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Preparation, fluorination and synthetic utility of a CFC–olefin adduct

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Abstract

1,1,1-Trichlorotrifluoroethane was added to ethylene using the catalyst system Fe/triethylphosphite, which eliminated the need for a solvent and avoided the corrosion problems inherent in CuCl-catalyzed reactions. The adduct, $CF_3CCl_2CH_2CH_2Cl$, was fluorinated with HF over a chromium(III) oxide catalyst. A series of alternating dehydrochlorinations and HF additions to internal C=C double bonds was proposed and supported by thermodynamic calculations to explain the formation of $CF_3CF_2CH{=}CH_2$ as the principal fluorination product. An intermediate, $CF_3CCl{=}CHCH_2Cl$, formed cleanly by dehydrochlorination of the adduct in the absence of HF, was converted into 4,4,4-trifluorobutanol and other compounds of the type $CF_3CCl{=}CHCH_2X$ (X = OAc, OH, Br, I, H).

Keywords: Fluorination; CFC–olefin adduct; Thermodynamic calculations

1. Introduction

The addition of fluoroalkyl bromides and iodides to both simple and functionalized olefins has been extensively employed as a means of preparing a variety of organic compounds [1–5]. Similarly, the addition of chlorofluorocarbons (CFCs) to olefins has been a key step in the synthesis of bioactive compounds such as insecticidal pyrethrins, where incorporation of the $CF_3CCl{=}CH-$ group enhances both stability and effectiveness [6,7]. In recent years, we have studied the addition of chlorocarbons and chlorofluorocarbons to olefins as a means of preparing hydrofluorocarbons (HFCs) by reduction of the adducts [8] or by partial fluorination followed by reduction [9]. We report here the results of studies on the preparation of HFCs by complete halogen exchange fluorination of the adducts, and describe briefly the potential utility of the isolable reaction intermediates.

2. Results and discussion

As anticipated from earlier work on the fluorination of low molecular weight adducts of chlorocarbons and simple olefins [10,11], antimony(V) halides were effective in catalyzing HF fluorinations of highly chlorinated 4- and 5-carbon adducts characterized by alternating non-halogenated and perhalogenated carbon atoms [12].

$$CCl_3CH_2CCl_2CH_2CCl_3 \xrightarrow{HF/SbCl_5} CF_3CH_2CF_2CH_2CF_3$$

More challenging and less predictable are fluorinations involving compounds in which adjacent carbons are halogenated. An illustrative example is the fluorination of $CCl_3CH_2CCl_2CH_2F$ (**1**), in which all chlorines were replaced by fluorine and vice versa – a true halogen exchange. The product **2** is readily understood on a thermodynamic basis: the conversion of the $-CH_2Cl$ group to a $-CH_2F$ group using HF is enthalpically disfavored (at 298 K) by nearly 7 kcal mol^{-1} [13].

$$\underset{(\mathbf{1})}{CCl_3CH_2CCl_2CH_2F} \xrightarrow{HF/SbCl_5} \underset{(\mathbf{2})}{CF_3CH_2CF_2CH_2Cl}$$

The possibility of fluorinating adducts of CFCs (as opposed to chlorocarbons) and olefins, was much less certain. In the case of the adduct of CF_3CCl_3 and ethylene (**3**), for example, aside from uncertainties associated with the presence of the terminal $-CH_2Cl$ group, halogen exchanges at a carbon adjacent to a CF_3 group could result in halogen migration. We are unaware of any reports on the fluorination of CFC–olefin adducts containing four or more carbons, or of the exchange fluorination of a CCl_2 group flanked by CF_2 and CH_2 groups.

$$\underset{(\mathbf{3})}{CF_3CCl_2CH_2CH_2Cl} \xrightarrow[?]{HF/cat} \underset{(\mathbf{4})}{CF_3CF_2CH_2CH_2F}$$

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The formation of CFC–olefin adducts of low molecular weight olefins such as ethylene and propylene is also a challenge on a large scale due to the pressure limitations of large batch reactors and the costs associated with solvent handling and recycling. Consequently, we undertook a study of the formation and fluorination of $CF_3CCl_2CH_2CH_2Cl$ (**3**) as an exemplar of simple CFC–olefin adducts.

