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REACTIONS OF ALKOXIDES WITH ALKOXYSULFONIUM SALTS[1]

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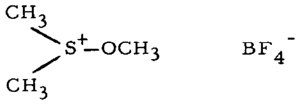


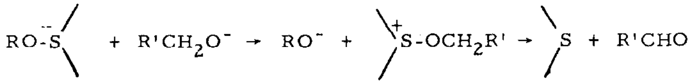
I

The reaction of alkoxides with simple alkoxysulfonium salts such as dimethyl methoxysulfonium fluoroborate (I) proceeds _via_ rapid interchanges of the alkoxy group followed by base-catalyzed elimination to provide carbonyl compounds. This procedure focuses attention concurrently on two types of reactions which have previously been observed. Earlier studies of Kornblum and co-workers[2] had established the ability of sulfoxides, especially dimethyl sulfoxide to oxidize halides and tosylates according to the equation (1). Alkoxysulfonium salts have often

$$RCH_2X + CH_3SOCH_3 \xrightarrow[\Delta]{NaHCO_3} RCHO + CH_3SCH_3 + HX \quad (1)$$

been postulated as intermediates in these reactions. Work in our laboratories has established that these salts are subject to back-side displacement on the sulfur atom.[3]

Treatment of dimethylmethoxysulfonium fluoroborate (I) labeled with carbon-14 in the O-methyl group with sodium hydride in dimethyl sulfoxide yielded correspondingly radioactive formaldehyde; however, when sodium methoxide in methanol was employed as base the formaldehyde (35 cpm/μ mole) obtained exhibited less than one percent of the radioactivity of the starting salt (4340 cpm/μ mole), indicating that methoxy interchange with solvent occurs much more rapidly than elimination of the salt to the carbonyl compound and sulfide (equation (2)). The formaldehyde was characterized and its radioactivity determined as the methone

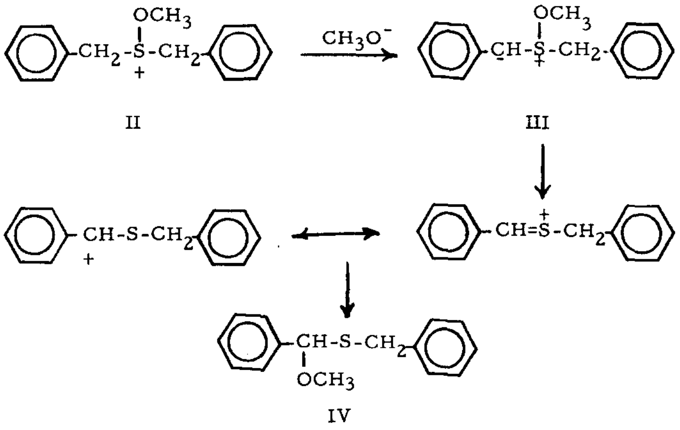


$$RO\text{-}\overset{+}{S}\langle \;+\; R'CH_2O^- \rightarrow RO^- \;+\; >\overset{+}{S}\text{-}OCH_2R' \rightarrow\; >S \;+\; R'CHO \quad (2)$$

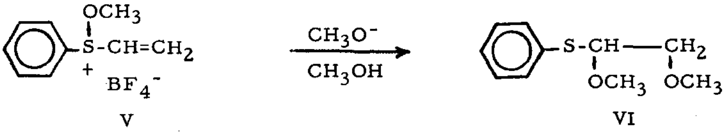
derivative. Exchange was also dictated by the observation that when the reaction was run part-way, recovered salt showed considerable reduction in radioactivity. Equilibration of the alkoxy groups of the salt with alcohol solvent was also observed in the following reactions. Titration of dimethylmethoxysulfonium fluoroborate with sodium ethoxide in ethanol provides acetaldehyde in 72 percent yield. Similarly, when the same salt is titrated with isopropoxide in isopropanol acetone is formed in 50 percent yield. Use of *t*-butoxide in *t*-butanol provides an intermediate *t*-butoxysulfonium salt which cannot eliminate to carbonyl compound, but which yields isobutylene and dimethyl wulfoxide by carbon-oxygen cleavage. The isobutylene was identified as 1, 2-dibromo-2-methylpropane.

