

fer processes in mixtures of pyrimidines and purines will be published.

E. Hayon

Pioneering Research Laboratory, U. S. Army Natick Laboratories  
Natick, Massachusetts 01760

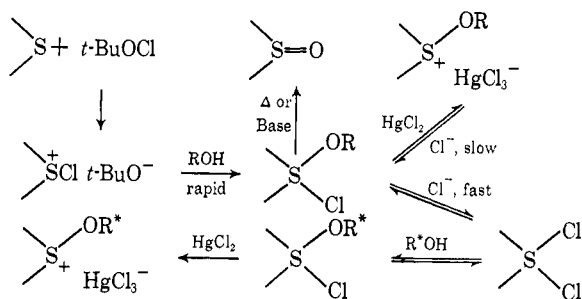
Received June 10, 1969

### Oxidation of Sulfides with *t*-Butyl Hypochlorite. Evidence for a Tetravalent Sulfur Intermediate<sup>1</sup>

Sir:

*t*-Butyl hypochlorite is an excellent reagent for the oxidation of sulfides to sulfoxides without concomitant formation of sulfones.<sup>2</sup> In certain cases, interesting and synthetically useful stereochemical control of such oxidations is possible.<sup>3</sup> It has been proposed that alkoxy-sulfonium salts intervene in these oxidations;<sup>2</sup> such salts have been isolated after the addition of halide traps such as antimony pentachloride, mercuric chloride, or certain silver salts.<sup>4</sup> Several papers have already appeared with mechanistic suggestions concerning such reactions.<sup>5</sup> We now wish to report convincing evidence for the intervention of tetravalent sulfur species in such oxidations; we believe Scheme I describes the essential features of these reactions.

Scheme I



The hypochlorite oxidations are conducted at  $-78^\circ$ . To thiane in methylene chloride was added 2 equiv of *t*-butyl hypochlorite followed by 1 equiv of mercuric chloride. Addition of ethyl ether caused the precipitation of the relatively unstable salt **1** ( $R = t\text{-C}_4\text{H}_9$ ). The solid was rapidly analyzed by ir spectroscopy. A spectrum characteristic of a *t*-butoxy-sulfonium trichloromercurate was obtained. If ethanol (as little as 1 or 2 equiv) is present at the time of addition of the hypochlorite the principal product is salt **1** ( $R = \text{C}_2\text{H}_5$ ). On the other hand, if the ethanol is added after the addition of the *t*-butyl hypochlorite the salt obtained upon addition of mercuric chloride is again the *t*-butyl salt. The reaction of *t*-butyl hypochlorite in ethanol is much faster than the reaction of ethyl hypochlorite; therefore, we are confident that, in the former case, ethyl hypochlorite is not the effective reagent. These results led to the suggestion that the chlorosulfonium salt **2** is the first intermediate

(1) Part XX in the series Chemistry of Sulfoxides and Related Compounds. We gratefully acknowledge support by the National Science Foundation (Grant GP-8648).

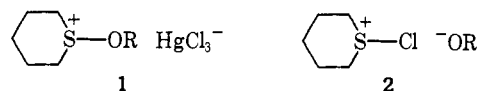
(2) P. S. Skell and M. F. Epstein, Abstracts, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964, p 26N

(3) C. R. Johnson and D. McCants, Jr., *J. Amer. Chem. Soc.*, **87**, 1109 (1965).

(4) C. R. Johnson and M. P. Jones, *J. Org. Chem.*, **32**, 2014 (1967).

(5) C. Walling and M. J. Mitz, *ibid.*, **32**, 1286 (1967); L. Skattebøl, B. Boulette, and S. Solomon, *ibid.*, **32**, 3111 (1967).

along the reaction coordinate and that this chlorosulfonium salt reacts quickly even at  $-78^\circ$  to give an alkoxy intermediate. This alkoxy intermediate could be an alkoxy-sulfonium chloride (which may or may not exist as a tight ion pair)<sup>6</sup> or it could be a tetravalent sulfur species. The evidence outlined below indicates the latter to be correct.



When alkoxy-sulfonium fluoroborates or trichloromercurates are dissolved in ethanol-1-<sup>14</sup>C, the rate of exchange is quite slow (less than 5% per hour) even at room temperature. However, when trace amounts of hydrogen chloride (added as a saturated solution in methylene chloride) are added, alkoxy exchange is rapid and statistical (based on total available alkoxy groups in the reaction system). Thiane was allowed to react with *t*-butyl hypochlorite in ethanol at  $-78^\circ$  and the reaction mixture allowed to warm to room temperature over a 30-min period, followed by the addition of ethanol-1-<sup>14</sup>C. The mixture then was allowed to stir for an additional 30 min at room temperature. Mercuric chloride was added; 1-ethoxy-thioniacyclohexane trichloromercurate (**1**,  $R = \text{C}_2\text{H}_5$ ) was obtained at high yield and found to contain negligible radiolabel. These experiments indicate that the intermediate produced by the reaction of *t*-butyl hypochlorite and sulfide in alcohols has a relatively long lifetime even at room temperature and does not undergo rapid alkoxy interchange.

When the above reaction sequence was repeated, but with the addition of a catalytic amount of dry hydrogen chloride at the time of addition of the labeled ethanol, scrambling of the ethoxy group was found to be statistical after 15 min at room temperature. On the other hand, sulfuric acid does not catalyze the exchange, suggesting that catalysis is due to chloride ion rather than the acidity of hydrogen chloride. Salts such as tetra-*n*-butylammonium chloride are also effective catalysts. Apparently the trichloromercurate ion is not an effective source of halide ion under these conditions. Hydrogen chloride does not catalyze the exchange at  $-78^\circ$ .

The observation that catalytic amounts of chloride ion catalyze exchange of alkoxy-sulfonium salts, coupled with the fact that the intermediate seems to be stable in the absence of chloride ion, leads to the suggestion that attack of chloride ion on the salt may be slow compared to subsequent steps leading to alkoxy interchange. If this were not true, small amounts of chloride ion would be rapidly consumed by the formation of the stable tetravalent intermediate and hence chloride ion in small amounts would not be an effective catalyst for statistical alkoxy exchange.

The nmr spectrum of the product of the reaction of methyl phenyl sulfide and *t*-butyl hypochlorite differs significantly from the spectrum of methylphenyl-*t*-butoxy-sulfonium fluoroborate. We do not anticipate that such differences could be entirely accounted for by ion-pairing phenomena and suggest that the data summarized in Table I provide additional evidence for a

(6) For a recent discussion of tetravalent sulfur intermediates and related ion pairs see H. Kwart, E. N. Givens, and C. J. Collins, *J. Amer. Chem. Soc.*, **90**, 7162 (1968).