2.1. Preparation of $CF_3CCl_2CH_2CH_2Cl$ (3)

The more economical CFCs, e.g. CF_3CCl_3 and especially $CF_2ClCFCl_2$, are less reactive with respect to olefin additions than the more commonly used perfluoroalkyl iodides. Although several new redox catalysts have been developed recently for such addition reactions [14–16], their effectiveness is still limited to the more reactive halides and/or they are not truly catalytic, requiring stoichiometric quantities of a co-catalyst such as zinc. While the use of the well-established CuCl/amine system [17] was adequate for laboratory preparations of adducts such as $CCl_3CH_2CCl_2CH_2CCl_3$, $CCl_2CH_2CCl_2CH_2F$ and even **3**, the deficiencies of this system, including corrosion of metal reactors, low reaction rates and/or high pressures at temperatures necessary to achieve a good reaction rate, are significant, especially for gaseous olefins such as ethylene. In the addition of CF_3CCl_3 to ethylene with acetonitrile as solvent, pitting of Monel, Inconel, and Hastelloy C autoclave surfaces was observed. After a preparation conducted in a Hastelloy C reactor, it was also observed that CuCl, recovered as the pot residue following distillation of **3**, was contaminated with nearly all the metals present in Hastelloy C, and in a subsequent run this recovered catalyst was more active compared to CuCl alone. Chlorides of these metals were then tested as co-catalysts along with CuCl. The catalyst system $CuCl/WCl_4$ (15:1 ratio) was about 10-times more reactive than CuCl alone. However, we found the catalyst system Fe/triethylphosphite, introduced by Astrologes for the addition of CCl_4 to ethylene [18], to be superior overall in terms of cost, selectivity and rate. Further, as it eliminated the need for a solvent, productivity and process simplicity were improved as well. The procedure was successfully scaled up in a 50 gal reactor in which > 300 lb of product was prepared per batch.

$$CF_3CCl_3 + CH_2{=}CH_2 \xrightarrow[(EtO)_3P]{Fe} \underset{(3)}{CF_3CCl_2CH_2CH_2Cl}$$

The isomeric $CF_2ClCFCl_2$ was essentially unreactive under these conditions (< 1% conversion after 46 h). However, this addition has been reported recently using an iron catalyst in a vapor-phase process, although conversions were <2% [19].

2.2. Fluorination of $CF_3CCl_2CH_2CH_2Cl$ (3) to $CF_3CF_2CH{=}CH_2$ (5)

In contrast to the successful fluorination of adducts containing CCl_2 groups which are flanked by CH_2 groups, all attempts to fluorinate **3** using $HF/SbCl_5$ at 175–225 °C failed. Starting material was recovered, along with only small amounts of dehydrochlorination and single Cl–F exchange ($C_4H_3Cl_2F_4$) products (GC–MS). Halogen exchange did occur, however, in the vapor phase.

$$\underset{(3)}{CF_3CCl_2CH_2CH_2Cl} \xrightarrow[250\ °C]{HF/Cr_2O_3} \underset{(5)}{CF_3CF_2CH{=}CH_2} + \text{intermediates}$$

The main product, in 60–73% selectivity (ca. 80% conversion of **3**, at operating pressures of 50–200 psig), was the dehydrochlorination product *E*/*Z*-$CF_3CCl{=}CHCH_2Cl$ (**6**), which was the sole product in the absence of HF. Assignment of *Z*-**6** as the major isomer was based on estimated heats of formation (PM3) which indicate that the *Z*-isomer is more stable than the *E*-isomer by about 1.7 kcal mol^{-1}, in good agreement with the observed isomer ratio of 93.5:6.5.

The main fluorinated product, in about 23% selectivity, was $CF_3CF_2CH{=}CH_2$ (**5**). Minor reaction products (totalling 3%–16% of the product mixture) were $CF_3CF_2CH_2CH_2F$ (**4**), $CF_3CCl_2CH{=}CH_2$ (**7**), $CF_3CF_2CH_2CH_2Cl$ (**8**), $CF_3CCl{=}CHCH_2F$ (**9**) and $CF_3CCl_2CH_2CH_2F$ (**10**). Recycle of crude $CF_3CCl{=}CHCH_2Cl$ resulted in the formation of $CF_3CF_2CH{=}CH_2$ with 79% selectivity at about 50% conversion.

It is interesting to note that the internal olefin **6**, and not the isomeric $CF_3CCl_2CH{=}CH_2$ (**7**), was the main dehydrochlorination product of **3**. The main fluorination product, however, was the terminal olefin **5** and not $CF_3CF{=}CHCH_2F$ (**11**). When **3** was dehydrochlorinated with NaOH in ethylene glycol, the main product was $CF_3CCl_2CH{=}CH_2$ (**7**). Estimated heats of formation suggest this terminal olefin ($\Delta H_f = -154.3$ kcal mol^{-1}) is a kinetically controlled product; its heat of formation being 5.5 kcal mol^{-1} less negative than the isomeric *Z*-**6** ($\Delta H_f = -159.8$ kcal mol^{-1}).

$$\underset{(7)}{CF_3CCl_2CH{=}CH_2} \xrightarrow[105\ °C,\ 90\ min]{LiCl,\ DMF} \underset{(6)}{CF_3CCl{=}CHCH_2Cl}$$

As anticipated then, **7** isomerized readily (LiCl, DMF) to give *Z*/*E*-**6** with essentially the same isomer ratio as obtained in the gas phase (95.2:4.8). Calculated heats of formation for the observed products and other likely intermediates are given in Table 1. Calculated (PM3) heats of formation for **5** and **11** indicate that, for this pair, ΔH_f is more negative for the terminal olefin **5** (-240.9 kcal mol^{-1}) than for its internal isomer **11** (-235.3 kcal mol^{-1}) by 5.6 kcal mol^{-1}, a complete reversal compared to the chlorinated analogs **7** and **6**.

