

Reaction of Hexafluoroacetone with Ortho Esters

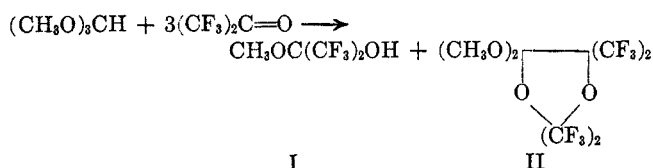
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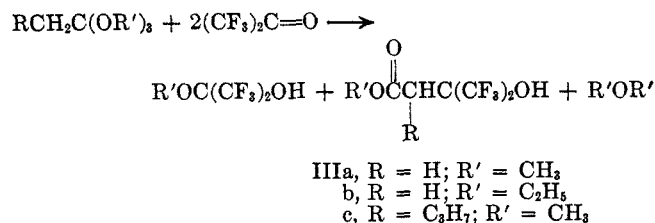
Received April 18, 1966

The reaction of hexafluoroacetone with aliphatic ortho esters, other than orthoformates, has been found to afford the hydroxy esters III. The reaction of hexafluoroacetone with the cyclic ortho ester 2-methyl-2-ethoxy-1,3-dioxolane gives the hydroxy ketal ester IV. Evidence in support of these structures has been obtained from infrared, proton nmr, and mass spectral data.

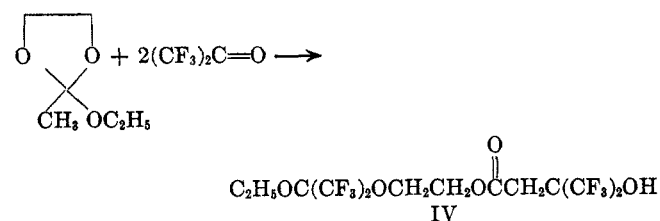
In earlier papers we described the reaction of hexafluoroacetone with orthoformates.^{1,2} A typical reaction is that of hexafluoroacetone with trimethyl orthoformate to give the hemiketal (I) and the 1,3-dioxolane



(II). We now deal with the reaction of hexafluoroacetone with ortho esters other than orthoformates. Trimethyl orthoacetate, triethyl orthoacetate, and trimethyl orthovalerate reacted readily with hexafluoroacetone at 150° to give a hemiketal and hydroxy esters IIIa-c. Ether, (R')₂O, is suspected to be the third product although it has not been isolated from the reaction. Compound IIIb has been prepared previously



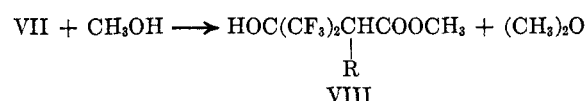
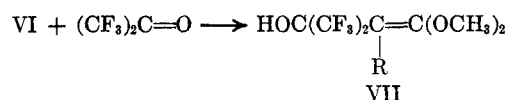
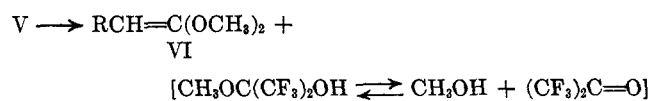
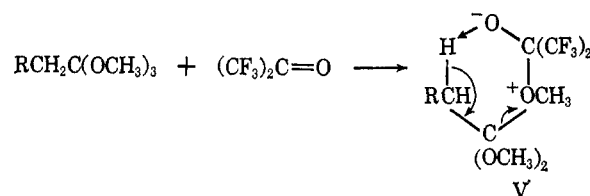
from the reaction of hexafluoroacetone with ethyl chloroacetate and zinc.³ With the cyclic ortho ester 2-methyl-2-ethoxy-1,3-dioxolane, the only product is the hydroxy ketal ester IV, when 2 or more molar equiv of hexafluoroacetone are used. The structures of these mate-



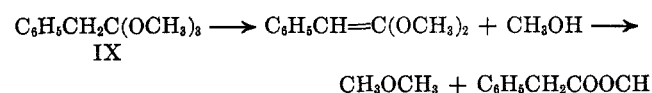
rials were established by infrared, proton nmr, and mass spectral analysis along with elemental analysis.

