Fluorothiocarbonyl Compounds. IV.[1] Hexafluorothioacetone–Olefin Adducts

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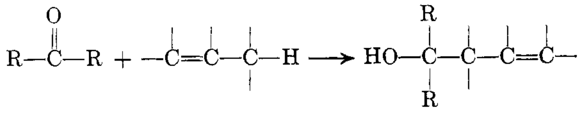
Hexafluorothioacetone reacts rapidly at low temperatures with olefins containing allylic hydrogen to give 1:1 adducts that are allyl sulfides. The reaction appears to involve a concerted mechanism with an allylic shift of the double bond. Hexafluorothioacetone also forms 1:1 adducts with vinyl ethers and vinyl sulfides. These adducts, however, are thietanes formed by a cycloaddition reaction.

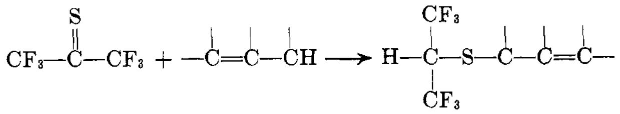
A number of ketones possessing electron-withdrawing groups have been reported to react with olefins containing allylic hydrogens to give unsaturated alcohols corresponding to I. Examples are the reactions of hexafluoroacetone[2] and hexafluorocyclobutanone[3] with propylene, and of carbonyl cyanide[4] with α-methylstyrene.



$$R{-}\overset{\overset{O}{\|}}{C}{-}R + {-}\overset{|}{C}{=}\overset{|}{C}{-}\underset{|}{\overset{|}{C}}{-}H \longrightarrow HO{-}\underset{R}{\overset{R}{C}}{-}\underset{|}{\overset{|}{C}}{-}\overset{|}{C}{=}\overset{|}{C}{-}$$

I

We have found that hexafluorothioacetone (HFTA) also reacts with propylene and other olefins that possess allylic hydrogens to give 1:1 adducts. The products are not unsaturated mercaptans as would be expected by analogy with the ketone reactions, but instead are allyl sulfides (II).

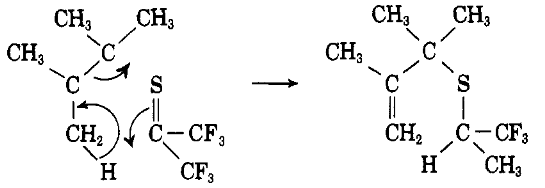


$$CF_3{-}\overset{\overset{S}{\|}}{C}{-}CF_3 + {-}\overset{|}{C}{=}\overset{|}{C}{-}\overset{|}{C}H \longrightarrow H{-}\underset{CF_3}{\overset{CF_3}{C}}{-}S{-}\overset{|}{C}{-}\overset{|}{C}{=}\overset{|}{C}{-}$$

HFTA II

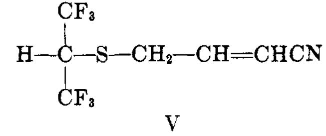
The reaction of HFTA with propylene is extremely fast, occurring instantaneously when the two reactants are mixed at −78° to give 1,1,1,3,3,3-hexafluoro-2-propyl allyl sulfide in high yield. This speed of reaction is in marked contrast to the reaction of hexafluoroacetone with propylene, which is relatively slow and requires the use of heat and pressure.[2]

Reaction occurs with a number of other olefins under essentially the same conditions to give allyl sulfides. For example, reaction of HFTA with tetramethylethylene (III) gives IV. Other olefins, including 1-heptene, cyclopentene, isobutylene-α-pinene, and α-methylstyrene also give 1:1 adducts.



III IV

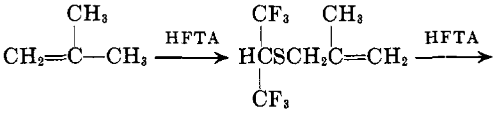
From the nature of the products it appears that more than simple addition of an allylic hydrogen across the thiocarbonyl bond has occurred. The double bond of the olefin has also undergone an allylic shift. This shift also occurs in the reaction of HFTA with allyl cyanide to give a product which contains a conjugated nitrile (V).



$$\mathrm{HFTA} + CH_2{=}CH{-}CH_2CN \xrightarrow{-78^\circ} H{-}\underset{CF_3}{\overset{CF_3}{C}}{-}S{-}CH_2{-}CH{=}CHCN$$