In order to evaluate the sequence of events leading to these products, reactions such as A–H can initially be considered (Table 2). Reaction free energies were calculated for each of these reactions using the program CHETAH™, which employs group contributions to enthalpies, entropies and heat capacities. The required groups were not available for reac-

Table 1
Calculated ΔH_f values for chlorofluorobutenes and butanes

Compound No.	Structure	ΔH_f (kcal mol^{-1})
5	$CF_3CF_2CH{=}CH_2$	−240.9
6	$CF_3CCl{=}CHCH_2Cl$	−159.8
7	$CF_3CCl_2CH{=}CH_2$	−154.3
9	$CF_3CCl{=}CHCH_2F$	−197.2
10	$CF_3CCl_2CH_2CH_2F$	−225.9
11	$CF_3CF{=}CHCH_2F$	−235.3
12	$CF_3CF{=}CHCH_2Cl$	−197.8
13	$CF_3CFClCH{=}CH_2$	−194.9
14	$CF_3CFClCH_2CH_2Cl$	−228.6

tions F and G. Reaction I was substituted as a model for Rxn G.

The calculated values for ΔG_{rxn} (for all reactants and products in the gaseous state) are consistent with the formation of $CF_3CCl{=}CHCH_2Cl$ as the principal dehydrochlorination product at a reaction temperature of about 525 K (compare reactions A and B) and the addition of HF to internal olefins like **6** with the observed regioselectivity (compare H and I).

As indicated by the results in Table 2, alternating HF additions to internal double bonds and HCl eliminations provide a thermodynamically favorable pathway leading to the main fluorination product **5**:

$$\underset{(\mathbf{3})}{CF_3CCl_2CH_2CH_2Cl} \xrightarrow{-HCl} \underset{(\mathbf{6})}{CF_3CCl{=}CHCH_2Cl} \xrightarrow{+HF}$$

$$\underset{(\mathbf{14})}{CF_3CFClCH_2CH_2Cl} \xrightarrow{-HCl}$$

$$\underset{(\mathbf{12})}{CF_3CF{=}CHCH_2Cl} \xrightarrow{+HF}$$

$$\underset{(\mathbf{8})}{CF_3CF_2CH_2CH_2Cl} \xrightarrow{-HCl}$$

$$\underset{(\mathbf{5})}{CF_3CF_2CH{=}CH_2}$$

Calculated values for ΔG_{rxn} are positive, however, for reactions involving the formation of a terminal CH_2F group via HF addition to $CF_3CXYCH{=}CH_2$ (Rxn C) or by direct exchange of a terminal $-CH_2Cl$ to a terminal $-CH_2F$ (Rxn D). Consistent with the estimated reaction free energy for the latter are Bell's [20] results on the cognate vapor-phase fluorination of CF_3CH_2Cl to CF_3CH_2F using HF/Cr_2O_3. In this case, using an HF/organic ratio of 4, an 18% conversion of CF_3CH_2Cl to CF_3CH_2F was realized at a reaction temperature of 350 °C. Given the uncertainty in estimating ΔG (probably not better than about ± 2 kcal mol^{-1} for fluorinated compounds) and our experimental conditions (20:1 HF/organic ratio, 250 °C), the conversion of a $-CH_2Cl$ to a $-CH_2F$ group via HF halogen exchange could account for the small amounts of these compounds which are observed. Unlike the conversion of CF_3CH_2Cl to CF_3CH_2F, however, thermodynamically more attractive processes are possible in the present case. These include an S_N2'-like exchange (reaction E) and isomerizations such as **12** to **9** (Rxn F, $\Delta\Delta H_f = 0.6$ kcal mol^{-1}).

