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Electrophilic, catalytic alkylation of polyfluoroolefins by some fluoroalkanes[☆]

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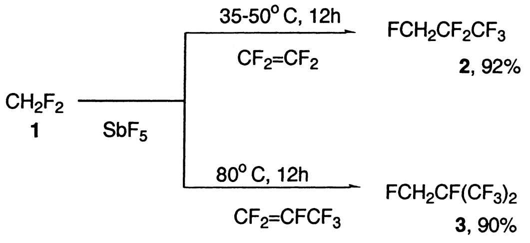
Abstract

New data are presented on the antimony pentafluoride catalyzed reaction of hydrofluorocarbons such as CH_3F, CH_2F_2, CH_3CHF_2 and $R_fCH_2CH_2F$ with fluoroolefins. The condensation of CH_2F_2 and fluoroolefins $CF_2{=}CFX$ ($X = F$, CF_3) proceeds under mild conditions producing the corresponding propanes FCH_2CFXCF_3 in moderate to high yield. Under similar conditions methyl fluoride reacts with tetrafluoroethylene giving $CH_3CF_2CF_3$. However, a complex mixture of products forms in the analogous reaction with hexafluoropropene. The structures of the products of the reactions of CH_3CHF_2 and tetrafluoroethylene and *F*-butylethylene were determined. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Polyfluoroolefins; Fluoroalkanes; Electrophilic; Alkylation; Difluormethane; Methyl fluoride

1. Introduction

The electrophilic condensation of polyfluoroalkanes with fluoroolefins is an important synthetic route for the synthesis of higher polyfluoroalkanes. Some condensation reactions involving simple alkyl fluorides or chlorides and fluoroolefins are catalyzed effectively by a solution of antimony pentafluoride in anhydrous HF [1,2]. A key property of this superacid system is the elimination of the pronounced oxidizing power of antimony pentafluoride. Additions of chlorofluoroalkanes to polyfluoroethylenes catalyzed by antimony pentafluoride are limited to easily activated molecules such as $CClF_2CCl_2F$ [3] or CH_3CF_3 [4]. Aluminum chlorofluoride, ACF [5] is a potent Lewis acid catalyst which has no oxidizing capability. However, ACF has a much higher sensitivity to protic impurities. This requires particular care in excluding materials such as water or hydrocarbons and also limits the range of substrates to highly fluorinated materials. Within these limits the range of materials compatible with ACF is broad [6]. A recent example is the ACF catalyzed condensation of trifluoromethanes, CF_3X ($X = H$, Cl, Br, I) with fluoroethylenes [7]. In this paper, we report new data on the antimony pentafluoride catalyzed reaction of hydrofluorocarbons such as CH_3F, CH_2F_2, CH_3CHF_2 and $R_fCH_2CH_2F$ with fluoroolefins. Reaction of difluoromethane (**1**) in the presence of antimony pentafluoride with either tetrafluoroethylene (TFE) or hexafluoropropylene (HFP) at ambient or elevated temperature gave the corresponding dihydrofluoroalkanes, 1,1,1,2,2,3-hexafluoropropane (**2**) and 2-trifluoromethyl-1,1,1,2,3-pentafluoropropane (**3**), respectively. Both reactions proceed rapidly in the presence of 2–10 mol% antimony pentafluoride.



(1)

The reactions are exceptionally clean and only produce the one to one adducts. No evidence for the formation of compounds resulting from the further condensation of alkanes **2** and **3** with a second mole of fluoroolefin was found. The reactions could be scaled up to kilogram scale by

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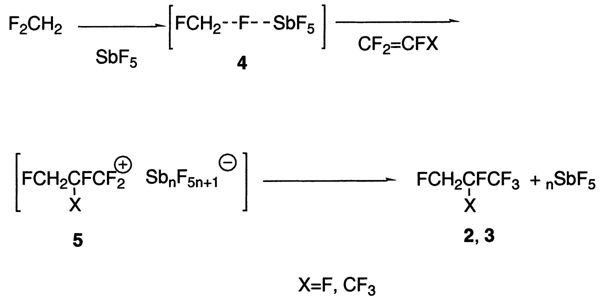


Scheme 1.