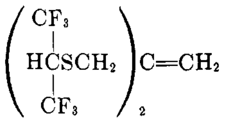
V

With certain olefins, it is possible to prepare 2:1 adducts with HFTA. Isobutylene reacts with HFTA to give either the 1:1 adduct (VI) or the 2:1 adduct (VII), depending upon the amount of thio ketone added to the reaction mixture.



$$CH_2{=}\overset{CH_3}{C}{-}CH_3 \xrightarrow{\mathrm{HFTA}} H\underset{CF_3}{\overset{CF_3}{C}}SCH_2\overset{CH_3}{C}{=}CH_2 \xrightarrow{\mathrm{HFTA}}$$

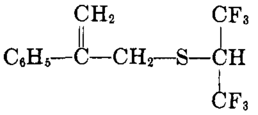
VI



$$\left(H\underset{CF_3}{\overset{CF_3}{C}}SCH_2\right)_2C{=}CH_2$$

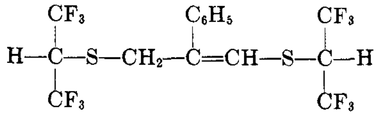
VII

α-Methylstyrene also reacts to give both a 1:1 adduct (VIII) and a 2:1 adduct (IX). Since styrene reacts as a diene with HFTA to form a Diels–Alder adduct,[1] it appears that HFTA reacts with allylic hydrogens more readily than it forms Diels–Alder adducts with aromatic rings.



$$C_6H_5{-}\overset{\overset{CH_2}{\|}}{C}{-}CH_2{-}S{-}\underset{CF_3}{\overset{CF_3}{C}}H$$

VIII



$$H{-}\underset{CF_3}{\overset{CF_3}{C}}{-}S{-}CH_2{-}\overset{C_6H_5}{C}{=}CH{-}S{-}\underset{CF_3}{\overset{CF_3}{C}}{-}H$$

IX

The reaction of α-vinylthiophene with HFTA is an example in which both a Diels–Alder reaction and an allylic hydrogen addition occur. Since only a 2:1 adduct (XI) could be isolated from the reaction regardless of the ratio of reactants, the second step, which involves allylic addition, is apparently much faster than the first step, which involves formation of a Diels–Alder adduct (X).

Polyolefins containing more than one unconjugated double bond would be expected to react with a number of HFTA units to form higher adducts. This is the case with crepe rubber (natural polyisoprene). A toluene solution of this polymer reacts rapidly with an excess of HFTA to give a modified polymer that con-

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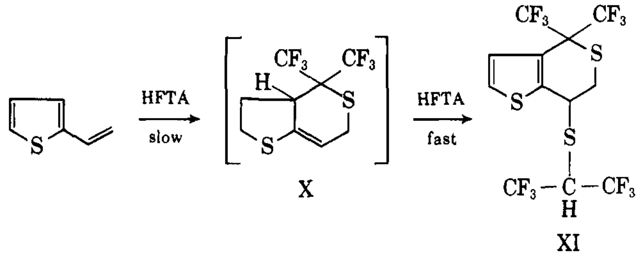
[1] Paper III: W. J. Middleton, *J. Org. Chem.*, **30**, 1390 (1965).

[2] H. R. Davis, Abstracts of the 140th Meeting of the American Chemical Society, Chicago, Ill., Sept. 1961, p. 25M.

[3] D. C. England, *J. Am. Chem. Soc.*, **83**, 2205 (1961).

[4] O. Achmatowicz, M. Leplawy, and A. Zamojski, *Roczniki chem.*, **30**, 215 (1956).

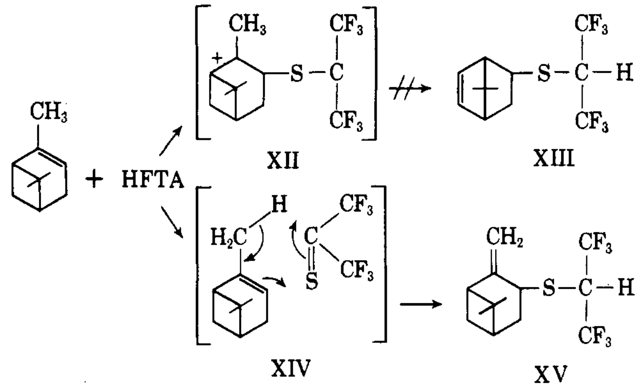


(or isomer)

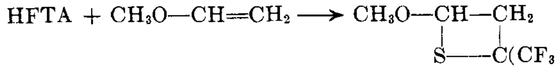
tains approximately one unit of HFTA for each double bond in the original polymer. Other polyunsaturated natural products also react with HFTA to form adducts. A 6:1 adduct was prepared from squalene, and a 5:1 adduct was prepared from β-carotene.