2.3. Hydrofluorination of $CF_3CF_2CH{=}CH_2$ (5)

Perfluoroalkyl ethylenes are electron-deficient and do not add hydrogen halides readily [21–23]. With the aid of the corresponding aluminum trihalides as catalysts, Henne and Kaye succeeded in adding HCl or HBr, in the anti-Markovnikov sense, to $CF_3CH{=}CH_2$ (ca. 25% yield) at 100 °C [21]. These and similar results [22] have led to the general conclusion that the electrophilic addition of a hydrogen halide to such olefins requires strong catalysts and forcing conditions [23]. As shown in Table 2 (Rxn C), for the addition of HF to the homologous **5**, ΔG_{rxn} is positive at 250 °C but decreases with temperature. This suggested that the addition of HF to **5** should be achievable, even at low temperatures. Gratifyingly, antimony(V) halides were sufficiently potent catalysts to effect the conversion of **5** to **4** at an appreciable rate, *even at 0 °C*. Tin and titanium tetrachlorides were comparatively ineffective.

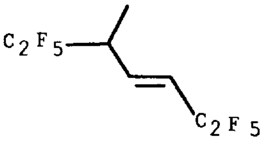
$$\underset{(\mathbf{5})}{CF_3CF_2CH{=}CH_2} \xrightarrow[0\,°C]{HF/SbCl_5} \underset{(\mathbf{4})}{CF_3CF_2CH_2CH_2F}$$

Myhre and Andrews [24] have provided evidence that $CF_3CH{=}CH_2$ is not protonated in the superacid HSO_3F, but

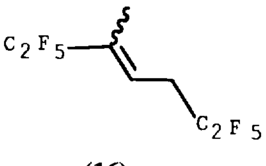
Table 2
Calculated ΔG_{rxn} values at various temperatures

		ΔG_{rxn} (kcal mol^{-1}) at			
		300 K	400 K	500 K	600 K
Rxn A	$CF_3CCl_2CH_2CH_2Cl \rightarrow CF_3CCl{=}CHCH_2Cl + HCl$	+0.8	−2.7	−6.3	−9.7
Rxn B	$CF_3CCl_2CH_2CH_2Cl \rightarrow CF_3CCl_2CH{=}CH_2 + HCl$	+4.3	+1.0	−2.4	−5.7
Rxn C	$CF_3CF_2CH{=}CH_2 + HF \rightarrow CF_3CF_2CH_2CH_2F$	+1.3	+4.6	+7.9	+11.2
Rxn D	$CF_3CCl{=}CHCH_2Cl + HF \rightarrow CF_3CCl{=}CHCH_2F + HCl$	+5.7	+5.7	+5.6	+5.6
Rxn E	$CF_3CCl_2CH{=}CH_2 + HF \rightarrow CF_3CCl{=}CHCH_2F + HCl$	+2.2	+1.9	+1.7	+1.6
Rxn F	$CF_3CF{=}CHCH_2Cl \rightarrow CF_3CCl{=}CHCH_2F$				
Rxn G	$CF_3CF{=}CHCH_2Cl + HF \rightarrow CF_3CF_2CH_2CH_2Cl$				
Rxn H	$CF_3CCl{=}CHCH_2Cl + HF \rightarrow CF_3CHClCHFCH_2Cl$	+3.8	+7.0	+10.1	+13.2
Rxn I	$CHF{=}CHCH_2Cl + HF \rightarrow HCF_2CH_2CH_2Cl$	−9.7	−6.3	−2.8	+0.6

dimerizes via the difluoroallyl cation. An analogous process for the conversion of **5** to **4** would involve the cation $CF_3CF^+CH{=}CH_2$. Trapping of this cation by fluoride or chloride ion (from $SbF_nCl_{6-n}^-$), or by **5** would then be expected. Observed by-products included both $CF_3CF_2CH_2CH_2Cl$ and dimers of **5**. The major dimer (**15**) had spectral properties indicating a structure analogous to the dimer formed from $CF_3CH{=}CH_2$.



(15)



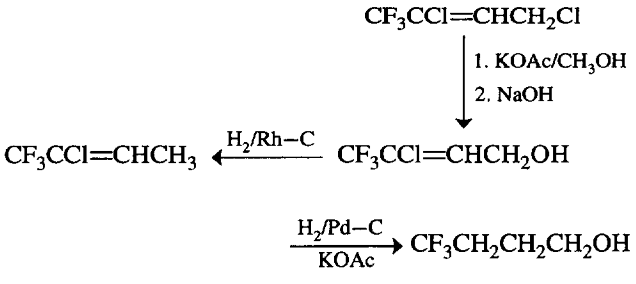
(16)

2.4. Synthetic utility of 6

Adducts of CFCs and olefins are perhaps still under-utilized as fluorinated chemical intermediates. In addition to the utility of perfluoroalkyl ethylenes like **5**, compound **6** is also an attractive raw material which is relatively easy to make and has the following desirable features: (1) a trifluoromethyl group; (2) a reactive, allylic chlorine for displacement by other nucleophiles; and (3) a CCl=CH group which is a latent or masked carbonyl group.

