

## A-7.1.1 Basic Research for the Preparation of Chlorofluorocarbon Alternatives

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**Total Budget for FY1990 - FY1992** 51,168,000 Yen

### Abstract

Since it was found that chlorofluorocarbons (CFCs) currently in use destroy the ozone layer in the stratosphere, and tend to produce a global warming effect, it was decided to abolish them totally by the beginning of 1996. Consequently, in order to solve the CFCs problem, it has become most important to develop pollution-free CFCs alternatives.

To obtain the basic knowledge of new CFCs' alternatives, several new synthetic reactions were achieved. It means that synthesis of hydrochlorofluorocarbon (HCFC-253ca) from allene, new selective monofluorination of hydrofluorocarbon (HFC), synthesis of fluorine containing ether derivatives (HFES) by fluorination of ether derivatives using fluorine gas or high valent metal fluoride as fluorination reagent, preparation of trifluoromethyl ether by addition of trifluoromethyl hypofluorite to ethylene derivatives, and so on.

The synthesized compounds were analyzed on some physical properties and environmental effect.

**Key Words** Synthesis, Fluorine, CFC, Alternatives

### 1. Introduction

The legislated chlorofluorocarbons<sup>1,2)</sup> (CFC-11, 12, 113, 114, 115) are used in various area of our life as refrigerant, foam blowing agent, solvent, aerosol, and so on, so that these CFCs are very important materials to our life. But these CFCs cause the depletion of the stratospheric ozone layer. The ozone layer protects lives on the earth from harmful ultraviolet irradiation and keeps the temperature of the stratosphere, consequently, the depletion of the ozone layer would have serious influence on the life system and the climate. Now the world is going toward the abolish of CFCs and the development of non-pollution CFCs' alternatives is most important subject to maintain the present society.

### 2. Research Object

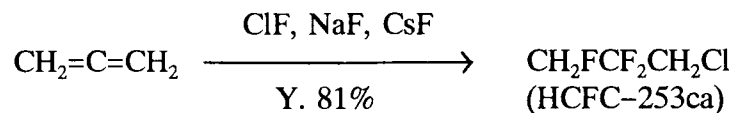
In order to search for the CFCs' alternatives, various possible compounds as the alternatives are extracted, and these candidates should be synthesized to analyze the basic physical properties. In this point, this study aims to get basic knowledge of CFCs' alternatives by developing the several new synthetic methods of hydrochlorofluorocarbon (HCFC), hydrofluorocarbon (HFC), and fluorine containing ether derivatives (HFES) and also analyzing the physical properties of these candidates.

### 3. Results and Discussion

#### 3.(1). Investigation of synthetic method of candidate compounds.

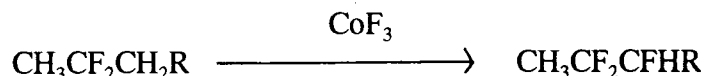
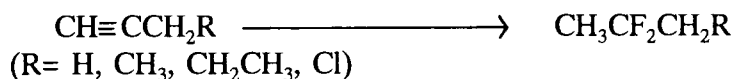
##### 3.(1).A. Synthesis of HCFC

HCFCs are one of the possible CFCs alternative because of similar physical properties as CFCs and less environmental effects compared with CFCs. We decided to use allene which is reactive and industrially available compound as starting material. And high yield preparation of 1-chloro-2,2,3-trifluoropropane (HCFC-253ca) was achieved by the reaction between allene and ClF in the presence of CsF.

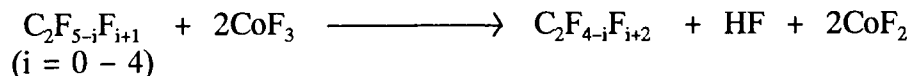


##### 3.(1).B. Synthesis of HFCs

HFCs have no ozone depletion effects and are the most possible CFCs' alternative. In this work, fluorination of HFCs containing gem-difluoromethylene group using cobalt trifluoride ( $\text{CoF}_3$ ) was attempted as the synthetic method of HFCs, and regioselective fluorination at the methylene group neighboring gem-difluoroethylene group was achieved.