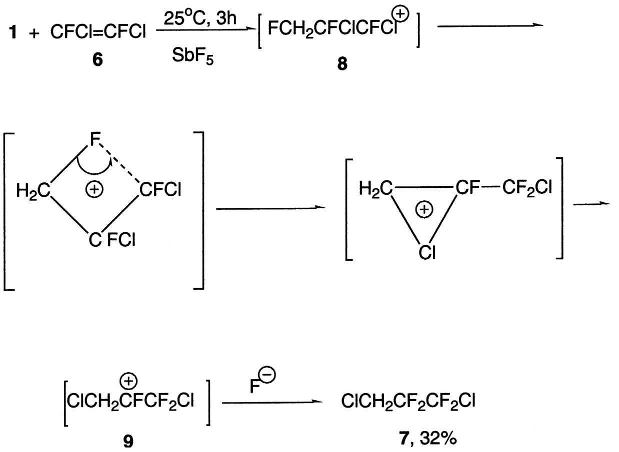
adding the fluoroolefin to excess difluoromethane under pressure at 35–50°C (TFE) or at 60–80°C (HFP). The regiospecificity of the product with HFP is that expected for an electrophilic reaction [8].

We believe that the probable mechanism involves the formation of an ionized complex **4**, between difluoromethane (**1**) and the Lewis acid followed by reaction with the fluoroolefin to intermediate **5**. Stabilization of **5**, by addition of fluoride from the counter ion leads to the final product and reformation of the catalyst. The mechanism is similar to that proposed for the Lewis acid condensation of fluoroolefins with CF_3CH_3 [4] and CF_3X [7] (Scheme 1).

The reaction of difluoromethane (**1**) and 1,2-dichlorodifluoroethylene (**6**), resulted in extensive tar formation. Surprisingly, 1,3-dichloro-2,2,3,3-tetrafluoropropane (**7**), formed in 32% yield, was the only product isolated. We believe that the formation of **7** is the result of process represented by Scheme 2.

Carbocation **8** formed by the reaction of **1** and **6** undergoes two rearrangements: a 1,3-migration of fluorine [9] followed by a 1,2-migration of chlorine [10]. This results in formation of cation **9**, which is converted into the final product by addition of fluoride anion from the counter anion.

Methyl fluoride (**10**) reacted similarly with fluoroolefins. Reaction of **10** with tetrafluoroethylene gave 1,1,1,2,2-pentafluoropropane (**11**). Reaction of **10** with trifluoroethylene at ambient temperature produced 1,1,1,2-tetrafluoropropane (**12**) in moderate yield. In addition a small amount of 1,1,1,2-tetrafluoroethane (**13**), was formed by the Lewis acid catalyzed addition of adventitious HF to trifluoroethylene. No further condensation products from either **12** or **13** and trifluoroethylene were found.



Scheme 2.

$$\underset{\mathbf{10}}{CH_3F} + CF_2{=}CF_2 \xrightarrow[SbF_5]{50^{\circ}C,\ 10h} \underset{\mathbf{11},\ 67\%}{CH_3CF_2CF_3} \tag{2}$$

$$\underset{\mathbf{10}}{CH_3F} + CFH{=}CF_2 \xrightarrow[SbF_5]{25^{\circ}C,\ 14h} \underset{\mathbf{12}}{CH_3CFHCF_3} + \underset{\mathbf{13}}{CF_3CH_2F} \tag{3}$$

ratio 9 : 1

yield of **12**, 39%

A similar lack of higher condensation products was reported in the reaction of tetrafluoroethylene and 1,1,1,2,3,3,3-heptafluoropropane [11].