Displacement of the allylic chlorine readily afforded other compounds of the type $CF_3CCl{=}CHCH_2X$ in good yield (X = Br, 82%; X = I, 75%; X = OAc, 79%; and X = OH, 73% yield), having the same *Z*/*E* ratio as **6** [25].

Catalytic reduction of the alcohol $CF_3CCl{=}CHCH_2OH$ in the presence of base (KOAc) provided the expected $CF_3CH_2CH_2CH_2OH$, but reduction in the absence of base gave mainly $CF_3CCl{=}CHCH_3$ [25], which is a potential precursor to the interesting dienophile $CF_3C{\equiv}CCH_3$. Apparently, HCl generated by partial hydrodechlorination catalyzes the reduction of the hydroxy group, which then becomes kinetically favored relative to reduction of the electron-deficient double bond.



3. Experimental details

PM3 calculations of ΔH_f were performed using the MOPAC program resident in the CAChe™ Scientific WorkSystem, Version 3.5. Calculations of ΔG versus T were made using the program CHETAH™, Version 7.0 (1994), available from the American Society for Testing and Materials (ASTM), Philadelphia, PA.

NMR spectra were recorded in $CDCl_3$ solution with a Finnegan TSQ-700, 360 MHz multinuclear spectrometer. Chemical shifts are reported in ppm downfield (positive) from standard (TMS for ^1H and ^{13}C, $CFCl_3$ for ^{19}F).

The catalyst for vapor-phase fluorination of **3** was 1/8 in pelletized Cr_2O_3 available from Mallinckrodt Specialty Chemicals Co., St. Louis, MO.

Caution! All operations with aqueous or anhydrous HF should be conducted with suitable personal protective equipment (rubber gloves, face shield and plastic apron or suit) and operators should be familiar with procedures for treating HF burns.

3.1. 1,1,1,3,3-Pentachloro-4-fluorobutane (1)

An autoclave was charged with 400 ml of NMP, 112.2 g of 2,3-dichloroprop-1-ene, 115 g of KF and 4 g of tetrabutylammonium bromide and heated to 155 °C for 23 h. The volatile materials were removed at ≤ 90 °C at a pressure ≥ 15 mmHg (66 g), and re-distilled to give 49.3 g (52% yield) of 97% pure $CH_2{=}CClCH_2F$, b.p. 43–46 °C (lit. b.p. 44 °C [26]).

A mixture consisting of 47 g of $CH_2{=}CClCH_2F$, 154 g of CCl_4, 0.5 g of CuCl, 0.8 g of diethylamine hydrochloride and 43 g of acetonitrile was heated in an autoclave to 105 °C for 7 d. The contents were washed with brine, dried (Na_2SO_4) and distilled to give 99.3 g (80% yield) of 99% pure $CCl_3CH_2CCl_2CH_2F$ (**1**), b.p. 81–82 °C/5 mmHg. ^1H NMR δ: 3.79 (2H, s); 4.85 (2H, d, J = 47 Hz) ppm. ^{19}F NMR δ: −202.9 (t, J = 47 Hz) ppm. ^{13}C NMR δ: 93.5 (CCl_3, s); 86.5 (CH_2F, d, J = 193 Hz); 83.0 (CCl_2, d, J = 22 Hz); 62.1 (CH_2, s) ppm. MS *m/z* (%): 215 (26.2); 213 (47.3); 211 (35.8, P − Cl); 179 (15.2); 177 (42.0); 175 (42.0, P − Cl_2); 121 (16.2); 119 (52.7); 117 (100); 115 (92.5).

3.2. 1,1,1,3,3-Pentafluoro-4-chlorobutane (2)

An autoclave was charged with 14.6 g of SbF_5, cooled to −40 °C and evacuated. Anhydrous HF (100 g) was then added, followed by 61.2 g of $CCl_3CH_2CCl_2CH_2F$. Provisions were made to pass gaseous products from the reactor through an aqueous KOH scrubber which was connected to a −78 °C cold trap. The contents were heated to 140–145 °C for 10 h during which time pressure in excess of 400 psig was vented to the scrubber and cold trap. After 10 h, the contents were vented completely. The organic material in the scrubber and cold traps was combined, washed with 2 × 25 ml of 5% Na_2CO_3 solution, 2 × 25 ml of water and dried (4 Å sieves). Distillation provided 14.5 g (32% yield) of $CF_3CH_2CF_2CH_2Cl$ (**2**), b.p. 78 °C. ^1H NMR δ: 3.75 (2H, t, J = 12.4 Hz); 2.98 (2H, tq, J = 13.9, 9.8 Hz) ppm. ^{19}F NMR δ: −62.8 (3F, t, J = 9.8 Hz); −99.4 (2F, m) ppm. ^{13}C NMR δ; 123.6 (CF_3, qt, J = 276, 5.4 Hz); 118.3 (CF_2, tq, J = 245, 3.3 Hz); 44.0 (CH_2Cl, tq, $J=33.6$, 1.9 Hz); 38.3 (CH_2, tq) ppm. MS *m/z*: 182 (P); 69 (base).

