

# Intramolecular cyclization with participation of the cyano group in reactions of fluoro-olefins with hexafluoroacetone cyanohydrin

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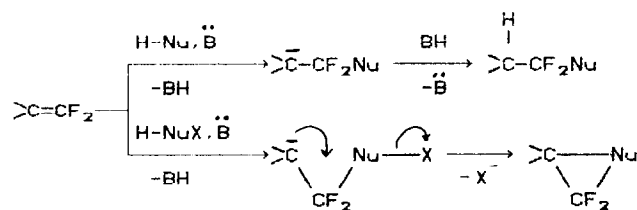
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## Abstract

The reaction of fluoro-olefins (I) with hexafluoroacetone cyanohydrin (II) catalyzed by Et<sub>3</sub>N gives fluorinated 3-iminotetrahydrofurans (III), whose structures have been confirmed by spectral methods and various chemical transformations. A mechanism for the formation of products III is suggested including nucleophilic addition of an O-anion to a C=C bond followed by intramolecular cyclization in the intermediate C-anion with participation of the C≡N group.

## Introduction

The interaction for fluoro-olefins with proton-containing nucleophiles usually leads to addition of the reagent to a multiple bond. However, intramolecular cyclization can take place in those cases when the nucleophile contains groups attached to the nucleophilic centre (or to more distant positions) and is capable of being split off as an anion (Scheme 1).

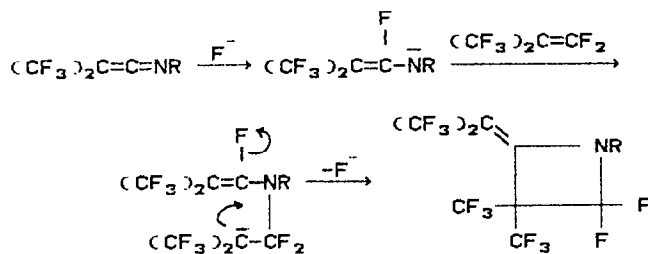


Scheme 1.

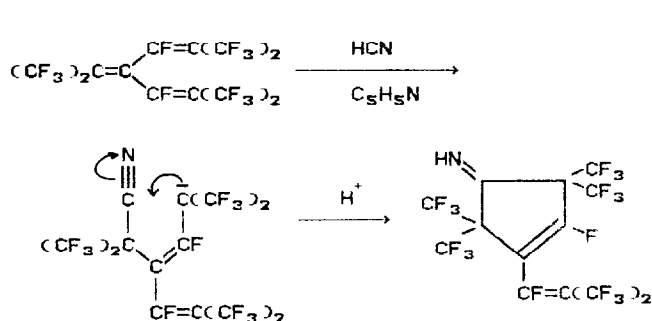
Typical examples of similar processes, resulting in formation of three-membered rings, are the epoxidation of fluoro-olefins with hydrogen peroxide in an alkaline medium [1] or hypochlorites [2] and their epimerization with *N*-chloro-, *N*-acyloxy- and *N*-(*p*-nitrobenzenesulphonyloxy)amides in the presence of organic bases [3, 4].

The cycloaddition of fluorine-containing ketene imines [5] or allenes [6] to perfluoroisobutene, which gives four-membered rings, proceeds in accordance with the same reaction scheme under nucleophilic catalytic conditions. In this case, the nucleophile with a leaving group in the position  $\alpha$  to the charged centre is generated during the course of the reaction (Scheme 2).

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Scheme 2.



Scheme 3.

In the above examples, cyclization occurs as a result of intramolecular nucleophilic substitution which proceeds via an intermediate fluorinated carbanion. A similar process affording fluorine-containing derivatives of tetrahydrofuran appears to take place when perfluoro-2-methyl-pent-2-ene interacts with O-anions containing a chlorine atom in the  $\beta$ -position [7, 8].

In the other variation, the addition of an intermediate carbanion to an electrophilic multiple bond introduced into the molecule as part of the nucleophile occurs during the cyclization step. Both the ester group [9]

and the cyano group [10] can participate in such a cyclization (Scheme 3).

