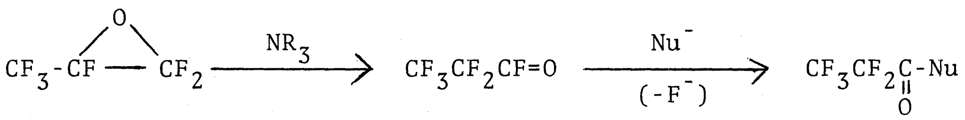
CHEMISTRY LETTERS, pp. 1407-1408, 1976. Published by the Chemical Society of Japan

PREPARATION OF CARBOXYLIC ACID FLUORIDES USING HEXAFLUORO-1,2-EPOXYPROPANE

Nobuo ISHIKAWA and Shigekuni SASAKI
Department of Chemical Technology, Tokyo Institute of
Technology, Ookayama, Meguro-ku, Tokyo 152

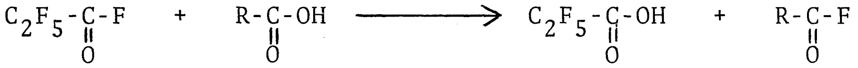
Carboxylic acid fluorides were prepared by treating free carboxylic acids with hexafluoro-1,2-epoxypropane in the presence of triethylamine or N,N-dimethylaniline under mild conditions.

Hexafluoro-1,2-epoxypropane (HFPO, hexafluoropropylene oxide) is known to rearrange to pentafluoropropionyl fluoride (1) with bases.[1-3] We already reported a convenient preparative method for esters and amides of pentafluoropropionic acid starting from HFPO and alcohols or amines.[4]



(1)

Since pentafluoropropionic acid has a strong acidity, its fluoride is expected to fluorinate other nonfluorinated carboxylic acids according to the following exchange reaction:



$$C_2F_5\text{-}\underset{\underset{O}{\|}}{C}\text{-}F \quad + \quad R\text{-}\underset{\underset{O}{\|}}{C}\text{-}OH \longrightarrow C_2F_5\text{-}\underset{\underset{O}{\|}}{C}\text{-}OH \quad + \quad R\text{-}\underset{\underset{O}{\|}}{C}\text{-}F$$

Thus, fluorination of several carboxylic acids was examined, by treating them with hexafluoro-1,2-epoxypropane in the presence of triethylamine or N,N-dimethylaniline. In each case, the reaction proceeded smoothly within a short period and carboxylic acid fluoride was obtained in excellent yield. In this reaction, another product, pentafluoropropionic acid, is easily removed as non-volatile onium salt from the acid fluoride.

For example, a mixture of benzoic acid (2.44 g, 20 mmol), triethylamine (2.02 g, 20 mmol) and sulfolane (5 ml) was placed in a pressure vessel and cooled to -75°C. Liquefied HFPO (bp -27°C, 3.40 g, 20.5 mmol) was then introduced into the vessel and the whole was brought to room temperature. After 30 min of stirring at this temperature, the reaction mixture was subjected to distillation under reduced pressure and a crude product (bp 75 - 81°C/46 mmHg, 2.33 g, 94%) was obtained. Redistillation gave pure benzoyl fluoride (bp 76°C/50 mmHg, 1.97 g) in a yield of 79%.

The other carboxylic acids such as propionic, isobutyric, octanoic and p-toluic acids were converted into their fluorides in a similar manner (Table 1). In some cases, N,N-dimethylaniline was used instead of triethylamine.

Table 1. Preparation of carboxylic acid fluorides

R-CO_2H	NR_3	Reaction conditions Time (min)	 Temp (^oC)	Product (R-COF) Yield[a)] (%)	 B.p. (^oC/mm)	 (Lit)
$CH_3CH_2CO_2H$	$PhNMe_2$	90	r.t.	86	——	43[b)]
$(CH_3)_2CHCO_2H$	〃	90	〃	87	——	61[b)]
$CH_3(CH_2)_6CO_2H$	Et_3N	30	〃	89	68.5/25	62/15[b)]
$PhCO_2H$	〃	30	〃	79	76/50	157[b)]
p-$CH_3C_6H_4CO_2H$	〃	60	〃	77	90-91/25	——

a) Yield of the products purified by distillation. Structures were confirmed by ir and ^{19}F nmr.

b) G. A. Olah and S. J. Kuhn, J. Org. Chem., 26, 237 (1961).

Carboxylic acid fluorides have commonly been prepared from carboxylic acid chlorides or anhydrides with potassium fluoride or hydrogen fluoride, or more recently, directly from free carboxylic acids by fluorination with cyanuric fluoride,5) 1,3-dimethyl-2-fluoropyridinium salt6) or other reagents.6) Although the direct fluorination of free carboxylic acids is more versatile than fluorination of carboxylic acid halides or anhydrides, the direct-fluorinating agents listed above are difficult to prepare or obtain. HFPO is attracting attention recently for its use in several fluoropolymers, and is obtainable semi-commercially. The reaction proceeds under mild conditions, i.e., at room temperature in short periods (30 - 90 min), and the separation of acid fluoride is easily accomplished by direct distillation. From these standpoints, the above method seems to be a new and versatile preparative route to carboxylic acid fluorides.

References

1) Review: P. Tarrant, G. G. Allison, and K. P. Barthold, "Fluorine Chemistry Reviews," Vol.5, Marcel Dekker, Inc., New York, (1971), p.77.
2) D. Sianesi, A. Pasetti, and F. Tarli, J. Org. Chem., 31, 2312 (1966).
3) I. L. Knunyants, V. V. Shokina, and I. V. Galakhov, Khim. Geterotsikl. Soedin, 1966, 873; Chem. Abstr., 66, 115673t (1967).
4) N. Ishikawa and S. Sasaki, Nippon Kagaku Kaishi, in press.
5) G. A. Olah, M. Nojima, and I. Derekes, Synthesis, 1973, 487.
6) T. Mukaiyama and T. Tanaka, Chem. Lett., 1976, 303, and references cited therein.

(Received October 25, 1976)