

A New Preparative Method for 1-Chloro-2,2,3-trifluoropropane (HCFC-253ca)

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Allene was both fluorinated and chlorofluorinated with chlorine monofluoride serving as a well-known chlorofluorinating and chlorinating reagent. 1-Chloro-2,2,3-trifluoropropane was obtained as a major product in the presence of cesium fluoride.

Recently, chlorofluorinated propanes as well as ethanes have been focused as chlorofluorocarbons (CFCs) alternatives. An object of our study is to synthesize the CFCs alternatives based on cumulene series by the use of various fluorinating reagents. Chlorine monofluoride (ClF) is a useful reagent, acting as a chlorofluorinating reagent as well as a chlorinating reagent toward olefin and alkyne derivatives.¹⁾ However, there is no information on the chemical behavior of the cumulene series with ClF. In this paper we report a new finding that ClF serves as a fluorinating reagent to allene in the presence of cesium fluoride (CsF).

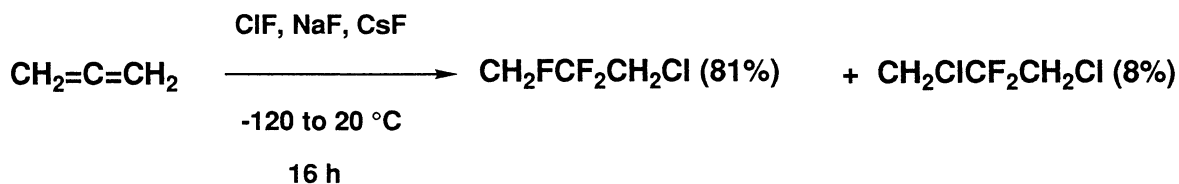
Typical results of the reaction of allene with ClF are summarized in Table 1. The reaction conditions²⁾ and the products are given for each reaction. Some of the products were identified from mixtures by ¹⁹F-NMR and ¹H-NMR spectral data. Yields were determined by ¹⁹F-NMR (CFCl₃ was used as an internal standard). As shown in entry 1 of Table 1, treatment of allene (1 mmol) with ClF (2.2 mmol) afforded a mixture consisting of 1,3-dichloro-2,2-difluoropropane[HCFC-252ca] (25%), 1-chloro-2,2,3-trifluoropropane[HCFC-253ca] (8%), 1-chloro-2,2-difluoropropane (13%), and 2,2-difluoropropane (10%), 2-chloro-2-fluoropropane (6%) with recovery of allene (10%). In contrast, when the reaction was carried out in the presence of sodium fluoride (NaF) to trap the generated hydrogen fluoride (entry 2), allene was both fluorinated and chlorofluorinated. Generally, it is well known that ClF reacts via an ionic mechanism.^{1a)} In addition, CsF is required to catalyze the ionic reaction to generate a naked fluoride ion.³⁾ In the next step, we examined the effect of CsF in the reaction of ClF. Treatment of allene with ClF in the presence of CsF and NaF afforded HCFC-253ca (31%), HCFC-252ca (5%), and unreacted allene (45%) (entry 3). This is because most of ClF form Cs⁺ClF₂⁻ (CsF + ClF) at -10 °C. When the reaction temperature was raised to 20 °C

(entry 4), HCFC-253ca was obtained as a major product in 81% yield. Furthermore, HCFC-253ca was obtained in 82% yield in the presence of only CsF. However, none of the fluorinated products were formed in the case of other unsaturated compounds by ClF. For example, four unsaturated compounds (fluoroethene, chloroethene, propene, propyne) were tested as a reactant for ClF under the similar condition as entry 4. We found that all reactants react with ClF to give the chlorofluorinated products (major) and the chlorinated products (minor) even in the presence of CsF (and/or NaF). A mechanism for the formation of HCFC-253ca from allene is not clear. Attack of nascent fluorine from $\text{Cs}^+\text{ClF}_2^-$ would occur to allene.

Table 1. Reaction of Allene with $\text{ClF}^{\text{a)}$

Entry	Allene (mmol)	ClF (mmol)	Products (Yield/%) ^{b)}
1	1	2.2	allene(10), $\text{CH}_2\text{ClCF}_2\text{CH}_2\text{Cl}$ (25), $\text{CH}_2\text{FCF}_2\text{CH}_2\text{Cl}$ (8), $\text{CH}_2\text{ClCF}_2\text{CH}_3$ (13), $\text{CH}_3\text{CF}_2\text{CH}_3$ (10), $\text{CH}_3\text{CFClCH}_3$ (6)
2 ^{c)}	1	7	$\text{CH}_2\text{ClCF}_2\text{CH}_2\text{Cl}$ (72), $\text{CH}_2\text{FCF}_2\text{CH}_2\text{Cl}$ (10)
3 ^{d)}	1	7	allene(45), $\text{CH}_2\text{ClCF}_2\text{CH}_2\text{Cl}$ (5), $\text{CH}_2\text{FCF}_2\text{CH}_2\text{Cl}$ (31)
4 ^{d,e)}	1	7	$\text{CH}_2\text{ClCF}_2\text{CH}_2\text{Cl}$ (8), $\text{CH}_2\text{FCF}_2\text{CH}_2\text{Cl}$ (81)

a) Conditions: -120 to -10 °C, 12 h. b) Yields of products listed were based on the allene. c) Reaction in the presence of NaF (300 mg). d) Reaction in the presence of NaF (300 mg) and CsF (1.2 g). e) Conditions: -120 to 20 °C, 16 h.



In conclusion, this paper has shown for the first time that treatment of allene with ClF in the presence of CsF affords HCFC-253ca in good yield. We have examined the possibility, HCFC-253ca serves as CFCs alternatives. Further work on the fluorination of cumulene series as well as the application of the fluorinated cumulene for CFCs alternatives is currently continued in our laboratory.

References

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