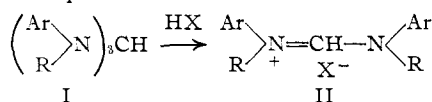


particularly useful because of their ready conversion to formamidinium salts, an extremely interesting class of compounds.

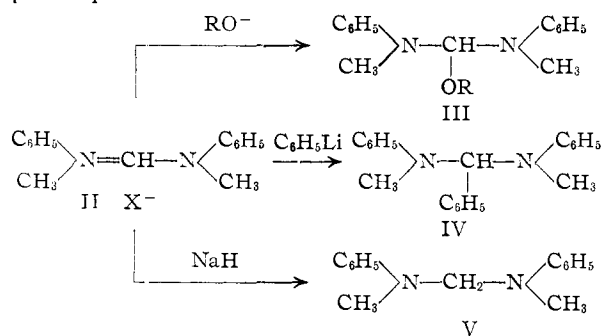


The sodium salt of N-methylaniline on treatment with gaseous chlorodifluoromethane in 1,2-dimethoxyethane produced Ia (Ar = C₆H₅; R = CH₃), m.p. 263–265° dec. (*anal.* Calcd. for C₂₂H₂₅N₃: C, 79.72; H, 7.60; N, 12.68. Found: C, 79.43; H, 7.65; N, 12.82) in 58% yield. Similarly were prepared Ib (Ar = C₆H₅; R = C₂H₅), m.p. 183–186° (21%) (*anal.* Calcd. for C₂₅H₃₁N₃: C, 80.38; H, 8.37; N, 11.25. Found: C, 80.13; H, 8.38; N, 11.03) and Ic (Ar = *p*-NO₂C₆H₄; R = CH₃), m.p. 260–265° dec. (23%) (*anal.* Calcd. for C₂₂H₂₂N₃O₂: C, 56.64; H, 4.76; N, 18.02. Found: C, 56.30; H, 4.96; N, 17.73).

The orthoamide Ia (Ar = C₆H₅; R = CH₃) also was prepared by heating ethyl orthoformate and N-methylaniline at reflux (21%) and by the reaction of II (Ar = C₆H₅; R = CH₃; X = I) with the sodium salt of N-methylaniline.

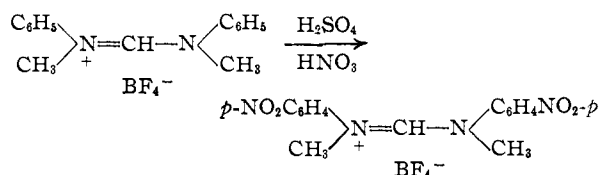
The orthoamides I react smoothly with strong acids, alkyl halides and acyl halides to produce formamidinium salts. IIa (Ar = C₆H₅; R = CH₃; X = BF₄), m.p. 117–119° (*anal.* Calcd. for C₁₅H₁₇N₂BF₄: C, 57.72; H, 5.49; N, 8.98. Found: C, 57.90; H, 5.29; N, 8.98) was prepared in 75% yield by heating 30 g. of I (Ar = C₆H₅; R = CH₃) with 200 cc. of water and 60 cc. of 48% fluoroboric acid, then diluting and crystallizing. In a similar manner were prepared I Ib (Ar = *p*-NO₂C₆H₄; R = CH₃; X = BF₄), m.p. 159–161° and I Ic (Ar = C₆H₅; R = CH₃; 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 = C₆H₅; R = CH₃; X = BF₄) with sodium methoxide, isopropoxide or *t*-butoxide the corresponding diaminoalkoxymethane III is formed in good yields. Treatment of I Ic (Ar = C₆H₅; R = CH₃; 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 = C₆H₅; R = CH₃; X = BF₄) to V, m.p. 33–34° (reported² 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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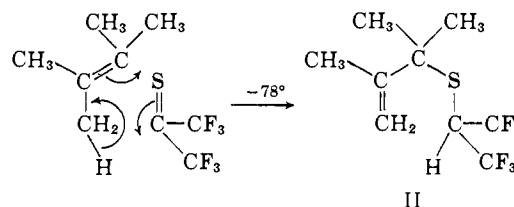
PERFLUOROTHIOCARBONYL COMPOUNDS

Sir:

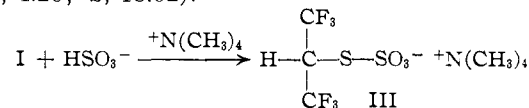
We have found the C=S group in fluorothiocarbonyl compounds has exceptional ability to undergo a variety of addition reactions. This reactivity is best exemplified in hexafluorothioacetone (I), the simplest member of a new class of compounds, the perfluorothioketones.