A similar cyclization also occurs during the interaction of fluoro-olefins **Ia–d** with hexafluoroacetone cyanohydrin (**II**) in the presence of  $\text{Et}_3\text{N}$  as a catalyst.

## Experimental

$^1\text{H}$  NMR spectra were recorded using a Bruker WP-200 SY (200 MHz) spectrometer; chemical shifts are reported in parts per million (ppm) from TMS as external standard. Infrared spectra were obtained with a UR-20 spectrometer. Mass spectroscopic data were obtained with a VG-7070E instrument employing an ionization potential of 70 eV at an ion source temperature of 140 °C [ $m/z$ , tentative assignment and relative intensity (%) are given]. The analytical and preparative GLC columns used were packed with Crytox and FS-1265 on Chromosorb W.

### Preparation of hexafluoroacetone cyanohydrin (**II**)

Hexafluoroacetone (70 g) was passed into suspension consisting of 28 g KCN in 200 ml anhydrous MeCN with stirring and cooling to 0–5 °C. The mixture was heated up to 20 °C for 0.5 h and then poured into a 1:5 aqueous solution of HCl; the organic layer was separated and mixed with an equal volume of conc.  $\text{H}_2\text{SO}_4$  under cooling. The crude cyanohydrin **II** was distilled off *in vacuo* (5 mmHg pressure). Repeated distillation gave 63 g (77%) cyanohydrin **II**, b.p. 106–108 °C.  $^{19}\text{F}$  NMR  $\delta$ : –0.1 s (lit. value, see ref. 11).

### Preparation of (2-hydrohexafluoropropoxy)hexafluoroisobutyric acid nitrile (**III**) and perfluoro-2,2,4-trimethyl-3-iminotetrahydrofuran (**IVa**)

A mixture consisting of 8.8 g cyanohydrin **II**, 0.3 ml  $\text{Et}_3\text{N}$ , 8.0 g olefin **Ia** and 15 ml anhydrous DMF was left to stand in a sealed tube at 20 °C for 2 d; olefin **Ia** was then added in two portions (5 g and 8 g) until complete conversion of cyanohydrin **II** was achieved (7 d, GLC methods). The mixture was then poured into HCl (1:5), and distillation of the oil separated over conc.  $\text{H}_2\text{SO}_4$  gave a fraction (12.8 g, 82%, b.p. 90–97 °C) containing 30% nitrile **III** and 70% imine **IVa** (GLC methods). Analysis: Found: C, 24.65; H, 0.41; F, 65.65%.  $\text{C}_7\text{HF}_{12}\text{NO}$  requires: C, 24.49; H, 0.29; F, 66.47%. Preparative GLC afforded imine **IVa** b.p. 93–94 °C. Analysis: Found: C, 24.52; H, 0.29; F, 66.40%.

### Preparation of perfluoro-2,2,4,4-tetramethyl-3-iminotetrahydrofuran (**IVb**)

To a solution consisting of 10.5 g cyanohydrin **II** and 0.4 ml  $\text{Et}_3\text{N}$  in 30 ml anhydrous ether, olefin **Ib** (10.0 g) was added; the mixture was stirred at 20 °C for 1.5

h and after 12 h unreacted olefin **Ib** and most of the ether were distilled off. Distillation of the residue *in vacuo* over conc.  $\text{H}_2\text{SO}_4$  gave imine **IVb** (16.5 g, 75.8%), b.p. 111–112 °C,  $n_{\text{D}}^{20}$  1.3085. Analysis: Found: C, 24.53; H, 0.50; F, 67.33%.  $\text{C}_8\text{HF}_{14}\text{NO}$  requires: C, 24.43; H, 0.25; F, 67.68%.  $^1\text{H}$  NMR  $\delta$ : 11.9 (br. s) ppm. IR ( $\text{cm}^{-1}$ ): 1690 (C=N); 3330 (NH).

