Organic Chemistry

Isomerization of monohydroperfluoroalkenes

T. I. Filyakova,[a]* A. Ya. Zapevalov,[a] M. I. Kodess,[a] M. A. Kurykin,[b] and L. S. German[b]†

[a]*Institute of Organic Synthesis, Ural Branch of the Russian Academy of Sciences,*
20 ul. S. Kovalevskoi, 620219 Ekaterinburg, Russian Federation.
Fax: +7 (343) 244 0026
[b]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,*
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085

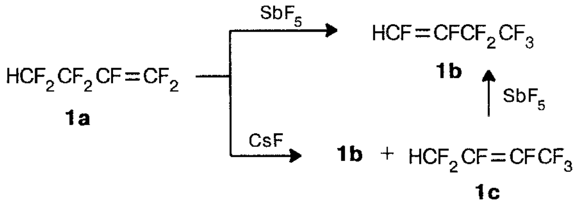
Isomerization of monohydroperfluoro-1-alkenes $HC(CF_2)_nCF=CF_2$ (n = 2 to 8) catalyzed by Lewis bases or acids (CsF, KHF_2, and SbF_5) under conditions of thermodynamic control affords equilibrium mixtures of all of the possible isomers resulting from migration of the double bond along the carbon chain. Under conditions of kinetic control, isomerization through the action of SbF_5 gives ω-H-perfluoro-2-alkenes. The substantially higher proportion of *cis*-isomers in the resulting monohydroperfluoroalkenes than in their perfluorinated analogs has been attributed to the effect of an intramolecular hydrogen bond.

Key words: monohydroperfluoroalkenes, isomerization, isomeric ratio; nucleophilic and electrophilic catalysis.

Isomerization of higher perfluoro-1-alkenes accompanied by migration of the multiple bond along the chain occurs through the action of both nucleophilic (alkali metal fluorides)[1—3] and electrophilic (SbF_5)[4] catalysts. The rearrangement is, as a rule, stereoselective and yields predominantly *trans*-isomers, whose proportion increases as the size of the substituent increases.[4,5] Polychlorofluoroalkenes also afford only *trans*-isomers.[6]

The use of monohydroperfluoroalkenes allows this isomerization to be studied in more detail. For example, 4-H-heptafluoro-1-butene (**1a**) is converted into 1-H-heptafluoro-1-butene (**1b**)[7] under the action of SbF_5, and treatment of **1a** with CsF in diglyme at 180 °C results in an equilibrium mixture of **1b** and 1-H-heptafluoro-2-butene (**1c**).[8] Alkene **1b** is formed as well from **1c** when the latter is treated with SbF_5 (Scheme 1).

Scheme 1



Treatment of ω-H-perfluoro-1-octene with KHF_2 in DMF at an elevated temperature affords 1-H-perfluoro-1-octene.[9]

In the present work we report the results of a study of isomeric transformations of ω-H-perfluoroalkenes with 5 to 10 carbon atoms.

---

† Deceased in 1994.

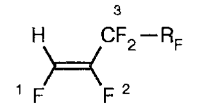
Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 9, pp. 1614—1619, September, 1994.

Table 1. Reaction conditions and the ratio of the products of catalytic isomerization of ω-H-perfluoro-1-alkenes **1a—4a**

