Journal of Fluorine Chemistry, *37* (1987) 171–176

Received: January 19, 1987; accepted: July 7, 1987

SOLVENT EFFECTS ON THE REACTION OF 4-CHLOROOCTAFLUOROBUTYLIODIDE WITH COPPER

QING-YUN CHEN*, ZHEN-YU YANG and Ya-BO HE

Shanghai Institute of Organic Chemistry, Academia Sinica,
345 Lingling Lu, Shanghai (China)

SUMMARY

A linear relationship between the differences of chemical shift in ^{19}F-NMR of $IC\underline{F}_2(CF_2)_3Cl$ and the donor number (DN) of various solvents has been found and the mechanism of the reaction of fluoroalkyl iodide with copper depends on the DN of the solvent used, which influences the product distribution in the reaction of fluoroalkyl iodide and copper with the mixture of olefin and iodobenzene in various solvents.

INTRODUCTION

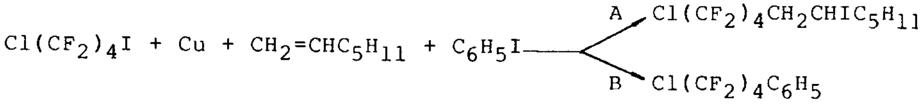
Some reactions take diverse pathways depending on the solvents used, e.g. diazonium salts decompose quite differently in various solvents[1]. In literature[2] fluoroalkylation of alkyl halides or aromatic halides in the presence of copper in DMSO, DMF, pyridine, CH_3CN, or HMPA have been accomplished, however, little was known about the different approaches prior to our finding that reaction of fluoroalkyl iodides with copper may involve radical intermediates in acetic anhydride but fluoroalkylcopper intermediates in DMSO [3]. Thus, we have extended the study of this reaction in various solvents and established the relationship between solvent properties and reaction mechanisms.

0022-1139/87/$3.50

RESULTS AND DISCUSSION

Fluoroalkyl iodides, because of the strong electron attracting properties of fluoroalkyl group, contain an iodine-carbon bond with the partial positive charge residing at iodine [4]. These molecules may be complexed with Lewis bases containing nitrogen to form molecular adducts [5] or interact with electron donating solvent molecule, the ability of which is represented by donor number (DN) [6]. Due to the interaction of electron donor with iodine of fluoroalkyl iodide the electron densities at the fluorine atoms increases resulting in changes in ^{19}F-NMR spectra. Figure 1 shows the linear correlation between the chemical shift of ^{19}F-NMR and DN of various solvents.

In the reaction of fluoroalkyl iodides with copper, a fluoroalkyl radical could be trapped by olefin to form adduct (path A) or a fluoroalkylcopper intermediate by iodobenzene to give a coupling product (path B) depending on the solvent used. Therefore, if both fluoroalkyl iodide and copper were added to the mixture of olefin and iodobenzene in various solvents it should give the products which reveal the possible intermediates, *i.e.* fluoroalkyl radical or fluoroalkylcopper.



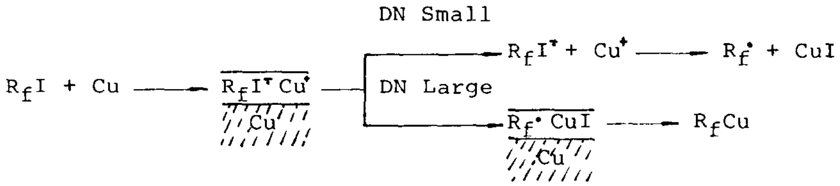
$$Cl(CF_2)_4I + Cu + CH_2{=}CHC_5H_{11} + C_6H_5I \longrightarrow \begin{cases} \xrightarrow{A} Cl(CF_2)_4CH_2CHIC_5H_{11} \\ \xrightarrow{B} Cl(CF_2)_4C_6H_5 \end{cases}$$

The experiments in which a fluoroalkyl iodide reacted with copper in the presence of both heptene-1 and iodobenzene in ten different solvents were carried out at 110°C for 4-16 h. Products were isolated and identified, and the results are summarized in Table 1.