The reaction of methyl fluoride (**10**), and hexafluoropropylene at 50°C led to a complex mixture of products. The major product was 1,1,1,2,3,3,3-heptafluoropropane (**14**). In addition approximately equal amounts of three hydrofluoroalkanes (**15**, **16**, **17**) were formed. The structures of the alkanes were established by GC/MS and NMR spectroscopy. The formation of **16** and **17** containing C_2H_5– and $(CH_3)_3C$– fragments most likely resulted from addition of $C_2H_5^+$ and $(CH_3)_3C^+$ to hexafluoropropylene. These cations are well known to form in the self-condensation reaction of methyl fluoride in magic acid [12]. The hydrogen fluoride formed in this process will react with hexafluoropropylene to give major product **14**. However, it is possible that formation of **14** could be the result of the protonation of a C–C bond of **17** by superacid followed by bond cleavage to give $(CH_3)_3C^+$ and **14**. Although this process is unknown at present for hydrofluorocarbons it has been reported for hydrocarbons [13].

$$\mathbf{10} + CF_2{=}CFCF_3 \xrightarrow[SbF_5]{50^{\circ}C,\ 12h} \underset{\mathbf{14}}{HCF(CF_3)_2} + \underset{\mathbf{15}}{CH_3CF(CF_3)_2} + \underset{\mathbf{16}}{C_2H_5CF(CF_3)_2} + \underset{\mathbf{17}}{(CH_3)_3CCF(CF_3)_2} + \tag{4}$$

ratio **14** :**15** : **16** : **17** = 75 : 11 : 5 : 9

yield mixture 70 %

$$(CH_3)_3C\text{-}CF(CF_3)_2 \xrightarrow[SbF_5]{H^+} (CH_3)_3C^+ + \underset{\mathbf{14}}{HCF(CF_3)_2} \tag{5}$$

Tetrafluoroethylene reacted with 1,1-difluoroethane (**18**) in the presence of SbF_5 to give the isomeric butanes **19a** and

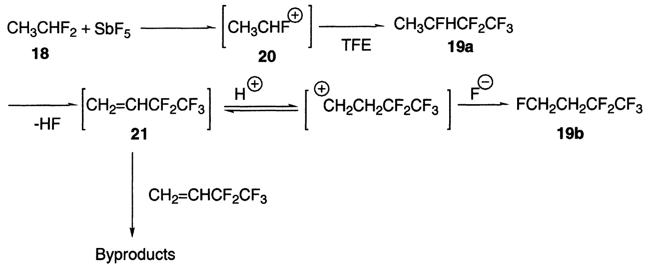
19b in moderate yield in addition to some higher boiling materials of unknown structure.

$$\underset{\mathbf{18}}{CH_3CHF_2} + TFE \xrightarrow[SbF_5]{40\text{-}50^{\circ}C,\ 10h} \underset{\mathbf{19a}}{CH_3CFHCF_2CF_3} + \underset{\mathbf{19b}}{FCH_2CH_2CF_2CF_3} + \text{others} \tag{6}$$

ratio **19a** : **19b** = 9 : 1

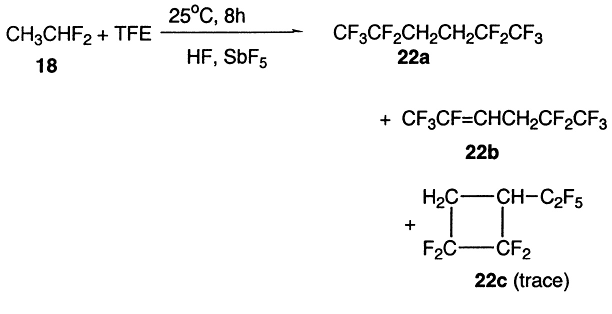
yield mixture 40%

A possible mechanism for the formation of **19a** and **19b** is shown in Scheme 3. Reaction of α-fluoroethyl cation (**20**) [14] with tetrafluoroethylene leads to the major product **19a**. Under the reaction conditions elimination of HF from **19a** produces olefin **21**. Readdition of HF to **21** yields the isomeric butane **19b**. The addition of HF to the carbon–carbon double bond of perfluoroalkylethylenes is known to result in the formation of 1-perfluoroalkyl-2-fluoroethanes [15,16]. The formation of higher boiling materials may well be due to the self-condensation of **21**.



