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

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We wish to report the preparation of trimethylthiomethyl fluoroborate (I) and several of the reactions which it undergoes. Although the preparation of stable alkoxymethyl 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 tetramethylorthothiocarbonate (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  $167.5-169^{\circ}$  and its nmr spectrum showed a single resonance at  $\tau 6.91$  intrifluoracetic acid.<sup>8</sup> (<u>Anal</u>. 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).

$$(CH_{3}S)_{4}C + (C_{6}H_{5})_{3}C^{+}BF_{4} \longrightarrow (CH_{3}S)_{3}C^{+}BF_{4} + (C_{6}H_{5})_{3}C_{-}S_{-}CH_{3}$$
(1)  
II  
$$(CH_{3}S)_{2}C=S + (CH_{3})_{3}O^{+}BF_{4} \longrightarrow I + CH_{3}OCH_{3}$$
(2)

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. <u>Attack at Central Carbon</u>. Both water and methanethiol, the latter in a reversible reaction, attack I at the central carbon, although the reaction with water is surprisingly sluggish.<sup>9</sup> Approximately 24 hr at 60° is necessary to completely discharge the ion from an acetonitrile solution initially containing equimolar amounts of ion and water. Significantly, no dimethyltrithiocarbonate (III) is produced, indicating that attack by water is on the central carbon atom. Monitoring the reaction by nmr, by thin layer chromatography (tlc), and by product analysis reveals the early production of tetramethylorthothiocarbonate (II) as well as dimethyldithiocarbonate (IV). Production of IV is irreversible, but the thiol produced can react with I in a reversible step. Scheme 1 indicates a possible reaction sequence.

## SCHEME I

$$(CH_{3}S)_{3}C^{+} + H_{2}O \longrightarrow (CH_{3}S)_{3}C^{\pm}O \overset{H}{\underset{H}{\longrightarrow}} (CH_{3}S)_{2}C=O + H^{+} + CH_{3}SH$$

$$I \qquad IV$$

$$CH_{3}SH + I \longrightarrow (CH_{3}S)_{4}C + H^{+}$$

$$II$$

The equilibrium involving thicl and I has been demonstrated and represents a second example of attack on the central carbon atom of the ion.

<u>Attack at Methyl</u>. A number of substances are methylated by ion I. Attempts to prepare the iodide salt of I led instead to varying amounts of dimethyltrithiocarbonate (III). Iodine was also produced by this reaction possibly <u>via</u> a one-electron transfer from iodide to the cation. Treatment of I with other inorganic ions including bromide, cyanide, and thiocyanate, also gave complex reaction mixtures containing some of the ester III.

Treatment of a solution of I in 1,2-dichloroethane with a slight molar excess of pyridine gave, after 18 hr at 80°, methyl pyridinium fluoroborate (V) and III (eq 3).

$$I + C_5H_5N \longrightarrow C_5H_5NCH_3 BF_7 + III (3)$$

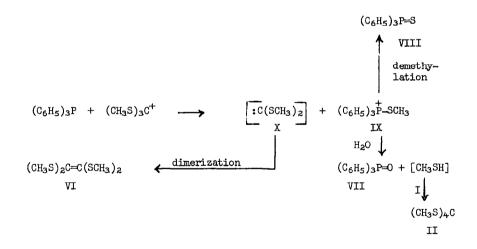
The pyridinium salt was characterized by elemental analysis, nur and independent synthesis. Surprisingly, V remained a liquid at room temperature.<sup>>D</sup>

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. (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 carbone intermediate (X).<sup>16</sup> Nucleophilic

$$(CH_{3}S)_{3}C^{+} + (C_{6}H_{5})_{3}P \longrightarrow (CH_{3}S)_{2}C=C(SCH_{3})_{2} + (C_{6}H_{5})_{3}P=0 + VI VII (C_{6}H_{5})_{3}P=S + (C_{6}H_{5})_{3}P=S-CH_{3} + (CH_{3}S)_{4}C$$
(4)  
VIII IX II

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

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- (a) R. Gompper and E. Kutter, <u>Angew. Chem. Internat. Edit.</u>, <u>2</u>, 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, <u>Ber.</u>, <u>98</u>, 1365(1965).
- (3) L. Soder and R. Wizinger, <u>Helv. Chem. Acta</u>, <u>42</u>, 1733(1959).
- (4) E. Klingsberg, J. Am. Chem. Soc., 85, 3244(1963).
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- (6) E. Campaigne and R. D. Hamilton, <u>J. Org. Chem</u>., <u>29</u>, 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., <u>88</u>, 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, <u>J. Chem. Soc</u>., 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 mmr 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 \tau2.1-2.8 region, and a doublet for the methyl protons (J=14 cps) centered at \tau7.60.
- (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) <u>Cf.</u> 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., pl05.
- (18) (a) U. Schöllkopf and E. Wiskott, <u>Angew. Chem.</u>, <u>75</u>, 725(1963). (b) D. M. Lemal and E. H. Banitt, <u>Tetrahedron Letters</u>, 245(1964).