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Acetyl Hypofluorite, the First Member of a New Family of Organic Compounds

Summary Some sodium salts in acetic acid-Freon 11 (CFCl₃) when treated with elemental fluorine produce acetyl hypofluorite, CH_3CO_2F , a new electrophilic fluor-inating agent.

THE search for electrophilic fluorinating agents has so far yielded several compounds which all possess a fluoroxygroup attached to a perfluoroalkyl moiety.¹ Except for some theoretical studies on the unknown CH_3OF ,² no organic compound with a fluoroxy-group bonded to a non-fluorinated alkyl radical is known. It had always been believed that such compounds would be very unstable because of their tendency to eliminate HF. Recently, however, it has been shown that CF_3OH is unexpectedly stable, since the distance between the fluorine and the hydrogen atoms is quite large.³ We thought, therefore, that acetyl hypofluorite, CH_3CO_2F , (1), should be even more stable and thus of use in organic synthesis.

Elemental fluorine does not react with acetic acid and is practically insoluble in it, nor does it dissolve in a mixture of CH_3CO_2H and $CFCl_3$ (Freon 11) at - 78 °C, and thus it does not form an oxidising solution.[†] When, however, nitrogen-diluted fluorine is passed through suspensions of sodium fluoride, acetate, or trifluoroacetate in acetic acid-

[†]D. Cech and A. Holy, *Collect. Czech. Chem. Commun.*, 1976, **41**, 3335. The authors stated that they were dissolving fluorine in acetic acid at various concentrations. These fluorine solutions were oxidative and were used for converting uracil into 5-fluorouracil. We, however, were unable to prepare such a 'fluorine solution.' It is possible that various amounts of some salts were present in the reaction mixtures in their experiments, thus forming oxidising solutions owing to the formation of the fluoroxy-moiety which can convert uracil into 5-fluorouracil.

Freon (1:9) at -78 °C, oxidising solutions are formed. The concentrations of these solutions depend on the amounts of salt present.

In order to elucidate the nature of this oxidant, we added to it trans-stilbene (2) (1g) and, after a minute, stopped the reaction by sweeping nitrogen through and pouring the mixture into water. From the mixture we isolated threo-1acetoxy-2-fluoro-1,2-diphenylethane (3a) (yield 45%), m.p. 60 °C, accompanied by the corresponding erythro-isomer (3b) (7%), m.p. 41 °C.[‡] This result indicates that the oxidative power may be due to acetyl hypofluorite which adds across the double bond mainly in the syn mode.

In order to eliminate the possibility that free acetic acid was solvating the intermediate α -fluorocarbocation⁴ we transferred the acetyl hypofluorite (1) with the aid of a stream of nitrogen into another vessel containing Freon 11 alone at -78 °C. During this process, although (1) was exposed for a short time to room temperature, no appreciable amount of the oxidising power was lost. The new solution also reacts with (2) with the same results as before. What is more, when fluorine was passed through a suspension of sodium acetate in Freon 11 alone, an oxidising solution was also formed and reacted with (2) to give (3), although only in 24% yield.

cis-Stilbene (4) also reacts with (1) with high stereoselectivity, forming (3b) (syn addition) in 51% yield, accompanied by the *threo*-isomer (3a) (11%).

$$\begin{array}{ccc} \text{CH}_3\text{CO}_2\text{F} + \text{PhCH=CHPh} \rightarrow \text{PhCH}(\text{OAc})\text{CHFPh} \\ (1) & trans (2) & (3) \\ cis (4) & \mathbf{a}; threo & \mathbf{b}; erythro \end{array}$$

Compound (1) also reacts with ethyl trans-cinnamate (5) and methyl cis-cinnamate (6). However, since in these cases the resulting α -fluorocarbocation is obviously less stable than in the stilbene case, the tightly bound ion pair (7)collapses immediately¹ so that only the corresponding syn adducts (8) (57%), oil, and (9) (44%), m.p. 68 °C, could be isolated.

PhCH=CHCO₂R + (1)
$$\rightarrow \begin{bmatrix} PhCHCHFCO_2R \\ AcO^- \end{bmatrix}$$

(5); trans; R = Et (7)
 \downarrow
PhCH(OAc)CHFCO₂R
(6); cis; R = Me (8); threo; R = Et
(9); erythro; R = Me

The results described and the full regiospecificity confirm

the electrophilic character of the oxygen-bound fluorine.^{1a,b} We believe that the formation of (1) proceeds as in equation 1.

$$\label{eq:NaX} \begin{split} \mathrm{NaX} + \mathrm{CH}_3\mathrm{CO}_2\mathrm{H} &\to \mathrm{HX} + \mathrm{CH}_3\mathrm{CO}_2\mathrm{Na} \xrightarrow{\mathrm{F}_2} \mathrm{CH}_3\mathrm{CO}_2\mathrm{F} \\ &+ \mathrm{NaF} \quad (1) \end{split}$$

$$X = F, CH_3CO_2, CF_3CO_2$$

The reaction is not a catalytic one, since eventually the insoluble NaHF₂ is formed and the reaction stops. Thus the yield of the oxidiser is 50-80% based on the salts present in the reaction mixture. In the case of CF₃CO₂Na, trifluoroacetyl hypofluorite CF₃CO₂F can be formed,^{1c} but a nucleophilic attack on the oxygen-bonded fluorine by the large excess of acetic acid takes place to produce (1) again. It should also be noted that when only CH₃CO₂Na is present, without acetic acid, the unsolvated NaF formed may attack the carbonyl group,^{1b} thus leading to unstable species which can decompose rapidly. This may explain the low yields of the oxidisers (about 10% based on salt added) and the low yields of the fluoroacetoxy-compounds (3) (based on the reacting olefin).

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‡ Yields were based on the olefin used. The spectral properties (i.r., ¹H n.m.r., ¹⁹F n.m.r., and m.s.) of the fluorinated compounds were in excellent agreement with the proposed structures. For detailed discussions see ref. 1c. All new compounds gave correct microanalyses.

¹ The main perfluoroalkyl fluoroxy-reagents used as electrophilic reagents are; (a) CF₃OF: R. H. Hesse, *Isr. J. Chem.*, 1978, 17, 60 and references therein; (b) CF₃CF₂OF: O. Lerman and S. Rozen, *J. Org. Chem.*, 1980, 45, 4122; (c) CF₃CO₂F: S. Rozen and O. ¹ Lerman, *ibid.*, p. 672.
² J. S. Wright and L. Salem, J. Am. Chem. Soc., 1972, 94, 2371.
³ K. Seppelt, Angew. Chem., Int. Ed. Engl., 1977, 16, 322.
⁴ D. H. R. Barton, R. H. Hesse, G. P. Jackman, L. Ogunkoya, and M. M. Pechet, J. Chem. Soc., Perkin Trans. 1, 1974, 739.