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The monofluorination of hydrofluorocarbons over cobalt trifluoride

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Abstract

Hydrofluorocarbons (HFCs) have been fluorinated via the high-valency metal fluorides CoF_3, MnF_3 and $KCoF_4$. The fluorinating powers of these reagents for the monofluorination of 2,2-difluoropropane are in the order $CoF_3 > MnF_3 > KCoF_4$. The fluorinations of fluorinated ethanes with CoF_3 have been examined in detail. The effects of temperature and the distribution of products are described. Furthermore, regioselective monofluorination of *gem*-difluoro compounds (C_3–C_5) with CoF_3 was achieved at the methylene position adjacent to the *gem*-difluoro group. The trifluoro compounds were obtained in good yield at low reaction temperatures.

Introduction

The legislated chlorofluorocarbons (CFCs) are used for a wide range of applications such as refrigerants, aerosol propellants, blowing agents and cleaning agents. Hence these CFCs are very important materials [1], but when released to the atmosphere they can cause the depletion of the stratospheric ozone layer and lead to global warming [2]. The development of alternative CFCs which cause no pollution is thus a most important subject. Among the possibilities for alternative CFCs are aliphatic hydrofluorocarbons (HFCs) [3]. Because aliphatic HFCs possess no chlorine, the ozone depletion potential is zero and, in addition, their physical and chemical properties are close to those of CFCs [4].

The high-valency metal fluorides (CoF_3, MnF_3, $KCoF_4$, etc.) have been used as important fluorinating agents, particularly for the exhaustive fluorination of organic compounds via the Fowler process [5]. Tatlow and coworkers have investigated their use extensively for the fluorination of alkanes [6–10], cycloalkanes [11, 12], aromatic compounds [13, 14] and others [15, 16]. In most cases, these reactions were carried out at high temperature, and monofluorination, which is useful for preparing aliphatic HFCs, was not

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achieved because of the small differences between the reactivities of the C—H bonds in hydrocarbons. The well-studied cases of partial fluorination are those of ethane [6], propane [7], 2-methylpropane [8] and butane [9]: the distribution of hydrogens in the partially fluorinated products was almost random in the first two cases, and in the last two gave a mixture of at least 30 or 51 components. In addition, extensive skeletal rearrangements occurred during the fluorination of saturated aliphatics: for example, octane over CoF_3 gave only about 50% of straight-chain perfluoro-octane, the rest being perfluorinated branched-chain C_8 isomers or C_8 cyclic compounds [10]. It is well known that if some fluorine is already present in the organic substrate, undesirable side-reactions are much reduced. In this paper, we describe monofluorination, by the use of various metal fluorides such as CoF_3, $KCoF_4$ and MnF_3, of HFCs with 2–5 carbon atoms. The content of this article has been published partially previously [17].

Experimental

General

All volatile compounds were handled in glass and stainless-steel vacuum systems similar to those described previously [18]. Pressures in the glass system were measured with a MKS Baratron® absolute pressure gauge (type 122A) and transformed with power supply/digital readout (model PDR-C-2C). The differential pressure was measured by means of a differential pressure gauge (type 127A) in the metal system. Amounts of the volatile products were determined by PVT measurements. Temperatures were measured with a copper–constantan thermocouple associated with an Advantest digital multi-thermometer (model TR2114). ^1H and ^{19}F NMR spectra (chemical shifts in ppm from an internal reference) were recorded at 22 °C on JEOL GX-500 (500 MHz) and Hitachi R-1200F (56.47 MHz) spectrometers with $(CH_3)_4Si$ and $CFCl_3$, respectively, as reference compounds in $CDCl_3$ (as solvent). Spectral data for all compounds were cited in the literature [19–22] except 2,2,3-trifluoropentane (**12a**). GC–MS analyses were performed on a JEOL JMS-DX 300 instrument (EI = 70 eV, capillary column with PEG 20M).

Reagents

All reagents were obtained from commercial sources. Fluorine (Takachiho Co.) was used after passing through an NaF scrubber. Sodium fluoride was purchased from Nakarai Co. Metal fluorides (CoF_3, $KCoF_4$ and MnF_3) were purchased from Hashimioto Kasei Co. The *gem*-difluoro compounds **11–13** were prepared from hydrogen fluoride and the corresponding acetylenes according to literature methods [23]. The products were distilled *in vacuo*, and the major ones (**11a–13a**) were obtained in 85 to 40% yield (purity 99%). 1,1,1,2-Tetrafluoroethane (**7**) was a gift from the Du Pont–Mitsui Fluorochemicals Co., and other HFCs were obtained to PCR guaranteed grade. Solids were dried under vacuum and liquids were distilled under vacuum before use.