### Preparation of perfluoro-2,2,4,4-tetramethyl-5-ethyl-3-iminotetrahydrofuran (**IVc**)

A mixture consisting of 4.4 g cyanohydrin **II**, 0.1 ml  $\text{Et}_3\text{N}$ , 6.8 g olefin **Ic** and 10 ml anhydrous MeCN was stirred at 20 °C for 16 h and poured into a 1:5 aqueous solution of HCl. The oil which separated was treated with conc.  $\text{H}_2\text{SO}_4$ , allowed to stand at 100 °C for 1 h to remove unreacted **II** and then distilled. Imine **IVc** (6.4 g, 57%, b.p. 141–142 °C,  $n_{\text{D}}^{20}$  1.3090) was obtained. Analysis: Found: C, 24.28; H, 0.30; F, 69.31%.  $\text{C}_{10}\text{HF}_{18}\text{NO}$  requires: C, 24.34; H, 0.20; F, 69.37%.  $^1\text{H}$  NMR  $\delta$ : 12.55 (br. s) ppm. IR ( $\text{cm}^{-1}$ ): 1690 (C=N); 3330 (NH).

### Preparation of perfluoro-3,5,5-trimethyl-4-iminotetrahydrofuran-3-carbonic acid methyl ester (**IVd**)

To a solution consisting of 1.2 g cyanohydrin **II** and two drops of  $\text{Et}_3\text{N}$  in 3 ml anhydrous ether was added 1.2 g olefin **Id** in 3 ml ether; when the exothermal reaction had ceased, 1.9 g (79%) of imine **IVd** was isolated by distillation, b.p. 43–44 °C/3 mmHg,  $n_{\text{D}}^{20}$  1.3445. Analysis: Found: C, 28.31; H, 1.09; F, 54.50%.  $\text{C}_9\text{H}_4\text{F}_{11}\text{NO}_3$  requires: C, 28.20; H, 1.04; F, 54.57%.  $^1\text{H}$  NMR  $\delta$ : 4.05 (s, CH); 12.15 (br. s, NH) ppm. IR ( $\text{cm}^{-1}$ ): 1695 (C=N); 1750 (C=O); 3320 (NH). MS: 383 ( $\text{M}^+$ ) 2; 364 ( $\text{M}^+ - \text{F}$ ) 1.5; 344 ( $\text{M}^+ - \text{F} - \text{HF}$ ) 2.5; 332 ( $\text{M}^+ - \text{HF} - \text{OMe}$ ) 9.8; 158 ( $\text{C}_4\text{F}_5\text{NH}$ ) 14.1; 148 ( $\text{M}^+ - \text{C}_3\text{F}_6\text{O} - \text{COOMe}$ ) 2.7; 138 ( $\text{C}_4\text{F}_4\text{N}$ ) 4.4; 69 ( $\text{CF}_3$ ) 25.8; 59 (COOMe) 100.

### Preparation of perfluoro-N-isobutenyl-2,2,4,4-tetramethyl-3-iminotetrahydrofuran (**VIa**)

To a suspension of 4.4 g KCN in 25 ml anhydrous MeCN was added hexafluoroacetone (8.0 g) at 5–10 °C and the precipitate filtered. Olefin **Ib** (20.0 g) was added to the filtrate at 0–5 °C and when the exothermal reaction had ceased the mixture was allowed to stand at 20 °C for 12 h and then poured into a 1:5 aqueous solution of HCl. The oil which separated was washed with  $\text{NaHCO}_3$  solution and distilled *in vacuo* over conc.  $\text{H}_2\text{SO}_4$ . The product **VIa** (21.8 g, 79%) was obtained, b.p. 73–74 °C/3 mmHg,  $n_{\text{D}}^{20}$  1.3290. Analysis: Found: C, 25.18; F, 69.89%.  $\text{C}_{12}\text{F}_{21}\text{NO}$  requires: C, 25.13; F, 69.63%. IR ( $\text{cm}^{-1}$ ) 1685 (C=N); 1755 (C=C).

