

CHEMISTRY OF TRIALKYLTHIOMETHYL IONS. I. THE PREPARATION  
AND PROPERTIES OF TRIMETHYLTHIOMETHYL CATION

William P. Tucker and Glenn L. Roof

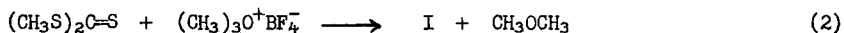
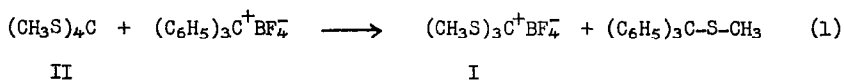
Department of Chemistry, North Carolina State University

Raleigh, North Carolina 27607

(Received 19 April 1967)

We wish to report the preparation of trimethylthiomethyl fluoroborate (I) and several of the reactions which it undergoes. Although the preparation of stable alkoxyethyl cations has been previously reported<sup>1</sup>, few of the divalent sulfur analogs of these compounds have been characterized.<sup>2-6</sup>

The cation is formed either by treatment of tetramethylthiothiocarbonate (II) with trityl cation in methylene chloride (eq 1) or by methylation of dimethyltrithiocarbonate (III) with trimethyloxonium fluoroborate<sup>7</sup> (eq 2) in yields ranging from 60 to 80%. The white crystalline product melted without decomposition at 167.5-169° and its nmr spectrum showed a single resonance at  $\tau$ 6.91 in trifluoroacetic acid.<sup>8</sup> (Anal. Calcd for C<sub>4</sub>H<sub>9</sub>S<sub>3</sub>BF<sub>4</sub>: C, 20.00; H, 3.78. Found: C, 19.99 H, 3.79).

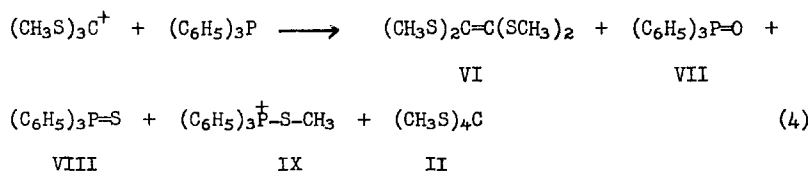


The reactions of I are of special interest since it is possible to direct attack of nucleophiles to (a) the central carbon atom, (b) a methyl carbon atom, or (c) a sulfur atom. We have used water, methanethiol, various inorganic ions, pyridine, and triphenylphosphine to demonstrate this spectrum of reactivity.



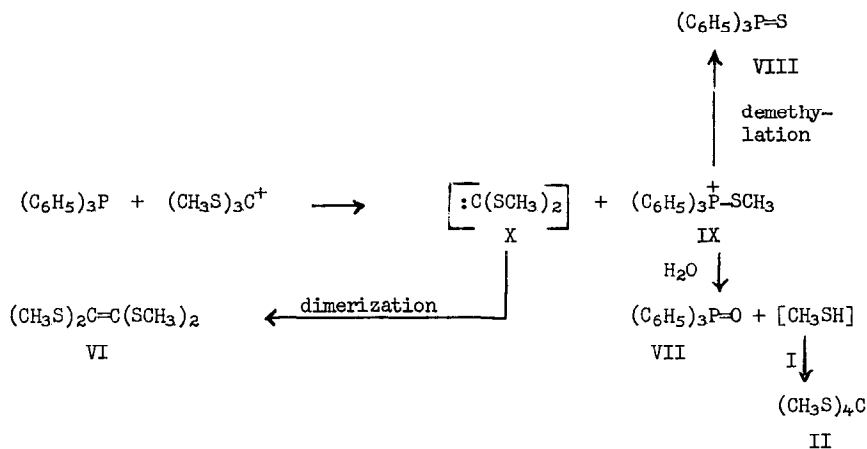
The pyridinium salt was characterized by elemental analysis, nmr and independent synthesis. Surprisingly, V remained a liquid at room temperature.<sup>12</sup>