The rate of reaction of HFTA with olefins is much too fast to be easily measured. However, an approximation of the relative rates of reaction with propylene and with isobutylene was obtained by competitive reactions. Thus, it was found that HFTA reacts more than six times as fast with isobutylene than it does with propylene. Since isobutylene is more susceptible to electrophilic reagents than is propylene, it appears that the reaction proceeds by attack of a positively charged sulfur and the allylic hydrogen is abstracted as a proton by the negatively charged carbon of the C=S group. In other words, the C=S group reacts as though it were polarized in a manner opposite to that of a normal carbonyl compound.[5]

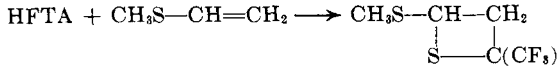
The addition of HFTA to olefins is believed to involve a concerted mechanism and not a two-step ionic reaction. The reaction product (XV) obtained from HFTA and α-pinene supports this conclusion. Ionic addition should give XII, an intermediate that would be expected to rearrange to XIII by analogy with other ionic reactions of α-pinene. However, XV is the only product formed. This result indicates that the reaction takes place as shown by XIV.



Although hexafluorothioacetone (HFTA) will not react with ethylene at low temperatures, it will form adducts with certain electron-rich olefins, even though they possess no allylic hydrogens. For example,



$$\text{HFTA} + \text{CH}_3\text{O—CH=CH}_2 \longrightarrow \begin{array}{l}\text{CH}_3\text{O—CH—CH}_2\\ \qquad\quad\ \text{S——C(CF}_3)_2\end{array}$$



$$\text{HFTA} + \text{CH}_3\text{S—CH=CH}_2 \longrightarrow \begin{array}{l}\text{CH}_3\text{S—CH—CH}_2\\ \qquad\quad\ \text{S——C(CF}_3)_2\end{array}$$

methyl vinyl ether and methyl vinyl sulfide react rapidly to form 1:1 cyclic adducts with HFTA, even at −78°.

Adducts with other electron-rich olefins have also been prepared. These include dihydropyran, dioxene, ethyl vinyl ether, and *t*-butyl vinyl sulfide.

The structures of these vinyl ether and sulfide adducts have not been conclusively proved, but they are believed to be 2-alkoxy- (or 2-alkylthio-) thietanes rather than 3-alkoxy- (or 3-alkylthio-) thietanes on the basis of their mass spectrometer patterns. Major peaks in the patterns of these adducts correspond to the charged fragments that would result by cleaving the thietane ring in all possible ways. For example, the most abundant peak for the HFTA–methyl vinyl ether adduct is *m/e* 76, $(C_2H_4SO)^+$, which is most probably $\left[\text{H-C}{<}^{\text{S}}_{\text{OCH}_3}\right]^+$. Unfortunately, thermal pyrolysis of these adducts proceeds unilaterally to give HFTA and vinyl ethers or sulfides as the only isolated products.

Experimental[6]

Propylene–HFTA Adduct.[7]—Propylene, 7 ml. (4.2 g., 0.1 mole), was condensed in a calibrated receiver and cooled to −78° by a Dry Ice–acetone bath. HFTA was distilled into the cooled receiver until a faint blue color persisted. The reaction mixture was allowed to warm to room temperature and then was distilled to give 18.7 g. (84% yield) of 1,1,1,3,3,3-hexafluoro-2-propyl allyl sulfide as a colorless oil, b.p. 57–58° (100 mm.), $n^{25}\text{D}$ 1.3637.

The infrared spectrum contained bands at 6.05 (C=C) and at 11.3 μ (terminal methylene). The proton n.m.r. spectrum showed a doublet centered at 3.37 (J = 8 c.p.s.) for methylene, a septet at 3.68 (J = 8 c.p.s.) for $(CF_3)_2CH$, and a multiplet from 5.0–6.3 p.p.m. for $CH=CH_2$. The fluorine n.m.r. spectrum contained a doublet centered at 0.55 p.p.m. (J = 8 c.p.s.).

Anal. Calcd. for $C_6H_6F_6S$: C, 32.15; H, 2.70; F, 50.85; S, 14.31. Found: C, 32.45; H, 2.93; F, 50.61; S, 14.32.

The dibromide derivative of this adduct, 2,3-dibromopropyl 1,1,1,3,3,3-hexafluoro-2-propyl sulfide, m.p. 36°, was prepared in carbon tetrachloride and recrystallized from pentane.

