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Synthesis of Perfluoroethylmethylether by Direct Fluorination

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The direct fluorination of trifluoromethylethers prepared from ethylene or fluorinated ethylenes with trifluoromethyl hypofluorite proceeded in excellent yield to obtain perfluoroethylmethylethers.

Chlorofluorocarbons (CFCs) are useful materials for refrigerant, electronics solvent, flexible and rigid foam, aerosol, and so on. But CFCs have caused the depletion of ozone layer and the global warming effect. So the development of CFCs alternatives has seriously expected. To find out the substitute of CFCs, it is necessary to synthesize the compound which is expected as alternatives and to analyze the environmental effects of this compound before using. New several types of CFCs substitutes are under consideration. One of the possibilities for future CFCs alternatives is the chlorine free polyfluoroethers,1) because polyfluoroethers possess better lipophilic property than polyfluorocarbons by the reason of containing oxygen atom and fluorine containing compounds have the excellent vaporization properties in general. For example, it was reported that perfluoroethylmethylether 1 has a high latent heat of vaporization and a low ratio of compression,2) and has been expected to be a useful refrigerant. However, low yield syntheses of ether 1 were only known. For example, ether 1 was prepared by the electrochemical fluorination of ethylene glycol ether3) or p-dioxan4) in low yield (less than 1%). Herein, we wish to describe a novel synthetic method of perfluoroethylmethylether 1 and some hydrofluoroethers 2 as following scheme.

$$\underset{(X\ =\ H,\ F)}{X_2C{=}CX_2} \xrightarrow{CF_3OF} \underset{\underline{2}}{CF_3OCX_2CX_2F} \xrightarrow{F_2} \underset{\underline{1}}{CF_3OCF_2CF_3}$$

Hydrofluoroethers 2 were prepared in good yield (75 - 84%) by the reaction between ethylene or fluorinated ethylenes and trifluoromethyl hypofluorite 3. Results are shown in Table 1. Trifluoromethyl 2-fluoroethyl ether 2a was previously prepared by the UV irradiation of ethylene with 3. Also it was noticed that an explosion was observed if the reaction was carried out without irradiation.[5] In this case, the reaction was carried out in lower temperature (from -111 to 20 °C) and 2a was obtained in 83% yield without an explosion. The compounds 2b, 2c (as a mixture of 2b and 2c; 9 : 1) and 2d were prepared in good yields in the reported manner[6] except that no solvent was employed. The mixture of 2e and 2f was previously prepared with the formation of other six types of by-products by electrochemical fluorination of methyl 2-methoxypropionate in low yield.[7] Table 1 shows that the mixture of 2e and 2f (2 : 1) was obtained in 75% yield by the addition of 3 to trifluoroethylene.

Table 1. Preparation[a] of Trifluoromethylethers

Olefin	Product	2	Yield/%
$CH_2=CH_2$	$CF_3OCH_2CH_2F$	2a	83
$CH_2=CHF$	$CF_3OCH_2CHF_2$	2b	84 (2b/2c=9/1)
	$CF_3OCHFCH_2F$	2c	
$CH_2=CF_2$	$CF_3OCH_2CF_3$	2d	83
$CHF=CF_2$	$CF_3OCHFCF_3$	2e	75 (2e/2f=2/1)
	$CF_3OCF_2CF_2H$	2f	

a) Reaction conditions; Olefin (5 mmol), CF_3OF (5 mmol), at -111 to 20 °C for 20 h.

A typical procedure of direct fluorination of 2 is as follows; Sodium fluoride was placed into the reactor made by stainless steel or poly(chlorotrifluoroethylene). The ether 2 (1 mmol) and a slightly excess of fluorine were introduced into the reactor at -194 °C using vacuum line system. The reactor was then placed in cold bath (-111 °C) and allowed to warm up slowly to ambient temperature (20 °C) for 20 h. The mixture was cooled to -194 °C, and excess fluorine was pumped out. Then the reaction mixture was fractionated through traps at temperature low enough to trap the product 1. In the -150 °C trap, 1 was isolated. The structure of 1 was determined by ^{19}F-NMR,[8] IR spectra, and molecular weight in usual manner.[9] The results of direct fluorination of 2 are listed in Table 2.