Combining the data in Figure 1 with those in Table 1, shows that if the reactions were carried out in solvents with smaller DN (DN<19) (or $\Delta\delta_F<6$) only adduct was formed, but in the solvents with larger DN (DN>31) (or$\Delta\delta_F>9.5$) the major product was the coupling product, and in the solvents with medium DN (19<DN<31)(or $6<\Delta\delta_F<9.5$),both adduct and coupling product were obtained. Interestingly, the reactions in the solvents with smaller DN could be suppressed by a radical inhibitor(hydroquinone) and a single electron transfer scavenger(p-dinitrobenzene). All the results seem to show that the mechanism of the reaction of fluoroalkyl iodide with copper depends on the solvent used, i.e. in solvents with smaller DN, the radical intermediate is required but in solvents with larger DN, the fluoroalkylcopper intermediate is involved.

The above competitive reactions depend on the reactivity of olefin used. If a less reactive(relative to fluoroalkyl radical) olefin such as cyclohexene was used as a trap in DMSO, only the coupling product was formed, but for the more reactive olefin, diallyl ether,27% of coupling product and 54% of tetrahydrofuran derivative were obtained,which is an excellent probe for elucidating radical intermediates. This result may imply that when fluoroalkylcopper is formed a radical intermediate is also involved.

In summary, we propose that the first step of the reaction of fluoroalkyl iodide with copper in various solvents takes place with single electron transfer to form an ion pair within the solvent cage. In the solvent with smaller DN, diffusional separation of the caged ion pair produces fluoroalkyl radical, but in the solvent with larger DN this ion pair decomposes to give a radical in solvent cage, which absorbs on the surface of copper to form fluoroalkylcopper. Furthermore, the solvents with larger DN can very well stablilize the fluoroalkylcopper which plays also an important role during the course of the reaction.



Thus, if differences of chemical shift or DN of solvent are known the possible intermediates in the reaction may, then, be predicted. This appears to be important in the synthesis of organofluorine compounds and throw light on the mechanisms in the reactions of fluoroalkyl iodide with copper.

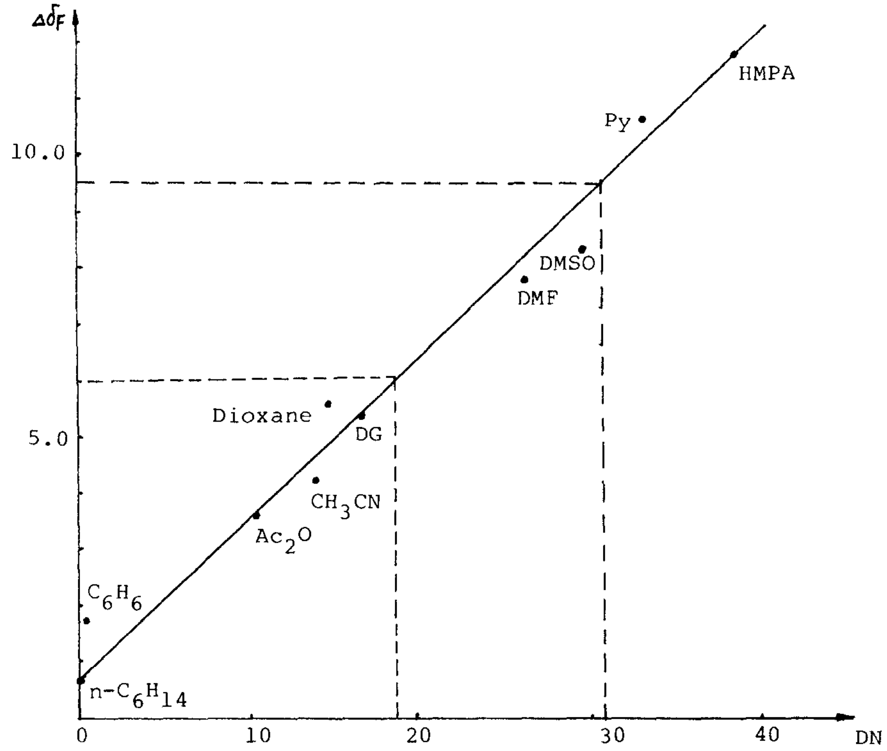


Fig. 1.