The probable first step in these reactions is the electrophilic attack of the hexafluoroacetone at an ether oxygen. The proposed reaction paths are consistent with the products obtained and our previous experience with the nature of hexafluoroacetone reaction, but have not been rigorously proven. The anionic center of the initial complex (V) could attack an available C-H group and in the case of the aliphatic ortho esters, the probably intermediate ketene acetal (VI) would be immediately

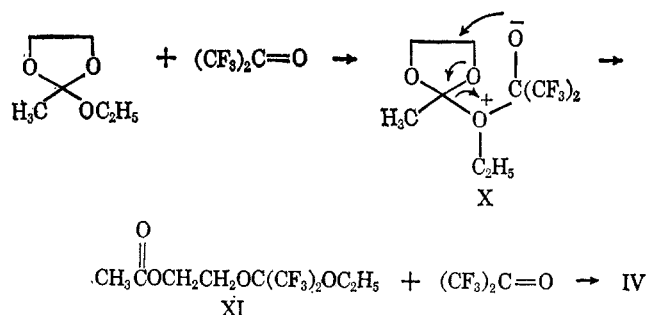
attacked by the electrophilic hexafluoroacetone to give VII.² The hydroxyketene acetal (VII) could react with methanol to give the observed product (VIII) and dimethyl ether. The precedent for the last step of this



sequence is the reported formation of methyl phenylacetate and dimethyl ether by heating IX.⁴ In the case



of the cyclic ortho ester, the anionic center of the intermediate (X) apparently attacks a CH₂ carbon of the cyclic ortho ester to give XI. This type of reaction has been observed before.² If the excess hexafluoroacetone is used the final product is the hydroxy ketal esters (IV) resulting from the attack of another molecule of hexafluoroacetone at the activated acetate methyl group. The related reactions of hexafluoroacetone with ketals will be discussed in a future report.



(1) R. A. Braun, *J. Am. Chem. Soc.*, **87**, 5516 (1965).

(2) R. A. Braun, *J. Org. Chem.*, **31**, 1147 (1966).

(3) I. L. Knuyants, *Bull. Acad. Sci. USSR Div. Chem. Sci.*, 647 (1960).

(4) S. M. McElvain, *Chem. Rev.*, **45**, 453 (1949).

Experimental Section⁵

2-Methyl-2-ethoxy-1,3-dioxolane.—Ethylene glycol (96.0 g, 1.55 moles), triethyl orthoacetate (251.0 g, 1.55 moles), and 0.2 g of concentrated sulfuric acid were slowly heated, and 147 g of ethanol was recovered by distillation after 2 hr. Potassium carbonate (5.0 g) was added and the mixture was fractionated to give 117 g (57.1%) of 2-methyl-2-ethoxy-1,3-dioxolane, bp 140° (760 mm). The infrared and proton nmr spectra are consistent with the proposed structure.

Anal. Calcd for C₆H₁₂O₃: C, 54.53; H, 9.15. Found: C, 54.56; H, 9.13.

Methyl 2-Hydroxy-2-trifluoromethyl-3,3,3-trifluorobutanoate (IIIa).—Trimethyl orthoacetate (24.0 g, 0.2 mole) and hexafluoroacetone⁶ (67.0 g, 0.4 mole) were heated in a stainless steel bomb at autogenous pressure for 6 hr at 150°. The crude product (84.3 g) was fractionated to give CH₃OC(CF₃)₂OH, bp 83° (760 mm), 30.7 g; and IIIa, 31.1 g (64.9%), bp 143–144° (760 mm). The infrared spectrum contained bands at 3.05 (C(CF₃)₂-OH) and 5.76 μ (ester C=O). The proton nmr spectrum showed a singlet at τ 3.56 (OH), a singlet at 6.31 (2 OCH₃), and a singlet at 7.21 (CCH₂C).

Ethyl 2-Hydroxy-2-trifluoromethyl-3,3,3-trifluorobutanoate (IIIb).—In a similar manner IIIb was prepared from triethyl orthoacetate and hexafluoroacetone (65.8%), bp 149° (760 mm), *n*_D²⁰ 1.3419.

Anal. Calcd for C₇H₈O₃F₆: C, 33.09; H, 3.17; F, 44.85. Found: C, 33.28; H, 3.18; F, 44.59.

Methyl α-(1-Hydroxy-1-trifluoromethyl-2,2,2-trifluoromethyl-*n*-valerate (IIIc).—Similarly, IIIc was obtained from trimethyl ortho-*n*-valeranoate and hexafluoroacetone in 72.1% yield, bp

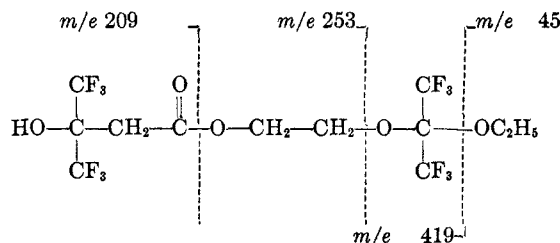
(5) Proton resonance spectra were obtained with a Varian Associates A-60 spectrometer.

