Reaction between Methyl-*p*-tolylmethoxysulfonium Salt and Nucleophiles[1]

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The reactions of methyl-*p*-tolylmethoxysulfonium ion with such nucleophiles as tertiary amines, triphenylphosphine, thiophenolate anion and *p*-toluenesulfinate anion were investigated. The points of attack vary with nucleophile; the sulfonium ion receives nucleophilic attacks at its methoxy oxygen, methoxy carbon, sulfonium sulfur, S-CH_3 hydrogen or O–CH_3 hydrogen atoms. Optically active methyl-*p*-tolylmethoxysulfonium ion was also synthesized, and its reactions with benzylethylphenylamine, benzylmethylphenylphosphine and benzyl ethyl sulfide were studied. In the cases of the amine and the sulfide, the methylated products had optical activity. Thus, the methoxysulfonium ion can act as an optically active methylating agent.

Several alkoxysulfonium ions, $R_1R_2\overset{\oplus}{S}OR_3$, were prepared by alkylating the corresponding sulfoxides with trialkyloxonium ions.[2)] Although alkoxysulfonium ions are expected to undergo interesting reactions with various nucleophiles, only a few papers have been published on these reactions. Johnson and Phillips reported that removal of the proton on the α-carbon of the alkoxy group of an alkoxysulfonium ion yields an aldehyde and a sulfide, and removal of the proton on the carbon atom adjacent to the sulfonium sulfur results in a Stevens-type rearrangement, an α-alkoxysulfide being formed.[2a,3)] Johnson and McCants studied the reaction between an optically active alkoxysulfonium salt and hydroxide anion and found that the sulfoxide obtained possessed inverted configuration.[2b)] Reaction with arylmagnesium halides gave triarylsulfonium salt with inverted configuration.[4)]

Studies on the reactions of alkoxysulfonium ions with amines, phosphines, and sulfides seemed to be of great interest, and such investigations have been carried out in our laboratories. The results are described in this paper.

Results and Discussion

Reactions between methyl-*p*-tolylmethoxysulfonium tetrafluoroborate (I) and several nucleophiles in dichloromethane were studied at room temperature by means of NMR spectroscopy.

Reactions between I and Amines. Reaction of I with triethylamine or pyridine was rapid and completed soon after mixing, but that with *N*,*N*-dimethylaniline took 4 days and that with benzylethylphenyl amine took 7 days for completion. The results are shown in Table 1.

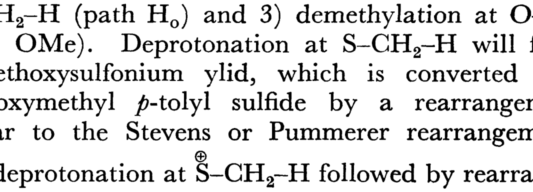
The reactions between I and amines can be summarized in the following scheme.

Table 1. Products of reactions between I and amines

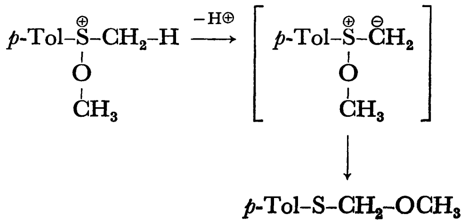
Product (mol/100 mol I)	Amines Et_3N	Me_2-NPh	C_5H_5N	PhEt-NCH_2Ph	Path[c)]
p-Tol-S-Me	45	9.1	4.8	10	H_o
p-Tol-$\overset{\oplus}{S}Me_2$	0	0	0	13	H_o
(CH_2O)[a)]	(45)	(9.1)	(4.8)	(25)	H_o
p-Tol-S-CH_2OMe	55	27	48	43	H_s
$H\overset{\oplus}{N}R_3$	97	32	(52.8)[b)]	(66)[b)]	H_s+H_o
p-Tol-$\underset{\overset{\downarrow}{O}}{S}$-Me	0	63	47	33	OMe
$Me\overset{\oplus}{N}R_3$	0	61	32	17	OMe

a) Estimated from the amounts of p-Tol-S-Me and p-Tol-$\overset{\oplus}{S}Me_2$.

b) Estimated from the amounts of p-Tol-S-Me, p-Tol-$\overset{\oplus}{S}Me_2$ and p-Tol-S-CH_2OMe c) See text and schemes.



Three paths are possible for these amines; 1) deprotonation at $\overset{\oplus}{S}$–CH_2–H (path H_S), 2) deprotonation at O–CH_2–H (path H_o) and 3) demethylation at O–Me (path OMe). Deprotonation at S–CH_2–H will form a methoxysulfonium ylid, which is converted into methoxymethyl *p*-tolyl sulfide by a rearrangement similar to the Stevens or Pummerer rearrangement. The deprotonation at $\overset{\oplus}{S}$–CH_2–H followed by rearrangement of the methoxy group appears to be the most plausible path for the formation of methoxymethyl *p*-tolyl sulfide.



$$p\text{-Tol-}\underset{\underset{CH_3}{|}}{\underset{O}{\overset{\oplus}{S}}}\text{-}CH_2\text{-}H \xrightarrow{-H^{\oplus}} \left[p\text{-Tol-}\underset{\underset{CH_3}{|}}{\underset{O}{\overset{\oplus}{S}}}\text{-}\overset{\ominus}{C}H_2\right] \longrightarrow p\text{-Tol-S-}CH_2\text{-}OCH_3$$

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1) Organic Sulfur Compounds. Part XLVI.