Relationship between the differences of chemical shift in $I C\underline{F}_2(CF_2)_3Cl$ complexes and DN of the solvents. $\Delta\delta_F$ in ppm, related to CF_3COOH as external standard. (recorded on EM-360L NMR spectrometer at 60 MHz).

$I(CF_2)_4Cl$: Solvent = 1 : 3 (mol/mol).

TABLE 1

Reaction of 4-chlorooctafluorobutyliodide with copper in the presence of both heptene-1 and iodobenzene[a]

Solvent	DN	t (h)	Conversion (%)	Adduct (%)	Coupling Product(%)
None		6	100	94	0
n-C_6H_{14}	0	12	100	91	0
C_6H_6	0.1	12	100	89	0
Ac_2O	10.5	10	100	83	0
CH_3CN	14.1	10	100	88	0
Diglyme	-	10	100	79	0
Dioxane	14.8	10	100	85	0
DMF	26.6	13	100	61	34
DMSO	29.8	10	94	41	50
Pyridine	33.1	11	100	0	66
HMPA	38.8	16	58	0	86

[a] $Cu : Cl(CF_2)_4I : C_5H_{11}CH{=}CH_2 : C_6H_5I = 4 : 1 : 2 : 2$
The reactions were carried out at 100-110°C

EXPERIMENTAL

A typical procedure is as follows: A mixture of 4-chlorooctafluorobutyliodide(1.8g, 5mmol), 1-heptene(1.0g, 10mmol), iodobenzene(2.0g, 10mmol) and copper(1.0g, 15.6mmol) in DMF (10ml) was stirred at 100°C for 12 h under nitrogen.The mixture was filtered. The solid was washed twice with ether, the combined extracts hydrolyzed with dilute acid. The organic layer was separated,and aqueous layer was extracted twice with ether. The combined extracts were washed with water, dried over anhydride Na_2SO_4 and ether distilled off.Distillation in vacuo gave 0.52g(34%) of 4-chlorooctafluorobutylbenzene and 1.4g(61%) of 1-(4-chlorooctafluorobutyl)-2-iodo-heptane.

REFERENCES

1 H.Zollinger, Angew. Chem., 90 (1978) 151.

2 a V.C.R.Mcloughlin, J.Thrower, Tetrahedron, 25 (1969) 5921;
  b P.L.Coe, N.E.Milner, J. Fluorine Chem., 2 (1972/73) 167;
  c Y.Kabayashi, I.Kumadaki, S.Sato, N.Hara, E.Chikami, Chem. Pharm. Bull., 18 (1970) 2334.

3 Q.Y.Chen, Z.Y.Yang, J. Fluorine Chem., 28 (1985) 399.

4 P. Calas, A.Commeyras, J. Electroanal. Chem., 89 (1979) 363.

5 a Q.Y.Chen, Z.M.Qiu, 'International Symposium on Celebrating centenary of the Isolation of Fluorine', 1986, Paris, p. 75;
  b A.Mishar, A.D.E.Pullin, Aust. J. Chem., 24 (1971) 2493; I.J.Nanght, A.D.E.Pullin, ibid, 27 (1974) 987; ibid, 27 (1974) 973;
  c Q.Y.Chen, Z.M.Qiu, Youji Huaxe, to be published.

6 V.Gutmann, "The Donor-Acceptor Approach to Molecular Interaction ", Plenum Press, New York and London, 1978, p. 19.