Anal. Calcd. for $C_6H_6Br_2F_6S$: C, 18.77; H, 1.57; Br, 41.63. S, 8.37. Found: C, 18.88; H, 1.54; Br, 41.91; S, 8.43.

Tetramethylethylene–HFTA Adduct.—1,1,1,3,3,3-Hexafluoro-2-propyl 1,1,2-trimethylallyl sulfide, b.p. 61° (20 mm.), $n^{25}\text{D}$ 1.3960, was prepared in a similar manner from HFTA and tetramethylethylene (72% yield). The infrared spectrum contained bands at 3.22 (=CH), 3.35, 3.4, and 3.45 (saturated CH), 6.1 (C=C), and 11.3 μ (terminal methylene). The fluorine n.m.r. spectrum contained a signal at −0.48 p.p.m. split to a doublet (J = 8 c.p.s.). The proton n.m.r. spectrum, in addition to other bands, contained a septet centered at 3.4 p.p.m. (J = 8 c.p.s.).

Anal. Calcd. for $C_9H_{12}F_6S$: C, 40.58; H, 4.55; F, 42.82; S, 12.04. Found: C, 40.79; H, 4.71; F, 42.57; S, 11.82.

Cyclopentene–HFTA Adduct.—1,1,1,3,3,3-Hexafluoro-2-propyl 3-cyclopentenyl sulfide, b.p. 67° (21 mm.), $n^{25}\text{D}$ 1.4021, was prepared in a similar manner from HFTA and cyclopentene (76% yield).

Anal. Calcd. for $C_8H_8F_6S$: C, 38.41; H, 3.23; F, 45.56; S, 12.81. Found: C, 38.95; H, 3.48; F, 45.48; S, 13.25.

1-Heptene–HFTA Adduct.—1,1,1,3,3,3-Hexafluoro-2-propyl 2-(1-heptenyl)sulfide, b.p. 51° (3.5 mm.), $n^{25}\text{D}$ 1.3942, was prepared in a similar manner from 1-heptene and HFTA.

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(5) Paper II: W. J. Middleton and W. H. Sharkey, *J. Org. Chem.*, **30**, 1384 (1965).

(6) Fluorine n.m.r. spectra were obtained with Varian Associates high-resolution n.m.r. spectrometer operating at 56.4 Mc./sec. Spectra were calibrated in terms of higher field displacement in parts per million from the F^{19} resonance of 1,2-difluoro-1,1,2,2-tetrachloroethane used as an external reference. Proton resonance spectra were obtained with a Varian Associates A-60 spectrometer. Spectra were calibrated in terms of lower field displacement in parts per million from the proton resonance of tetramethylsilane used as an internal reference.

(7) W. J. Middleton, U. S. Patent 3,052,726 (1962).

Anal. Calcd. for $C_{10}H_{14}F_6S$: C, 42.85; H, 5.03; F, 40.68; S, 11.44. Found: C, 43.31; H, 5.27; F 40.52; S 11.32.

Isobutylene–HFTA Adduct.—HFTA, 18.2 g. (0.1 mole), was added dropwise to 9 ml. (0.1 mole) of isobutylene cooled to −78°. The reaction mixture was distilled under reduced pressure to give 18.05 g. (76%) of 1,1,1,3,3 3-hexafluoro-2-propyl 2-methylallyl sulfide, b.p. 60° (74 mm.) n^{25}D 1.3729. The fluorine n.m.r. spectrum contained a doublet centered at −2.81 p.p.m. (J = 8 c.p.s.). The infrared spectrum contained a band at 6.05 (C=C) and at 11.25 μ (terminal methylene).

Anal. Calcd. for $C_7H_8F_6S$: C, 35.30; H, 3.39; F, 47.86; S, 13.44. Found: C, 35.78; H, 3.58; F, 47.65; S, 13.54.

Isobutylene–HFTA 1:2 Adduct.—HFTA, 7.3 g. (0.4 mole), was distilled into 9.5 g. (0.4 mole) of 1,1,1,3,3,3-hexafluoro-2-propyl 2-methylallyl sulfide stirred and cooled to −78°. The reaction mixture solidified as the blue color faded. Crystallization of the solid from pentane gave 12.1 g. (72%) of 4-methylene-1,1,7,7-tetrakis(trifluoromethyl)-2,6-thiaheptane as colorless needles, m.p. 41–42°. The fluorine n.m.r. spectrum indicated all fluorines were equivalent. The infrared spectrum showed bands at 6.05 for C=C and 11.25 μ for terminal methylene.