Alkene	Catalyst	T /°C	Duration of the reaction/h	The ratio of the products (mol. %)[a]		
				$HCF=CFR_F$	$HCF_2CF=CFR_F$	Other isomers
1a	CsF	20	12	—	100 (**1c**)	
	CsF	150	26	85 (**1b**)	15 (**1c**)	
	SbF_5	20	1	100 (**1b**)		
				[53:47][b]		
2a	CsF	20	20	—	55 (**2c**)	45 (**2d**)
	CsF	150	8	2 (**2b**)	59 (**2c**)	39 (**2d**)
	CsF	190	15	14 (**2b**)	51 (**2c**)	35 (**2d**)
	SbF_5	20	1	40 (**2b**)	37 (**2c**)	23 (**2d**)
	$SbF_5/(C_4F_9)_3N$	20		47 (**2b**)	35 (**2c**)	18 (**2d**)
	SbF_5	45		67 (**2b**)	24 (**2c**)	9 (**2d**)
	$SbF_5/(C_4F_9)_3N$	50		75 (**2b**)	19 (**2c**)	6 (**2d**)
					[55:45]	[18:82]
3a	CsF	150	20	8 (**3b**)	18 (**3c**)	57 (**3d**) + 17 (**3e**)
	CsF	190	8	10 (**3b**)	19 (**3c**)	54 (**3d**) + 17 (**3e**)
	CsF	190	100	11 (**3b**)	19 (**3c**)	53 (**3d**) + 17 (**3e**)
	SbF_5	20	1	—	—	— 100 (**3e**)
	$SbF_5/(C_4F_9)_3N$	20		9 (**3b**)	10 (**3c**)	19 (**3d**) + 62 (**3e**)
	SbF_5	60	1	—	—	27 (**3d**) + 73 (**3e**)
	SbF_5	100	10	18 (**3b**)	21 (**3c**)	52 (**3d**) + 9 (**3e**)
	SbF_5/C	110	20	11 (**3b**)	18 (**3c**)	56 (**3d**) + 15 (**3e**)
					[55:45]	[11:89] [15:85]
4a	KHF_2/DMF	100	20	—	21 (**4c**) + 12 (**4d**)	52 (**4e**) + 15 (**4f**)
	CsF	150	100	3 (**4b**)	7 (**4c**) + 34 (**4d**)	48 (**4e**) + 8 (**4f**)
	SbF_5	20	1	—	—	— 100 (**4f**)
	SbF_5	100	20	6 (**4b**)	45 (**4c** + **4d**)	46 (**4e**) + 3 (**4f**)
	SbF_5/C	120	20	—	64 (**4c** + **4d**)	31 (**4e**) + 5 (**4f**)
					[55:45] (**4c**)	[12:88] [14:86]

[a] The overall yield of the isomerization products is nearly quantitative and decreases at elevated temperatures owing to dimerization of the alkenes. [b] The ratios of the *cis*- and *trans*-isomers are given in brackets.

Table 2. ^1H and ^{19}F NMR spectra of *cis*-1-H-perfluoro-1-alkenes **2b—4b**

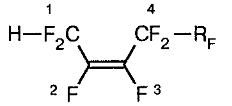


Compound	R_F	δ ^1H, Φ ^{19}F	J/Hz
2b	$\overset{4}{CF_2}\overset{5}{CF_3}$	6.82 (H); 152.07 (F-1); 153.80 (F-2); 119.24 (F-3); 126.37 (F-4); 79.89 (F-5)	$J_{H,1}$ = 69.0; $J_{H,2}$ = 14.0; $J_{1,2}$ = 5.0; $J_{2,3}$ = 18.0; $J_{2,4}$ = 8.5; $J_{2,5}$ = 2.5; $J_{3,5}$ = 10.0
3b	$\overset{4}{CF_2}\overset{5}{CF_2}\overset{6}{CF_3}$	6.84 (H); 151.90 (F-1); 153.47 (F-2); 118.08 (F-3); 129.59 (F-4, F-5); 80.17 (F-6)	$J_{H,1}$ = 69.0; $J_{H,2}$ = 14.0; $J_{1,2}$ = 5.0; $J_{3,6}$ = 2.5; $J_{4,6}$ = 10.5
4b	$\overset{4}{CF_2}\overset{5}{CF_2}\overset{6}{CF_2}\overset{7}{CF_3}$	7.38 (H); 150.54 (F-1); 151.60 (F-2); 118.53 (F-3); 128.96 (F-4); 129.49 (F-5, F-6); 80.10 (F-7)	$J_{H,1}$ = 68.0; $J_{H,2}$ = 14.8; $J_{1,2}$ = 6.0

Note. ^1H and ^{19}F NMR spectra of alkene **1b** have been presented previously.[7]

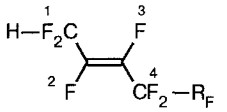
The products were analyzed by GLC, ^{19}F and ^1H NMR, and IR spectroscopy. The isomeric composition was determined from the NMR spectra using the literature data.[5,10] The results are summarized in Table 1. Parameters of the NMR spectra are listed in Tables 2—5.