2) a) C. R. Johnson and W. G. Phillips, *J. Org. Chem.*, **32**, 1926 (1967); b) C. R. Johnson and D. Mc Cants, Jr., *J. Amer. Chem. Soc.*, **87**, 5404 (1965).

3) a) C. R. Johnson and W. G. Phillips, *Tetrahedron Lett.*, **1965**, 2101; b) C. R. Johnson and W. G. Phillips, *J. Amer. Chem. Soc.*, **91**, 682 (1969).

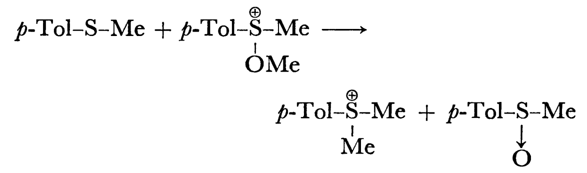
4) a) K. K. Andersen, M. Cinquini, and N. E. Papanikolaov, *J. Org. Chem.*, **35**, 706 (1970); b) K. K. Andersen and N. E. Papanikolaov, *Tetrahedron Lett.*, **1966**, 5445.

Table 2. Comparison of the points of attack of amines

Amine	OMe Attack[a] (%)	H Attack (%) $\mathrm{H_o}$[b]	$\mathrm{H_s}$[c]	Total	pK_a[e]	$\mathrm{N_{MeI}}$[f]
$\mathrm{Et_3N}$	0	45	55	100	10.7	6.66
$\mathrm{C_5H_5N}$	47	5	48	53	5.19	5.23
$\mathrm{Me_2NPh}$	63	9	27	36	5.21	5.64
$\mathrm{PhEtNCH_2Ph}$	33[d]	23	43	66	—	—

a) Yield of methyl *p*-tolyl sulfoxide. b) Yield of methyl *p*-tolyl sulfide and dimethyl-*p*-tolylsulfonium ion. c) Yield of methoxymethyl *p*-tolyl sulfide. d) (Yield of methyl *p*-tolyl sulfoxide) – (yield of dimethyl-*p*-tolylsulfonium ion). e) pK_a of $\mathrm{H\overset{\oplus}{N}R_3}$: Ref. 5. f) Pearson's nucleophilicity constant, $\mathrm{N_{MeI}} = \log(k/k_{\mathrm{MeOH}})$; Ref. 6.

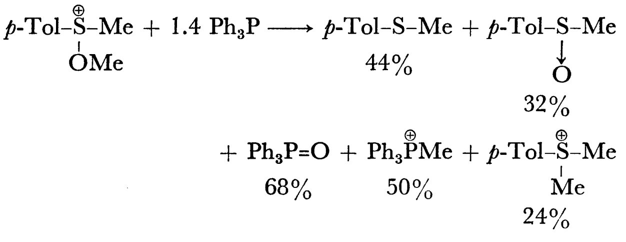
Dimethyl-*p*-tolylsulfonium salt was found only when benzylethylphenylamine was used. The reaction of I with this amine was very slow, and the methyl *p*-tolyl sulfide formed by the path $\mathrm{H_0}$ must have been further methylated by the methoxysulfonium ion still remaining unreacted in the medium.



$$p\text{-Tol-S-Me} + p\text{-Tol-}\overset{\oplus}{\underset{\text{OMe}}{\text{S}}}\text{-Me} \longrightarrow p\text{-Tol-}\overset{\oplus}{\underset{\text{Me}}{\text{S}}}\text{-Me} + p\text{-Tol-}\underset{\underset{\text{O}}{\downarrow}}{\text{S}}\text{-Me}$$

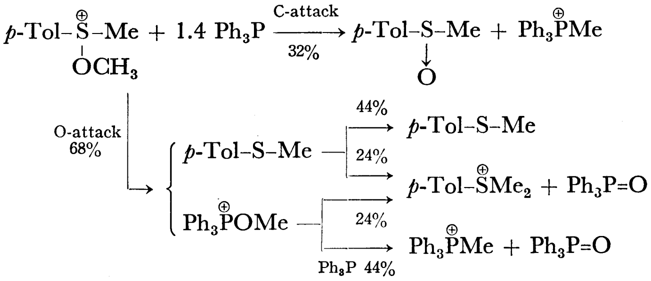
Table 2 summarizes the points of attack of the amines on I. The variations in the attacking points can be explained as follows. Since triethylamine is the strongest base among the four amines, its reaction is 100% H-attack and no C-attack was observed. *N,N*-Dimethylaniline is a much weaker base than triethylamine by a factor of 320000, but its nucleophilicity is smaller only by a factor of 10. Therefore, its main reaction was C-attack. Pyridine is a base of about equal strength but a slightly weaker nucleophile than *N,N*-dimethylaniline, and its H-attack percentage is greater than that of *N,N*-dimethylaniline. Though the basicity of benzyl ethyl phenyl amine is not available in the literature, it is expected to be comparable to or slightly greater than that of *N,N*-dimethylaniline. The much greater percentage of its H-attack is ascribable mainly to a steric factor; the crowded tertiary amine can attack the O–Me group only slowly and H-attack predominates.