TABLE 1

Fluorination of 1,1-difluoropropane (**1a**) over CoF_3, MnF_3 and $KCoF_4$

Metal fluoride	Temp. (°C)	Time (h)	Recovery (%)	Product yield[a] (%)		
				1b	**1c**	**1d**
CoF_3	0	300	0	89	9	2
CoF_3	25	6	40	51	4	5
CoF_3	100	6	0	73	6	20
MnF_3	25	6	90	10	0	0
MnF_3	50	6	71	27	0	2
MnF_3	100	6	37	58	0	5
$KCoF_4$	25	6	100	0	0	0
$KCoF_4$	100	6	100	0	0	0

1a: $CH_3CF_2CH_3$; **1b**: $CFH_2CF_2CH_3$; **1c**: $CF_3CH_2CH_3$; **1d**: $CFH_2CF_2CFH_2$.

[a] Yields and recovery of **1a** were determined by means of ^{19}F NMR spectroscopic methods.

General procedure for the fluorination of hydrofluorocarbons over metal fluoride

A typical procedure for the fluorination of HFCs [eqns. (1)–(3)] is as follows. The metal fluoride (200 mmol) was placed in a batchwise reactor. The reactor was constructed from a stainless-steel cylinder (Hoke, 4HS150) and a stop valve (Nupro, SS-4JB) [17]. The reactant (3 mmol) was introduced into the reactor at −196 °C using a vacuum line system. The reactor was allowed to warm up slowly to ambient temperature (20 °C) for 1.5 h, then heated at the temperature and for the time indicated in Table 1. It was then cooled to −196 °C and the volatile products were pumped out. Hydrogen fluoride was removed from the crude mixture by means of dried sodium fluoride (0.2 g). The products were determined by ^{19}F NMR, ^{1}H NMR and GC–MS analyses. The yields of the products and recoveries of reactants were identified by ^{19}F NMR spectroscopy ($CFCl_3$ being used as an internal standard).

The spent metal fluoride was subsequently regenerated at 200–250 °C by contact with elementary fluorine prior to the next fluorination reaction.

Results and discussion

Comparison of the monofluorinating powers of reagents

First, we examined the reactivity of fluorination among the various metal fluorides studied. The fluorinations of 2,2-difluoropropane (**1a**) over various metal fluorides are summarized in Table 1. The reactions proceed according to eqn. (1):

$$\underset{(MF_n;\ CoF_3,\ KCoF_4,\ MnF_3)}{CH_3CF_2CH_3 + 2MF_n} \longrightarrow \underset{(MF_{n-1};\ CoF_2,\ KCoF_3,\ MnF_2)}{CH_3CF_2CFH_2 + HF + 2MF_{n-1}} \qquad (1)$$

2,2-Difluoropropane (**1a**) was monofluorinated with a series of metal fluorides to give the major product 1,2,2-trifluoropropane (**1b**). The monofluorination reactivity of each metal fluoride is obviously different, decreasing in the order $CoF_3 > MnF_3 > KCoF_4$. When **1a** was fluorinated with CoF_3 for 6 h at 100 °C, **1b** was obtained as the major product with no recovery of **1a**, while 1,1,1-trifluoropropane (**1c**) and 1,2,2,3-tetrafluoropropane (**1d**) were also obtained in low yield as by-products. Fluorination of **1a** over MnF_3 for 6 h at 100 °C afforded **1b** in 58% yield with 37% recovery of **1a**. Fluorination of **1a** did not take place using $KCoF_4$ for 6 h at 100 °C. If the reaction temperature was raised to 200 °C, polyfluorinated compounds were obtained. For this reason CoF_3 was the most effective monofluorinating reagent.

Comparison of the fluorination reactivity of fluorinated ethanes over CoF_3

$$C_2H_{6-i}F_i + 2CoF_3 \longrightarrow C_2H_{5-i}F_{i+1} + HF + 2CoF_2 \qquad (2)$$

$(i = 0\text{–}5)$

The results of the stepwise fluorination [eqn. (2)] of ethanes $C_2H_{6-i}F_i$ ($i = 0$–5) are listed in Table 2. Fluorination of ethane (**1**) was slow below 50 °C, and the difluoroethanes [1,1-difluoroethane (**3**) and 1,2-difluoroethane (**4**)] were obtained in only 8% and 9% yield; no 1-fluoroethane (**2**) was detected. Fluorination of **1** gave mainly di- or tri-fluoroethanes at 100 °C, while tetra- or penta-fluoroethane were obtained at 200 °C. As expected, the yield of polyfluorinated products increased with an increase in the reaction temperature.