Table 3. ^1H и ^{19}F NMR spectra of *cis*-1-H-perfluoro-2-alkenes **1c—4c**



Compound	R_F	δ ^1H, Φ ^{19}F	J/Hz
1c	$\overset{4}{F}$	6.48 (H); 123.73 (F-1); 149.87 (F-2); 147.63 (F-3); 66.47 (F-4)	$J_{H,1}$ = 52.5; $J_{H,2}$ = 13.3; $J_{H,3}$ = 1.7; $J_{1,2}$ = 19.5; $J_{1,3}$ = 12.4; $J_{1,4}$ = 4.6; $J_{2,3}$ = 1.7; $J_{2,4}$ = 8.0
2c	$\overset{5}{CF_3}$	6.38 (H); 123.71 (F-1); 145.64 (F-2); 144.73 (F-3); 120.23 (F-4); 83.79 (F-5)	$J_{H,1}$ = 51.0; $J_{H,2}$ = 16.0; $J_{H,3}$ = 1.5; $J_{1,2}$ = 19.0; $J_{1,3}$ = 12.0; $J_{1,4}$ = 6.0; $J_{2,3}$ = 2.5; $J_{2,4}$ = 2.5; $J_{3,5}$ = 6.0; $J_{4,5}$ = 2.0
3c	$\overset{5}{CF_2}\overset{6}{CF_3}$	6.35 (H); 123.79 (F-1); 145.27 (F-2); 143.38 (F-3); 122.60 (F-4); 126.50 (F-5); 79.71 (F-6)	$J_{H,1}$ = 50.5; $J_{H,2}$ = 16.0; $J_{H,3}$ = 3.5; $J_{1,2}$ = 19.3; $J_{1,3}$ = 12.2; $J_{1,4}$ = 6.1; $J_{2,3} \approx J_{2,4} \approx$ 3.5; $J_{3,4}$ = 9.5; $J_{3,6}$ = 2.5; $J_{4,6}$ = 9.5
4c	$\overset{5}{CF_2}\overset{6}{CF_2}\overset{7}{CF_3}$	6.72 (H); 123.70 (F-1); 144.47 (F-2, F-3); 121.05 (F-4); 129.84 (F-5, F-6); 79.70 (F-7)	$J_{H,1}$ = 50.5; $J_{H,2}$ = 14.5; $J_{5,7}$ = 9.8