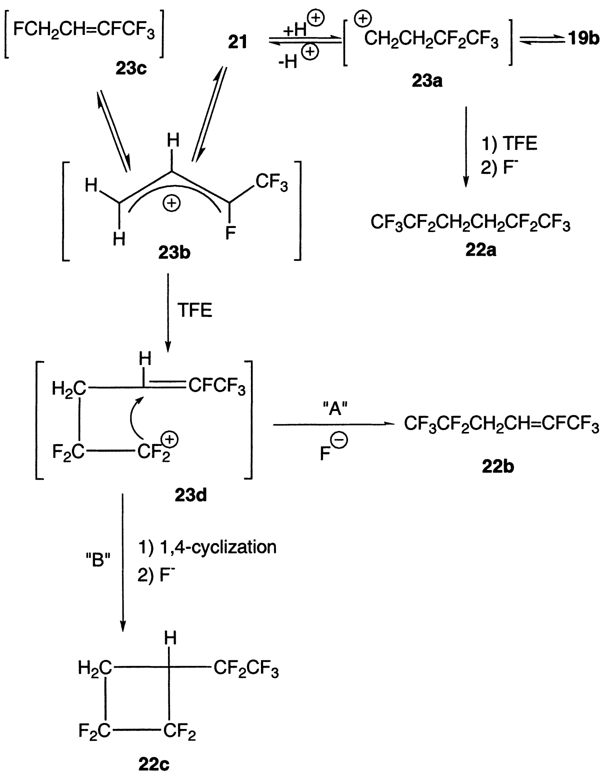
Scheme 3.

Surprisingly when the above reaction of **18** and tetrafluoroethylene was carried out in the presence of SbF_5 with HF as a solvent the major reaction products were hexane **22a** and hexene **22b**. In addition a trace amount cyclobutane **22c**, identified by GC/MS, as well as some higher boiling materials were formed.



ratio **22a** : **22b** = 7 : 1
yield mixture 50%

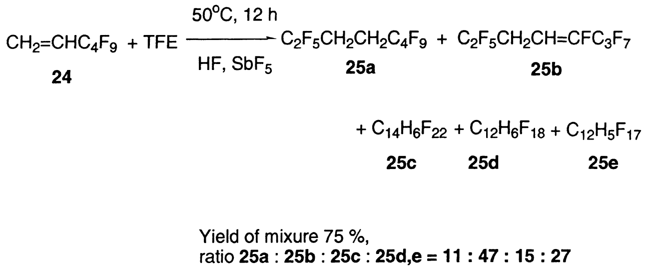
(7)



Scheme 4.

The formation of the observed products is shown in Scheme 4. The intermediate is believed to be $CH_2{=}CHCF_2CF_3$ (**21**) formed as shown in Scheme 3. Protonation of **21** may give cation **23a** which may yield (**19b**) or may yield the mesomeric cation **23b**, which in turn will yield $FCH_2CH{=}CFCF_3$ (**23c**) [16]. Under the reaction conditions both carbocations **23a** and **23b** may be in equilibrium with **23c** and **19b**. Reaction of carbocation **23a** with tetrafluoroethylene leads to the observed decafluorohexane **22a**. The reaction of carbocation **23b** with tetrafluoroethylene leads to the formation of the relatively stable α,α-difluorocarbocation **23d**. It may either add fluoride ion via path "A" to give the observed olefinic product **22b** or undergo an intramolecular cyclization via path "B" to yield cyclobutane **22c** the minor product of the reaction. Intramolecular cyclization of perhalogenated carbocations resulting in the formation of a cyclobutane was first reported by Krespan and Dixon [9] and later also observed in the reaction of hexafluoroisobutene and tetrafluoroethylene [17].

The formation of products **25a** and **25b** in the reaction of perfluorobutylethylene **24** and TFE in a mixture of HF and SbF_5 support the mechanism proposed in Scheme 4. The isolated products, octane **25a** and octene **25b** are analogous to those found from the reaction of CH_3CHF_2 (**18**) and tetrafluoroethylene carried out in the presence of SbF_5 with HF as a solvent where (**21**) was the proposed intermediate (Eq. (7) and Scheme 4).



