CHEMISTRY LETTERS, pp. 211-214, 1975. Published by the Chemical Society of Japan

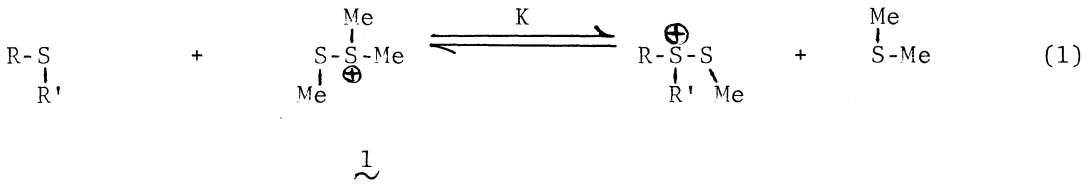
TETRACOVALENT SULFUR INTERMEDIATES IN SULFIDE-SULFONIUM ION REACTIONS

Hiroshi MINATO,* Takashi MIURA, Fumio TAKAGI, and Michio KOBAYASHI
Department of Chemistry, Tokyo Metropolitan University, Fukazawa, Setagaya, Tokyo 158

Methyl sulfide was very rapidly t-butylated by di-t-butylmethylsulfonium ion, forming t-butyldimethylsulfonium ion. Benzylation of methyl sulfide with dibenzylmethylsulfonium ion was a little slower, and i-propylation with methyldi-i-propylsulfonium ion was not observed. A mechanism presented involves the formation of a tetracovalent sulfur intermediate.

Recently Kim and Caserio suggested possible occurrence of 1,2-degenerate rearrangement in alkylated dimethyl disulfide.[1] We wish to report our findings on the reactions between sulfides and sulfonium ions, and suggest a plausible mechanism.

We studied the reactions between dimethylmethylthiosulfonium fluoroborate (1) and various sulfides in nitromethane. When an equimolar amount of ethyl sulfide was added to a nitromethane solution of 1, the $Me_2\overset{\oplus}{S}-$ absorption (δ, 3.22 ppm) was shifted to 2.46 ppm and the -SMe absorption (2.88 ppm) was shifted to 2.82 ppm. This finding suggests that the following equilibrium was established and both the forward and backward reactions were very rapid in the nmr time scale.



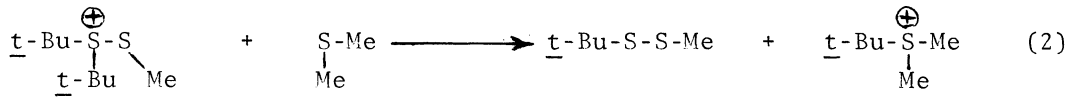
(1)

1

The equilibrium constants obtained were 1.0 for MeSEt, 2.6 for MeS-i-Pr, 4.5 for Et_2S, and 0.0047 for Ph_2S.

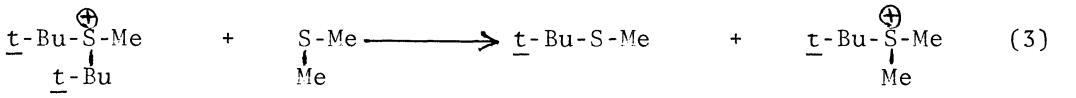
However, when t-butyl sulfide was allowed to react with 1, such an equilibrium was not observed, and further change did take place. When the nmr spectrum was determined 90 sec after the mixing of the reactants (about 0.4 M in each), all the four components of the equilibrium (1) were absent and t-butyl-

dimethylsulfonium ion and t-butyl methyl disulfide were present. Apparently the following reaction took place very rapidly.