An equimolar mixture of imine **IVb**, olefin **Ib** and a few drops of  $\text{Et}_3\text{N}$  in MeCN was allowed to stand for 30 h. The product **IVb** containing 10% **VIa** (GLC

methods) was obtained. To 4.0 g imine **VIa** in 15 ml acetone and 1 ml water was added  $\text{KMnO}_4$  in portions with stirring until a stable violet colour appeared. The reaction mass was poured into a 1:5 aqueous solution of  $\text{HCl}$ , the crystals precipitated extracted with ether and the solution evaporated. Sublimation of the residue *in vacuo* (2 mmHg) gave 2.2 g (55%) of product **VIb**, m.p. 137–138 °C. Analysis: Found: C, 24.50; F, 64.89; N, 2.45%.  $\text{C}_{12}\text{HF}_{20}\text{NO}_3$  requires: C, 24.53; F, 64.74; N, 2.39%.

#### Preparation of *N*-chloroperfluoro-2,2,4,4-tetramethyl-3-iminotetrahydrofuran (**VIII**)

To a mixture consisting of 3.2 g imine **IVb**, 2 ml anhydrous  $\text{MeCN}$  and 2 g chlorine was added 2 g pyridine dropwise over 0.5 h; the reaction mass was stirred until the reaction was completed (GLC methods), then treated with conc.  $\text{H}_2\text{SO}_4$  followed by distillation *in vacuo* which gave 2.5 g (71%) of imine **VIII**, b.p. 49–50 °C/40 mmHg,  $n_D^{20}$  1.3340. Analysis: Found: C, 22.46; F, 61.92%.  $\text{C}_8\text{ClF}_{14}\text{NO}$  requires: C, 22.45; F, 62.22. IR ( $\text{cm}^{-1}$ ): 1640 ( $\text{C}=\text{N}$ ).

#### Preparation of perfluoro-2,2,5-trimethyl-3-ketotetrahydrofuran (**IX**)

A mixture (11.8 g) containing 35% nitrile **III** and 65% imine **IVa** was heated with 50 ml conc.  $\text{H}_2\text{SO}_4$  at 70 °C for 5 h with stirring. The resulting mixture, consisting of 60% ketone **IX**, 38% nitrile **III** and 2% imine **IVa**, distilled off. Following fractionation, this gave pure ketone **IX**, b.p. 72 °C,  $n_D^{20} < 1.3$ . Analysis: Found: C, 24.29; F, 66.22%.  $\text{C}_7\text{F}_{12}\text{O}_2$  requires: C, 24.42; F, 66.28%. IR ( $\text{cm}^{-1}$ ): 1810 ( $\text{C}=\text{O}$ ). MS: 344 ( $\text{M}^+$ ) 4.9; 325 ( $\text{M}^+ - \text{F}$ ) 4.2; 297 ( $\text{C}_6\text{F}_{11}\text{O}$ ) 10.0; 197 ( $\text{C}_4\text{F}_7\text{O}$ ) 1.5; 150 ( $\text{C}_3\text{F}_6$ ) 100; 147 ( $\text{C}_3\text{F}_5\text{O}$ ) 3.8; 97 ( $\text{C}_2\text{F}_3\text{O}$ ) 4.3; 131 ( $\text{C}_3\text{F}_5$ ) 29.7; 119 ( $\text{C}_2\text{F}_5$ ) 2.4; 69 ( $\text{CF}_3$ ) 46.3.