$$\underset{\mathbf{24}}{CH_2{=}CHC_4F_9} + TFE \xrightarrow[HF,\ SbF_5]{50^\circ C,\ 12\ h} \underset{\mathbf{25a}}{C_2F_5CH_2CH_2C_4F_9} + \underset{\mathbf{25b}}{C_2F_5CH_2CH{=}CFC_3F_7} + \underset{\mathbf{25c}}{C_{14}H_6F_{22}} + \underset{\mathbf{25d}}{C_{12}H_6F_{18}} + \underset{\mathbf{25e}}{C_{12}H_5F_{17}}$$

Yield of mixture 75 %,
ratio **25a** : **25b** : **25c** : **25d,e** = 11 : 47 : 15 : 27

(8)

Higher boiling compounds **25c–e** were also products of this reaction. Although these materials were not isolated GC/MS and NMR spectra data strongly suggest that **25c** has the formula $C_{14}H_6F_{22}$ and is the product of the condensation of 1 mol of tetrafluoroethylene with 2 mol of starting *F-n*-butylethylene. Compounds **25d** and **25e** with the formulas $C_{12}H_6F_{18}$ and $C_{12}H_5F_{17}$, respectively, are the result of the dimerization of starting olefin **24**. Formation of compounds with similar composition has been reported in reaction of **24** in superacidic media [16]. The presence of significant amounts of **25c–e** (>40%, see Section 2) indicates that under these conditions the rate of reaction of **24** with tetrafluoroethylene is comparable to the rate of self-condensation. Interestingly, neither **25a** nor **25b** were formed when **24** was reacted with tetrafluoroethylene in HF with BF_3 as the catalyst [16]. This is consistent with the use, in the present work, of the more powerful Lewis acid, antimony pentafluoride, which serves to increase the effective concentrations of the intermediate cations analogous to **23a** and **23b**.

2. Experimental

^{19}F and ^{1}H NMR spectra were recorded on a QE-300 (General Electric, 200 MHz) or Brucker DRX-400 instruments (400.5524 and 376.8485 MHz, respectively) using $CFCl_3$ as internal standard or chloroform-*d* or acetone-d_6 as a lock solvent. IR spectra are recorded on Perkin-Elmer 1600 FT spectrometer in a liquid film. CF_2H_2, CH_3F (Aldrich), SbF_5, $CFH{=}CF_2$, $CFCl{=}CFCl$ (PCR), CH_3CF_2H, $C_4F_9CH{=}CH_2$, TFE and HFP (DuPont) are commercially available and were used without further purification. Compounds **13**, **14** were identified by comparison with authentic samples. Compounds **2**, **12** [18], **3**, **15**, **16** [19], **7**, **11** [20], **16** [21], **19b** [15] were identified by comparison of their ^{19}F and ^{1}H NMR spectra data with their reported literature values.

2.1. Reaction of difluoromethane (1) and tetrafluoroethylene (TFE)

A 250 ml stainless steel shaker tube was loaded with 45 g of SbF_5, 39 g of **1** and 30 g of TFE. The reaction vessel was agitated for 8 h at 50°C, second portion of TFE (30 g) added and the reaction vessel heated at 80°C for another 20 h. The gaseous products were bleed out of the reactor and collected in a −78°C cold trap. Distillation of the crude product gave 75 g of **2**, bp 0–1°C. The yield of **2** was 80%.

The reaction was carried out using same amount of reagents, but 5 g of SbF_5. In this experiment compound **2** was isolated in 92% yield.

2.2. Reaction of difluoromethane (1) and hexafluoropropene (HFP)

A 250 ml stainless steel shaker tube was loaded with 45 g of SbF_5, 39 g of **1** and 66 g of HFP. The reaction vessel was agitated for 8 h at 50°C, a second portion of HFP (30 g) added and the reaction vessel heated at 50°C for another 8 h. The gaseous products were bleed out of the reactor and collected in a −78°C cold trap. Distillation of the crude product gave 80 g of **3**, bp 22–24°C. The yield of **3** was 90%.

2.3. Reaction of difluoromethane (1) and CFCl=CFCl

A 250 ml stainless steel shaker tube was loaded with 22 g of SbF_5, 36 g of **1** and 26 g of CFCl=CFCl. The reaction vessel was agitated for 3 h at 20°C. Crude product is collected in cold trap (−78°C) while the reactor is heated in hot water bath. Crude product is collected in cold trap (−78°C) while the reactor is heated in hot water bath. Collected in cold trap product was washed with water, dried over $MgSO_4$ and distilled to give 12 g (36% yield) of compound **7**, bp 62–64°C.