Table 4. ^1H и ^{19}F NMR spectra of *trans*-1-H-perfluoro-2-alkenes **1c—4c**

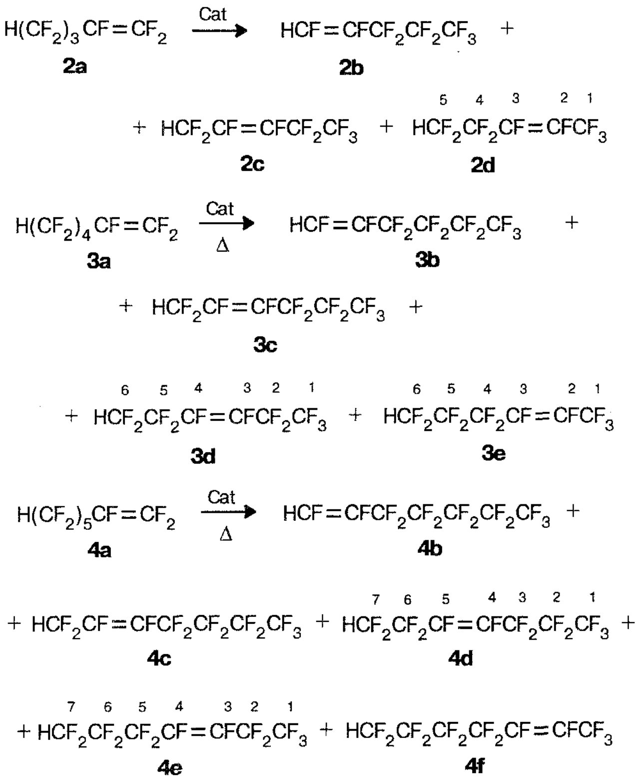


Compound	R_F	δ ^1H, Φ ^{19}F	J/Hz
1c	$\overset{4}{F}$	6.48 (H); 123.87 (F-1); 164.08 (F-2); 167.6 (F-3); 68.28 (F-4)	$J_{H,1}$ = 52.5; $J_{H,2}$ = 13.8; $J_{1,2}$ = 16.9; $J_{1,3}$ = 2.3; $J_{2,3}$ = 135.7; $J_{2,4}$ = 21.1; $J_{3,4}$ = 8.5
2c	$\overset{5}{CF_3}$	6.37 (H); 126.78 (F-1); 160.41 (F-2); 167.46 (F-3); 120.51 (F-4); 83.86 (F-5)	$J_{H,1}$ = 52.5; $J_{H,2}$ = 14.5; $J_{H,3}$ = 3.5; $J_{1,2}$ = 16.0; $J_{1,3}$ = 2.0; $J_{1,4}$ = 2.0; $J_{2,3}$ = 138; $J_{2,4}$ = 25.0; $J_{3,4}$ = 9.0; $J_{4,5}$ = 2.5
3c	$\overset{5}{CF_2}\overset{6}{CF_3}$	6.43 (H); 126.95 (F-1); 160.69 (F-2); 164.25 (F-3); 124.90 (F-4); 126.9 (F-5); 79.93 (F-6)	$J_{H,1}$ = 52.0; $J_{H,2}$ = 14.0; $J_{1,3}$ = 4.0; $J_{3,6}$ = 2.0; $J_{2,5} \approx J_{3,5} \approx$ 6.1; $J_{4,6}$ = 9.0; $J_{5,6}$ = 1.0; $J_{2,3}$ = 132.5
4c	$\overset{5}{CF_2}\overset{6}{CF_2}\overset{7}{CF_3}$	6.88 (H); 127.12 (F-1); 161.77 (F-2); 163.0 (F-3); 121.05 (F-4); 129.4 (F-5, F-6); 80.18 (F-7)	$J_{H,1}$ = 51.5; $J_{H,2}$ = 12.7; $J_{H,3}$ = 3.8; $J_{1,3}$ = 13.4; $J_{2,3}$ = 142.64; $J_{4,7}$ = 2.5; $J_{5,7}$ = 9.8

The products of the isomerization of monohydroperfluoroalkenes differ substantially from those of perfluoroalkenes under similar conditions. Under conditions of thermodynamic control an equilibrium mixture of all of the possible isomers, including 1-H-perfluoro-1-alkenes, is formed with both nucleophilic and electrophilic catalysts (see Scheme 2 and Table 1). Under similar conditions, perfluoro-1-hexene and perfluoro-1-heptene afford an equilibrium mixture of 2- and 3-alkenes.[5,11]

Treatment of compounds **1a** and **2a** with SbF_5 at 20 °C results in a more complete shift of the double bond to the end of the chain (see Table 1). Perfluorotributylamine is efficient only with monohydroperfluoropentene **2a**. When compounds **3a** and **4a** are heated with a solution of SbF_5 in $(C_4F_9)_3N$, decom-

Scheme 2



$$\underset{\mathbf{2a}}{H(CF_2)_3CF{=}CF_2} \xrightarrow{Cat} \underset{\mathbf{2b}}{HCF{=}CFCF_2CF_2CF_3} + \underset{\mathbf{2c}}{HCF_2CF{=}CFCF_2CF_3} + \underset{\mathbf{2d}}{HCF_2CF_2CF{=}CFCF_3}$$

$$\underset{\mathbf{3a}}{H(CF_2)_4CF{=}CF_2} \xrightarrow[\Delta]{Cat} \underset{\mathbf{3b}}{HCF{=}CFCF_2CF_2CF_2CF_3} + \underset{\mathbf{3c}}{HCF_2CF{=}CFCF_2CF_2CF_3} + \underset{\mathbf{3d}}{HCF_2CF_2CF{=}CFCF_2CF_3} + \underset{\mathbf{3e}}{HCF_2CF_2CF_2CF{=}CFCF_3}$$

$$\underset{\mathbf{4a}}{H(CF_2)_5CF{=}CF_2} \xrightarrow[\Delta]{Cat} \underset{\mathbf{4b}}{HCF{=}CFCF_2CF_2CF_2CF_2CF_3} + \underset{\mathbf{4c}}{HCF_2CF{=}CFCF_2CF_2CF_2CF_3} + \underset{\mathbf{4d}}{HCF_2CF_2CF{=}CFCF_2CF_2CF_3} + \underset{\mathbf{4e}}{HCF_2CF_2CF_2CF{=}CFCF_2CF_3} + \underset{\mathbf{4f}}{HCF_2CF_2CF_2CF_2CF{=}CFCF_3}$$