Anal. Calcd. for $C_{10}H_8F_{12}S_2$: C, 28.59; H, 1.92; F, 54.25; S, 15.26. Found: C, 28.72; H, 2.07; F, 54.07; S, 15.06.

Allyl Cyanide–HFTA Adduct.—Allyl cyanide, 9 ml., was added dropwise to 9.1 g. (0.05 mole) of HFTA cooled to −78°. The reaction mixture was allowed to warm to room temperature and then was distilled to give 5.78 g. (46% yield) of (1,1,1,3,3,3-hexafluoro-2-propylthio)crotononitrile as a colorless oil, b.p. 75–76° (1 mm.), n^{25}D 1.4117. Infrared indicated a conjugated nitrile at 4.50 μ.

Anal. Calcd. for $C_7H_5F_6NS$: C, 33.74; H, 2.02; F, 45.76; N, 5.62; S, 12.87. Found: C, 33.96; H, 2.48; F, 45.19; N, 5.69; S, 12.65.

α-Pinene–HFTA Adduct.—α-Pinene[8] was added dropwise to 18.2 g. (0.1 mole) of HFTA cooled to −78° until the blue color faded to light yellow. The reaction mixture was distilled under reduced pressure to give 5.3 g. of HFTA dimer and 15.7 g. of the adduct XIV as a colorless oil, b.p. 68–69° (0.1 mm.), n^{25}D 1.4371, $[\alpha]^{24}$D −47.81°. The infrared spectrum contained bands at 6.1 (C=C) and 11.3 μ (terminal methylene). The H and F n.m.r. spectra were complex. The F^{19} spectrum showed nonequivalent CF_3 groups coupled to each other and to hydrogen. Structure XIV would be expected to have nonequivalent CF_3 groups due to the assymetric center present. Integration of the hydrogen spectrum indicated that the methyl groups contained about 38% of the total hydrogens, and thus supports structure XIV. The methyl groups of structure XIII would contain 56% of the total hydrogens.

Anal. Calcd. for $C_{13}H_{16}F_6S$: C, 49.05; H, 5.07; F, 35.82; S, 10.07. Found: C, 49.31; H, 5.08; F, 35.94; S, 10.66.

α-Methylstyrene–HFTA 1:2 Adduct.—HFTA was added dropwise to a stirred solution of 5.9 g. (0.05 mole) of α-methylstyrene in 10 ml. of methylene chloride cooled to −78° until a faint blue color persisted. The reaction mixture was distilled under reduced pressure to give 19.2 g. (80%) of α-(1,1,1,3,3,3-hexafluoro-2-propylthiomethyl)-β-(1,1,1,3,3,3-hexafluoro-2-propylthio)styrene as a colorless oil, b.p. 112–113° (1.1 mm.), n^{25}D 1.4540. The fluorine n.m.r. spectrum contained two resonance lines, each split to a doublet. The infrared spectrum contained aromatic bands at 6.3, 6.35, and 6.7 μ.

Anal. Calcd. for $C_{15}H_{10}F_{12}S_2$: C, 37.35; H, 2.09; F, 47.27; S, 13.29. Found: C, 37.77; H, 2.34; F, 47.59; S, 13.18.

α-Methylstyrene–HFTA 1:1 Adduct.—HFTA, 9.1 g. (0.05 mole), was added dropwise to a stirred solution of 5.9 g. (0.05 mole) of α-methylstyrene in 20 ml. of methylene chloride cooled to −78°. The blue color faded immediately. The reaction mixture was distilled under reduced pressure to give 13.1 g. of a colorless oil, b.p. 70° (0.8 mm.), that solidified to a white solid on standing overnight. The solid was recrystallized from pentane to give 9.9 g. of α-(1,1,1,3,3,3-hexafluoro-2-propylthiomethyl)styrene as large, colorless prisms, m.p. 50°. The fluorine n.m.r. spectrum contained a doublet. The infrared spectrum showed a band at 11.3 μ for $C{=}CH_2$.

Anal. Calcd. for $C_{12}H_{10}F_6S$: C, 48.00; H, 3.36; F, 37.93; S, 10.69. Found: C, 48.31; H, 3.24; F, 38.07; S, 10.93.

α-Vinylthiophene–HFTA Adduct.—HFTA was added dropwise to a solution of 5.5 g. (0.05 mole) of α-vinylthiophene in 20 ml. of methylene chloride cooled to −78° until a faint blue color persisted. The reaction mixture was distilled under reduced pressure to give 18.7 g. (79%) of a 2:1 adduct as a colorless oil, b.p. 80–81° (0.35 mm.), n^{25}D 1.4506. The fluorine n.m.r. spectrum showed one doublet and a pair of quadruplets. The infrared and ultraviolet spectrum [$\lambda_{\max}^{\text{isooctane}}$ 255 mμ (ε 3860) and mμ (ε 5200)] appeared to be consistent with structure XI.