Reaction between I and Triphenylphosphine. The products of the reaction between I and triphenylphosphine are summarized as follows.



$$p\text{-Tol-}\overset{\oplus}{\underset{\text{OMe}}{\text{S}}}\text{-Me} + 1.4\ \text{Ph}_3\text{P} \longrightarrow \underset{44\%}{p\text{-Tol-S-Me}} + \underset{32\%}{p\text{-Tol-}\underset{\underset{\text{O}}{\downarrow}}{\text{S}}\text{-Me}} + \underset{68\%}{\text{Ph}_3\text{P=O}} + \underset{50\%}{\text{Ph}_3\overset{\oplus}{\text{P}}\text{Me}} + \underset{24\%}{p\text{-Tol-}\overset{\oplus}{\underset{\text{Me}}{\text{S}}}\text{-Me}}$$

These products can be explained by assuming that triphenylphosphine attacks I at both the $\text{O-}\underline{\text{Me}}$ and $\underline{\text{O}}\text{-Me}$ positions. A reaction scheme consistent with the experimental results is shown below.



$$p\text{-Tol-}\overset{\oplus}{\underset{\text{OCH}_3}{\text{S}}}\text{-Me} + 1.4\ \text{Ph}_3\text{P} \xrightarrow[32\%]{\text{C-attack}} p\text{-Tol-}\underset{\underset{\text{O}}{\downarrow}}{\text{S}}\text{-Me} + \text{Ph}_3\overset{\oplus}{\text{P}}\text{Me}$$

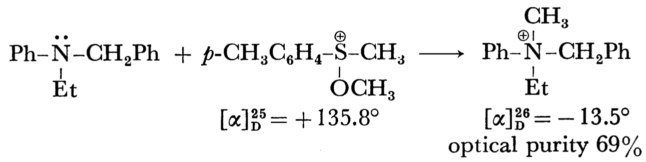
$$\xrightarrow[68\%]{\text{O-attack}} \left\{\begin{array}{l} p\text{-Tol-S-Me} \begin{cases} \xrightarrow{44\%} p\text{-Tol-S-Me} \\ \xrightarrow{24\%} p\text{-Tol-}\overset{\oplus}{\text{S}}\text{Me}_2 + \text{Ph}_3\text{P=O} \end{cases} \\ \text{Ph}_3\overset{\oplus}{\text{P}}\text{OMe} \begin{cases} \xrightarrow{24\%} \\ \xrightarrow[\text{Ph}_3\text{P}\ 44\%]{} \text{Ph}_3\overset{\oplus}{\text{P}}\text{Me} + \text{Ph}_3\text{P=O} \end{cases} \end{array}\right.$$

Since triphenylphosphine is a very weak base, it does not give the products of deprotonation. Although the nucleophilic attack of amines takes place only at the methoxy carbon atom, that of triphenylphosphine is mainly at the methoxy oxygen atom and the methoxy carbon attack is a minor reaction.

When triphenylphosphine attacks the methoxy oxygen atom of I, methoxytriphenylphosphonium ion is produced, which is expected to react further with triphenylphosphine. The experimental results show that this was what took place. When equal moles of I and triphenylphosphine were mixed, about 30% of I remained unreacted. The amounts of products formed were determined after a sufficient amount of triphenylphosphine was added and all of I present was consumed. Methoxyphosphonium ion has been postulated as an intermediate in the reaction of a phosphine with peroxides,[7a)] or Arbuzov reactions.[7b,c)]

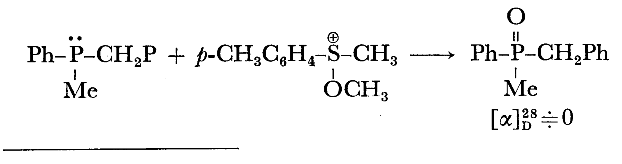
Reactions between Optically Active I and Nucleophiles. When optically active I is let to react with nucleophiles, it is expected that the products have some optical activity. In order to check this possibility, the reactions with benzylethylphenylamine, benzylmethylphenylphosphine and benzyl ethyl sulfide were studied.

When R-(+)-I was let to react with benzyl ethyl phenyl amine, a salt-like product obtained was found to be a 77:23 mixture of $(\text{Ph})(\text{PhCH}_2)\overset{\oplus}{\text{N}}(\text{Me})(\text{Et})$ and $p\text{-CH}_3\text{C}_6\text{H}_4\overset{\oplus}{\text{S}}(\text{CH}_3)_2$(by NMR). The optical purity of the methylated amine was 33%.



$$\text{Ph-}\underset{\text{Et}}{\overset{\cdot\cdot}{\text{N}}}\text{-CH}_2\text{Ph} + \underset{[\alpha]_{\text{D}}^{25} = +135.8^\circ}{p\text{-CH}_3\text{C}_6\text{H}_4\text{-}\overset{\oplus}{\underset{\text{OCH}_3}{\text{S}}}\text{-CH}_3} \longrightarrow \underset{\substack{[\alpha]_{\text{D}}^{26} = -13.5^\circ \\ \text{optical purity 69\%}}}{\text{Ph-}\overset{\text{CH}_3}{\underset{\text{Et}}{\overset{\oplus|}{\text{N}}}}\text{-CH}_2\text{Ph}}$$

When R-(+)-I was let to react with benzylethylphenylphosphine, the phosphine oxide produced was found to have no optical activity.



$$\text{Ph-}\underset{\text{Me}}{\overset{\cdot\cdot}{\text{P}}}\text{-CH}_2\text{P} + p\text{-CH}_3\text{C}_6\text{H}_4\text{-}\overset{\oplus}{\underset{\text{OCH}_3}{\text{S}}}\text{-CH}_3 \longrightarrow \underset{[\alpha]_{\text{D}}^{28} \doteqdot 0}{\text{Ph-}\overset{\overset{\text{O}}{\|}}{\underset{\text{Me}}{\text{P}}}\text{-CH}_2\text{Ph}}$$

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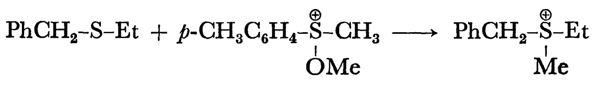
5) C. D. Hodgman (ed.), "Handbook of Chemistry and Physics," Chemical Rubber Publ. Co., Cleveland (1960), p. 1742.

