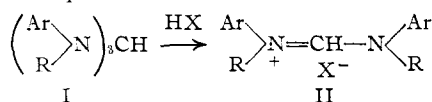




particularly useful because of their ready conversion to formamidinium salts, an extremely interesting class of compounds.

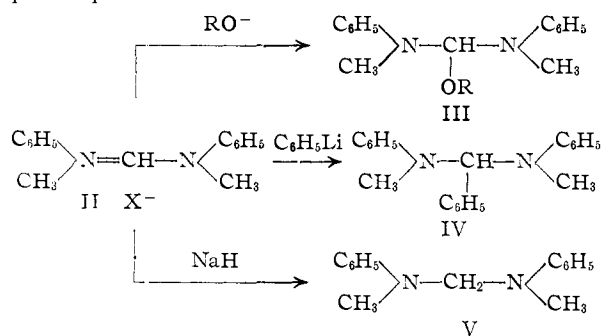


The sodium salt of N-methylaniline on treatment with gaseous chlorodifluoromethane in 1,2-dimethoxyethane produced Ia (Ar = C<sub>6</sub>H<sub>5</sub>; R = CH<sub>3</sub>), m.p. 263–265° dec. (*anal.* Calcd. for C<sub>22</sub>H<sub>25</sub>N<sub>3</sub>: C, 79.72; H, 7.60; N, 12.68. Found: C, 79.43; H, 7.65; N, 12.82) in 58% yield. Similarly were prepared Ib (Ar = C<sub>6</sub>H<sub>5</sub>; R = C<sub>2</sub>H<sub>5</sub>), m.p. 183–186° (21%) (*anal.* Calcd. for C<sub>25</sub>H<sub>31</sub>N<sub>3</sub>: C, 80.38; H, 8.37; N, 11.25. Found: C, 80.13; H, 8.38; N, 11.03) and Ic (Ar = *p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>; R = CH<sub>3</sub>), m.p. 260–265° dec. (23%) (*anal.* Calcd. for C<sub>22</sub>H<sub>22</sub>N<sub>3</sub>O<sub>2</sub>: C, 56.64; H, 4.76; N, 18.02. Found: C, 56.30; H, 4.96; N, 17.73).

The orthoamide Ia (Ar = C<sub>6</sub>H<sub>5</sub>; R = CH<sub>3</sub>) also was prepared by heating ethyl orthoformate and N-methylaniline at reflux (21%) and by the reaction of II (Ar = C<sub>6</sub>H<sub>5</sub>; R = CH<sub>3</sub>; X = I) with the sodium salt of N-methylaniline.

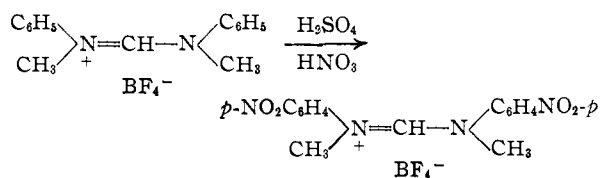
The orthoamides I react smoothly with strong acids, alkyl halides and acyl halides to produce formamidinium salts. IIa (Ar = C<sub>6</sub>H<sub>5</sub>; R = CH<sub>3</sub>; X = BF<sub>4</sub>), m.p. 117–119° (*anal.* Calcd. for C<sub>15</sub>H<sub>17</sub>N<sub>2</sub>BF<sub>4</sub>: C, 57.72; H, 5.49; N, 8.98. Found: C, 57.90; H, 5.29; N, 8.98) was prepared in 75% yield by heating 30 g. of I (Ar = C<sub>6</sub>H<sub>5</sub>; R = CH<sub>3</sub>) with 200 cc. of water and 60 cc. of 48% fluoroboric acid, then diluting and crystallizing. In a similar manner were prepared IIB (Ar = *p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>; R = CH<sub>3</sub>; X = BF<sub>4</sub>), m.p. 159–161° and IIC (Ar = C<sub>6</sub>H<sub>5</sub>; R = CH<sub>3</sub>; X = I), m.p. 162–164°.

The formamidinium salts undergo a variety of reactions, most of which involve attack of nucleophilic species on the central carbon atom.



For example, on stirring IIa (Ar = C<sub>6</sub>H<sub>5</sub>; R = CH<sub>3</sub>; X = BF<sub>4</sub>) with sodium methoxide, isopropoxide or *t*-butoxide the corresponding diaminoalkoxymethane III is formed in good yields. Treatment of IIC (Ar = C<sub>6</sub>H<sub>5</sub>; R = CH<sub>3</sub>; X = I) with phenyllithium produced IV, m.p. 127–130°, identified by an analysis in agreement with formula and by hydrolysis to benzaldehyde. It is interesting that reduction of IIa (Ar = C<sub>6</sub>H<sub>5</sub>; R = CH<sub>3</sub>; X = BF<sub>4</sub>) to V, m.p. 33–34° (reported<sup>2</sup> 35°) was achieved easily with sodium hydride in 1,2-dimethoxyethane.

(2) J. V. Braun, *Ber.*, **41**, 2147 (1908).



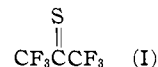
Nitration of IIa gave a 63% yield of IIB, an extremely interesting result in view of the fact that only para substitution was observed. Other reactions of the orthoamides and formamidinium salts are being examined and will be reported in a later issue of THIS JOURNAL.

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RECEIVED MAY 1, 1961

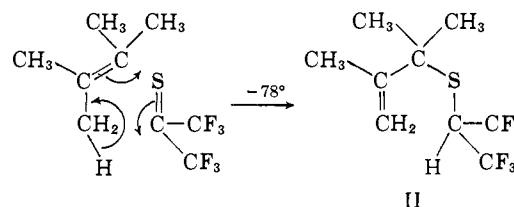
## PERFLUOROTHIOCARBONYL COMPOUNDS

Sir:

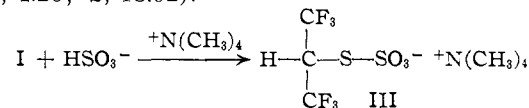
We have found the C=S group in fluorothiocarbonyl compounds has exceptional ability to undergo a variety of addition reactions. This reactivity is best exemplified in hexafluorothioacetone (I), the simplest member of a new class of compounds, the perfluorothioketones.



The remarkable reactivity of fluorothiocarbonyl compounds is illustrated by the ease with which hexafluorothioacetone (I) combines with olefins possessing allyl hydrogen atoms. For example, I reacts very rapidly at -78° with tetramethylethylene to give the allyl sulfide II, b.p. 61° (20 mm.), *n*<sub>D</sub><sup>25</sup> 1.3960, infrared bands at 6.1 μ (C=C) and 11.3 μ (terminal CH<sub>2</sub>), (*Anal.* Found: S, 11.82).



In many of the reactions of fluorothiocarbonyl compounds, the C=S group behaves as though the sulfur is more electrophilic than the carbon, a situation opposite to that of a C=O group. For example, hexafluorothioacetone reacts in a reverse manner with aqueous bisulfite ion to give a Bunte salt, isolated as the tetramethylammonium salt III, m.p. 196–198° (*Anal.* Found: F, 33.91; N, 4.26; S, 18.92).



Another example of reverse addition is reaction of hydrogen chloride with I, which gives the disulfide IV, b.p. 67° (48 mm.), *n*<sub>D</sub><sup>25</sup> 1.3598 (*Anal.* Found: Cl, 8.69; S, 16.08).