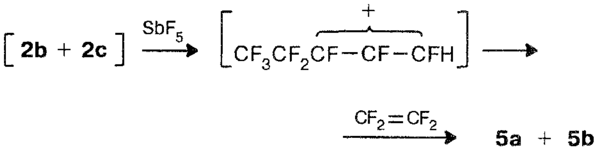
Cat = CsF, KHF_2/DMF, SbF_5, SbF_5/C (graphite), $SbF_5/(C_4F_9)_3N$

position of the solvent and dimerization of the alkene occur. The action of SbF_5 without a solvent at a temperature >100 °C also results in partial dimerization of monohydroperfluoroalkenes.

One piece of indirect evidence for the existence of the equilibrium is that the reaction of 5-H-perfluoro-1-pentene **2a** with tetrafluoroethylene (TFE) in the presence of SbF_5 yields 3-H-perfluoro-2- and -3-heptenes (**5a** and **5b**, respectively).

$$\mathbf{2a} \xrightarrow[SbF_5]{CF_2=CF_2} \underset{\mathbf{5a}}{CF_3CF_2CF_2CF_2CH{=}CFCF_3} + \underset{\mathbf{5b}}{CF_3CF_2CF_2CF{=}CHCF_2CF_3}$$

We believe that the interaction of the intermediate monohydroperfluoropentenes **2b** and **2c** with SbF_5 gives an asymmetrical allyl cation, which adds a TFE molecule exclusively at the CFH group. 5-H-Perfluoro-2-pentene **2d** does not add TFE, but is converted into alkenes **2b** and **2c**, which react with TFE to give heptenes **5a** and **5b**.



$$[\mathbf{2b} + \mathbf{2c}] \xrightarrow{SbF_5} \left[CF_3CF_2\overset{+}{CF{-}CF{-}CFH}\right] \longrightarrow \xrightarrow{CF_2=CF_2} \mathbf{5a} + \mathbf{5b}$$

Table 5. ^1H и ^{19}F NMR spectra of monohydroperfluoroalkenes **2d**, **3d**, **3e**, **4d**, and **4e**

