CHEMISTRY LETTERS, pp. 1421−1424, 1991.

Fluorination of Chlorinated Trifluoromethyl Ethers

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Chlorine atoms in the chlorinated trifluoromethyl ether prepared from the reaction between chlorinated ethylenes and trifluoromethyl hypofluorite were fluorinated directly by fluorine gas. Tin(II) fluoride/sodium fluoride system was effective in the fluorination.

Chlorofluorocarbons (CFCs) are useful materials for refrigerant, propellants, plastic form blowing agents, aerosol, and so on. But CFCs have caused the depletion of stratospheric ozone layer. So the development of CFCs substitutes is expected to solve this serious problem. Now several types of CFCs substitutes are under consideration. One of the possibilities for future CFCs substitutes is the ether derivatives containing fluorine atom,[1,2] because of the thermal and chemical stability, a high latent heat of vaporization, and so on. On the other hand, it is known that the chlorine atom derived from CFCs and chlorocarbons causes the decomposition of ozone in the stratosphere, consequently, the future CFCs alternatives should be chlorine free. So that development of the substitution reaction of fluorine atom or hydrogen atom for chlorine atom in CFCs alternatives is important to synthesize the better alternatives. Only low yield substitutions of fluorine for chlorine in chlorinated ethers by the Swartz reaction [3] or KF[3] were reported. The fluorinations of alkyl chlorides[4,5] or CFCs[6] by the use of fluorine gas have been known. Recently we have developed the synthetic method of perfluoroethyl methyl ether $\underline{1}$ as refrigerant by the direct fluorination.[2] Herein, we wish to describe a substitution reaction of fluorine for chlorine in chlorinated ether $\underline{2}$ using fluorine gas as shown in Scheme.

$$\underset{X=Cl,H}{CX_2=CXCl} \xrightarrow{CF_3OF\ \underline{3}} \underset{\underline{2}}{CF_3OCX_2CFClX} \xrightarrow{F_2} \underset{\underline{4}\ \ Y=F,Cl}{CF_3OCY_2CFClY} + \underset{\underline{1}}{CF_3OCF_2CF_3}$$

The ethers 2 were prepared by the reaction of chlorinated ethylenes with trifluoromethyl hypofluorite (CF_3OF, 3) in good yields (76 - 86%). The preparation of $CF_3OCHClCFClH$ (2a) and $CF_3OCH_2CFCl_2$ (2b) was carried out in the reported manner[7)] except that no solvent was employed. Addition of the compound 3 to trichloroethylene and tetrachloroethylene also proceeded to obtain $CF_3OCHClCFCl_2$ (2c)[8)] and $CF_3OCCl_2CFCl_2$ (2d),[9)] respectively, in good yields.

A typical procedure of direct fluorination of ether 2 is as follows; The ether 2 (1.0 mmol) and an excess of fluorine were introduced into the stainless steel reactor containing metal fluoride at -194 °C using vacuum line system. The reactor was then placed in cold bath (-111 °C) and allowed to warm up to ambient temperature (20 °C) for 20 h, and then heated at 100 °C for 6 h. After removal of unreacted fluorine, the reaction mixture was fractionated through traps at temperature low enough to trap the products 4 and 1. The mixture of ethers 4 and 1 was isolated in -150 °C trap. The structures of 4 and 1 were determined by ^{19}F-NMR, IR spectra, and molecular weight in usual manner.[2)] The yields of 4,[7,10)] and 1[2)] were determined by ^{19}F-NMR. The results of direct fluorination of 2 are listed in Table 1.

The direct fluorination of 2a proceeded smoothly without addition of metal fluoride to obtain 4a in 83% yield in the case of using 2.2 molar ratio of fluorine. In this reaction, by-product 4b which was yielded by substitution of fluorine for α-chlorine in product 4a was obtained in 11% yield. This result indicates that fluorine was effective in substitution of fluorine atom for chlorine atom in halogenated ethers. Then fluorine-substitution for chlorine in 2a was examined using 3.3 molar ratio of fluorine. First, sodium fluoride was placed in the reactor to remove hydrogen fluoride which was formed by fluorine-substitution for the hydrogen atom in 2a. In this reaction, the sodium fluoride was also effective in fluorine-substitution for α-chlorine atom in 2a to obtain 4b in higher yield (53%) than that (28%) of the reaction without sodium fluoride. So next, various metal fluoride (KF, PbF_2, CoF_3, SbF_3, SnF_2)/NaF system was examined to see the effects on the fluorination.