6) R. G. Pearson, H. Sobel, and J. Songstad, *J. Amer. Chem. Soc.*, **90**, 319 (1968).

7) a) M. A. Greenbaum, D. B. Denney, and A. K. Hoffman, *ibid.*, **78**, 2563 (1956); b) A. Macgaekus and R. Kaehne, *Ber.*, **31**, 1048 (1898); c) E. A. Arbuzov, *Zh. Russ. Fiz. Khim. Obshch.*, **38**, 687 (1906).

If the reactions taking place were simply the nucleophilic attack of the phosphine on the oxygen atom adjacent to the asymmetric sulfur atom, some optical activity is expected. The fact that no optical activity was found indicates that what took place was more complex than a simple S_N2 reaction of the phosphine on the methoxy oxygen atom.

When R-(+)-I was let to react with benzyl ethyl sulfide, the benzylethylmethoxysulfonium tetrafluoroborate produced was found to have some optical activity.



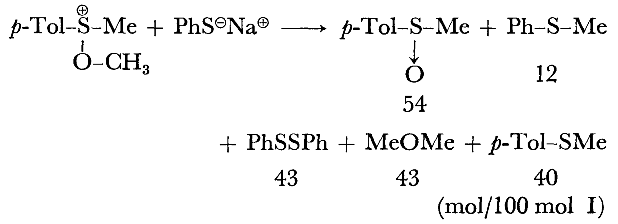
$$\mathrm{PhCH_2\text{-}S\text{-}Et} + p\text{-}\mathrm{CH_3C_6H_4}\text{-}\underset{\mathrm{OMe}}{\overset{\oplus}{\mathrm{S}}}\text{-}\mathrm{CH_3} \longrightarrow \mathrm{PhCH_2}\text{-}\underset{\mathrm{Me}}{\overset{\oplus}{\mathrm{S}}}\text{-}\mathrm{Et}$$

$[\alpha]_D^{27} = +4.9°$
optical purity 60%

Since this salt was not crystalline, it was subjected to anion-exchange on an $\mathrm{NaClO_4}$ column. However, the crystalline sulfonium perchlorate obtained showed no optical activity. It is possible that racemization took place during the anion-exchange procedure.

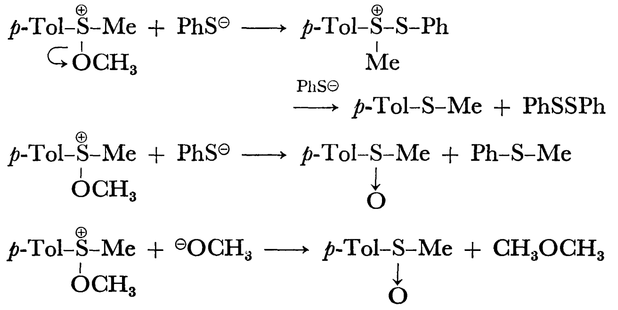
Thus, it has been established that optically active I can be used as stereoselective methylating agent for amines and sulfides.

Reaction between I and Sodium Thiophenolate. The products of the reaction between I and sodium thiophenolate are summarized as follows.



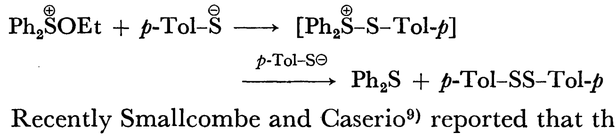
$$p\text{-Tol-}\underset{\mathrm{O\text{-}CH_3}}{\overset{\oplus}{\mathrm{S}}}\text{-Me} + \mathrm{PhS^{\ominus}Na^{\oplus}} \longrightarrow \underset{54}{p\text{-Tol-}\underset{\underset{\mathrm{O}}{\downarrow}}{\mathrm{S}}\text{-Me}} + \underset{12}{\mathrm{Ph\text{-}S\text{-}Me}}$$
$$+ \underset{43}{\mathrm{PhSSPh}} + \underset{43}{\mathrm{MeOMe}} + \underset{40}{p\text{-Tol-SMe}} \quad \text{(mol/100 mol I)}$$

These results indicate that the following reactions probably took place.



