reaction, are understandable. The iodide ion is the best electron transfer agent of the halides, and, if the triphenylsulfonium iodide exists mainly in the form of contact ion pairs, as the ultraviolet absorption studies suggest, whereas the other halide salts exist mainly as solvent-separated ion pairs, it is clear that the opportunity for electron transfer is at a maximum in the case of the sulfonium iodide.

Table III. Photolysis of Triphenylsulfonium Salts in Ethanol at 45° for 61 Hr

$(C_6H_5)_3S^+$, X^-	Products, % yield				Recovered
	C_6H_5S-C_6H_5	C_6H_5X	C_6H_6	C_6H_5–C_6H_5	$(C_6H_5)_3$-S^+,X^-
Cl	23	1	14	2.1	38
Br	37	12	24	1.4	24
I	47	36	31	1.4	4[a]
NO_3	30	. .	34	1.4	29

[a] As the triiodide.

$$(C_6H_5)_3S^+, X^- \rightleftarrows (C_6H_5)_3X \rightleftarrows (C_6H_5)_3S\cdot, X\cdot \longrightarrow C_6H_5SC_6H_5 + C_6H_5\cdot, X\cdot \longrightarrow C_6H_5X$$

Experimental Section

General. All melting points and boiling points are uncorrected. The procedure of Potratz and Rosen[23] 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 carried out by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Triphenylsulfonium Fluoroborate. A slurry of 14.6 g (0.04 mol) of diphenyliodonium fluoroborate[24] in 8.67 g (0.045 mol) of diphenyl sulfide was heated at 185° for 35 hr with vigorous stirring, and the hot mixture was poured into 150 ml of benzene. The benzene solution was decanted from a brown semisolid residue, most of which was then extracted into two 300-ml portions of boiling water, a brown oily residue being left behind. The combined aqueous extract, when concentrated, afforded crystalline triphenyl-

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(20) Diphenyl sulfide, sulfoxide, and sulfone, and the corresponding phenyl *p*-chlorophenyl compounds exhibit C–H stretching absorption peaks in the 3070–3090-cm^{-1} region. Diphenyl-*p*-chlorophenylsulfonium and diphenyl-*p*-anisylsulfonium iodides show a strong peak at 2910 cm^{-1}. This peak shows up at 2990 cm^{-1} for both triphenylsulfonium nitrate and triiodide.

(21) This evidently is of importance in certain reactions of benzyl halides with anions: *cf.* R. C. Kerber, G. W. Urry, and N. Kornblum, *J. Am. Chem. Soc.*, 86, 3904 (1964); N. Kornblum, T. M. Davies, G. W. Earl, G. S. Green, N. L. Holy, R. C. Kerber, J. W. Manthey, M. T. Musser, and D. H. Snow, *ibid.*, **89**, 5714 (1967), and papers cited therein.

(22) T. D. Walsh and R. C. Long, *ibid.*, **89**, 3943 (1967).

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

(24) F. M. Beringer, R. A. Falk, M. Karniol, I. Lillien, G. Masullo, M. Mausner, and E. Somer, *J. Am. Chem. Soc.*, **81**, 342 (1959).

sulfonium fluoroborate, mp 190–191° after recrystallization from water. The yield of purified salt was 64%.

Triphenylsulfonium Iodide. This compound precipitated when NaI was added to a hot aqueous solution of triphenyl-sulfonium fluoroborate. The melting point of the iodide was 245–246° dec after crystallization from ethanol–ether (lit.[25] mp 250°).

Triphenylsulfonium Bromide. To a solution of 3.85 g (0.01 mol) of triphenylsulfonium iodide in 30 ml of methanol was added 2.3 g (0.01 mol) of silver oxide. The mixture was stirred rapidly for 5 hr at room temperature, and the insoluble material (silver iodide plus unreacted silver oxide) was removed by filtration. The filtrate was neutralized with concentrated hydrobromic acid and concentrated to dryness and the residue dissolved in chloroform. The chloroform solution, dried over anhydrous magnesium sulfate, gave an oil on evaporation. A solution of this oil in ethanol–ether gave 2.7 g (80%) of crystalline triphenylsulfonium bromide, mp 288–290° dec. A mixture melting point with an authentic sample[26] of triphenylsulfonium bromide showed no depression.

Triphenylsulfonium Chloride. This salt was prepared in 75% yield from triphenylsulfonium iodide by the same method as described above for the corresponding bromide, concentrated hydrochloric acid being used to neutralize the filtrate from the silver oxide treatment. The melting point of the salt crystallized from ethanol–ether was 294–295° dec (lit.[25] mp 297°).