#### Interaction of hexafluoroacetone cyanohydrin (**II**) with perfluoromethylcyclopentene

A mixture consisting of 4.6 g cyanohydrin **II**, 6.2 g olefin **X**, 1.4 g  $\text{KF}$  and 15 ml anhydrous  $\text{MeCN}$  was stirred at c. 20 °C for 1 h, poured into water, the organic layer dried over  $\text{MgSO}_4$  and distilled. Dinitrile **XI** (4.3 g, 59%) was obtained, b.p. 59–60 °C/3 mmHg,  $n_D^{20}$  1.3250. Analysis: Found: C, 27.54; F, 62.65%.  $\text{C}_{14}\text{F}_{20}\text{N}_2\text{O}_2$  requires: C, 27.63; F, 62.50%. IR ( $\text{cm}^{-1}$ ): 1695, 1725 ( $\text{C}=\text{C}$ ); 2285 ( $\text{C}=\text{N}$ ). MS: 608 ( $\text{M}^+$ ) 7.2; 589 ( $\text{M}^+ - \text{F}$ ) 67.2; 539 ( $\text{M}^+ - \text{CF}_3$ ) 17.1; 432 ( $\text{M}^+ - \text{C}_3\text{F}_6\text{N}$ ) 73.9.

## Results and discussion

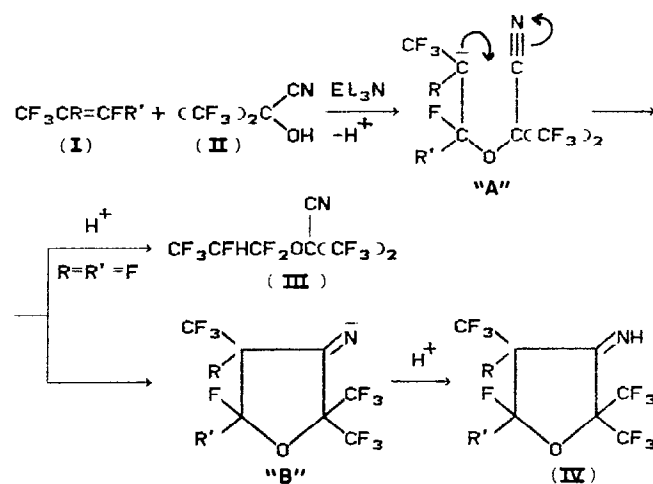
Under mild conditions (c. 20 °C, DMF), it has been shown that hexafluoropropene (**1a**) reacts with cy-

anohydrin **II** in the presence of  $\text{Et}_3\text{N}$  to give a mixture of two products, i.e. alkoxy nitrile **III** and iminotetrahydrofuran **IVa** in a total yield of c. 80%. The structures of isomers **III** and **IVa** are readily obtained by comparison of their spectral characteristics. Thus, the IR spectra of isomers **III** and **IVa** exhibit bands at 2285  $\text{cm}^{-1}$  ( $\text{C}\equiv\text{N}$ ) and 1700  $\text{cm}^{-1}$  ( $\text{C}=\text{N}$ ), respectively. In addition, a multiplet  $\text{CH}$  ( $\delta$  4.8 ppm) with a typical geminal coupling constant  $J(\text{F}-\text{H}) = 44$  Hz and a broad signal  $\text{NH}$  ( $\delta$  11.5 ppm) also exist in the  $^1\text{H}$  NMR spectra of isomers **III** and **IVa**, respectively.

It should be noted that nitrile **III** does not isomerize into imine **IVa** under conditions similar to those employed in the reaction ( $\text{DMF}$ ,  $\text{Et}_3\text{N}$  or  $\text{CsF}$  as catalyst). Thus the 30:70 ratio of products **III** and **IVa** obtained, which remains constant during the course of the reaction, indicates the extent to which the two independent transformations of the intermediate fluorocarbanion **A** (protonation and cyclization) proceed (Scheme 4).

Interaction of perfluoroisobutene (**IIb**), perfluoro-2-methylpentene (**IIc**) or methylperfluoromethacrylate (**IId**) with cyanohydrin **II** and  $\text{Et}_3\text{N}$  also led to the formation of the corresponding iminotetrahydrofurans **IVb–d**. In contrast to that mentioned above, these reactions proceed in only one direction and are not accompanied by the formation of the usual products of nucleophilic HO addition.

