BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (4), 1267—1268 (1978)

Preparation of Aroyl and Arenesulfonyl Fluorides from the Corresponding Chlorides Using Zinc Fluoride–Pyridine System

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(Received December 17, 1977)

Synopsis. Convenient preparation of aroyl and arenesulfonyl fluorides in high yields was achieved by the reaction of the corresponding chlorides with zinc fluoride in pyridine.

A number of methods for the conversion of carboxylic acid chlorides or bromides into fluorides have been reported. In earlier days, various metal fluorides such as SbF_3,[1a,b] AsF_3, AgF,[1a] KF, KHF_2,[1c] HgF_2,[1d] and ZnF_2[1e] were used for this purpose, although they do not give satisfactory results. In recent years, more complex fluorides, such as Na_2SiF_6,[2] potassium fluorosulfinate,[3] triethylammonium fluoride,[4] hexafluoroacetone-KF adduct[5] or morpholinosulfur trifluoride[6] have been reported as fluorinating reagents.

In our earlier paper[7] it was mentioned that smooth formation of a ketone from (heptafluoro-1-methylethyl)-zinc iodide and benzoyl chloride was induced in the zinc fluoride–pyridine system, in which an in situ conversion of benzoyl chloride into fluoride was recognized. Further investigation has revealed that zinc fluoride is surprisingly effective in pyridine for the conversion of not only aroyl chlorides but also arenesulfonyl chlorides into the corresponding fluorides under mild conditions.

Several decades ago, the reaction of zinc fluoride with acetyl chloride (no solvents) for three days[8] and the reaction of zinc fluoride with organic sulfonyl chlorides in water were reported,[9] the results being, however, unsatisfactory yields of the corresponding fluorides. We describe here a practically useful method for the preparation of aroyl and arenesulfonyl fluorides by reaction in the zinc fluoride–pyridine system.

After addition of benzoyl chloride to an equimolar amount of zinc fluoride in pyridine at room temperature (25 °C), tracing of the reaction by ^{19}F NMR analyses revealed rapid conversion of the chloride into fluoride, which was completed quantitatively within 20 min. However, on using a half-molar amount of zinc fluoride the reaction was much slower, and 73 and 88% conversions after 40 min and 12 h respectively were observed.

Replacement of zinc fluoride by potassium fluoride, or of pyridine by other tertiary amines (Et_3N, $PhNMe_2$, or *N*-methylpiperidine) or by other solvents (DMSO, DMF, MeCN, or THF) gave no satisfactory results, showing almost no occurrence of conversion. The exclusive effectiveness of pyridine is presumably due

Table 1. Preparation of aroyl and arenesulfonyl fluorides

$$\underset{(\text{or } ArSO_2Cl)}{ArCOCl} + ZnF_2 \xrightarrow[\text{r.t.}]{\text{Pyr.}} \underset{(\text{or } ArSO_2F)}{ArCOF} + ZnClF$$

ArCOF or $ArSO_2F$	Preparation			Bp[c] (°C/mmHg)	Mp[c] (°C)	^{19}F NMR[d] COF or SO_2F
	Method[a]	Time (min)	Yield[b] (%)			
p-$MeOC_6H_4COF$	A	40	83	74/5[e]	——	−93.3 (neat)
p-MeC_6H_4COF	A	20	84	110/94 (90—91/25)[f]	——	−94.8 (neat)
C_6H_5COF	A	20	82	101/130 (154—155)[g(i)]	——	−94.8 (neat)
p-ClC_6H_4COF	B	20	82	——	59—60[h]	−96.0 (CCl_4)
p-$NO_2C_6H_4COF$	B	20	100	——	138—139 (144—146)[i]	−97.6 (C_6H_6)
p-$MeC_6H_4SO_2F$	B	120	80	——	42.5—43.5 (43—44)[g(ii)]	−144.3 (CCl_4)
$C_6H_5SO_2F$	B	120	82	62—65/2 (203—204)[g(iii)]	——	−144.6 (neat)
p-$ClC_6H_4SO_2F$	B	120	90	——	53—54 (48—49)[i]	−142.0 (MeCN)
p-$BrC_6H_4SO_2F$	B	120	94	——	66—67 (65—66)[k]	−142.0 (MeCN)

a) See experimental section. b) Yields are those of the products actually isolated. c) Values in the literature are shown in parentheses. d) Chemical shifts in the solvents in parentheses are shown in δ ppm from ext. CF_3CO_2H. e) Calcd, C, 62.34%; H, 4.58%; Found, C, 61.68%; H, 4.55%. f) N. Ishikawa and S. Sasaki, *Chem. Lett.*, **1976**, 1407. g) "Dictionary of Organic Compounds" 4th ed, Eyre and Spottiswoode Pub. Ltd., (1965), (i) Vol. 1, p. 359; (ii) Vol. 1, p. 330; (iii) Vol. 5, p. 3072. h) Calcd, C, 53.02%; H, 2.54%; Found, C, 53.21%; H, 2.61%. i) L.N. Markovskij, V.E. Pashinnik, and A.V. Kirsanov, *Synthesis*, **1973**, 787. j) M. Kulka, *J. Am. Chem. Soc.*, **72**, 1215 (1950). k) M.E. Aberlin and C.A. Bunton, *J. Org. Chem.*, **35**, 1825 (1970).

to its ability to weaken the Zn–F linkage through an appropriate coordination to the zinc atom.

The reaction was extensively studied using aroyl chlorides with varied substituents. As summarized in Table 1, the corresponding fluorides were obtained in sufficiently high yields in all the runs. However, when phenylacetyl chloride, an aliphatic acid chloride, was employed, the yield of fluoride was only 57% (^{19}F NMR analysis) even after 4 h's reaction.

Conversion of arenesulfonyl chlorides into fluorides was also examined in a similar manner. For example, conversion of benzenesulfonyl chloride into the fluoride occurred quantitatively after 2 h (^{19}F NMR). Results of experiments with several other arenesulfonyl chlorides are shown in Table 1.

Experimental

Anhydrous Zinc Fluoride. Anhydrous zinc fluoride was easily prepared as follows. An aqueous solution of zinc chloride (two molar equiv.) was added to an aqueous solution of potassium fluoride and the precipitates obtained were collected by filtration, washed thoroughly with water and dried over phosphorus pentaoxide at 180 °C in vacuo. Yield was almost quantitative.

General Procedures for Fluorination. To a solution of zinc fluoride (0.03 mol) in pyridine (30 ml) aroyl chloride or arenesulfonyl chloride (0.03 mol) was added with stirring at room temperature (25 °C). Stirring was continued until the reaction was completed (checked by ^{19}F NMR) then treated by either method (A) or (B), as follows:

(A) In the case of low-boiling products resistant to hydrolysis; the reaction mixture was poured into ice-cold 25% hydrochloric acid. The liberated aroyl fluoride was extracted with ether and the ethereal solution was washed with water and dried over magnesium sulfate. Evaporation of ether gave the aroyl fluoride, which was purified by distillation under reduced pressure.

(B) The reaction mixture was concentrated under reduced pressure and the resulting residue was extracted with warm hexane or benzene. Evaporation of the solvent gave crude aroyl fluoride or arenesulfonyl fluoride which was purified by distillation under reduced pressure or by recrystallization.

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