The fluorination of 1-fluoroethane (**2**) afforded its monofluorinated compound, 1,1-difluoroethane (**3**), as the major product below 75 °C, and its difluorinated compound, 1,1,2-trifluoroethane (**6**), was the major product at 100 °C. When 1,1-difluoroethane (**3**) was fluorinated for 8 h at 50 °C, its monofluorinated compound, 1,1,1-trifluoroethane (**5**), was obtained as the major product, but the yield was low. When the reaction time was extended to 400 h at 50 °C, compound **5** was obtained in 58% yield. When the reaction temperature was increased to 100 °C, the yield of **5** increased from 11% to 34%, but by-products such as 1,1,2-trifluoroethane (**6**), 1,1,1,2-tetrafluoroethane (**7**) and 1,1,2,2-tetrafluoroethane (**8**) were also formed, and the major product was no longer **5** but **6** at 100 °C.

Fluorination of **5** did not proceed over 8 h at 100 °C, but **5** gave its monofluorinated compound, **7**, at 200 °C. Little fluorination of **6** had occurred after 8 h at 100 °C, but **6** gave its monofluorinated compound, **8**, at 200 °C. The main product of monofluorinating **6** was changed from **7** into **8** at 200 °C. Fluorination of **7** and **8** did not progress over 8 h at 100 °C, but the monofluorinated product of these compounds, pentafluoroethane (**9**), was formed at 200 °C. Fluorination of **9** did not proceed over 8 h at 100 °C, but a little of **9** was converted to hexafluoroethane (**10**) at 200 °C. The polyfluorinated HFCs show low fluorination reactivity.

TABLE 2

Fluorination of fluorinated ethanes by the use of CoF_3

Reactant	Substrate No.[a]	Temp. (°C)	Recovery[b] (%)	Product yield (%)							
				3	**4**	**5**	**6**	**7**	**8**	**9**	**10**
$C_2F_0H_6$											
CH_3CH_3[c]	**1**	50	83	8	9	0	0	0	0	0	0
CH_3CH_3[c]	**1**	100	1	26	30	8	30	2	3	0	0
CH_3CH_3[c]	**1**	200	0	0	0	4	4	39	30	23	0
$C_2F_1H_5$											
CH_3CFH_2	**2**	50	74	14	7	0	5	0	0	0	0
CH_3CFH_2	**2**	75	0	37	23	6	31	1	2	0	0
CH_3CFH_2	**2**	100	0	13	3	18	54	5	7	0	0
$C_2F_2H_4$											
CH_3CF_2H	**3**	50	86	–	–	11	2	1	0	0	0
CH_3CF_2H	**3**	50[d]	4	–	–	58	12	25	1	0	0
CH_3CF_2H	**3**	75	53	–	–	29	14	4	0	0	0
CH_3CF_2H	**3**	100	6	–	–	34	49	7	4	0	0
$C_2F_3H_3$											
CF_3CH_3	**5**	200	57	–	–	–	–	28	0	15	0
CFH_2CF_2H	**6**	100	87	–	–	–	–	7	4	1	0
CFH_2CF_2H	**6**	200	39	–	–	–	–	12	47	2	0
$C_2F_4H_2$											
CF_3CFH_2	**7**	200	61	–	–	–	–	–	–	36	3
CF_3CFH_2	**7**	200[e]	10	–	–	–	–	–	–	83	7
CF_2HCF_2H	**8**	200	89	–	–	–	–	–	–	11	0
$C_2F_5H_1$											
CF_3CF_2H	**9**	200	91	–	–	–	–	–	–	–	9

The fluorination reaction was carried out for 8 h.

[a] Substrate numbers as follows: **1**, CH_3CH_3; **2**, CH_3CFH_2; **3**, CH_3CF_2H; **4**, CFH_2CFH_2; **5**, CF_3CH_3; **6**, CFH_2CF_2H; **7**, CF_3CFH_2; **8**, CF_2HCF_2H; **9**, CF_3CF_2H; and **10**, CF_3CF_3.

[b] Reactant recovery.

[c] Yields and recovery of **1** were determined by ^{19}F and ^1H NMR spectroscopy (int. stand. TMS).

[d] Reaction time was 400 h.