The highly electrophilic olefins **IIb,d** interact exothermally with cyanohydrin **II** even in a slightly polar solvent such as ether in accordance with their reactivity order in nucleophilic reactions, whereas the less active olefins **IIa,c** react with a noticeable rate only in highly polar  $\text{MeCN}$  or  $\text{DMF}$ . As would be expected, the cyanohydrin potassium salt **V** reacts more readily with olefins **I** than does cyanohydrin **II**. The reaction of salt **V** with olefin **IIb** yields the *N*-perfluoroisobutenyl derivative **VIa** in



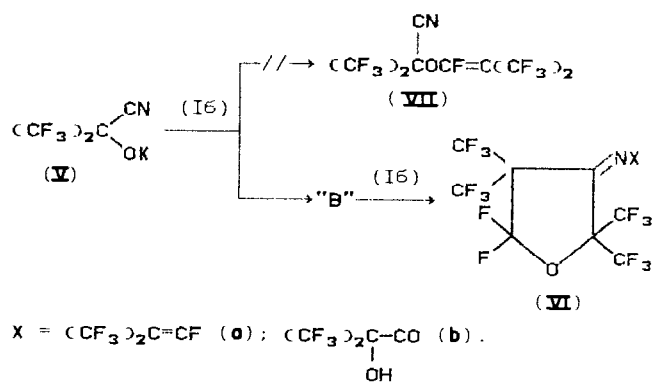
$\text{R}=\text{R}'=\text{F}$  (a);  $\text{R}=\text{CF}_3$ ,  $\text{R}'=\text{F}$  (b);  $\text{R}=\text{CF}_3$ ,  $\text{R}'=\text{C}_2\text{F}_5$  (c);  $\text{R}=\text{COOMe}$ ,  $\text{R}'=\text{F}$  (d).

Scheme 4.

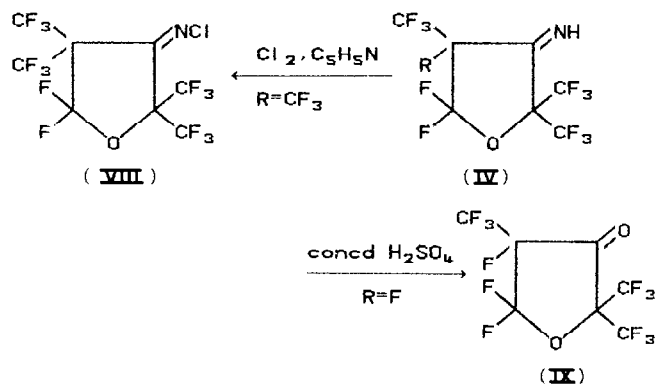
high yield as a result of cyclization followed by the involvement of the intermediate N-anion **B** in reaction with a second molecule of **Ib**. In this case, the usual product of vinyl substitution, **VII**, is not formed. Attempts to complete the reaction of **Ib** with the salt **V** at the stage of 1:1 adduct formation failed; compound **Vla** was the sole product irrespective of the ratio of reactants employed. When insufficient amounts of olefin **Ib** were employed, unreacted salt **V** was isolated from the reaction mixture together with the product **Vla** (Scheme 5).

The structure of **Vla** has been confirmed from the spectral data and from its transformation into the  $\alpha$ -oxyamide **Vlb** by the action of  $\text{KMnO}_4$  (cf. ref. 12). The perfluoroisobutenyl derivative **Vla** is also formed in the reaction of iminotetrahydrofuran **IVb** with olefin **Ib** catalyzed by bases in a highly polar medium. In addition, the imine **IVb** can be chlorinated in the presence of pyridine to produce the *N*-chloro derivative **VIII**. At the same time, imine **IVb** showed unusual stability towards the action of strong mineral acids; this is not typical of compounds containing the  $\text{C}=\text{N}$  group, including the fluorinated analogues [13]. This means that imine **IVb** remains unchanged after prolonged heating with concentrated  $\text{H}_2\text{SO}_4$  at *c.* 100 °C. Such resistance to acid hydrolysis appears to be associated with steric hindrance caused by the presence of four bulky  $\text{CF}_3$  groups in positions  $\alpha, \alpha'$  to the imino group. This assumption is supported by the fact that the imine **IVa**, which contains only three  $\text{CF}_3$  groups in  $\alpha, \alpha'$ -positions, yields the corresponding ketone **IX** quite readily by the action of  $\text{H}_2\text{SO}_4$  (Scheme 6).