The results, as shown in Table 1, indicate that SnF_2/NaF system was most effective in fluorine-substitution for chlorine using fluorine gas and afforded 4b and 1 in better yield than the other metal fluoride. In this system, NaF is necessary to obtain the fluorinated compounds 4b and 1. If the reaction was carried out with only SnF_2 as metal fluoride in the reactor, the reaction mixture contained many decomposed products (CF_4 etc.) without the formation of 4a, 4b, and 1. Furthermore, the effect of the amount of SnF_2 was investigated by the reaction of 2a (1.0 mmol) with

Table 1. The direct fluorination of the ether 2

Reaction conditions[a]			Products[b] (Yield/%[c])						
Sub.2 (1 mmol)	F_2 (mmol)	MF_n (mmol)	Recov. 2	4a	4b	4c	4d	4e	1
2a[d]	2.2	-	42	30	0	-	-	-	0
2a	2.2	-	9	75	11	-	-	-	0
2a[e]	2.2	-	0	83	11	-	-	-	0
2a	3.3	-	9	29	53	-	-	-	0
2a[e]	3.3	-	0	57	28	-	-	-	0
2a	4.4	-	0	23	69	-	-	-	0
2a	6.0	-	0	23	57	-	-	-	8
2a	3.3	KF (1.0)	0	50	41	-	-	-	0
2a	3.3	PbF_2(1.0)	6	44	37	-	-	-	5
2a	3.3	CoF_3(1.0)	18	5	27	-	-	-	11
2a	3.3	SbF_3(1.0)	13	23	50	-	-	-	0
2a	3.3	SnF_2(1.0)	11	9	54	-	-	-	9
2a	3.3	SnF_2(0.1)	6	27	54	-	-	-	0
2a	3.3	SnF_2(0.2)	0	26	61	-	-	-	4
2a	3.3	SnF_2(0.35)	0	4	74	-	-	-	8
2a	3.3	SnF_2(0.5)	10	8	53	-	-	-	12
2a[e]	3.3	SnF_2(0.35)		dec. (CF_4, etc.)					
2a	-[f]	SnF_2(2.0)	97	0	0	-	-	-	0
2a	4.4	SnF_2(0.35)	0	0	60	-	-	-	22
2a	6.0	SnF_2(0.35)	0	0	51	-	-	-	34
2b	3.3	SnF_2(0.35)	0	-	66	7	-	-	12
2b	6.0	SnF_2(0.35)	0	-	72	0	-	-	22
2c	3.3	SnF_2(0.35)	0	5	43	26	9	-	0
2c	6.0	SnF_2(0.35)	0	10	53	10	0	-	0
2d	4.4	SnF_2(0.35)	0	19	38	16	9	12	0
2d	6.0	SnF_2(0.35)	0	10	48	14	0	0	0

a) Reaction conditions; NaF(10 mmol), -111 to 20 °C(20 h) and 100 °C (6 h).

b) 4a: $CF_3OCFClCF_2Cl$; 4b: $CF_3OCF_2CF_2Cl$; 4c: $CF_3OCF_2CFCl_2$; 4d: $CF_3OCFClCFCl_2$; 4e: $CF_3OCCl_2CF_2Cl$; 1: $CF_3OCF_2CF_3$.

c) Yield was determined by ^{19}F-NMR.

d) Reaction temperature; -111 to 20 °C(20 h).

e) No NaF was employed.

f) No fluorine was employed.

fluorine (3.3 mmol) in the presence of NaF using various amount (0 to 1.0 mmol) of SnF_2, and the results, as shown in Table 1, indicate that 4b was obtained in the highest yield when 0.35 mmol of SnF_2 was employed.

From the analysis of the used metal fluoride (mixture of SnF_2 and NaF) after the fluorination, chloride ion was not detected.11) And without fluorine gas, no fluorination of 2a by SnF_2 proceeded. These results suggested that SnF_2 worked as a catalyst in this fluorination. It is assumed that SnF_2 interacted with the chlorine atom as a Lewis acid and promoted the fluorine-substitution for the chlorine atom.

The fluorination of several ethers containing chlorine atoms 2b-d was carried out using SnF_2 (0.35 mmol) and NaF (10 mmol) on similar reaction condition. The fluorine-substitution for chlorine atoms proceeded smoothly to obtain the products 4 and 1 in good yields, as shown in Table 1. In all cases, 4b was obtained as the major product, and perfluoroether 1 was the minor product or was not obtained. According to this result, the fluorine-substitution for chlorine atom of 4b is difficult to proceed, which indicates that the reactivity of the chlorine atom at $-CF_2Cl$ group is much lower than that at -CFCl-, $-CCl_2-$, or $-CFCl_2$ group.

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(Received May 28, 1991)