Anal. Calcd for $C_{18}H_{15}SCl$: C, 72.34; H, 5.06; S, 10.73; Cl, 11.87. Found: C, 72.51; H, 5.06; S, 10.59; Cl, 12.02.

Triphenylsulfonium Nitrate. This salt was prepared in 85% yield from triphenylsulfonium iodide by the same method described above for the corresponding bromide, concentrated nitric acid being used to neutralize the filtrate from the silver oxide treatment. The melting point of the salt crystallized from ethanol–ether was 228–229° (lit.[25] mp 227–227.5°).

Tri-*p*-tolylsulfonium Fluoroborate. This compound, mp 160–161° after crystallization from ethanol–ether or from water, was prepared in the same manner as described for triphenylsulfonium fluoroborate. The yield of the purified salt was 18%.

Anal. Calcd for $C_{21}H_{21}SBF_4$: C, 64.29; H, 5.40; S, 8.18. Found: C, 64.55; H, 5.39; S, 8.36.

Tri-*p*-tolylsulfonium Bromide. This salt, mp 241–244° dec, was prepared in 46% yield from di-*p*-tolyl sulfoxide and *p*-tolylmagnesium bromide by the method of Wildi, Taylor, and Potratz.[26] It was purified by crystallization from ethanol–ether.

Tri-*p*-tolylsulfonium Iodide. This compound precipitated when sodium iodide was added to a hot aqueous solution of tri-*p*-tolylsulfonium bromide. It had a melting point of 213–215° dec after crystallization from ethanol–ether.

Anal. Calcd for $C_{21}H_{21}SI$: C, 58.33; H, 4.90; S, 7.42; I, 29.35. Found: C, 58.71; H, 4.73; S, 7.60; I, 29.58.

Tri-*p*-tolylsulfonium Chloride. To a solution of tri-*p*-tolylsulfonium iodide in methanol was added a slight excess of a saturated solution of silver oxide in concentrated ammonia water. The precipitate of silver iodide was removed by filtration, the filtrate neutralized with concentrated hydrochloric acid, the solution extracted with chloroform, and the chloroform evaporated. The oil which remained was induced to crystallize from a mixture of ethanol, acetone, and ether. The tri-*p*-tolylsulfonium chloride obtained had a melting point of 236–237° dec.

Anal. Calcd for $C_{21}H_{21}SCl$: C, 73.98; H, 6.21; S, 9.41; Cl, 10.40. Found: C, 73.93; H, 6.40; S, 9.38; Cl, 10.41.

Reactions of Triphenylsulfonium and Tri-*p*-tolylsulfonium Salts with Sodium Methoxide. A 0.00050-mol sample of each of the salts listed in Table I was dissolved in 1.00 ml of a 1.01 *M* solution of sodium methoxide in absolute methanol contained in a Pyrex tube, which was then sealed. Each reaction was allowed to proceed for 60 hr at 72°. The reaction mixture was then directly analyzed by use of a flame ionization gas chromatograph equipped with a 6 ft × $^1/_8$ in. diameter SE 30 column. Internal standards were used and peak areas were determined. The results are summarized in Table I.

Each reaction mixture was homogeneous at the start of reaction. During the course of the reactions of the triarylsulfonium chlorides and fluoroborates, sodium chloride and sodium tetrafluoroborate, respectively, precipitated. The tri-*p*-tolylsulfonium salts turned light yellow while dissolving in the sodium methoxide solution.

Reactions of Triarylsulfonium Salts with Various Sodium Alkoxides. A 0.00075-mol sample of each of the salts listed in Table II was dissolved in 2.0 ml of the appropriate absolute alcohol, and to this solution was added 2.0 ml of a 0.00075 *M* solution of the corresponding sodium alkoxide in the alcohol. The reactions were allowed to take place at the temperatures and for the periods indicated in Table II. The solutions were subjected to vapor phase chromatographic analysis without neutralization or prior work-up. Either an F & M 609 flame ionization gas chromatograph equipped with a 5-ft Carbowax 20M column or an F & M 500 chromatograph equipped with a thermal detector and a 2-ft Silicone rubber column was used for the analytical work. Internal standards were used and peak areas were measured. The results are given in Table II.

All of the reaction mixtures turned brown after several minutes of reaction. In most cases a resin deposited on the sides of the flask. Sodium bromide precipitated from each reaction mixture in which a triarylsulfonium bromide was used as a reagent.