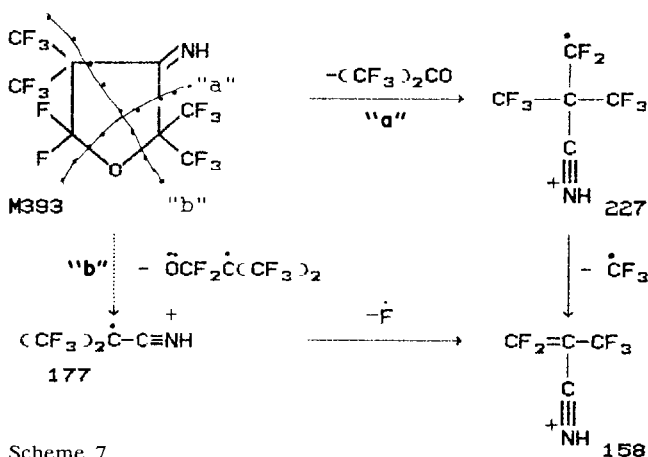
The iminotetrahydrofurans **IV**, **VI** and **VIII** exist as mixtures of stereoisomers, thus making it difficult to interpret their  $^{19}\text{F}$  NMR spectra. However, their mass spectra unambiguously confirm the structures of the above compounds (see Table 1). These spectra contain ions (together with  $\text{M}^+$  and  $[\text{M} - \text{F}]^+$ ) which are formed as a result of successive  $\text{M}^+$  fragmentation of hexafluoroacetone and one of the substituents in the 4-



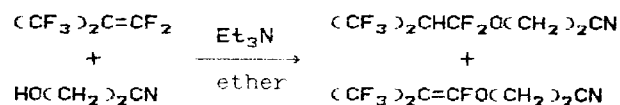
Scheme 5.



Scheme 6.



Scheme 7.

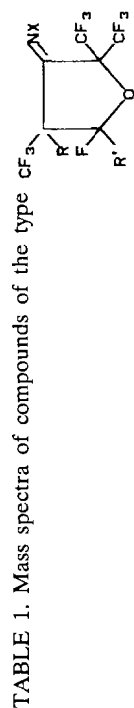


Scheme 8.

position: F or  $\text{CF}_3$  in **IVa** ( $m/z$  158 and 108),  $\text{COOMe}$  or  $\text{CF}_3$  in **IVd** ( $m/z$  158 and 148). The mass spectra of the other compounds containing geminal trifluoromethyl groups in position 4 contain ions with  $m/z$  158 (**IVb**), 192 (**XII**), 258 (**IVc**), 338 (**IVa**) and 352 (**Vb**) [ $\text{M}^+ - \text{C}_3\text{F}_6\text{O} + \text{CF}_3$ ]. Both the steps a and b in the fragmentation of compounds **IVb** have been confirmed by analysis of the metastable ions (Scheme 7). The fragmentation scheme for  $\text{M}^+$  (from **IVc**) is similar.

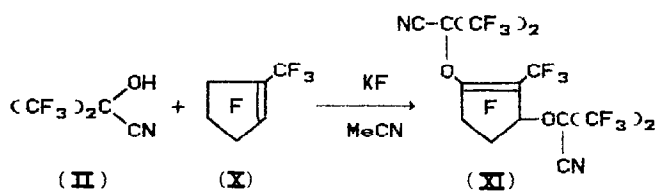
Ion 158 (from **IVb**) could also be formed as a result of fragmentation proceeding via route b, but this assumption has only been confirmed by observation of the metastable transition 177  $\rightarrow$  158. In addition, irrespective of its formation route, the presence of ion 158 supports the cyclic structure of imine **IVb**.