3.3. *1,3,3-Trichloro-4,4,4-trifluorobutane (3)*

The reaction was performed in a 100 ml glass pressure bottle using magnetic stirring and heating via a constant temperature oil bath. The bottle was fitted with a pressure gauge and ball valve inlet. Iron powder (0.37 g, 6.6 mmol) was charged under a nitrogen atmosphere. After evacuating the reactor, 0.48 g (2.9 mmol) of triethyl phosphite and 48 g (0.256 mmol) of CF_3CCl_3 were charged via a syringe. The system was degassed with three freeze–thaw cycles, heated to 120 °C and pressurized to 80 psig with ethylene. Ethylene was fed into the reactor on demand at a pressure of 80 psig over 30 h. The contents were then distilled at atmospheric pressure to recover 24.8 g of unreacted CF_3CCl_3 and further distilled at 85 mmHg to give 17.4 g (65% yield) of $CF_3CCl_2CH_2CH_2Cl$, b.p. 55 °C. ^1H NMR δ: equal intensity, distorted triplets at 3.9 and 2.77 ppm. ^{19}F NMR δ: -81 (s) ppm. IR (cm^{-1}): strong bands characteristic of the $CF_3CCl_2CH_2$– grouping [8] at 1255, 1210, 1180. Analysis: Calc. for $C_4H_4Cl_3F_3$: C, 22.30; H, 1.87%. Found: C, 22.08; H, 1.86%.

3.4. *Fluorination of 1,3,3-trichloro-4,4,4-trifluorobutane (3)*

The Cr_2O_3 catalyst was pretreated as follows. While maintaining a nitrogen flow of 350 $cm^3\ min^{-1}$, the catalyst (150 cm^3) contained in a 1 in tube reactor was heated to 350 °C at the rate of 50 °C h^{-1}, maintained at 350 °C for 8 h and cooled to 200 °C at a rate of 40 °C h^{-1}. Hydrogen fluoride was then metered in at a rate to keep the temperature below 250 °C (about 0.8 ml min^{-1}). After the exotherm had moved through the catalyst bed, the temperature was increased to 350 °C at 50 °C h^{-1}, maintained at 350 °C for 2 h and finally cooled to a reaction temperature of 250 °C at 50 °C h^{-1}. In a typical experiment, the operating pressure was 200 psig and **3** was fed in at 1 g min^{-1} and HF at a 20:1 HF/organic mole ratio. The nitrogen flow was reduced to obtain a contact time of about 30 s. These conditions resulted in a 79% conversion and a selectivity of 1% for $CF_3CF_2CH_2CH_2F$, 23.4% for $CF_3CF_2CH{=}CH_2$, 72.5% for $CF_3CCl{=}CHCH_2Cl$ and 3.1% for other products (identified by GC–MS) including $C_4H_3ClF_4$ isomers, $CF_3CF_2CH_2CH_2Cl$ and $CF_3CCl_2CH_2CH_2F$. 3,3,4,4,4-Pentafluoro-1-butene (b.p. 3–6 °C) was recovered from the crude product mixture (collected in -78 °C cold traps) by bulb-to-bulb distillation. The liquid products were then fractionated. The fraction boiling at 95–101 °C consisted of 10% of $CF_3CCl_2CH_2CH_2F$ [^1H NMR δ: 2.74 (dt, CH_2CH_2F, $J=18.6$, 6.3 Hz); 4.83 (dt, CH_2CH_2F, $J=46.2$, 6.3 Hz) ppm. ^{19}F NMR δ: -80.7, -222.4 ppm] and 90% of **6**, while the fraction boiling at 101 °C was 97% pure **6** [^1H NMR δ: 6.61 ($=CH$, $^3J_{HH}=7.2$ Hz); 4.24 (CH_2, $^3J_{HH}=7.2$ Hz) ppm. ^{19}F NMR δ: -70.1 ppm (major isomer (*Z*)) and -63.2 (*E*-isomer) ppm].

In the absence of HF, **6** was produced cleanly, Thus, **3** (747 g) was fed (at 40 ml h^{-1}, N_2 at 10 $cm^3\ min^{-1}$) into a reactor containing 250 cm^3 of Cr_2O_3 catalyst at 285 °C (atmospheric pressure). The organic products (643 g), collected in cold traps, consisted of 37% of **6** and 62% starting material, for a conversion of 38% and a selectivity for **6** of 97%.