Attack at Sulfur. Allowing a solution of I and triphenylphosphine in acetonitrile to stand overnight at room temperature led to the mixture of products shown in eq 4 (see 12). The appearance of major product VI<sup>13</sup>, and products VII, VIII and IX<sup>15</sup> can be rationalized as desulfurization of I by trivalent phosphorus to form a carbene intermediate (X).<sup>16</sup> Nucleophilic



demethylation of IX to produce the sulfide VIII seems reasonable since phosphonium salts exhibit a strong tendency to become pentavalent. Triphenylphosphine oxide (VII) most likely results from hydrolysis of IX by traces of moisture, and the small amount of ortho ester (II) found is probably formed during the reaction from I and methanethiol. Scheme 2 outlines a possible reaction sequence.

SCHEME 2



We are currently investigating further details of electrophilic reactions of ion I and its homologs.

## REFERENCES

- (1) H. Meerwein, K. Bodenbenner, P. Borner, F. Kunert and K. Wunderlich, Ann., 632, 38(1960).
- (2) (a) R. Gompper and E. Kutter, Angew. Chem. Internat. Edit., 2, 687(1963). These authors prepared several trialkylthiomethyl ions, including the trimethyl as the methyl sulfate salt. No physical properties, however, were reported. (b) R. Gompper and E. Kutter, Ber., 98, 1365(1965).
- (3) L. Soder and R. Wizinger, Helv. Chem. Acta, 42, 1733(1959).
- (4) E. Klingsberg, J. Am. Chem. Soc., 85, 3244(1963).
- (5) E. Klingsberg, ibid., 86, 5290(1964).
- (6) E. Campaigne and R. D. Hamilton, J. Org. Chem., 29, 2877(1964).
- (7) H. Meerwein, G. Hinz, P. Hofmann, E. Kroning and E. Pfeil, J. Prakt. Chem., 147, 257(1937).
- (8) Nmr spectra throughout were recorded with a Varian HA-100 spectrometer using TMS as an internal standard.
- (9) B. G. Ramsey and R. W. Taft, J. Am. Chem. Soc., 88, 3058(1966) showed that the reaction of the analogous trimethoxymethyl cation with water is rapid, producing dimethylcarbonate and methanol. In this case it is not clear if attack by water is on the central carbon followed by loss of proton and methanol, or if water is directly methylated by the ion to produce the same products.
- (10) Ethyl pyridinium fluoroborate (mp 59°)<sup>7</sup> and pyridinium fluoroborate (mp 210°)<sup>11</sup> are both solids. The methyl derivative, V, has not been previously reported.
- (11) M. F. Lappert, J. Chem. Soc., 784(1955).
- (12) Characterization of products included comparison of their nmr spectra, melting points, tlc behavior, and mixture melting points with those of authentic samples.
- (13) This product was formed in 55% yield, mp 58.5-60° (lit.<sup>14</sup> mp 59-60°).
- (14) J. Hine, R. P. Bayer and G. G. Hammer, J. Am. Chem. Soc., 84, 1751(1962).
- (15) This ion, methylthiotriphenylphosphonium cation, was not obtained in a pure state but was identified on the basis of a comparison of its nmr spectrum with that of the product obtained from the reaction of trimethyloxonium fluoroborate with triphenylphosphine sulfide. These spectra were superimposable, exhibiting aromatic resonance in the  $\tau$ 2.1-2.8 region, and a doublet for the methyl protons ( $J=14$  cps) centered at  $\tau$ 7.60.
- (16) Both desulfurization of organic compounds by trivalent phosphorus<sup>17</sup> and the existence of bis-(alkylthio)-carbenes<sup>18</sup> are well documented.
- (17) Cf. L. Goodman and E. J. Reist in "The Chemistry of Organic Sulfur Compounds", Vol. 2, edited by N. Kharasch and C. Meyers, Pergamon Press, New York, N. Y., p105.
- (18) (a) U. Schöllkopf and E. Wiskott, Angew. Chem., 75, 725(1963). (b) D. M. Lemal and E. H. Banitt, Tetrahedron Letters, 245(1964).