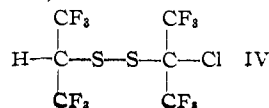
The remarkable reactivity of fluorothiocarbonyl compounds is illustrated by the ease with which hexafluorothioacetone (I) combines with olefins possessing allyl hydrogen atoms. For example, I reacts very rapidly at -78° with tetramethylethylene to give the allyl sulfide II, b.p. 61° (20 mm.), *n*_D²⁵ 1.3960, infrared bands at 6.1 μ (C=C) and 11.3 μ (terminal CH₂), (*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*_D²⁵ 1.3598 (*Anal.* Found: Cl, 8.69; S, 16.08).

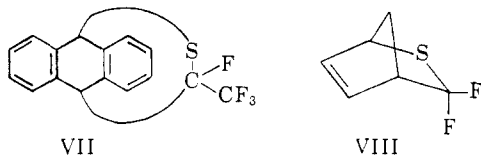


Hexafluorothioacetone is an exceedingly active dienophile. It reacts instantaneously with butadiene at -78° to give a quantitative yield of the cyclic adduct, 2,2-bis-(trifluoromethyl)-3,6-dihydro-2H-1-thiapyran, b.p. 65° (30 mm.), n_D^{25} 1.4042 (*Anal.* Found: S, 13.87). Under the same conditions, I also reacts rapidly with the two conjugated diene systems in styrene to give a 2:1 adduct, b.p. $103-104^\circ$ (1.2 mm.), n_D^{25} 1.4512 (*Anal.* Found: F, 48.62; S, 13.89).

Other fluorothiocarbonyl compounds, for example, trifluorothioacetyl fluoride (V) and thiocarbonyl fluoride (VI), are also very reactive dienophiles.

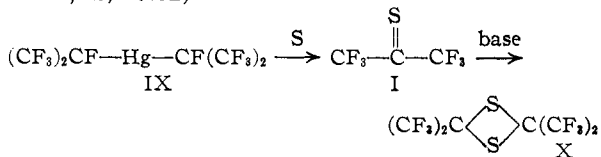


Although less reactive than I, trifluorothioacetyl fluoride (V) reacts with anthracene at room temperature to give the adduct VII, m.p. 85° (*Anal.* Found: S, 10.03). Thiocarbonyl fluoride (VI) reacts rapidly with cyclopentadiene at -20° to give the adduct VIII, m.p. 48° (*Anal.* Found: S, 21.36).



Bistrifluoromethyl trithiocarbonate and ethyl dithiotrifluoroacetate are additional examples of fluorothiocarbonyls that are active dienophiles. Surprisingly, the diene reaction is also applicable to such non-fluorine-containing thiocarbonyl compounds as thiophosgene and thiofluorenone.

A general method for preparation of perfluorothioketones is reaction of perfluoro-*sec*-alkylmercurials with sulfur. Hexafluorothioacetate was obtained in 60% yield by dropwise addition of bis-(heptafluoroisopropyl)-mercury (IX)¹ to boiling sulfur. The thioketone is a deep blue liquid, b.p. 8° , $\lambda_{\text{max}}^{\text{CH}_2\text{Cl}_2}$ 580 m μ (*Anal.* Found: C, 19.84; F, 62.41; S, 17.71). It is not sensitive to water or to oxygen but dimerizes in the presence of a trace of base to give the dithietane X, b.p. 110° , m.p. 23.6° , n_D^{25} 1.3357 (*Anal.* Found: C, 19.64; F, 62.36; S, 17.52).



The reaction of secondary fluoroalkylmercurials with sulfur has been used to prepare a number of other fluorothioketones.