2.4. Reaction of methyl fluoride (10) and tetrafluoroethylene (TFE)

A 400 ml Hastelloy shaker tube was loaded with 15 g of SbF_5, 35 g of **10** and 50 g of TFE. The reaction vessel was agitated for 6 h at 25°C and 10 h at 50°C. The gaseous products were bleed from the reactor and collected in a −78°C cold trap. Distillation of the 40 ml crude reaction mixture gave 45 g (67%) of $CH_3CF_2CF_3$ (98% purity), bp −13 to −12°C.

2.5. Reaction of methyl fluoride (10) and hexafluoropropene (HFP)

A mixture of 20 g of **10**, 75 g of $CF_2{=}CFCF_3$ and 15 g of SbF_5 was heated for 14 h at 50°C. Isolation gave 68 g of a mixture containing 77% of **14**, 11% of **15**, 5% of **16** and 9% $(CF_3)_2CFC(CH_3)_3$ (**17**) based on ^{1}H and ^{19}F NMR analysis. The yield of **17** was 4%. Compound **17** was characterized in the reaction mixture. ^{1}H NMR: 1.12 (s). ^{19}F NMR: −74.13 (6F, d; 6 Hz), −211.73 (1F, m). MS, *m/e*: 211.0364 $(M{-}CH_3)^+$, $C_6H_6F_7{}^+$, calc. 211.0358.

2.6. Reaction of methyl fluoride (10) and trifluoroethylene

A mixture of 10 g of **10**, 24 g of $CF_2{=}CFH$ and 10 g of SbF_5 was heated for 14 h at 25°C. Isolation gave 12 g of a fraction, bp 0–2°C, which contained 90% CF_3CFHCH_3 and 10% CF_3CFH_2 as determined by ^{19}F NMR. The yield of fluoropropane was 38.6%.

*2.7. Reaction of 1,1-difluoroethane (**18**) and tetrafluoroethylene (TFE)*

Compound **18** (53 g), antimony pentafluoride (44 g) and TFE (30 g) were heated in a 250 ml stainless steel shaker tube at 40–50°C for 10 h. The products were transferred to a -78°C cold trap. The excess **18** was removed by distillation, the residue washed with water, dried and distilled to give 20 g of a mixture, bp 23–27°C. This mixture contained 89% **19a** and 11% **19b** based on NMR analysis. The total yield was 40%. The residue (20 g) was not analyzed. Compound **19a** was characterized in the mixture. ^{19}F NMR: -84.0 (3F, m; 10 Hz), -131.5 (2F, typical AB pattern; 230; 16; 7 Hz), -196.5 (1F, m; 45; 17 Hz). ^{1}H NMR: 1.7 (3H), 5.25 (1H).

*2.8. Reaction of 1,1-difluoroethane (**18**) and tetrafluoroethylene (TFE) in HF*

