Notes A department for short papers of immediate interest.

Organic Fluorine Compounds. XXVII.[1] Preparation of Acyl Fluorides with Anhydrous Hydrogen Fluoride. The General Use of the Method of Colson and Fredenhagen

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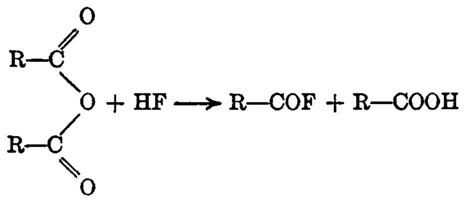
The preparation of acetyl and propionyl fluorides from the corresponding acid anhydrides and anhydrous hydrogen fluoride was described by Colson in 1897.[2] In 1933[3] Fredenhagen reported the quantitative formation of acetyl and benzoyl fluoride from the corresponding acyl chlorides and anhydrous hydrogen fluoride. No preparative investigation of the preparation of acyl fluorides based on anhydrous hydrogen fluoride, however, was reported, nor were the scope or experimental conditions of the reactions known. We therefore felt it useful to report briefly on the investigation of this method, which was found, with certain limitations, to be the most suitable way of preparing acyl fluorides. It is regrettable that so far the method of Colson and Fredenhagen has received little attention in the literature.

Our attention was directed to the method of Colson and Fredenhagen in connection with our previously reported investigation of the preparation of acyl fluorides from acyl chlorides and anhydrous potassium bifluoride.[4] We observed that both fluorine atoms of potassium acid fluoride reacted; thus potassium acid fluoride also acted as a source of hydrogen fluoride. A similar observation was made in the case of acid anhydrides and potassium acid fluoride by Mashentsev.[5] The reaction of potassium bifluoride with acyl chlorides and acid anhydrides needs higher temperatures which are sometimes inconvenient to apply. Therefore, we decided to investigate, in some detail, the reaction of anhydrous hydrogen fluoride with acyl chlorides (or bromides)

$$\text{R—COCl} + \text{HF} \longrightarrow \text{R—COF} + \text{HCl}$$

and acid anhydrides



$$(\text{R—CO})_2\text{O} + \text{HF} \longrightarrow \text{R—COF} + \text{R—COOH}$$

The reactions were carried out at atmospheric pressure, generally at a temperature between −10 and + 5°. A slight excess of anhydrous hydrogen fluoride was added to the corresponding acid anhydrides or passed into the corresponding acyl chloride. This resulted in a vigorous evolution of hydrogen chloride. Table I shows the yields obtained for twenty-one acyl fluorides investigated.

TABLE I

Yields of Acyl Fluorides

Compound	B.P.	Yield, % from Anhydride	Yield, % from Acyl Chloride
(1) Formyl fluoride	−29	61.0	—
(2) Acetyl fluoride	20	93.6	—
(3) Propionyl fluoride	43	91.5	89.0
(4) Butyric fluoride	69	—	91.0
(5) Isobutyric fluoride	61	—	90.0
(6) Valeric fluoride	90	—	92.0
(7) Isovaleric fluoride	81	—	87.5
(8) Caproic fluoride	122	—	81.0
(9) Heptanoic fluoride	40/15 mm.	—	80.5
(10) Octanoyl fluoride	62/15 mm.	—	86.0
(11) Pelargonic fluoride	81/15 mm.	—	83.0
(12) Decanoic fluoride	92/15 mm.	—	85.0
(13) Fluoroacetyl fluoride	54	—	89.0
(14) Chloroacetyl fluoride	77	—	87.5
(15) Dichloroacetyl fluoride	85	—	84.0
(16) Trifluoroacetyl fluoride	−57	85.0	—
(17) Trichloroacetyl fluoride	67	—	79.0
(18) Bromoacetyl fluoride	104	—	82.0
(19) Benzoyl fluoride	157	78.0	94.0
(20) Phthaloyl fluoride	84/15 mm.	—	89.0
(21) Phenylacetyl fluoride	85/15 mm.	—	87.0

In the reaction of acid anhydrides with anhydrous hydrogen fluoride it was found that only acetic and propionic anhydride (or their halogenated derivatives such as trifluoroacetic anhy-

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(1) Part XXVI, *J. Org. Chem.*, **26**, 225 (1961).

(2) A. Colson, *Bull. soc. chim. France* [3] **17**, 55 (1897); *Ann. Chim.* [7] 12, 255 (1897).

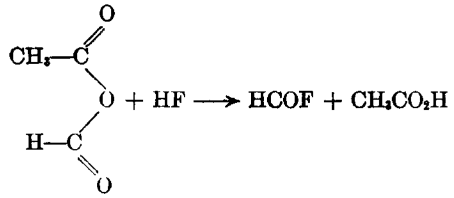
(3) K. Fredenhagen, *Z. phys. Chem. Abt.* A164, 189 (1933); K. Fredenhagen and G. Cadenbach, *Z. phys. Chem. Abt.*, A164, 201 (1933).

(4) G. Olah, S. Kuhn, and S. Beke, *Chem. Ber.* **89**, 862 (1956).