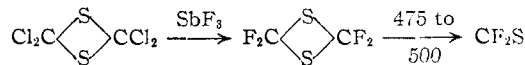
Trifluorothioacetyl fluoride was prepared in a similar manner from bis-(1-chloro-1,2,2,2-tetrafluoroethyl)-mercury² and sulfur. The thioacid fluoride was obtained in 80% yield and is a yellow gas, b.p. -21° (*Anal.* Found: C, 18.31; F, 57.28; S, 24.38). Upon ultraviolet exposure, it dimerized to a mixture of *cis* and *trans* 2,4-bis-(trifluoro-

(1) E. G. Howard and W. J. Middleton, U. S. Patent 2,970,173 (1961).

(2) C. G. Krespan, *J. Am. Chem. Soc.*, **25**, 105 (1960).

methyl)-2,4-difluoro-1,3-dithietane, b.p. 73° , n_D^{25} 1.3378 (*Anal.* Found: C, 18.58; F, 57.47).

Thiocarbonyl fluoride was prepared in almost quantitative yields by pyrolysis at $475-500^\circ$ of its cyclic dimer, 2,2,4,4-tetrafluoro-1,3-dithietane (XI). After distillation, the thiocarbonyl fluoride, b.p. -54° ,³ appeared to have no impurity other than about 15-25 ppm. of carbonyl sulfide. The dimer XI, b.p. 48° , n_D^{25} 1.3950 (*Anal.* Found: C, 14.73; F, 46.60; S, 39.16), was prepared from tetrachloro-1,3-diethietane⁴ by reaction with antimony trifluoride in tetramethylene sulfone.



(3) (a) N. N. Yarovenko and A. S. Vasil'eva, *J. Gen. Chem. (U.S.S.R.)*, **29**, 3754 (1959), English Translation, report a boiling point range of -57 to -54° for impure thiocarbonyl fluoride. (b) A. J. Downs and E. A. V. Ebsworth, *J. Chem. Soc.*, 3516 (1960), also have made this compound and have reported an infrared spectrum, which is in agreement with one taken on our compound.

(4) A. Schonberg and A. Stephenson, *Ber.*, **66B**, 567 (1933).

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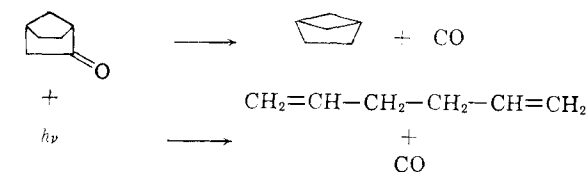
RECEIVED APRIL 26, 1961

A SIMPLE SYNTHESIS OF BICYCLO[2.1.1]HEXANE¹

Sir:

Bicyclo[2.1.1]hexane has been synthesized recently.² Till now, the only satisfactory method for the formation of the bicyclo[2.1.1]hexane ring system has been the photolysis of a diazoketone derived from bicyclo[2.2.1]heptane.³ The present method provides an alternative route to the synthesis of bicyclo[2.1.1]hexanes and may be particularly applicable to the hydrocarbons of this series.

It was found that the *vapor phase* photolysis of norcamphor led to the formation of bicyclo[2.1.1]hexane and 1,5-hexadiene along with an equivalent amount of carbon monoxide.



These reactions are analogous to the photochemical formation of bicyclo[2.2.0]hexane, 1,5-hexadiene, and carbon monoxide from bicyclo[3.2.0]heptanone-3.⁴

Bicyclo[2.1.1]hexane (m.p. $21.6-22^\circ$, b.p. 70.9° (751 mm.)) was separated from the other products by distillation and vapor phase chromatography.

Anal. Calcd. for C_6H_{10} : C, 87.74; H, 12.26; mol. wt., 82. Found: C, 87.70; H, 12.25; mol.

(1) This research was supported in part by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under Contract No. AF 18(600)1528 presently AF 49(638)679. Reproduction in whole or in part is permitted for any purpose by the United States Government.

(2) Professor K. Wiberg, private communication.

(3) L. Horner and E. Spietschka, *Ber.*, **88**, 934 (1955).

(4) S. Cremer and R. Srinivasan, *Tetrahedron Letters*, No. 21, p. 24 (1960).