$$p\text{-Tol-}\underset{\curvearrowleft\mathrm{OCH_3}}{\overset{\oplus}{\mathrm{S}}}\text{-Me} + \mathrm{PhS^{\ominus}} \longrightarrow p\text{-Tol-}\underset{\mathrm{Me}}{\overset{\oplus}{\mathrm{S}}}\text{-S-Ph} \xrightarrow{\mathrm{PhS^{\ominus}}} p\text{-Tol-S-Me} + \mathrm{PhSSPh}$$
$$p\text{-Tol-}\underset{\mathrm{OCH_3}}{\overset{\oplus}{\mathrm{S}}}\text{-Me} + \mathrm{PhS^{\ominus}} \longrightarrow p\text{-Tol-S-Me} + \mathrm{Ph\text{-}}\underset{\underset{\mathrm{O}}{\downarrow}}{\mathrm{S}}\text{-Me}$$
$$p\text{-Tol-}\underset{\mathrm{OCH_3}}{\overset{\oplus}{\mathrm{S}}}\text{-Me} + {}^{\ominus}\mathrm{OCH_3} \longrightarrow p\text{-Tol-}\underset{\underset{\mathrm{O}}{\downarrow}}{\mathrm{S}}\text{-Me} + \mathrm{CH_3OCH_3}$$

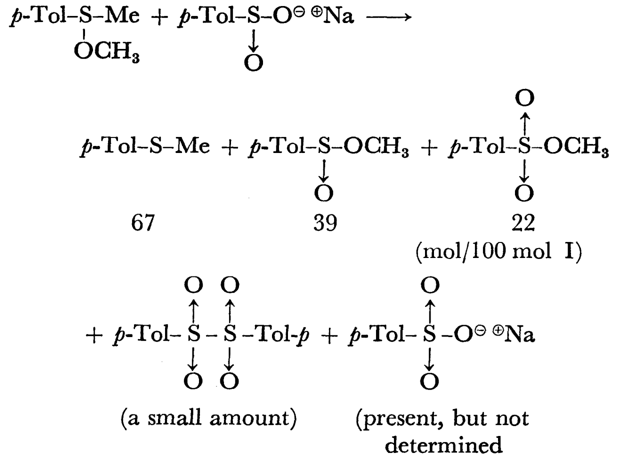
Thus thiophenolate anion attacks at both the sulfonium sulfur and methoxy carbon atoms. Oae and Khim reported that p-toluenethiolate anion attacks exclusively at the sulfonium sulfur atom of ethoxydiphenylsulfonium ion, and diphenyl sulfide and di-p-tolyl disulfide are the products.[8]



$$\mathrm{Ph_2\overset{\oplus}{S}OEt} + p\text{-Tol-}\overset{\ominus}{\mathrm{S}} \longrightarrow [\mathrm{Ph_2\overset{\oplus}{S}\text{-}S\text{-}Tol}\text{-}p] \xrightarrow{p\text{-Tol-S}^{\ominus}} \mathrm{Ph_2S} + p\text{-Tol-SS-Tol-}p$$

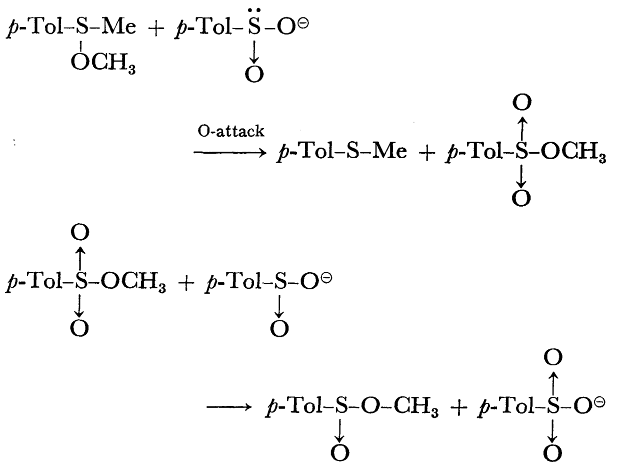
Recently Smallcombe and Caserio[9] reported that the rate constant k_2 for the reaction, $\mathrm{Me_2\overset{\oplus}{S}SMe} + \mathrm{MeSSMe} \rightarrow \mathrm{Me_2S} + \mathrm{Me\overset{\oplus}{S}(SMe)_2}$, is extremely large ($1.04 \times 10^4\ \mathrm{M^{-1}\,s^{-1}}$ at 40 °C). This suggests that the reaction between p-Tol(Me)$\overset{\oplus}{\mathrm{S}}$SPh and $\overset{\ominus}{\mathrm{S}}$Ph must be very fast, and as soon as p-Tol(Me)$\overset{\oplus}{\mathrm{S}}$SPh is formed by the S-attack of thiophenolate anion on I, it is quickly converted into methyl p-tolyl sulfide and diphenyl disulfide.

Reaction between I and Sodium p-*Toluenesulfinate.* The products of the reaction between I and sodium p-toluenesulfinate are summarized as follows.