TABLE 3

Fluorination of *gem*-difluoro HFCs by the use of CoF_3

Reactant	Substrate No.	Reaction conditions		Recovery[a] (%)	Monofluorinated product		
		Temp. (°C)	Time (h)		Main product	Product No.	Yield[b] (%)
$CH_3CF_2CH_2CH_3$	**11**	25	1	3	$CH_3CF_2CFHCH_3$	**11a**	78
$CH_3CF_2CH_2CH_3$	**11**	25	2	1	$CH_3CF_2CFHCH_3$	**11a**	82
$CH_3CF_2CH_2CH_3$	**11**	100	1	2	$CH_3CF_2CFHCH_3$	**11a**	26
$CH_3CF_2CH_2CH_2CH_3$	**12**	25	2	1	$CH_3CF_2CFHCH_2CH_3$	**12a**	67
$CH_3CF_2CH_2CH_2CH_3$	**12**	25	11	0	$CH_3CF_2CFHCH_2CH_3$	**12a**	69
$CH_3CF_2CH_2Cl$	**13**	25	2	89	CH_3CF_2CFHCl	**13a**	5
$CH_3CF_2CH_2Cl$	**13**	25	134	15	CH_3CF_2CFHCl	**13a**	50
$CH_3CF_2CH_2Cl$	**13**	100	8	2	CH_3CF_2CFHCl	**13a**	48

[a] Recovery of reactant was determined by GC methods (TCD detector).

[b] Yields were determined by ^{19}F NMR spectroscopic methods.

Comparison of the fluorination reactivity of gem-*difluoro compounds (C_3–C_5) over CoF_3*

The fluorination of *gem*-difluoro compounds (C_3–C_5) over CoF_3 are summarized in Table 3. The reactions progress according to eqn. (3):

$$CH_3CF_2CH_2R + 2\,CoF_3 \longrightarrow CH_3CF_2CFHR + HF + 2CoF_2 \qquad (3)$$

($R = CH_3$, CH_2CH_3, Cl)

2,2-Difluorobutane (**11**) was fluorinated at 25 °C for 1 h, and its monofluorinated compound, 2,2,3-trifluorobutane (**11a**), was obtained in 78% yield as the major product (Table 3). Extending the reaction time led to an increase in the yield of **11a**. When the reaction temperature was raised from 25 °C to 100 °C, the yield of **11a** decreased and polyfluorinated by-products such as 1,2,2,3-tetrafluorobutane, 2,2,3,3-tetrafluorobutane and 1,2,2,3,3-pentafluorobutane were generated. The major product was no longer **11a** at 100 °C. Hence, regioselective monofluorination via the use of CoF_3 was found to require low reaction temperatures. At high temperatures, the fluorination proceeds in a random manner.

2,2-Difluoropentane (**12**) and 1-chloro-2,2-difluoropropane (**13**) were monofluorinated to give 2,2,3-trifluoropentane (**12a**) and 1-chloro-1,2,2-trifluoropropane (**13a**), respectively, as the major products in good yield

The substituent R of $CH_3CF_2CH_2R$ may affect the reactivity of fluorination. Under the same reaction conditions (25 °C, 2 h), the reactivity of monofluorination of **11**–**13** decreased in the order $R = CH_3 > C_2H_5 > Cl$.

12a: ^{1}H NMR (from TMS) δ: 1.05 (t, 3H, CH_2CH_3, $J_{HH} = 7.3$ Hz); 1.61 (dt, 3H, CH_3CF_2, $J_{HF} = 18.9$ Hz, $J_{HF} = 2.5$ Hz); 1.70 (m, 2H, CH_2); 4.34 (m, 1H, CHF) ppm. ^{19}F NMR (from $CFCl_3$) δ: 97–109 (ddq, 2F, CF_2, $J_{FF} = 246$ Hz); 196 (m, 1F, CHF) ppm. MS: 126/1.5 (M^+); 111/2.3 ($C_4H_6F_3^+$); 65/100 ($C_2H_3F_2^+$); 61/83 ($C_3H_6F^+$).

Conclusions

It is concluded that CoF_3 is the most effective compound for reaction with HFCs for monofluorination. Fluorinated ethane derivatives were fluorinated further by CoF_3. A dependence of the reaction products on temperature and the low reactivity of polyfluorinated HFCs is apparent. Fluorinations of gem difluoro compounds over CoF_3 gave regioselective monofluorinations at low reaction temperatures. Metal fluorides such as CoF_3 were found to be useful for the monofluorination of fluorinated HFCs, a reaction which cannot be achieved by the use of elemental fluorine or electrochemical fluorination. Further investigation of the process is underway in this laboratory.

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