(2)

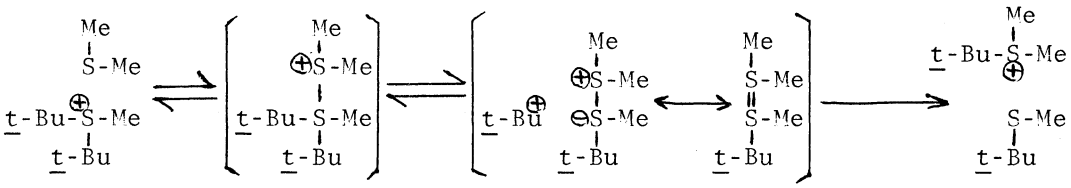
This rapid t-butylation of methyl sulfide seemed to be of great interest. It is peculiar that $R_2\overset{+}{S}$-SMe receives the nucleophilic attack of methyl sulfide only when R is t-butyl group. In an attempt to elucidate the mechanism of this reaction, we studied a simplified case, namely the reaction between di-t-butylmethylsulfonium fluoroborate and methyl sulfide in nitromethane. When the equimolar amounts of the reactants were mixed at room temperature (about 0.4 M in each reactant), the nmr spectra of the solution showed that methyl sulfide was very rapidly t-butylated; the reaction was 76% complete in 10 min and complete in 90 min. Again the reaction was exclusive t-butylation with no methylation accompanied.



(3)

If the reaction were a simple S_N2 displacement, the methyl carbon atom must receive the attack much more readily than the t-butyl carbon atom. Clearly reaction (3) is not a simple S_N2 displacement. A plausible mechanism for reaction (3) is the following, which involves nucleophilic addition of a sulfide to a sulfonium sulfur atom.

Scheme 1

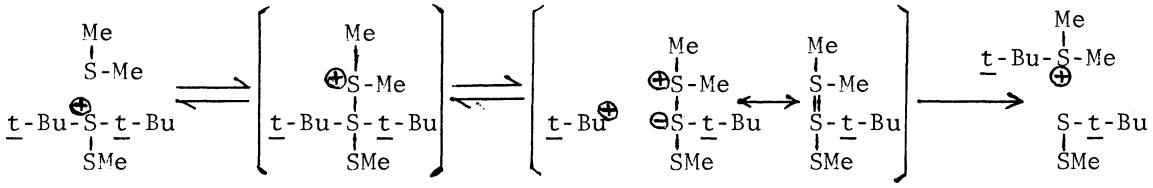


Another possible scheme is that involving the unimolecular dissociation of di-t-butylmethylsulfonium ion to t-butyl cation and t-butyl methyl sulfide, but this possibility can be rejected from the finding that t-butyl cation could not be trapped by styrene when a mixture of di-t-butylmethylsulfonium ion and styrene was allowed to stand at room temperature. Kim and Caserio found that optically active 1-phenylethyldimethylsulfonium ion does not racemize in nitromethane and it does not react with styrene.[1]

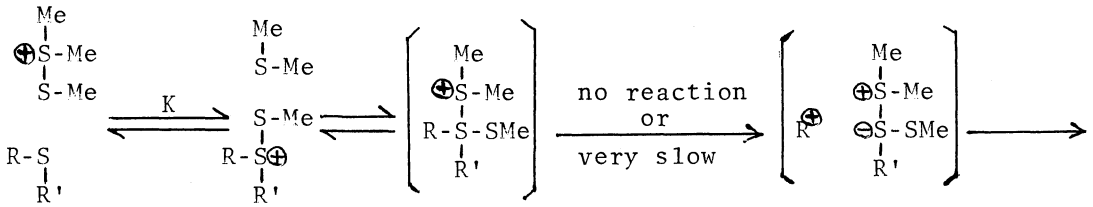
When methyldi-i-propylsulfonium ion was mixed with methyl sulfide, no measurable reaction took place. (The concentrations of the sulfonium ions were always about 0.4 M). The reaction between dibenzylmethylsulfonium ion and methyl sulfide (10 mol/mol of the sulfonium ion) was 60% complete in 120 min. The reaction was exclusive benzylation with no methylation accompanied. Thus, alkylation with trialkylsulfonium ion proceeds rapidly when an alkyl group can form a relatively stable cation. It is understandable that in the reactions between 1 and various sulfides (R = Me, Et, i-Pr, and Ph) only the reaction (1) was observed and no reaction similar to reaction (2) was observed in these cases.