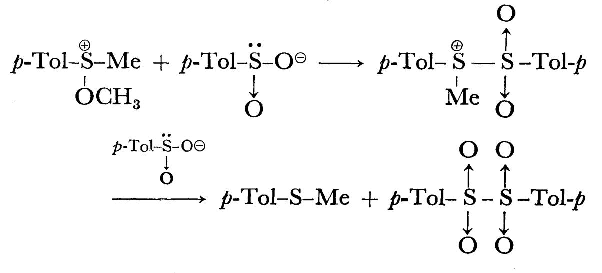
$$p\text{-Tol-}\underset{\mathrm{OCH_3}}{\mathrm{S}}\text{-Me} + p\text{-Tol-}\underset{\underset{\mathrm{O}}{\downarrow}}{\mathrm{S}}\text{-O}^{\ominus}\,{}^{\oplus}\mathrm{Na} \longrightarrow$$
$$\underset{67}{p\text{-Tol-S-Me}} + \underset{39}{p\text{-Tol-}\underset{\underset{\mathrm{O}}{\downarrow}}{\mathrm{S}}\text{-OCH_3}} + \underset{22}{p\text{-Tol-}\overset{\overset{\mathrm{O}}{\uparrow}}{\underset{\underset{\mathrm{O}}{\downarrow}}{\mathrm{S}}}\text{-OCH_3}} \quad \text{(mol/100 mol I)}$$
$$+ \underset{\text{(a small amount)}}{p\text{-Tol-}\overset{\overset{\mathrm{O}}{\uparrow}}{\underset{\underset{\mathrm{O}}{\downarrow}}{\mathrm{S}}}\text{-}\overset{\overset{\mathrm{O}}{\uparrow}}{\underset{\underset{\mathrm{O}}{\downarrow}}{\mathrm{S}}}\text{-Tol-}p} + \underset{\text{(present, but not determined}}{p\text{-Tol-}\overset{\overset{\mathrm{O}}{\uparrow}}{\underset{\underset{\mathrm{O}}{\downarrow}}{\mathrm{S}}}\text{-O}^{\ominus}\,{}^{\oplus}\mathrm{Na}}$$

These results suggest that the following reactions took place.



$$p\text{-Tol-}\underset{\mathrm{OCH_3}}{\mathrm{S}}\text{-Me} + p\text{-Tol-}\overset{\cdot\cdot}{\underset{\underset{\mathrm{O}}{\downarrow}}{\mathrm{S}}}\text{-O}^{\ominus} \xrightarrow{\text{O-attack}} p\text{-Tol-S-Me} + p\text{-Tol-}\overset{\overset{\mathrm{O}}{\uparrow}}{\underset{\underset{\mathrm{O}}{\downarrow}}{\mathrm{S}}}\text{-OCH_3}$$
$$p\text{-Tol-}\overset{\overset{\mathrm{O}}{\uparrow}}{\underset{\underset{\mathrm{O}}{\downarrow}}{\mathrm{S}}}\text{-OCH_3} + p\text{-Tol-}\underset{\underset{\mathrm{O}}{\downarrow}}{\mathrm{S}}\text{-O}^{\ominus} \longrightarrow p\text{-Tol-}\underset{\underset{\mathrm{O}}{\downarrow}}{\mathrm{S}}\text{-O-CH_3} + p\text{-Tol-}\overset{\overset{\mathrm{O}}{\uparrow}}{\underset{\underset{\mathrm{O}}{\downarrow}}{\mathrm{S}}}\text{-O}^{\ominus}$$

The formation of di-p-tolyl α-disulfone can be explained by the reaction steps involving the attack of the sulfinate on the S atom of I.



$$p\text{-Tol-}\underset{\mathrm{OCH_3}}{\overset{\oplus}{\mathrm{S}}}\text{-Me} + p\text{-Tol-}\overset{\cdot\cdot}{\underset{\underset{\mathrm{O}}{\downarrow}}{\mathrm{S}}}\text{-O}^{\ominus} \longrightarrow p\text{-Tol-}\underset{\mathrm{Me}}{\overset{\oplus}{\mathrm{S}}}\text{—}\overset{\overset{\mathrm{O}}{\uparrow}}{\underset{\underset{\mathrm{O}}{\downarrow}}{\mathrm{S}}}\text{-Tol-}p$$
$$\xrightarrow{p\text{-Tol-}\overset{\cdot\cdot}{\underset{\underset{\mathrm{O}}{\downarrow}}{\mathrm{S}}}\text{-O}^{\ominus}} p\text{-Tol-S-Me} + p\text{-Tol-}\overset{\overset{\mathrm{O}}{\uparrow}}{\underset{\underset{\mathrm{O}}{\downarrow}}{\mathrm{S}}}\text{-}\overset{\overset{\mathrm{O}}{\uparrow}}{\underset{\underset{\mathrm{O}}{\downarrow}}{\mathrm{S}}}\text{-Tol-}p$$

On the basis of these findings and other data reported in the literature, the reactions of methyl-p-tolylmethoxysulfonium ion with nucleophiles can be summarized as follows.

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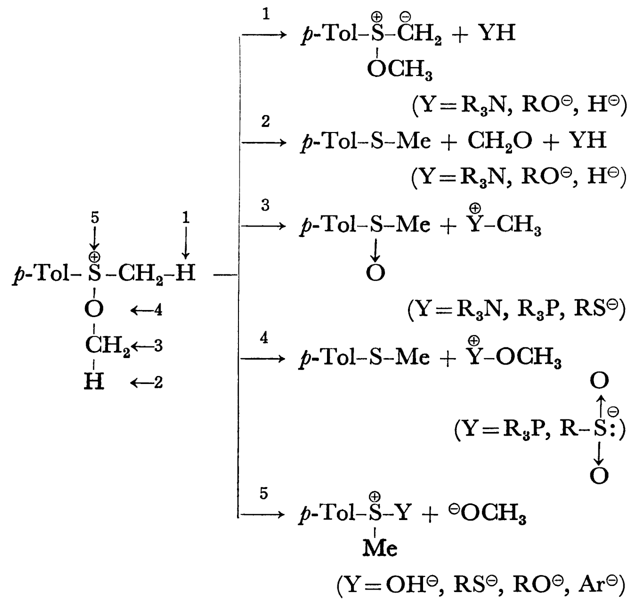
[8] S. Oae and Y. H. Khim, This Bulletin, **42**, 3528 (1969).

