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FLUORINATION BY USE OF TRANSITION METAL FLUORIDE-BIPYRIDINE COMPLEX IN APROTIC ORGANIC SOLVENTS

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Bipyridine complexes of transition metal fluorides which are soluble in aprotic organic solvents are used for the fluorination of organic halides under mild conditions.

Metal fluorides have been widely used as convenient reagents for the preparation of organic fluorine compounds because of their easy availability.$^{1)}$

Recently the use of KF-crown complex$^{2)}$ and "spray-dried" KF$^{3)}$ was developed to generate "naked" fluoride ion which enabled fluorine-replacement reactions to proceed under mild conditions, while transition metal fluorides such as described below have been rarely used seemingly because of their low reactivities and solubilities in aprotic organic solvents. We report here the successful fluorination of organic halides by use of transition metal fluorides which are solubilized in acetonitrile and dichloromethane by complexation with lipophilic nitrogen-containing ligands.

Figure 1 shows the results of the reactions of benzyl bromide (0.1 mol dm^{-3}) with transition metal fluorides (2 times mol) in the presence of 2,2'-bipyridine (bpy)$^{4)}$ (6 times mol) in refluxing acetonitrile to give predominantly benzyl fluoride. No reaction proceeded without bpy. The observed order of reactivity of the bivalent transition metal fluorides (Zn(II) < Cu(II) > Co(II) > Mn(II)) is in accord with the stability of transition metal complexes.$^{5)}$

Similarly the reaction of 1-bromooctane with copper(II) fluoride (2 times mol) and bpy (6 times mol) in refluxing acetonitrile for 128 h (93% conv.) gave 1-fluorooctane (95%) and 1-octene (2%). The reactivity of copper(II) fluoride under these conditions is comparable to those of KF-crown complex2) and "spray-dried" KF.3)

Fig. 1. Reactions of benzyl bromide in acetonitrile (0.1 mol dm^{-3}) with transion metal fluoride (MF_n) in the presence of bpy.

$$\mathrm{PhCh_2Br} \xrightarrow[\mathrm{CH_3CN,\ reflux}]{\mathrm{2MF_n,\ 6bpy}} \mathrm{PhCH_2F}$$

M = Cu(II), Co(II), Co(III), Zn(II), Fe(III), and Mn(II).

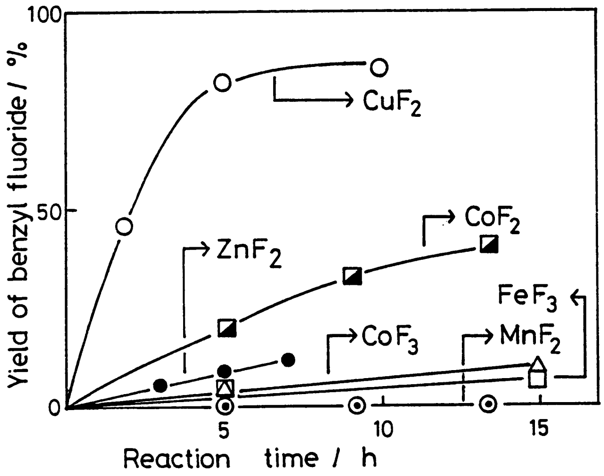

Table 1. Reactions of 2,4-dinitrochlorobenzene (0.1 mol dm^{-3}) with transition metal fluoride (2 times mol) in the presence of bpy (6 times mol) in refluxing acetonitrile

Run	MF_n	Reaction conditions			Conversion	Yield$^{a)}$
		Solvent	Temp/°C	Time/h	%	%
1	CuF_2	CH_3CN	82	5	93 - 96	37 - 39$^{b)}$
2	$CuF_2$$^{c)}$	CH_3CN	82	5	53	25
3	$CuF_2$$^{d)}$	CH_3CN	82	17	no reaction	-
4	CuF_2	CH_2Cl_2	40	125	83	45
5	CoF_2	CH_3CN	82	5	40	50
6	NiF_2	CH_3CN	82	5	22	50
7	CoF_3	CH_3CN	82	5	10	70
8	ZnF_2	CH_3CN	82	5	no reaction	-
9	FeF_3	CH_3CN	82	5	no reaction	-

a) Yield of 2,4-dinitrofluorobenzene determined by GLC by use of nitrobenzene as an internal standard.

b) 25% yield of 2,4-dinitrophenol was detected by HPLC.

c) With two times molar amounts of bpy.

d) With one third molar amount of bpy.

