

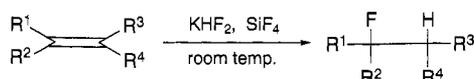
Hydrofluorination of Unsaturated Compounds with Solid Potassium Hydrogen Fluoride in the Presence of Silicon Tetrafluoride at Room Temperature

Masanori Tamura,* Motonari Shibakami, Shigeru Kurosawa, Takashi Arimura and Akira Sekiya*

National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, Ibaraki 305, Japan

Hydrofluorination of unsaturated compounds proceeds by reaction with solid potassium hydrogen fluoride and silicon tetrafluoride to afford the corresponding fluorides in high yields.

Hydrofluorination is a fundamental reaction in the synthesis of organofluorine compounds.¹ The addition of anhydrous hydrogen fluoride may be used but anhydrous hydrogen fluoride is a very hazardous reagent, and moreover the reaction must be carried out at low temperatures (−78 to 0 °C) to minimize the undesirable side reactions of rearrangement and polymerization of the substrate.^{1,2} Amine–hydrogen fluoride reagents, such as pyridine–hydrogen fluoride and melamine–hydrogen fluoride, have been investigated as alternative reagents to overcome these difficulties.^{2–4} However, these reagents are corrosive although, less so than anhydrous hydrogen fluoride itself, and a large amount of these reagents was used as the solvent. Recently, we have investigated the use of potassium fluoride–hydrogen fluoride salts for fluorinations.^{5,6} We now report new synthetic



Scheme 1

Table 1 Hydrofluorination of cyclohexene with MHF₂ and SiF₄^a

MHF ₂	Amount ^b of MHF ₂ /mmol	Amount ^b of SiF ₄ /mmol	Yield ^c of fluoro-cyclohexane (%)	Recovery of substrate (%)
KHF ₂	3	0	0	100
KHF ₂	2	2	67	15
KHF ₂	3	2	79 (73) ^d	7
KHF ₂	3	3	74	5
KHF ₂	4	2	79	2
NaHF ₂	3	2	33	57
NH ₄ HF ₂	3	2	74	12

^a The reaction was carried out at room temp. for 16 h. ^b Amount of the reagent relative to 1 mmol of cyclohexene. ^c Yield was determined by ¹⁹F NMR (C₆H₅CF₃ was used as internal standard). ^d Isolated yield.

Table 2 Hydrofluorination of unsaturated compounds with MHF₂ and SiF₄^a

Substrate	Product	Yield ^b (%)
		51 ^{c,d}
		73 ^e
		91 ^f
CH ₃ C≡CCH ₃	CH ₃ CF ₂ CH ₂ CH ₃	61
		95

^a The reaction was carried out at room temp. for 16 h. ^b Isolated yield. ^c 6 mmol of KHF₂ and 4 mmol of SiF₄ relative to 1 mmol of propene were used. ^d 47% of substrate was recovered. ^e 7% of substrate was recovered. ^f 9% of substrate was recovered.

methods for hydrofluorination using potassium hydrogen fluoride (KHF₂) and silicon tetrafluoride (SiF₄) as shown in Scheme 1.

Results for attempted hydrofluorination of cyclohexene using hydrogen fluoride salts are summarized in Table 1. Hydrofluorination did not proceed at all with only KHF₂, but the reaction proceeded in the presence of SiF₄, and fluoro-cyclohexane was obtained in 79% yield by the reaction of 1 mmol of cyclohexene with 3 mmol of KHF₂ and 2 mmol of SiF₄ at room temperature. Other alkali metal hydrogen fluorides, NaHF₂ and NH₄HF₂, were also effective, but, KHF₂ gave better results.

Results for the hydrofluorination of various unsaturated compounds, such as alkenes, alkynes and cyclopropane, with KHF₂ and SiF₄ are summarized in Table 2. The reaction was successful at room temperature and the corresponding fluorides were obtained in good to excellent yield. In the case of propene, the yield was fair but most of the unreacted substrate was recovered; *i.e.*, undesirable side reactions did not occur.

Concerning the mechanism of this reaction, the generation of hydrogen fluoride (HF) was observed from the reaction between KHF₂ and SiF₄ under the same condition as the hydrofluorination, but this hydrofluorination is not assumed to proceed by the reaction between substrates and HF because undesirable side reactions are suppressed even at room temperature.[†] Although the mechanism has not been elucidated in detail, it is assumed that the hydrofluorination may occur on the surface of the solid potassium salt. Possibly, some acidic centres, such as silicate-like species 'HKF₂-SiF₄' or 'HF-SiF₄' *etc.*, which can protonate an adsorbed unsaturated compound, may be formed on the surface of KHF₂ by the reaction with SiF₄ before HF is released into vapour phase. The carbocation formed may react with fluoride ion immediately on the surface to give the HF adduct.[‡] It is assumed that the carbocation will react with a fluoride ion much faster than with another organic molecule because of the low concentration of unsaturated compound adsorbed on the surface, with the result that side reactions are suppressed.

A typical experimental procedure is as follows. KHF₂ (6 mmol) was placed in a stainless-steel reactor equipped with a stop valve. The substrate (2 mmol) and SiF₄ (4 mmol) were introduced into the reactor at −196 °C from a vacuum line. The reactor was allowed to warm to ambient temperature and shaken vigorously for 16 h. Unreacted SiF₄ was removed from the reaction mixture by treatment with sodium fluoride, and the crude product was purified by trap-to-trap distillation.⁸

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Footnotes

[†] The addition of HF to unsaturated compounds at room temp. would be accompanied by formation of considerable amounts of by-products even if HF is released slowly from KHF₂ and SiF₄. For example, when the reaction between cyclohexene and anhydrous hydrogen fluoride (0.3 mmol relative to 1 mmol of cyclohexene) was carried out at room temperature for 16 h, the yield of fluorocyclohexane based on cyclohexene reacted, namely, the selectivity of hydrofluorination, was 58% (recovery of cyclohexene was

82%). On the other hand, the selectivity was 85% in reaction of cyclohexene with KHF_2 and SiF_4 .

‡ A similar mechanism was suggested in the ring-opening of epoxides with KHF_2 and AlF_3 .⁷

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