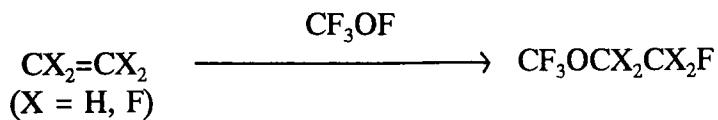
The fluorination of HFCs derived from ethane using  $\text{CoF}_3$  was investigated and the reaction condition of monofluorination was revealed.



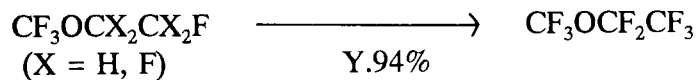
##### 3.(1).C. Synthesis of HFEs

HFEs are expected as the third generation CFCs' alternatives. Here, several new reactions were investigated.

Ethylmethylethers containing fluorine and hydrogen were prepared from ethylene or fluorinated ethylenes with trifluoromethyl hypofluorite.

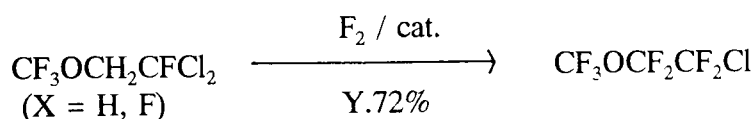
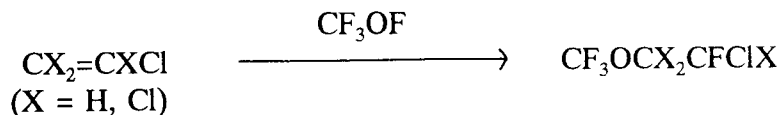


These ethylmethylethers in above scheme were reacted with fluorine gas, and the high yield synthetic method of perfluoroethylmethylether was achieved.

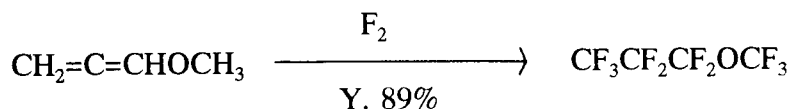


Previously, only low yield syntheses of perfluoroethylmethylether were known. And it was reported that perfluoroethylmethylether has a high latent heat of vaporization and a low ratio of compression.

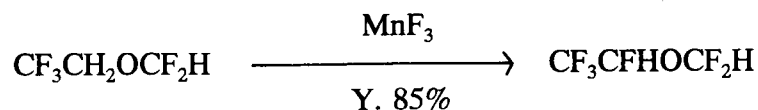
It is known that the compounds containing chlorine atom cause the depletion of ozone layer by decomposition in the stratosphere. Consequently, the conversion reaction of chlorine atom into other atom is important from the viewpoint of preserving the environment. Thus, the conversion reaction of chlorine atom into fluorine atom was investigated, with the result that chlorine atom could be converted into fluorine atom by direct fluorination using fluorine gas. The ethers containing chlorine atom were prepared by the reaction between chlorine-containing ethylenes and trifluoromethylhypofluorite, and chlorine atom in these chlorine-containing ethers was converted into fluorine atom by direct fluorination as follows;



The synthesis of fluorine-containing ether derivatives was carried out by other two methods. One is the direct fluorination of methoxyallene yielding perfluoroether in good yield.



The other is the selective monofluorination of ether derivatives using high valent metal fluoride as fluorination reagent.



### 3.(2). Thermal stability of candidates

The synthesized fluorine-containing candidate was heated in a closed system and the relation between pressure and temperature was measured. The decomposition point was determined from this relation and the thermal stability of these compounds were investigated. It was indicated that the stability more than 300 °C was observed in the case of some fluorinated ethers.

### 3.(3). Measurement of infrared (IR) spectra of candidates

The IR spectra of synthesized fluorine-containing candidates were measured. The absorption energy based on blackbody emission at 290 K as approximation of the emission from the earth were calculated from the IR spectra, and the value was corrected by absorption spectra of atmosphere. Then IR absorption energy of these compounds were investigated in Table 1.

Table 1. Comparison of the Amount of Infrared Absorption Energy of Fluorinated ethers

	Infrared Absorption	
	(/Weight)	(/Mole)
CFCl <sub>3</sub>	1.00	1.00
CF <sub>3</sub> OCF <sub>2</sub> CF <sub>3</sub>	1.08	1.61
CF <sub>3</sub> OCH <sub>2</sub> CF <sub>3</sub>	1.08	1.32
CF <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub> F	1.45	1.39

### Reference

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