Anal. Calcd. for $C_{12}H_6F_{12}S_3$: C, 30.38; H, 1.28; F, 48.06; S, 20.28. Found: C, 30.98; H, 1.44; F, 48.06; S, 20.44.

Crepe Rubber–HFTA Adduct.[9]—A solution of 10 g. of pale crepe rubber in 1000 ml. of toluene was cooled to 0°, and HFTA was added dropwise with vigorous stirring until a pale blue color persisted. The precipitate was collected on a filter and dried in a vacuum oven. There was obtained 40 g. of a plastic insoluble in hydrocarbons.

Anal. Calcd. for $(C_8H_8F_6S)_n$: F, 45.60. Found: F, 43.07.

Squalene–HFTA Adduct.—HFTA, 25.6 g. (0.14 mole), was added dropwise to a stirred solution of 9.45 g. (0.023 mole) of squalene in 25 ml. of methylene chloride cooled in a Dry Ice–acetone bath. The HFTA was decolorized rapidly. The reaction mixture was evaporated to dryness under reduced pressure to give 29.2 g. of a glassy, colorless residue. This product would flow slowly but could be shattered by a sharp blow. Elemental analysis indicates the product is a 6:1 adduct of HFTA with squalene.

Anal. Calcd. for $C_{48}H_{50}F_{36}S_6$: C, 38.35; H, 3.36; F, 45.50; S, 12.80. Found: C, 38.66; H, 3.44; F, 45.42; S, 13.34.

β-Carotene–HFTA Adduct.—A saturated solution of β-carotene in 2 lb. of carbon disulfide was cooled to 0° and HFTA was added portionwise until a faint blue color persisted. The reaction mixture was evaporated to dryness under reduced pressure. The residue was broken up and further dried in a vacuum desiccator to give 11.7 g. of an off-white crystalline solid, m.p. 105–175°. Sulfur analysis indicated the product to be a 5:1 adduct of HFTA with β-carotene.

Anal. Calcd. for $C_{55}H_{56}F_{30}S_5$: S, 11.08. Found: S, 11.16.

Comparative Rates of Reaction of HFTA with Propylene and Isobutylene.—HFTA, 18.2 g. (0.2 mole), was added dropwise to a stirred mixture of 13.7 ml. (0.2 mole) of propylene and 17.9 ml. (0.2 mole) of isobutylene cooled to −78°. The reaction mixture was distilled, and the material boiling in the range 50–100° (10 mm.) was collected (21.2 g.). This distillate consisted of 14% HFTA–propylene adduct and 86% HFTA–isobutylene adduct, determined by vapor phase chromatography.

Methyl Vinyl Ether–HFTA Adduct.—HFTA was added portionwise with stirring to 5.8 g. (0.1 mole) of freshly distilled methyl vinyl ether cooled to −78°. The addition was continued until a faint blue color persisted in the reaction mixture. Distillation under reduced pressure gave 9.9 g. of HFTA dimer and 20.05 g. (85% yield) of 2,2-bis(trifluoromethyl)-4- (or 3-) methoxythietane as a colorless liquid, b.p. 43° (18 mm.), n^{25}D 1.3750. The infrared spectrum contained bands at 3.35 and 3.45 μ for saturated CH, but showed no absorption for unsaturation. The fluorine n.m.r. spectrum contained a single unsplit resonance band. The mass spectrometer pattern of the sample contained major peaks at m/e 76 (major peak, $C_2H_4OS^+$), 240 (parent ion, $C_6H_6F_6OS^+$), 145 ($C_4H_2F_5^+$), 95 ($C_3H_2F_3^+$), and 164 ($C_4H_2F_6^+$).

Anal. Calcd. for $C_6H_6F_6OS$: C, 30.00; H, 2.52; F, 47.47; S, 13.35. Found: C, 30.63; H, 2.73; F, 46.96; S, 13.71.

Pyrolysis of this adduct at 600° gave only unchanged adduct, HFTA dimer, and a polymeric material containing no fluorine.

Ethyl Vinyl Ether–HFTA Adduct.—This adduct, b.p. 43° (10 mm.), n^{25}D 1.3793, was prepared in a similar manner from HFTA and ethyl vinyl ether. The fluorine n.m.r. spectrum contained a single unsplit resonance line. The proton n.m.r. spectrum showed a triplet at 5.28 (J = 6 c.p.s.), a doublet at 3.30 (J = 6 c.p.s.) and a singlet at 3.33 p.p.m.