3.5. *Addition of HF to $CF_3CF_2CH{=}CH_2$ to give $CF_3CF_2CH_2CH_2F$ (4)*

A 1-l, screw-capped PFA reactor with an inlet tube connected to a source of $CF_3CF_2CH{=}CH_2$ and an outlet vent was charged with 7.2 g (0.024 mol) of $SbCl_5$, and cooled to -30 °C (N_2 atmosphere). The reactor was then evacuated and charged with 102. 3 g of HF (5.12 mol). The resultant slurry was stirred vigorously while warming to 0 °C (30 min). Pentafluorobutene was then bubbled into the HF at about 24 g h^{-1}, maintaining the temperature at 0±2 °C. A total of 144.4 g of the olefin was fed over 6 h, after which stirring was continued for 15 min. The mixture was cooled to -20 °C and quenched by pouring into 1-l of ice-cold aqueous KOH (**Caution!**). The organic layer (145.8 g) was washed with aq. KOH, brine, water, dried ($MgSO_4$) and distilled to give 75.1 g (46% yield) of $CF_3CF_2CH_2CH_2F$, b.p. 43–44 °C. ^1H NMR δ: 4.69 (2H, dt, $J=46.4$, 5.6 Hz); 2.45 (2H, m) ppm. ^{19}F NMR δ: -87.1 (3F, s); -118.6 (2F, td, $J=17.8$, 6.4 Hz); -223.1 (1F, m) ppm. MS: 166 (M − 1); 97 ($M-CF_3$); 77; 69 (CF_3); 33 (CH_2F).

One minor reaction product was $CF_3CF_2CH_2CH_2Cl$, b.p. 52–55 °C [^1H NMR δ: 2.56 (2H, tt, $J=17.5$, 7.9 Hz); 3.7 (2H, t, $J=7.9$ Hz) ppm. ^{19}F NMR δ: -86.9 (3F); -119 (2F, t, $J=17.5$ Hz) ppm. ^{13}C NMR δ: 119 (qt, $^1J_{CF}=283$ Hz, $^2J_{CF}=33.9$ Hz); 114.5 (tq, $^1J_{CF}=214$ Hz, $^2J_{CF}=33.8$ Hz); 34.3; 34.4 ppm. MS (*m/z*): 182 (P); 184 (P + 2).

Other minor reaction products included $C_8H_6F_{10}$ isomers [MS (*m/z*): 292 (P)], boiling at 87–102 °C. The major isomer was identified as 2-(pentafluoroethyl)-3-methyl-4,4,5,5,5-pentafluoropent-1-ene (**15**). ^1H NMR δ: 6.37 (1H, dd, $J=16$, 9 Hz); 5.8 (1H, dt, $J=16$, 11 Hz); 2.9 (1H, m); 1.3 (3H, d, $J=7$ Hz) ppm. ^{19}F NMR δ: -83.7 (CF_3); -87.1 (CF_3); -118.0 (CF_2, d, $J=11$ Hz); -121.0 (1F of diastereotopic CF_2 fluorines, dd, $J=271$, 11.1 Hz); -124.0 (1F of CF_2, dd, $J=271$, 17.5 Hz) ppm. ^{13}C NMR δ: (of non-fluorinated aliphatic carbons; the others not readily assignable from the mixture of isomers) 40.5 (CF_2CHCH_3, t, $J=21$ Hz); 12.6 (CF_2CHCH_3, s) ppm. The minor isomer was identified as 1,1,1,2,2,6,6,7,7,7-decafluoro-3-methylhept-3-ene (**16**). ^1H NMR δ: 6.1 ($HC{=}C$, t, $J=7.3$ Hz); 2.9 (CH2, m); 1.8 (CH_3, s) ppm. ^{19}F NMR δ: -85.5 (CF_3); -86.9 (CF_3); -118.2 (CF_2CH_2, t, $J=16$ Hz); -119.9 ($CF_2C{=}C$, s) ppm. ^{13}C NMR δ: 30.8 (CH_2, t, $J=21$ Hz); 11.6 (CH_3, s) ppm; others not readily assignable from the mixture.

3.6. 3,3-Dichloro-4,4,4-trifluorobutene (7)

NaOH (10 g) was dissolved in 100 ml of ethylene glycol by heating to about 90 °C, and the solution was then allowed to cool. When the temperature reached 68 °C, $CF_3CCl_2CH_2CH_2Cl$ was added slowly with external heating or cooling as necessary to maintain the temperature between 65 °C and 75 °C. A total of 21 g was added over 45 min. Heating was continued for an additional 45 min before cooling and neutralizing with aqueous HCl. The volatile products were recovered by steam distillation (9.2 g) and re-distilled to give 6.3 g (36% yield) of $CF_3CCl_2CH{=}CH_2$, b.p. 73.5–75 °C (GC purity, 98.5%). ^{1}H NMR δ: 6.2 (1H, dd, $J = 16.2$, 9.9 Hz); 6.0 (1H, d, $J = 16.2$ Hz); 5.6 (1H, d, $J = 9.9$ Hz) ppm. ^{19}F NMR δ: -79.2 ppm.