(6) Commercial hexafluoroacetone of 99.54% purity from E. I. du Pont de Nemours and Co. was used.

56° (4.8 mm), *n*_D²⁰ 1.3675. The infrared spectrum contained bands at 2.98 (OH) and 5.85 μ (ester C=O).

Anal. Calcd for C₉H₁₂F₆O₃: C, 38.30; H, 4.29; F, 40.40; mol wt, 282. Found: C, 38.40; H, 3.60; F, 40.59; mol wt (cryoscopic in benzene), 277.

4,4-Bis(trifluoromethyl)-3,5-dioxoheptyl 3-Hydroxy-3-trifluoromethyl-4,4,4-trifluorobutanoate (IV).—2-Methyl-2-ethoxy-1,3-dioxolane (39.6 g, 0.3 mole) and hexafluoroacetone (100.0 g, 0.6 mole) were heated in a bomb at 150° for 8 hr. The crude liquid product (139.0 g) was fractionated to give IV, 48.0 g (34.6%), bp 114° (9 mm), 233–234° (760 mm), *n*_D²⁰ 1.3498, nmr signals at τ 3.68 (singlet, OH), 5.53 (quartet, OCH₂CH₂), 7.05 (singlet, CCH₂COO), and 8.70 (triplet, CH₂CH₂). The infrared spectrum contained bands at 3.01 (OH) and 5.83 μ (ester C=O). The mass spectrum did not contain the parent ion but all the major fragments are in agreement with the proposed structure.



Anal. Calcd for C₁₂H₁₂F₁₂O₆: C, 31.05; H, 2.61; F, 49.11; mol wt, 464. Found: C, 31.17; H, 2.25; F, 48.80; mol wt (freezing point in benzene), 472.

The low-boiling product, bp 66–68° (9 mm), 5.9 g, could not be obtained analytically pure but the infrared and nmr spectra indicated that it is the intermediate CH₃C(O)OCH₂CH₂OC(CF₃)₂OC₂H₅.

Ultraviolet and Electron Radiation Induced Addition to Olefins of Formamide

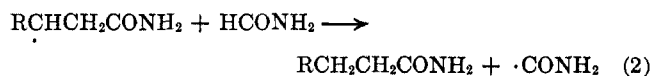
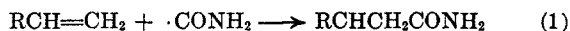
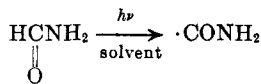
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Received April 8, 1966

Both the ultraviolet- and peroxide-induced addition of formamide to olefins has been reported in the literature.^{1–3} For the ultraviolet-induced reaction, no quantum efficiencies were reported; for the peroxide-induced reaction, the efficiency was low. The purpose of our investigation was not only to determine the quantum efficiency of the ultraviolet-induced reaction but also to study the previously unreported electron-induced reaction. Both the quantum yield for the ultraviolet-induced addition and the *G* value for the electron-induced reaction were found to be low.

The sequence of reactions suggested by Elad and Rokach¹ is as follows.



Some experimental difficulties were associated with the investigation of the formamide–1-hexene system. For example, the 1-hexene is only sparingly soluble in formamide and thus the irradiation must be run either under conditions where one of the reactants is in great excess or where a mutual solvent is added to the system.

(1) D. Elad and J. Rokach, *J. Org. Chem.*, **29**, 1855 (1964).
 (2) A. Rieche, E. Schmitz, and E. Gundermann, *Angew. Chem.*, **73**, 621 (1961).
 (3) J. E. Allen, J. I. G. Cadogan, and D. H. Hey, *J. Chem. Soc.*, 1918 (1965).

Both methods were used. The solubilizing system was similar to that used by Elad and Rokach.¹

For electron irradiation, both the rate of formation of heptanamide and the rate of disappearance of 1-hexene were measured. The simultaneous measurement of these two compounds permitted an estimate of the 1-hexene lost owing to side reactions. The results are expressed as *G* values (molecules formed or decomposed per 100 ev).

For the ultraviolet-irradiated systems the values for 1-heptanamide formation were always obtained while the 1-hexene content was determined in most cases.

Electron Irradiation Results.—Table I lists the *G* values for 1-heptanamide formation and for 1-hexene disappearance as a function of solvent and temperature. The results are averages for experiments conducted at 5, 10, 15, and 20 Mrads of radiation. At the highest dose, 30 to 60% of the 1-hexene originally present had disappeared.

The results may be summarized as follows: (1) the *G* values for 1-heptanamide formation are low, (2) re-