Anal. Calcd. for $C_7H_8F_6OS$: C, 33.07; H, 3.17; F, 44.85; S, 12.61. Found: C, 33.39; H, 3.02; F, 44.50; S, 12.71.

Dioxene–HFTA Adduct.—HFTA, 36.4 g. (0.2 mole), was added portionwise to a stirred solution of 8.6 g. (0.1 mole) of dioxene in 20 ml. of methylene chloride cooled to −78°. The solution became very dark and was almost black at the end of the additions. The reaction mixture was allowed to warm slowly for a few minutes. An exothermic reaction ensued, and the mixture became light yellow. The reaction mixture was distilled under reduced pressure to give 30.1 g. of HFTA dimer and 2.3 g. of 8,8-bis(trifluoromethyl)-2,5-dioxa-7-thiabicyclo[4.2.0]octane

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[8] Glidden Co., optical purity 90–92%.

[9] W. J. Middleton, U. S. Patent 3,012,995 (1961).

as a colorless oil, b.p. 72–73° (10 mm.), $n^{25}D$ 1.4068. The fluorine n.m.r. spectrum contained a pair of quadruplets. The proton n.m.r. spectrum showed an AB pattern at 5.13 and 5.87 (J = c.p.s.) of area 1 and a multiplet from 3.50–4.43 p.p.m. of area 2.

Anal. Calcd. for $C_7H_6F_6O_2S$: C, 31.35; H, 2.26; F, 42.51; S, 11.96. Found: C, 30.92; H, 2.28; F, 42.40; S, 12.08.

Dihydropyran–HFTA Adduct.—HFTA, 36.4 g. (0.2 mole), was added dropwise to a stirred solution of 8.4 g. (0.1 mole) of dihydropyran and 10 ml. of methylene chloride cooled to −78°. The reaction mixture was distilled to give 21 g. of HFTA dimer, and 15.5 g. of a pale purple oil, b.p. 57° (4.7 mm.), which solidified upon standing overnight. Recrystallization from pentane gave 10.9 g. of the adduct as colorless prisms, m.p. 36–37°. The fluorine n.m.r. spectrum showed two quadruplets of equal area. The infrared spectrum showed no evidence of unsaturation.

Anal. Calcd. for $C_8H_8F_6OS$: C, 36.09; H, 3.03; F, 42.82; S, 12.04. Found: C, 36.19; H, 3.03; F, 42.89; S, 12.00.

***t*-Butyl Vinyl Sulfide–HFTA Adduct.**—HFTA was added dropwise to a solution of 11.6 g. (0.1 mole) of *t*-butyl vinyl sulfide in 25 ml. of methylene chloride cooled to −78° until a faint blue color persisted. The reaction mixture was distilled to give 33.1 g. of HFTA dimer, b.p. 38° (40 mm.), and 27.7 g. (93%) of 2,2-bis(trifluoromethyl)-4- (or 3-) *t*-butylthiothietane as a colorless liquid, b.p. 38° (0.6 mm.), $n^{25}D$ 1.4252. The infrared, fluorine, and proton n.m.r. spectra appear to be consistent with the assigned structure. The fluorine n.m.r. spectrum showed a typical A_3B_3 pattern.

Anal. Calcd. for $C_9H_{12}F_6S_2$: C, 36.24; H, 4.06; F, 38.22; S, 21.50. Found: C, 36.51; H, 4.14; F, 38.26; S, 22.00.

A portion of this product was oxidized to the monosulfone by the following procedure. Hydrogen peroxide (30%), 10 ml., was added dropwise to a stirred solution of 6.06 g. (0.02 mole) of the thietane and 2 ml. of concentrated hydrochloric acid in 60 ml. of acetic acid at such a rate that the temperature of the reaction mixture remained between 50 and 80°. Water, 100 ml., was then added. The mixture was cooled, and the white precipitate that formed was collected on a filter, washed with water, and recrystallized from alcohol. There was obtained 3.6 g. of the sulfone as colorless prisms, m.p. 166–167°.

Anal. Calcd. for $C_9H_{12}F_6O_2S_2$: C, 32.72; H, 3.67; F, 34.51; S, 19.41. Found: C, 33.12; H, 3.55; F, 34.15; S, 19.55.