3.7. Isomerization of $CF_3CCl_2CH{=}CH_2$ (7) to $CF_3CCl{=}CHCH_2Cl$ (6)

A solution consisting of 2.0 g of $CF_3CCl_2CH{=}CH_2$ and 0.2 g of LiCl in 5 ml of DMF was heated to 105 °C for 90 min. By GC analysis the original olefin had isomerized almost completely to $CF_3CCl{=}CHCH_2Cl$. The product was distilled out completely, along with a little DMF, and washed with 5 ml of water. The lower layer was separated and dried to give 1.3 g of 97% pure $CF_3CCl{=}CHCH_2Cl$. Starting material was present to the extent of only 0.3%.

4. Conclusions

Simple CFC–olefin adducts such as **3** can be readily prepared on a large scale using Fe/triethylphosphite as a catalyst. Although the CCl_2 group in $CF_3CCl_2CH_2CH_2Cl$ is resistant to fluorination with HF/$SbCl_5$, vapor-phase fluorination successfully provided $CF_3CF_2CH{=}CH_2$. The addition of HF to perfluoroalkylethylenes is thermodynamically favored at low temperatures, but a powerful catalyst such as an antimony(V) halide is required to effect the addition. Dehydrochlorination of CFC–olefin adducts, as exemplified by the synthesis of $CF_3CCl{=}CHCH_2Cl$, gives access to conveniently functionalized olefins which should have considerable utility in the construction of more elaborate fluorinated compounds.

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References

[1] I. Rico, D. Cantacuzene and C. Wakselman, *Tetrahedron Lett., 22* (1981) 3405.
[2] M. Kotora, M. Hajek, B. Ameduri and B. Boutevin, *J. Fluorine Chem., 68* (1994) 49.
[3] J. Gonzalez, C.J. Foti and S. Elsheimer, *J. Org. Chem., 56* (1991) 4322.
[4] D. Holland, D.J. Milner and R.K. Huff, US Pat. 4 228 107, 1980.
[5] C.-M. Hu, Q.-S. Hu, Y.-L. Qiu and J. Chen, *J. Fluorine Chem., 66* (1994) 171.
[6] P.D. Bentley, R. Cheetham, R.K. Huff, R. Pascoe and J.D. Sayle, *Pestic. Sci., 11* (1980) 156.
[7] J. Crobsy and B.W.H. Terry, US Pat. 4 210 611, 1981.
[8] M. Van Der Puy, *J. Fluorine Chem., 61* (1993) 133.
[9] M. Van Der Puy and A. Thenappan, US Pat. pending.
[10] P. Tarrant, M.L. Brey and B.E. Gray, *J. Am. Chem. Soc., 80* (1958) 1711.
[11] L.L. Ferstandig, US Pat. 4 138 355, 1979.
[12] M. Van Der Puy, G.V.B. Madhavan and T.R. Demmin, US Pat. 5 395 997, 1995.
[13] Estimated by the method of R.M. Joshi, *J. Macromol. Sci. – Chem., A8* (1974) 861.
[14] C.-M. Hu and Y.-L. Qiu, *J. Fluorine Chem., 55* (1991) 109.
[15] Y. Ding, G. Zhao and W. Huang, *Tetrahedron Lett., 34* (1993) 1321.
[16] C.-M. Hu and J. Chen, *Tetrahedron Lett., 34* (1993) 5957.
[17] D.J. Burton and L.J. Kehoe, *Tetrahedron Lett.,* (1966) 5163.
[18] G.W. Astrologes, US Pat. 4 605 802, 1986.
[19] R.W. Johnson, M. Van Der Puy, G.J. Samuels, T.R. Demmin and W.C. Moeller, US Pat. pending.
[20] S.L. Bell, US Pat. 4 129 603, 1978.
[21] A.L. Henne and S. Kaye, *J. Am. Chem. Soc., 72* (1950) 3369.
[22] O.R. Pierce, E.T. McBee and R.E. Cline, *J. Am. Chem. Soc., 75* (1953) 5618.
[23] M. Hudlicky, *Chemistry of Organic Fluorine Compounds,* 2nd edn., Ellis Horwood Ltd., Chichester, UK, 1992, p. 228.
[24] P.C. Myhre and G.D. Andrews, *J. Am. Chem. Soc., 92* (1970) 7595, 7596.
[25] M. Van Der Puy, US Pat. pending.
[26] L.S. Boguslavskaya, A.B. Bulovyatova, A.P. Sineokov and V.S. Etlis, *J. Org. Chem. USSR, English Transl., 7* (1971) 645.