As for reaction (2), the following mechanism similar to Scheme 1 seems to best explain the experimental results.

Scheme 2



The non-occurrence of reaction (2) in the cases of R = Me, Et, i-Pr or Ph can be explained as follows. Methyl sulfide adds to the sulfonium sulfur atom of $R_2\overset{\oplus}{S}$-SMe reversibly in the same manner as in the case of R = t-Bu, but the next step, namely the unimolecular dissociation of the adduct forming R cation, is extremely slow in these cases.



Kim and Caserio found that the reaction between 1 and (-)-PhMeCHSCD$_3$ yielded (±)-PhMeCH-$\overset{\oplus}{S}$Me$_2$ and CH_3SSCD_3, and explained the results by assuming either the reversible dissociation of PhMeCH(D_3C)$\overset{\oplus}{S}$-SMe forming $\overset{\oplus}{PhMeCH}$ and D_3CSSCH_3 or an internal nucleophilic displacement in PhMeCH(D_3C)$\overset{\oplus}{S}$-SMe by the neighboring sulfur at the chiral center with inversion of configuration.

An objection to their first proposal is the findings that styrene did not react with either our sulfonium ions or their sulfonium ions. An objection to their second proposal is the fact that it is difficult to visualize how internal 1,2-rearrangement of an alkyl group proceeds with inversion of configuration; retention is expected in such 1,2-rearrangement of an alkyl group, and so far as we are aware, no 1,2-rearrangement with inversion has been reported in the literature. However, if one assumes the formation of the adduct from $PhMeCH(D_3C)\overset{\oplus}{S}$-SMe and MeSMe and the subsequent dissociation of the adduct forming $PhMeCH^{\oplus}$, one can rationalize their findings much more easily.

It has been shown that the reaction between trialkylsulfonium ions and nucleophiles has features different from the ordinary S_N1, S_N2 or competitive S_N1-S_N2 reactions. In ordinary S_N2 reactions the relative reactivities of benzyl and methyl compounds are not much different from unity,[2] whereas in the reaction of dimethyl-1-phenylethylsulfonium ion with nucleophiles benzylation predominates except one special case.[3]

The effect of added azide or iodide ions to the hydrolysis of benzyldimethylsulfonium ion could not be explained by S_N1, S_N2 or competitive S_N1-S_N2 mechanisms, and a unifying mechanism involving reversible dissociation of the sulfonium ion to benzyl cation-methyl sulfide assemblage has been proposed.[4] The hypothesis of nucleophile-sulfonium ion adducts is applicable to these cases, and it appears to be a reasonable mechanism.

Formation of tetracovalent sulfur compounds and intermediates has been reviewed.[5] Formation of tetracovalent sulfur intermediates in nucleophile-sulfonium reactions is a probable and useful hypothesis which can explain many data otherwise unexplainable.

REFERENCES

(1) J. K. Kim and M. C. Caserio, J. Amer. Chem. Soc., 96, 1930 (1974).
(2) A. Streitwieser, Chem. Rev., 56, 571 (1956).
P. B. D. de la Mare and E. D. Hughes, J. Chem. Soc., 1956, 845.
(3) H. M. R. Hoffmann, J. Chem. Soc., 1965, 823.
H. M. R. Hoffmann and E. D. Hughes, J. Chem. Soc., 1964, 1259.
S. H. Harvey, P. A. T. Hoye, E. D. Hughes, and C. Ingold, J. Chem. Soc., 1960, 800.
(4) R. A. Sneen, G. R. Felt, and W. C. Dickason, J. Amer. Chem. Soc., 95, 638 (1973).
(5) N. E. Hester, Int. J. Sulfur Chem., 8, 124 (1973).

(Received December 20, 1974)