Methyl Vinyl Sulfide–HFTA Adduct.—HFTA, 18.2 g. (0.1 mole), was added portionwise to a stirred solution of 3.7 g. (0.05 mole) of methyl vinyl sulfide in 15 ml. of methylene chloride cooled to −78°. The colorless reaction mixture was distilled to give 2.3 g. of adduct, b.p. 40–41° (3.6 mm.), $n^{25}D$ 1.4268. The fluorine n.m.r. spectrum contained two quadruplets of equal area.

Anal. Calcd. for $C_6H_6F_6S_2$: C, 28.12; H, 2.36; S, 25.02. Found: C, 28.21; H, 2.79; S, 25.83.

Fluorimines

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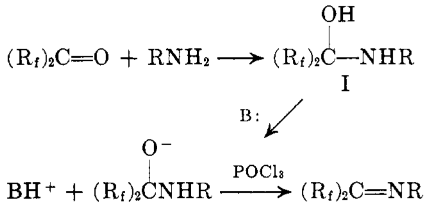
A new one-step procedure for the synthesis of fluorimines [$(R_f)_2C{=}NR$] in high yield is described. Reactions illustrating the predominately electrophilic character of fluorimines are presented along with some new derivatives to indicate their versatility as intermediates.

Reports that α-fluoro ketones can be converted to the usual ketone derivatives with carbonyl reagents are rare.[1] Similarly, attempts to prepare imines from fluoro ketones and amines have been unsuccessful until the present work. Imines of hexafluoroacetone have also been synthesized recently by Knunyants and his coworkers.[2] They used exchange with phosphine imines or an indirect route involving exchange with phenyl isocyanate since they believed the hydroxy amines formed from hexafluoroacetone and amines not to be subject to dehydration.

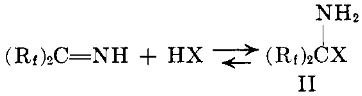
Amine and ammonia adducts of fluoro ketones are indeed very stable toward loss of water or of amine or ammonia, so that minor amounts of fluoro ketone and fluorimine must be present under equilibrium conditions at ordinary temperatures. Attempts to alter these equilibria by raising the temperature are complicated by a side reaction, similar to the haloform decomposition, in which the geminal hydroxy amine cleaves to fluoroalkane and fluoramide.[3] Chemical dehydration can be induced, however, by taking advantage of the acidity of the hydroxyl group in adduct I[4] to promote reaction at oxygen in basic media.[5]



$$(R_f)_2C{=}O + RNH_2 \longrightarrow \underset{\text{I}}{(R_f)_2\overset{\displaystyle OH}{\overset{|}{C}}{-}NHR} \xrightarrow{B:} BH^+ + (R_f)_2\overset{\displaystyle O^-}{\overset{|}{C}}NHR \xrightarrow{POCl_3} (R_f)_2C{=}NR$$

Conversion of a fluoro ketone to an imine, then, can be conveniently accomplished without isolation of the hydroxy amine I by using pyridine as the basic medium, adding the fluoro ketone, then ammonia or the primary amine, and lastly phosphorus oxychloride. Provided that the mixture is cooled to minimize side reactions, yields of 60–80% are easily attained.

The electronegative groups attached to the imine carbon make the double bond electron deficient, so that nucleophiles will attack to form stable adducts. Many of these adducts are without parallel in the chemistry of nonfluorinated amines. *gem* derivatives of type II, where X can be varied considerably, are easily prepared from the corresponding active hydrogen compounds. Adducts with one or more of the fluorimines have been prepared from ammonia, piperazine, hydrazine, methanol, ethylene glycol, cyanic acid,



$$(R_f)_2C{=}NH + HX \rightleftarrows \underset{\text{II}}{(R_f)_2\overset{\displaystyle NH_2}{\overset{|}{C}}X}$$

(X = NH_2, $NHNH_2$, NCO, N_3, OCH_3, F, etc.)

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[1] H. E. Simmons and D. W. Wiley [*J. Am. Chem. Soc.*, **82**, 2288 (1960)] noted that, except for hexafluoroacetone semicarbazone, no carbonyl derivatives of fluoro ketones had been claimed.

[2] Y. V. Zeifman, N. P. Gambaryan, and I. L. Knunyants, *Dokl. Akad. Nauk SSSR*, **153**, 1334 (1963).

[3] M. Hauptschein and R. A. Braun, *J. Am. Chem. Soc.*, **77**, 4930 (1955).

[4] Properties of various fluoro alcohols, including Brønsted acidity, are discussed by W. J. Middleton and R. V. Lindsey, *ibid.*, **86**, 4948 (1964).

[5] Simmons and Wiley[1] described a similar procedure for alkylating fluoro alcohols.