Attempts to extend the above reaction to other cyanohydrins have proved unsuccessful. In particular, it was shown that interaction of olefin **Ib** with ethylene cyanohydrin and  $\text{Et}_3\text{N}$  only afforded a mixture of addition and vinyl substitution products (Scheme 8).



Fragments	Substituents and corresponding compounds					
	R = F, R' = F, X = H (IVa)	R = CF <sub>3</sub> , R' = F, X = H (IVb)	R = CF <sub>3</sub> , R' = F, X = H (IVc)	R = CF <sub>3</sub> , R' = F, X = (CF <sub>3</sub> ) <sub>2</sub> C=CF (VIa)	R = CF <sub>3</sub> , R' = F, OH   X = (CF <sub>3</sub> ) <sub>2</sub> C-CO (VIb)	R = CF <sub>3</sub> , R' = F, X = Cl (VIII) <sup>a</sup>
M	343/18	393/9.6	493/9.9	573/17.4	587/7.2	427/20.4
M-F	324/7.2	374/6.1	474/8.2	554/22.4	568/9.7	408/7.4
M-HF	323/15.7	373/6.8	473/0.5			
M-F-HF	304/32.9	354/28.7	454/20.1		548/33.8	358/18.9
M-CF <sub>3</sub>	274/2.8		424/0.8		421/7.2	
M-C <sub>3</sub> F <sub>6</sub> O	177/33.6	227/6.4	327/4.5			
C <sub>3</sub> F <sub>9</sub> CNX			258/78.6			
C <sub>3</sub> F <sub>6</sub> CNX	177/33.6	177/3.6	177/10.8	357/1.8	371/5.0	211/1.0
C <sub>3</sub> F <sub>5</sub> CNX	158/9.2	158/71.1	158/5.8	338/28.8	352/10.0	192/16.7
C <sub>2</sub> F <sub>3</sub> CNX	108/3.6					
C <sub>2</sub> F <sub>5</sub> OCNX	124/7.2	124/11.8	124/20.7		318/12.7	158/14.2
C <sub>4</sub> F <sub>7</sub> O (197)	3.6	7.5	0.7	3.2	10.9	1.3
C <sub>3</sub> F <sub>5</sub> O (147)			10.1		1.2	
C <sub>2</sub> F <sub>3</sub> O (97)	2.0	3.0	6.5	6.3	4.8	2.1
C <sub>4</sub> F <sub>4</sub> N (138)	3.8	7.3	3.6		8.6	2.9
C <sub>2</sub> F <sub>3</sub> NH (96)	5.6	8.7	9.9		5.2	
C <sub>4</sub> F <sub>8</sub> (200)		6.4			1.6	7.2
C <sub>4</sub> F <sub>7</sub> (181)	100	3.4	2.7		3.1	1.3
C <sub>3</sub> F <sub>6</sub> (150)		26.7	11.1	18.4	15.6	9.2
C <sub>3</sub> F <sub>5</sub> (131)	17.2	6.3	1.1		2.6	3.2
C <sub>2</sub> F <sub>5</sub> (119)	2.7		10.7	1.7		1.6
CF <sub>3</sub> (69)	60.1	100	100	100	79.9	100

<sup>a</sup>The  $m/z$  values and intensities of the ions containing the <sup>35</sup>Cl isotope are listed for the chlorine-containing ions.



Scheme 9.

The cyano group was also not involved in the reaction of cyanohydrin **II** with the perfluoromethylcyclopentene **X**, the only product to be isolated (**XI**) arising from double vinyl substitution (Scheme 9).

In conclusion, it should be noted that the reaction of cyanohydrin **II** with fluoro-olefins provides the first example of interaction between cyanohydrins and activated olefins accompanied by cyclization involving the cyano group. A similar process is well known for the reactions of cyanohydrins with fluorocarbonyl compounds and their aza analogues, where the  $\text{C}\equiv\text{N}$  group is attacked by intermediate O- and N-anions during the cyclization step [11, 14].

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