In this reaction, sodium fluoride (10 mmol) was placed in the reactor to remove hydrogen fluoride which was formed in the reaction mixture. And 1 was prepared from 2d in excellent yield (94%). If large amount of sodium fluoride (20 mmol) was added to the reactor, fluorination of 2d proceeded slowly and it took long time to get 1 in high yield. However, without addition of sodium fluoride the direct fluorination smoothly occurred to obtain 1 in 93% yield.

Table 2. The direct fluorination of hydrofluoroethers 2

Substrate, 2	F_2	NaF	Reaction condition		Yielda)/%
(1 mmol)	(mmol)	(mmol)	Temp/ °C,	Time/h	1
2d	2.2	-	-111 — 20	20	93
2d	2.2	10	-111 — 20	20	94
2d	2.2b)	10	-111 — 20	20	57c)
2d	2.2	10	-60 — -50	8	0d)
2d	2.2	10	-35 — -30	24	25e,f)
2d	2.2	20	-111 — 20	20	27e,g)
2d	2.2	20	(-111 — 20	20	93
			20	24	
2a	5.5	10	(-111 — 20	20	85
			20	50	
2b/2c(=9/1)	4.5	10	(-111 — 20	20	90
			20	28	
2e/2f(=2/1)	1.1	10	-111 — 20	20	94

a) Isolated yield.
b) Diluted F_2 (F_2/N_2 = 3/2) was employed.
c) By-product 2e was also obtained in 33% yield.
d) Substrate 2d was recovered quantitatively.
e) Yield was determined by ^{19}F-NMR.
f) The reaction mixture contained 2d (24%) and 2e (50%) with 1.
g) By-product 2e was also obtained in 69% yield.

The fluorination of 2d with fluorine gradually occurred at around -35 °C. Because the substrate 2d was recovered quantitatively at -50 °C, and the fluorinated product 1 was obtained in 25% yield at -35 to -30 °C.

Diluted fluorine (F_2/N_2 = 3/2) instead of pure fluorine gas also worked well to the fluorination of 2d. The reaction rate reduced but the perfluorinated product 1 (57% yield) and the partially fluorinated 2e (33% yield) were obtained from the mixture of 2d and diluted fluorine.

Table 2 also indicates that the reaction of hydrofluoroethers 2a, 2b/2c, and 2e/2f with fluorine proceeded smoothly and perfluoroether 1 was obtained in high yield (85 - 94%). The yield of 1 was reduced from 94% to 85%, when the number of hydrogen atom in the starting materials 2 increased from 1 to 4. Probably the substrates which have more hydrogen atoms were easily decomposed by fluorine, and decomposition compounds, carbonyl difluoride and tetrafluoromethane were detected by IR spectra.

In the direct fluorination of 2d at lower temperature (-30 °C), by-product, 2e, which was fluorinated only one hydrogen atom was obtained in 50% yield (see Table 2). It suggests that the first hydrogen atom at α-position is fluorinated faster than second one at same position.

The comparison of the reactivity between α- and β-hydrogen atoms in 2b (containing three hydrogen atoms) was analyzed by the reaction of 2b (1 mmol) with fluorine (1.2 mmol) in the presence of sodium fluoride (10 mmol). The products 2d, $CF_3OCHFCHF_2$ (2g), 2e, 2f, and 1 were obtained in the yield of 12, 10, 33, 2, and 6%, respectively, with recovery of 2b (37%). According to the calculation of fluorinated percentage of first one hydrogen atom at α- and β-position in substrate (2b $CF_3OCH^aHCH^bF_2$), 51% of H^a (2e, 2g, 2f, and 1) and 51% of H^b (2d, 2e, and 1) were fluorinated in this reaction condition. There are two hydrogen atoms which could react with fluorine in H^a position, so that same fluorinated percentage of H^a and H^b indicates that H^b hydrogen atom in 2b reacts twice faster than H^a position.

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