These O-alkyl salts of sulfoxides undergo alkoxy exchange in alcohol solution in the absence of alkoxides although the exchange is considerably slower.[4] For example when dibenzyl ethoxysulfonium fluoroborate is dissolved in radioactive ethanol after one hour at 70° recovered salt shows only 4. 2 percent exchange of the ethoxy group with solvent. By employing optically active benzyl *p*-tolyl ethoxysulfonium fluoroborate in ethanol the exchange could be followed polarimetrically, but the situation is complicated by the formation of ethyl ether and sulfoxide.[5]

We have further observed that the ultimate course of the alkoxide reaction can be altered by increasing the acidity of the hydrogen on the carbons adjacent to the positive sulfur. In one example, the O-methyl salt (II) of dibenzyl sulfoxide was titrated with methoxide. When the reaction mixture was treated with 2, 4-dinitrophenylhydrazine reagent the derivative of benzaldehyde was recovered in good yield. When the reaction mixture was worked up in the absence of acid, α-methoxydibenzyl sulfide (IV) was obtained.

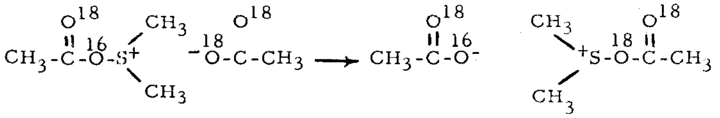


An entirely analogous reaction occurs with the salts of benzyl phenyl sulfoxide. Moreover, the same general type reaction could be initiated by the Michael-type addition of methoxide to vinyl phenyl methoxysulfonium fluoroborate (V). The product obtained was 1,2-dimethoxy-1-phenylthioethane (VI), whose structure was readily assigned from its mass spectrum.



Although it is not known at this time it is highly probable that these reactions proceed through ylid intermediates such as III. Should this be the case the reactions would be unique in that the loss of alkoxide from the ylid converts a carbon with carbanion character to one with carbonium ion character. An alternate pathway would involve concerted elimination of the elements of alcohol.

The similarity of these reactions to the familiar Pummerer reaction which yields α-acyloxy sulfides when the corresponding sulfoxide is treated with an acid anhydride is noteworthy. Furthermore, our observation of the facile exchange of alkoxy groups in alkoxysulfonium salts casts doubt upon the significance of the O-18 data obtained by Oae and co-workers[6] in their study of the Pummerer reaction. Their data which indicated oxygen scrambling could equally well be accounted for by acetoxy interchange of the type indicated by equation (3).



$$CH_3-\overset{O^{18}}{\overset{\|}{C}}-\overset{16}{O}-S^+(CH_3)_2 \quad {}^-\overset{18}{O}-\overset{O^{18}}{\overset{\|}{C}}-CH_3 \longrightarrow CH_3-\overset{O^{18}}{\overset{\|}{C}}-\overset{16}{O}{}^- \quad (CH_3)_2\,{}^+S-\overset{18}{O}-\overset{O^{18}}{\overset{\|}{C}}-CH_3 \qquad (3)$$

We are continuing to explore the scope and mechanism of reactions of alkoxysulfonium salts.

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2. N. Kornblum, W. J. Jones and G. J. Anderson, *ibid.*, **81**, 4113 (1959).

3. C. R. Johnson, *ibid.*, **85**, 1020 (1963); C. R. Johnson and D. McCants, Jr., in preparation.

4. Alkoxy exchange on alkoxysulfonium salts in alcohol solution has also been suggested by P. Skell and M. F. Epstein, Abstracts, p. 26N, 147th Meeting, American Chemical Society, April, 1964. We wish to thank Prof. Skell and Dr. Epstein for valuable discussions on this matter.

5. C. R. Johnson and J. B. Sapp, Jr., *ibid.*, p. 23Q, 145th Meeting, Sept. 1963.

6. S. Oae, T. Kitao, S. Kawamura and Y. Kitaoka, *Tetrahedron*, **19**, 817 (1963).