[9] S. H. Smallcombe and M. C. Caserio, *J. Amer. Chem. Soc.*, **93**, 5826 (1971).



Thus, methyl-*p*-tolylmethoxysulfonium ions can receive nucleophilic attack at five positions, and in this respect methylarylmethoxysulfonium ions are unique and interesting.

Experimental

Materials. Methyl-*p*-tolylmethoxysulfonium tetrafluoroborate (I) was synthesized by methylation of methyl *p*-tolyl sulfoxide with trimethyloxonium tetrafluoroborate in dichloromethane, and recrystallized from dichloromethane–ether;[2b] mp 65—68 °C; NMR, δ, 2.51 (s, $ArCH_3$), 3.57 (s, $S\text{–}CH_3$), 4.00 (s, $S\text{–}OCH_3$) ppm.

Methoxymethyl *p*-tolyl sulfide was prepared by condensation of chloromethyl *p*-tolyl sulfide with methanol in the presence of pyridine;[10] bp, 80—84 °C/4 mmHg; NMR, δ, 2.26 ppm ($ArCH_3$), 3.35 (s, OCH_3), 4.85 (s, SCH_2), 7.16 (q, ArH).

Dimethyl-*p*-tolylsulfonium tetrafluoroborate was synthesized by methylation of methyl *p*-tolyl sulfide with trimethyloxonium tetrafluoroborate, and recrystallized from dichloromethane–ether; NMR, δ, 2.50 ppm (s, $ArCH_3$), 3.27 (s, $S\text{–}CH_3$), 7.65 (q, ArH). Dimethylphenylsulfonium tetrafluoroborate was prepared in a similar manner; NMR, δ, 3.26 (s, $S\text{–}CH_3$), 7.87 (s, ArH).

Methyltriphenylphosphonium tetrafluoroborate was synthesized by methylation of triphenylphosphine with trimethyloxonium tetrafluoroborate; NMR, δ, 2.81 (d, CH_3), 7.77 (m, ArH).

General Procedure for the Reactions between I and Nucleophiles. An equimolar mixture of I and a nucleophile was let to react in dichloromethane, and the progress of the reaction was followed by means of NMR spectroscopy. The amounts of the products were determined from the integrated values on NMR spectra by using 1,1,2,2-tetrachloroethane as the internal standard. Each product was isolated by extraction, recrystallization or elution chromatography, and identified by comparing its melting point, glc retention time, IR or NMR spectrum with those of an authentic sample prepared separately.

Reaction between I and Pyridine. Pyridine (0.90 g, 11.4 mmol) was added to a dichloromethane solution (30 ml) of I (2.9 g, 11.4 mmol) in a 50 ml flask. Exothermic reaction took place, and pyridinium salts precipitated. After the white solids were filtered, the filtrate was concentrated, and the oily residue was extracted with hexane several times. Most of methyl *p*-tolyl sulfoxide remained unextracted. Evaporation and vacuum-distillation of the hexane extracts yielded methyl *p*-tolyl sulfoxide (bp, 110 °C/29 mmHg) and methoxymethyl *p*-tolyl sulfide (bp, 86—90 °C/3 mmHg). The pyridinium salts were recrystallized from dichloromethane–ether several times, and *N*-methylpyridinium chloride was isolated as crystals.

Reaction between I and Triphenylphosphine. Triphenylphosphine (3.1 g, 11.8 mmol) was added to a dichloromethane solution (15 ml) of I (3.0 g, 11.8 mmol). After 3 hr, the NMR spectrum of the solution indicated that 30% of I remained unreacted. When 1 g of phosphine was added, I disappeared completely. The solution was evaporated, and the residual oil was extracted with ether. Ether-isoluble residue was recrystallized from dichloromethane–ether, and methyltriphenylphosphonium salt and dimethyl-*p*-tolylsulfonium salt were isolated. The mother liquor of the recrystallization was evaporated, and elution chromatography of the residue yielded triphenylphosphine oxide. The ethereal extracts were evaporated, and the residue was subjected to elution chromatography on an alumina column; methyl *p*-tolyl sulfide and methyl *p*-tolyl sulfoxide were isolated.

Synthesis of Optically Active R-*(+)-Methyl* p-*Tolyl Sulfoxide.*[11] An anhydrous ether solution (100 ml) of methylmagnesium iodide (103 mmol) was added drop by drop to a stirred ether solution (500 ml) of (−)-menthyl *p*-toluenesulfinate (51.7 mmol) in 1 hr at 0 °C. The solution was stirred at room temperature for 3 hr, and then refluxed overnight. A saturated NH_4Cl solution (200 ml) was added for hydrolysis, and the ethereal layer was separated. The aqueous layer was extracted with ether three times, the combined ethereal extracts were dried over anhydrous magnesium sulfate, and the ether was evaporated. Elution chromatography (alumina, 300 mesh) of the residue gave *R*-(+)-methyl *p*-tolyl sulfoxide; $[\alpha]_D^{26}$ +136.5° (*c* 3.8, acetone).

Synthesis of Optically Active R-*(+)-Methyl-*p-*tolylmethoxysulfonium Tetrafluoroborate* (I_R). To a dichloromethane solution (20 ml) of *R*-(+)-methyl *p*-tolyl sulfoxide (2.0 g, 13.0 mmol) was added trimethyloxonium tetrafluoroborate (1.94 g, 13.0 mmol), and the mixture was stirred for 1.5 hr. After filtration, addition of ether to the cooled filtrate yielded white crystals, which were recrystallized from dichloromethane-ether; 2.4 g (9.4 mmol), 72%; $[\alpha]_D^{25}$ +135.8° (*c* 6.07, CH_2Cl_2).

