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Selective Electrochemical Formyl Hydrogen-Exchange Fluorination of Aliphatic Aldehydes to Prepare Acyl Fluorides Using HF-Base Solutions

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The selective displacement of formyl hydrogen (-(C=O)-H) to fluorine in aliphatic aldehydes was successfully carried out electrochemically to give acyl fluorides in base-nHF (base: pyridine or Et_3N, n=3-6) electrolyte solution with or without solvents such as acetonitrile and sulfolane.

HF-Base solution is well known as a good source of fluoro-substituents for the oxidative fluorination of organic compounds.1) Recently, the electrochemical fluorination of aromatic compounds has been extensively studied in the presence of R_4NF-mHF.2) We have carried out the electrochemical reaction of aliphatic aldehydes (2 mmol) using a platinum anode (20 mm × 20 mm) in 4 cm^3 of HF-Base (6HF-Pyridine, nHF-Et_3N with n=3-5) in an undivided cell (50 cm^3) made of Teflon PFA3) under a constant current (100 mA) or controlled potential of 2F (per mol of substrate) passage at 0-20 °C. The oxidative potential (vs. Ag/Ag^+) of substrates was measured using cyclic voltammetry to determine their controlled potentials for the electrolysis. After the usual work up of the resulting solution, the organic products were extracted using CH_2Cl_2 and then fully characterized by spectroscopy.

As shown in Table 1, the reaction of octylaldehyde was carried out in the presence of pyridine-6HF or Et_3N-nHF (n=3-5) as the electrolyte. The displacement of formyl hydrogen (-(C=O)-H) to fluorine took place selectively by electrolysis to afford octanoyl fluoride in good yields. Other fluorinated products were not observed in the CH_2Cl_2 extracts. Et_3N-5HF gave especially good results. The yield of octanoyl fluorides was also affected by the presence of solvent and was greatly improved by employing acetonitrile or sulfolane. However, the electrochemical fluorination of aldehydes was hindered by added solvents such as ethers, DMF and DMSO that diminished the yields of corresponding acyl fluorides. Et_4NF-4HF, which has been demonstrated as a prominent electrolyte for the electrochemical fluorination of aromatics,4) also exerted good results to afford the corresponding fluorides in high yields.

In Table 2, typical results are shown for the reaction of aliphatic aldehydes in the presence of Et_3N-5HF using acetonitrile. The replacement of formyl hydrogen to fluorine was not influenced by the bulk of the alkyl group in the aldehydes and preferentially took place to afford the corresponding acyl fluorides in good yields. The application to aldehydes having functional groups is currently under progress.

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Table 1. Preparation of Octanoyl Fluoride by Electrochemical Fluorination of Octylaldehyde

Electrolyte	Solvent	Electrolysis conditions	Temp °C	Conversion %	Yield of octanoyl fluoride/%
Pyridine-6HF	None	100 mA[a)]	0	81	37
″	Et_2O	″	″	20	7
″	CH_2Cl_2	″	″	81	28
″	MeCN	″	″	85	58
″	DMF	″	″	27	0
″	DMSO	″	″	33	6
″	THF	″	″	32	0
″	Sulforlane	″	″	58	42
Et_3N-3HF	None	″	″	55	23
″	Et_2O	″	″	26	8
″	CH_2Cl_2	″	″	79	25
″	MeCN	″	″	50	42
Et_4NF-4HF	None	″	″	73	51
″	MeCN	″	″	85	59
″	MeCN	″	20	93	66
″	MeCN	2.60V vs. Ag/Ag^+ [b)]	″	91	80
Et_3N-5HF	None	″	″	85	70
″	MeCN	″	″	90	75
″	Sulfolane	″	″	84	68
Et_3N-4HF	None	″	″	68	38
Et_3N-3HF	None	2.50V vs. Ag/Ag^+ [b)]	″	59	32

a) Constant current electrolysis. b) Controlled potential electrolysis.

Table 2. Electrochemical Fluorination of Aliphatic Aldehydes Using Et_3N-5HF[a)]

RCOH R:	Controlled potential V(vs. Ag/Ag^+)	Conversion %	Yield of RCOF %
n-pentyl-	2.60	93	70
3-Heptyl-	2.55	96	89
Cyclohexyl-	2.40	98	84
tert-Butyl-	″	97	66

a) React. conditions: Substrate (2 mmol), Electrolyte; Et_3N-5HF (4 ml), Solvent; CH_3CN (12 ml), Reaction temp ; 20 °C, Quantity of electricity passed; 2 F mol^{-1}.

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