Reaction of Tri-*p*-tolylsulfonium Bromide with Sodium *n*-Butoxide. To a solution of 0.58 g (0.0015 mol) of tri-*p*-tolylsulfonium bromide in 5 ml of anhydrous 1-butanol was added a solution of 0.003 mol of sodium 1-butoxide in 10 ml of absolute 1-butanol. After the mixture had been refluxed for 24 hr, it was cooled, filtered to remove sodium bromide which had precipitated, neutralized carefully with concentrated hydrochloric acid, and distilled at 15 mm pressure. The fraction of bp 90–105° was found to have an infrared spectrum identical with that of *n*-butyl *p*-cresyl ether. The residue of high boiling point was decanted from a brown resinous material and induced to crystallize from 95% ethanol. There was obtained di-*p*-tolyl sulfide, mp 57–58°, also in admixture with an authentic sample of the compound. Its infrared spectrum, taken in carbon tetrachloride solution, was identical with that of authentic di-*p*-tolyl sulfide.

The reaction was repeated, but this time the reaction mixture was subjected, without prior neutralization or work-up of any kind, to preparative-scale gas chromatography (F & M Model 500 gas chromatograph, 2-ft Silicone rubber column). The only readily volatile products were toluene, *n*-butyl *p*-cresyl ether, and di-*p*-tolyl sulfide. The ether was found to be at least 97.5% pure *n*-butyl *p*-cresyl ether by infrared spectral comparison with samples containing known mixtures of *n*-butyl *m*-cresyl and *n*-butyl *p*-cresyl ethers. The comparisons were made on carbon disulfide solutions, a Beckman IR5 spectrophotometer being used. Absorption peaks at 12.23 μ for the *para* isomer and at 14.52 μ for the *meta* isomer were used for the analyses.

4-Methyl 2-Diazo-1-benzoate. A 3-ml portion of concentrated hydrochloric acid was added to a solution of 3.0 g (0.02 mol) of 2-amino-4-methylbenzoic acid in 40 ml of absolute ethanol. The mixture was cooled to 0° and treated with 6 ml of *n*-butyl nitrite with rapid stirring for 15 min. About 50 ml of cold, absolute ether was added, and the mixture was filtered. The precipitate was washed with 15 ml of cold ether. The precipitate was dissolved in about 10 ml of cold water, and an excess of powdered silver oxide was added to the solution. The mixture was maintained at 0° for 1 hr with stirring and was then filtered. The filtrate was poured into a mixture of 100 ml of absolute ethanol and 50 ml of ether maintained at 0°. Additional ether was added until the diazobenzoate began to crystallize, and the mixture was placed in the refrigerator for 6 hr. The product was collected by filtration, washed with cold ether and dried over phosphorus pentoxide in an evacuated desiccator kept in the refrigerator. There was obtained 2.1 g (69%) of tan crystals of 4-methyl 2-diazo-1-benzoate.

Decomposition of 4-Methyl 2-Diazo-1-benzoate in 1-Butanol. To 5.0 ml of anhydrous 1-butanol maintained at 55° was added slowly 0.3 g of 4-methyl 2-diazo-1-carboxylate. Decomposition took place almost immediately with evolution of gas and formation of an orange-red solution. After the solution had been stirred for an additional 10 min, it was subjected to preparative-scale gas chromatography, and a mixture of *n*-butyl *p*-cresyl ether and *n*-butyl *m*-cresyl ether was obtained in 19% yield. Infrared analysis of a carbon disulfide solution of this mixture revealed that it contained 65% of the *meta* isomer and 35% of the *para* isomer, the absorption peaks at 12.23 μ for the *para* isomer and at 14.52 μ for the *meta* isomer being used in the quantitative determinations.

Photolysis of Triphenylsulfonium Salts. A solution of 0.0007 mol of each of the salts listed in Table III in 3.00 ml of absolute ethanol was sealed in a 12-mm quartz tube and exposed to a bank of 16 Rayonet Photochemical Reactor Lamps No. RP.R 2537 Å at 45° for 61 hr. At the end of the reaction period the tube was

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opened and the contents directly analyzed by gas chromatography (F & M Model 609 flame ionization gas chromatograph, 6-ft 5% Apiezon L column). The results are summarized in Table III. The unreacted sulfonium salts did not decompose under our conditions of analysis.