Compound **18** (11 g), antimony pentafluoride (45 g), TFE (40 g) and 80 g anhydrous HF were shaken in a 250 ml stainless steel shaker tube at 20°C for 8 h. The reactor was heated in boiling water and the crude product collected in a polyethylene wash bottle filled with water. The organic layer was separated, washed with water, dried over $MgSO_4$ and distilled to give 27 g of a fraction, bp 46–57°C. Based on GC and NMR data the mixture contained **22a** and **22b** and small amount of **22c** in the ratio of 70:29:3. The yield of the mixture was 50%. No attempt was made to separate compounds **22a–c**. The materials are characterized from the mixture. Compound **22a**: ^{19}F NMR: -87.5 (3F, s), -121.0 (2F, s). ^{1}H NMR: 2.5 (m). MS (*m/z*, relative intensities %): 247 (M–F, $C_6H_4F_9^+$, 0.1), 227 ($C_6H_3F_8^+$, 9.7), 197 ($C_5H_4F_7^+$, 18.9), 177 ($C_5H_3F_6^+$, 29.6), 157 ($C_5H_2F_5^+$, 6.7), 127 ($C_4H_3F_4^+$, 6.7), 77 ($C_2H_3F_2^+$, 100), 69 (CF_3^+, 68.4). Compound **22b**: ^{19}F NMR: -75.3 (3F, d; 10 Hz), -87.0 (3F, s), -119.0 (2F, t; 10 Hz), -131.5 (1F, m). ^{1}H NMR: 3.1 (2H, m; 7.5; 10 Hz), 5.8 (1H, dt; 30; 7.5 Hz). Raman spectrum: 1728 cm^{-1}. MS (*m/z*, relative intensities %): 246 (M^+, $C_6H_3F_9^+$, 9.6), 227 ($C_6H_3F_8^+$, 8.5), 207 ($C_6H_2F_7^+$, 2.3), 177 ($C_5H_3F_6^+$, 7), 157 ($C_5H_2F_5^+$, 0.7), 127 ($C_4H_3F_4^+$, 66), 113 ($C_3HF_4^+$, 20.3), 77 ($C_2H_3F_2^+$, 100), 69 (CF_3^+, 68.4). Compound **22c**: MS (*m/z*, relative intensities %): 227 (M–F, $C_6H_3F_8^+$, 0.8), 207 ($C_6H_2F_7^+$, 1.6), 177 ($C_5H_3F_6^+$, 1.8), 157 ($C_5H_2F_5^+$, 1.9), 127 ($C_4H_3F_4^+$, 4.5), 113 ($C_3HF_4^+$, 9.7), 77 ($C_2H_3F_2^+$, 13), 69 (CF_3^+, 10.6), 64 ($C_2H_2F_2^+$, 100).

*2.9. Reaction of perfluorobutylethylene (**24**) and TFE*

A 400 ml Hastelloy shaker tube was loaded with 10 g of SbF_5, 100 g of HF, 20 g of 24 and 20 g of TFE. The reaction vessel was agitated for 12 h at 50°C. After 100 ml of water was injected into reaction vessel, the organic layer was separated and dried over $MgSO_4$. The crude product (30 g) was found to be a mixture of four major components, which comprised >95% of the sample, **25a–d** in the ratio of 11:47:15:27, respectively. Distillation of the crude reaction mixture afforded 10 g of fraction, bp 105–110°C and 15 g of residue. The NMR spectrum of the first fraction showed it to consist of a mixture of compounds **25a** and **25b** in the ratio 15:85. The 90% of the residue were found to be a mixture of **25c** and **25d**. The remaining 10% were not identified.

25a: ^{19}F NMR: -81.60 (3F, m), -86.01 (3F, s), -117.00 (2F, m), -119.51 (2F, m), -124.79 (2F, m), -126.51 (2F, m). ^{1}H NMR: 2.20 (m). GC/MS (*m/z*, major peaks): 327 (M–HF_2, $C_8H_3F_{12}^+$), 277 ($C_7H_3F_{10}^+$), 213 ($C_5HF_8^+$), 197 ($C_5H_4F_7^+$), 177 ($C_5H_3F_6^+$, 100%), 157 ($C_5H_2F_5^+$), 127 ($C_4H_3F_4^+$), 113 ($C_3HF_4^+$), 77 ($C_2H_3F_2^+$), 69 (CF_3^+), 64 ($C_2H_2F_2^+$).

25b: ^{19}F NMR: -81.57 (3F, m), -86.66 (3F, s), -117.07 (2F, m), -119.51 (2F, m), -124.96 (1F, m), -127.97 (2F, m). ^{1}H NMR: 2.88 (2H, m), 5.52 (1H, dt; 31; 8 Hz). IR 1730 (w) cm^{-1}. GC/MS (*m/z*, major peaks): 346 (M^+, $C_8H_3F_{13}^+$), 327 (M–HF_2, $C_8H_3F_{12}^+$), 277 ($C_7H_3F_{10}^+$, 100%), 213 ($C_5HF_8^+$), 157 ($C_5H_2F_5^+$), 127 ($C_4H_3F_4^+$), 113 ($C_3HF_4^+$), 77 ($C_2H_3F_2^+$), 69 (CF_3^+).

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