Reaction between I_R *and Benzylethylphenylamine.* A mixture of I_R (3.0 g, 11.8 mmol) and benzylethylphenylamine (4.0 g, 19.0 mmol) in dichloromethane (30 ml) was let to react at room temperature for 8 days. After the solvent was evaporated, the residue was washed with ether and the ether-insoluble fraction was stirred with 30% $NH_3\text{–}H_2O$ (30 ml) and dichloromethane (20 ml) for 1 day. The solvents were evaporated, and the residue was extracted with dichloromethane. The extracts were dried over anhydrous $MgSO_4$ and evaporated. The NMR spectrum of the residue showed it to be a 77: 23 mixture of $(Ph)(PhCH_2)\overset{\oplus}{N}(Me)(Et)$ and $p\text{-}CH_3C_6H_4\overset{\oplus}{S}Me_2$. The optical activity of the salt was determined; $[\alpha]_D^{26}$ −13.5° (*c* 3.7, CH_2Cl_2), optical purity, 69% (optically pure $(Ph)(PhCH_2)\overset{\oplus}{N}EtMe$, $[\alpha]_D^{25}$ −19.6°).[12]

Reaction between I_R *and Benzylmethylphenylphosphine.*

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Dibenzylphenylphosphonium iodide was prepared by the reaction between dibenzylphenylphosphine and methyl iodide;[13] yield, 19.4%; mp, 206—209 °C (lit,[13] 207-208 °C). Lithium aluminium hydride (0.7 g, 18.4 mmol) was added to a stirred suspension of dibenzylmethylphenylphosphonium iodide (5.0 g, 11.6 mmol) in tetrahydrofuran (60 ml) under a nitrogen atmosphere. After the mixture was refluxed for 42 hr, dichloromethane (100 ml) was added. After 3 hr the jelly substance formed was filtered under a nitrogen atmosphere. To this filtrate containing benzylmethylphenylphosphine was added I_R (3.3 g, 12.9 mmol). After the mixture was allowed to stand at room temperature overnight, the solvent was evaporated, and the residue was extracted with ether. Repeated recrystallization of the ether-insoluble residue from CH_2Cl_2–Et_2O yielded $PhCH_2Ph\overset{\oplus}{P}Me_2\overset{\ominus}{B}F_4$, mp 120—122 °C. The mother liquor of the recrystallization was evaporated, and the residue was chromatographed on an alumina column; with CH_2Cl_2–Et_2O as the eluant MePhPh-CH_2P=O was obtained; mp 146—147 °C; $[\alpha]^{28}_D$ *ca.* 0 (*c* 6.7, CH_2Cl_2).

Reaction between I_R and Benzyl Ethyl Sulfide. A mixture of I_R (2.7 g, 10.6 mmol) and benzyl ethyl sulfide (2.0 g, 14.5 mmol) in dichloromethane (20 ml) was allowed to stand at room temperature for 3 days. Its NMR spectrum showed that I_R had disappeared completely. Ether (30 ml) was added, and the ether-insoluble fraction was dissolved in dichloromethane (20 ml), and again ether (30 ml) was added. This procedure was repeated for 6 times. Evaporation of the ether-insoluble fraction yielded solids; $[\alpha]^{27}_D$ +4.9° (*c* 6.08, CH_2Cl_2), optical purity, 60% (optically pure MeEt-$\overset{\oplus}{S}CH_2Ph\overset{\ominus}{Cl}O_4$, $[\alpha]^{25}_D = +8.20°$).[14]

The benzylethylmethylsulfonium tetrafluoroborate obtained was subjected to anion exchange by its aqueous acetone solution to an Amberlite IRA-400 column (ClO_4^-). Evaporation of the solvents and recrystallization of the residue from CH_2Cl_2–Et_2O gave crystals of $MeEt\overset{\oplus}{S}CH_2Ph\overset{\ominus}{Cl}O_4$; $[\alpha]^{25}_D$ *ca.* 0 (*c* 6.0, CH_2Cl_2).

Reaction between I and Sodium Thiophenolate. Sodium thiophenolate (1.3 g, 5.3 mmol) was added to a dichloromethane solution (10 ml) of I (0.70 g, 5.3 mmol). Reaction was soon completed. Diphenyl disulfide, methyl *p*-tolyl sulfoxide, methyl ether, methyl phenyl sulfide and methyl *p*-tolyl sulfide were obtained as the products. The amounts of methyl phenyl sulfide and methyl *p*-tolyl sulfide were determined by NMR spectroscopy.

Reaction between I and Sodium p-*Toluenesulfinate.* Anhydrous sodium *p*-toluenesulfinate (4.5 g, 25.3 mmol) was slowly added with stirring to a dichloromethane solution (30 ml) of I (3.9 g, 15.3 mmol). Exothermic reaction occurred. After one day, the solution was separated from the solids. Evaporation of the solution yielded crystals and oil. Crystals were found to be di-*p*-tolyl α-disulfone. Vacuum distillation of the oil yielded methyl *p*-tolyl sulfide (40 °C/0.02 mmHg) and a mixture of methyl *p*-toluenesulfinate and methyl *p*-toluenesulfonate (50—70 °C/0.02 mmHg).

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