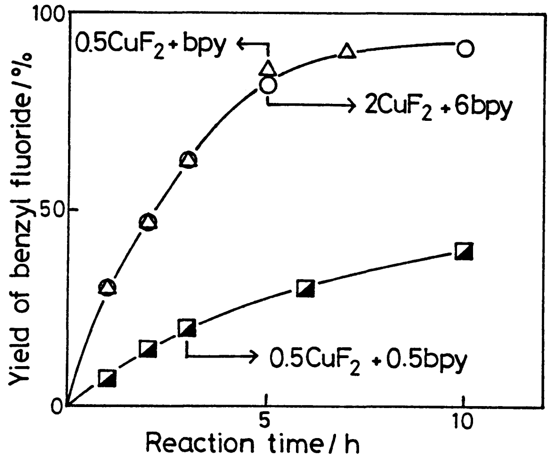

Fig. 2. The effect of molar ratios of CuF_2/bpy/substrate on the benzyl fluoride formation.

The reactions of 2,4-dinitrochlorobenzene with metal fluorides in the presence of bpy gave 2,4-dinitrofluorobenzene and 2,4-dinitrophenol which might result from nucleophilic attack of residual water in acetonitrile (Table 1).[6)]

Figure 2 shows the effect of molar ratios of copper(II) fluoride, bpy, and substrate on the fluorination of benzyl bromide in refluxing acetonitrile. With 1/2 and 1/3 molar ratios of copper(II) fluoride/bpy the reaction proceeded at similar rates, whereas the reaction was much retarded with 1/1 ratio of copper(II) fluoride/bpy. This means that two times molar amounts of bpy are required for copper fluoride to generate enough amounts of active fluoride ion and that the reaction rates are limited by the solubility of copper(II) fluoride in the reaction mixture in the presence of bipyridine. On the other hand, 1/0.5 molar ratio of substrate/copper(II) fluoride afforded more than 90% yield, which implies both fluoride ions of copper(II) fluoride to be used for fluorination. Similar results were obtained in the reaction of 2,4-dinitrochlorobenzene (see Table 1, Runs 1-3). According to these results, a reactive species might be considered to have two bpy ligands coordinated to copper(II) fluoride (Fig. 3).

In place of bpy was examined N-tetramethylcyclam[7)] (N-tmc, Fig. 4) as a ligand of higher chelating ability. Fluorination of 2,4-dinitrochlorobenzene (0.1 mol dm^{-3}) with copper(II) fluoride (half a mol) and N-tmc (half a mol) proceeded, however, in a sluggish manner (12% conv. after 11 h) in refluxing acetonitrile to give 2,4-dinitrofluorobenzene (80%) and 2,4-dinitrophenol (20%). The lower reactivity with N-tmc is probably due to lower solubility of N-tmc-copper(II) fluoride complex in acetonitrile.[8)]

The generation of reactive "naked" fluoride ion from the transition metal

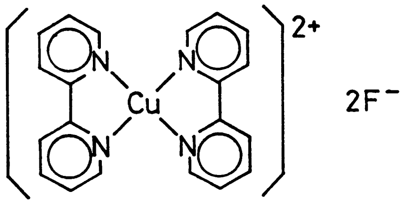

Fig. 3. Bis(2,2'-bipyridine)copper(II) fluoride.

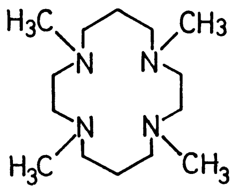

Fig. 4. N-Tetramethylcyclam.

complex fluorides and the application of fluoride ion thus generated to nucleophilic displacement are still under progress.

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References

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4) Although the solubility of N,N,N',N'-tetramethylethylenediamine (TMED) complex of copper(II) fluoride in acetonitrile was higher than that of the bpy-complex, the TMED-complex was not applicable to the present purpose because TMED itself reacted with 2,4-dinitrochlorobenzene even at room temperature.

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