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Amaryllidaceae Interconversions. Partial Syntheses of [2]Benzopyrano[3,4-*c*]indoles[1,2]

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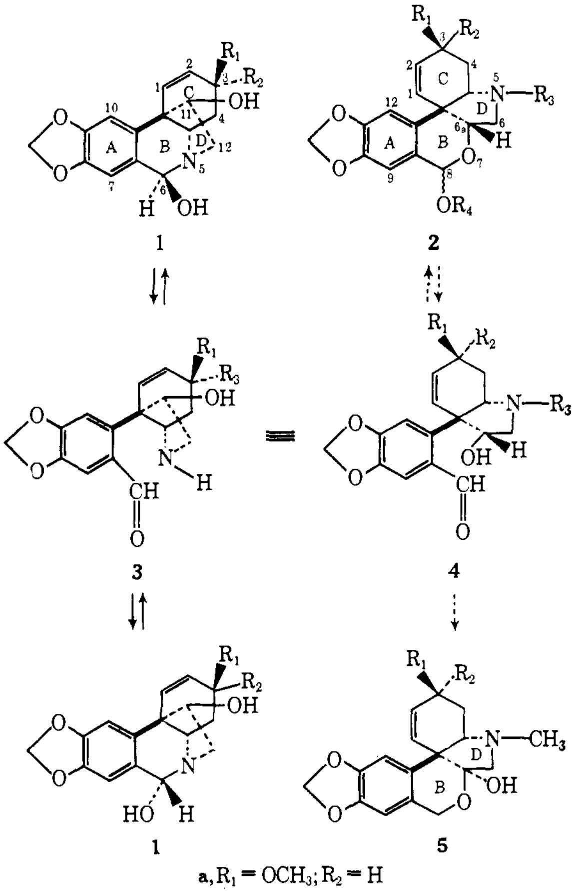
Abstract: Partial syntheses of pretazettine (**7a**), precriwelline (**7b**), and several related compounds are reported. Evidence is cited that haemanthidine (**1a**), 6-hydroxycrinamine (**1b**), and many derivatives of these alkaloids undergo a reversible rearrangement to the [2]benzopyrano[3,4-*c*]indole nucleus under mild conditions. Variations in temperature, solvent, or pH are often sufficient to alter the basic ring system. Biosynthetic implications of these transformations are outlined. Evidence for the α configuration of the C_{6a}-hydroxyl group of tazettine is presented.

Although the intermediate **3** and its rotational equivalent **4** (R_3 = H) have never been detected by spectral methods, these structures have considerable significance in the interrelationship of alkaloids related to structures **1**, **2**, and **5**. In a chemical sense the alkaloids haemanthidine (**1a**) and 6-hydroxycrinamine (**1b**) are amino alcohols formed by the ring closure of the intermediate amino aldehyde **3**. The dynamic nature of this N-C_6 bond formation was realized when **1a** and **1b** were shown to exist in solution as equilibrating mixtures of 6-hydroxyl epimers.[3] The epimeric forms were proposed to be interconvertible through **3**. The tendency of alkaloids of type **2** (pretazettine and precriwelline) to rearrange to the type **5** nucleus[4] (tazettine and criwelline) has been demonstrated.[5] This transformation was considered to proceed through **4** or the related alkoxide anion.



a, R_1 = OCH_3; R_2 = H
b, R_1 = H; R_2 = OCH_3

A number of examples are known for the conversion of the 6-hydroxy-5,10b-ethanophenanthridine alkaloids (**1**) to the [2]benzopyrano[3,4-*c*]indole ring systems (**2** and **5**). The first reported rearrangement of **1** to the type **5** nucleus was observed in the facile conversion of haemanthidine (**1a**) methiodide to tazettine (**5a**) upon treatment with aqueous sodium hydroxide.[7,8] Later, it was shown that N-demethyltazettine was produced when haemanthidine was treated with methanolic sodium methoxide.[9] Identical reactions were reported in the conversions of 6-hydroxycrinamine (**1b**) to criwelline (**5b**)[10] and to N-demethylcriwelline.[11] The reaction pathway for these rearrangements was studied with deuterated 6-hydroxycrinamine methiodide. It

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(2) This work is taken from the dissertation of D. T. Bailey submitted in partial fulfillment of the requirements for the Ph.D. degree, Iowa State University, 1968.

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(4) Compounds with the nucleus 2 have a β (steroid convention) C_{6a}-hydrogen,[5] while those with nucleus 5 have a C_{6a}-hydroxyl that has been reported to be α.[6]

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