(5) A. I. Mashentsev, *J. Appl. Chem.* (*U.S.S.R.*) **11**, 816, 1135 (1941); *Chem. Abstr.* **37**, 1190, 2716 (1943); *J. Appl. Chem.* (U.S.S.R.) **15**, 915 (1945); *Chem. Abstr.*, **40**, 6443 (1946).

dride) react at hydrogen fluoride reflux temperature fast enough for this to be used as a preparative method at atmospheric pressure. The higher homologous acid anhydrides (with the exception of benzoic anhydride) need higher temperatures and, consequently, super-atmospheric pressures. The acyl chlorides, however, react at −10 to +5° rapidly and smoothly, thus allowing the halogen exchange to proceed at atmospheric pressure.

Such a preparation of acetyl fluoride is inconvenient, of course, as its boiling point is very similar to that of hydrogen fluoride. It is, therefore, obvious that the two types of starting materials complement one another. It was found possible to apply the reaction of acid anhydrides with anhydrous hydrogen fluoride to mixed anhydrides; this method was found to be extremely useful in the preparation of formyl fluoride.[6] By carrying out the reaction at atmospheric pressure, with continuous removal of the low boiling formyl fluoride, it was possible to make the reaction go entirely in this direction.



$$CH_3C(=O)-O-C(=O)H + HF \longrightarrow HCOF + CH_3CO_2H$$

A 61% yield of formyl fluoride was obtained, with a minimum formation of acetyl fluoride.

EXPERIMENTAL

The acyl fluorides were analyzed by gas chromatography and infrared spectroscopy. A Perkin-Elmer Model 154C Vapour Fractometer, having as column material a silicone high vacuum grease and a Perkin Elmer Model 221 infrared spectrograph with sodium chloride optics and silver chloride cells were used. As comparative standards, acyl fluorides described by us but prepared by known methods[4] were used. The yields, however, as shown in Table I, are those obtained in preparative scale experiments and represent the amount of isolated acyl fluoride and *not* VPC data. All operations were carried out with the usual precautions to exclude moisture.

Reaction of acid anhydrides with anhydrous hydrogen fluoride. Into 2.0 moles of the corresponding acid anhydride, 45 g. (2.25 moles) anhydrous hydrogen fluoride was added. The additon was carried out at approximately −10° with stirring by means of a Teflon covered magnetic stirrer. The mixture was kept at this temperature for an hour. It was then allowed to warm to room temperature and left standing for 2 hr. The mixture was then treated with 15 g. of anhydrous sodium fluoride to remove excess hydrogen fluoride, and distilled. Operations involving anhydrous hydrogen fluoride were performed in fused silica or plastic equipment. Plastic materials used included polyethylene, polypropylene, Teflon, and Kel-F.

Reaction of acyl chlorides with anhydrous hydrogen fluoride. Into 2.0 moles of the corresponding acyl chloride, kept at −5° to 0°, a continuous stream of anhydrous gaseous hydrogen fluoride was introduced at a rate of approximately 1 g./min. for 1 hr. It is also possible to carry out the reaction by adding the required amount of anhydrous liquid hydrogen fluoride to the stirred, cold acyl chloride. The reaction was then allowed to warm to room temperature and was kept there for 2 hr. To remove excess hydrogen fluoride, the reaction mixture was treated with dry sodium fluoride, filtered, and distilled.

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[6] G. A. Olah and S. J. Kuhn, *J. Am. Chem. Soc.* **82**, 2380 (1960).

Oxidation of Olefins by Thallium Compounds

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Olefins have long been known to form complexes with various metallic compounds,[1] particularly those of platinum (II), mercury (II), palladium (II), and silver (I). In the case of mercury, a further reaction occurs in which the mercury compound adds across the double bond. For example, in glacial acetic acid, ethylene and mercuric acetate react as follows:[2]

$$C_2H_4 + Hg(OAc)_2 \longrightarrow AcOC_2H_4HgOAc \quad (1)$$

Under certain conditions it is possible to effect an oxidation of the olefin, producing an inorganic mercurous salt and the oxidized carbon compound.[3] For example, in moderately strong ($\sim 2M$) nitric acid solution, mercuric nitrate and 2-pentene react as follows:[(3a)]

$$CH_3CH{=}CHC_2H_5 + 2Hg^{++} \longrightarrow CH_3COC_3H_7 + 2Hg^{+} + 2H^{+} \quad (2)$$

Lead (IV), which is isoelectronic with mercury (II), has also been reported to oxidize olefins, both to carbonyl compounds[4] and also to glycol derivatives.[5] This report describes a similar reaction of olefins with a third isoelectronic species, thallium (III). The reaction of thallium (III) solutions with both ethylene and 2-hexene was investigated, and both carbonyl products and glycols or their esters were obtained. The thallium was meanwhile completely reduced to thallium (I).

In nitrate solutions, the highest yield of ethylene glycol obtained was about 32% of the ethylene consumed. The yield of nonvolatile carbonyl com-

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[3] (a) R. F. Morris, Thesis, University of Indiana, 1954. (b) F. E. Mertz and O. C. Dermer, *Proc. Oklahoma Acad. Sci.*, **30**, 134 (1949). (c) A. C. Cope, N. A. Nelson, and D. S. Smith, *J. Am. Chem. Soc.*, **76**, 1100 (1954). (d) W. Treibs, *Naturwiss.*, **35**, 125 (1948). (e) W. G. Toland, U. S. Patent **2,623,073** (1952).

[4] M. Finkelstein, *Ber.*, **90**, 2097 (1957).

[5] R. Criegee, *et al.*, *Ber.*, **90**, 1070 (1957).