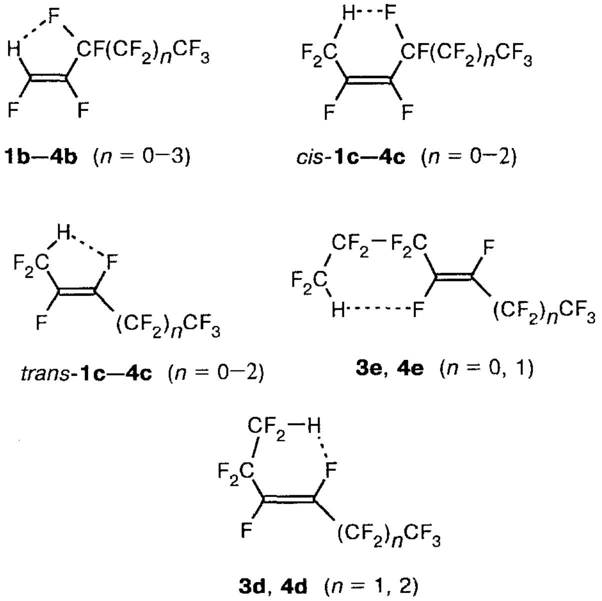
Compound	δ ^1H, Φ ^{19}F	J/Hz
trans- **2d**	68.22 (F-1); 161.52 (F-2); 155.22 (F-3); 117.59 (F-4); 135.58 (F-5); 5.84 (H)	$J_{1,2}$ = 8.0; $J_{1,3}$ = 20.0; $J_{1,4}$ = 1.5; $J_{2,5} \approx J_{3,5} \approx J_{4,5} \approx$ 4.5; $J_{3,4}$ = 9.0; $J_{4,H}$ = 2.8; $J_{5,H}$ = 53.5
cis- **2d**	64.56 (F-1); 140.35 (F-2); 139.18 (F-3); 117.06 (F-4); 135.26 (F-5); 5.84 (H)	$J_{1,2}$ = 9.0; $J_{1,3}$ = 7.5; $J_{1,4}$ = 17.0; $J_{1,5}$ = 3.0; $J_{5,H}$ = 54.0
trans- **3d**	83.77 (F-1); 120.40 (F-2); 158.98 (F-3); 153.04 (F-4); 120.40 (F-5); 135.66 (F-6); 5.84 (H)	$J_{1,2}$ = 2.3; $J_{1,3} \approx J_{1,4} \approx$ 5.3; $J_{3,4}$ = 139.0; $J_{5,H}$ = 3.3; $J_{6,H}$ = 53.0
trans- **3e**	68.15 (F-1); 157.44 (F-2); 155.15 (F-3); 118.30 (F-4); 129.55 (F-5); 136.12 (F-6); 5.92 (H)	$J_{1,2}$ = 6.7; $J_{1,3}$ = 20.0; $J_{2,3}$ = 140.0; $J_{2,4}$ = 24.0; $J_{5,6} \approx J_{5,H} \approx$ 6.0; $J_{6,H}$ = 52.5
cis- **3e**	64.43 (F-1); 136.85 (F-2); 138.88 (F-3); 115.83 (F-4); 128.56 (F-5); 136.12 (F-6); 5.92 (H)	$J_{1,2}$ = 9.0; $J_{1,3}$ = 8.5; $J_{1,4}$ = 17.0; $J_{1,5}$ = 5.0; $J_{2,3}$ = 9.5; $J_{2,4}$ = 2.6; $J_{3,4}$ = 21.5; $J_{3,5}$ = 8.5; $J_{3,6}$ = 4.5; $J_{6,H}$ = 52.5
trans- **4d**	79.89 (F-1); 126.86 (F-2); 117.73 (F-3); 156.48 (F-4); 153.56 (F-5); 120.20 (F-6); 136.84 (F-7); 6.55 (H)	$J_{1,3}$ = 9.0; $J_{2,4} \approx J_{25} \approx$ 6.1; $J_{3,4}$ = 9.0; $J_{3,5}$ = 24.5; $J_{4,5}$ = 139.2; $J_{6,H}$ = 3.0; $J_{7,H}$ = 52.5
trans- **4e**	83.70 (F-1); 120.49 (F-2); 155,23 (F-3); 152.78 (F-4); 118.27 (F-5); 129.49 (F-6); 136.21 (F-7); 6.47 (H)	$J_{1,2}$ = 2.5; $J_{1,3} \approx J_{1,4} \approx$ 5.0; $J_{3,4}$ = 139.2; $J_{3,5}$ = 24.0; $J_{5,H}$ = 8.0; $J_{6,H} \approx$ 4.9

A more convincing argument in favor of the equilibrium reaction is the fact that treatment of either alkene **1a** or **1b** with CsF at 150 °C affords mixtures of isomers **1b** and **1c** of the same composition.[8]

It has been noted that the ratio between the geometric isomers has a more intricate dependence on the structure of monohydroperfluoroalkenes than in the case of perfluoroalkenes. This is probably due to the effect of an intramolecular hydrogen bond, which is manifested in various isomers in different ways. The presence of H-bonds in monohydropolyfluorinated compounds has been shown previously.[12]

In fact, 1-H-perfluoro-1-alkenes **1b—4b** exist only in the *cis*(*E*)-form irrespective of the preparation method, which can be explained by the fact that the H-bond and the steric factors act in the same direction. In the case of 1-H-perfluoro-2-alkenes **1c—4c**, the ratio between the geometric isomers is practically identical for all of the homologs (*cis* : *trans* ≈ 55:45). It is likely that the formation of a six-membered ring made possible by the H-bond considerably increases the stability of the *cis*-isomers of **1c—4c**. In ω-H-perfluoro-2-alkenes and ω-H-perfluoro-3-alkenes, *trans*-isomers prevail (> 80 %), since both the H-bond and steric factors favor their stability (Scheme 3).

Scheme 3



1b—4b (*n* = 0—3)

cis-**1c—4c** (*n* = 0—2)

trans-**1c—4c** (*n* = 0—2)

3e, 4e (*n* = 0, 1)

3d, 4d (*n* = 1, 2)

The isomeric composition of the products of the rearrangement of monohydroperfluoroalkenes at elevated temperatures depends slightly on the type of the catalyst; this can be explained by the fact that the ratio between the structural and geometric isomers correlates with their thermodynamic stabilities.

At elevated temperatures, the equilibrium is reached rather quickly and a further increase in the duration of the reaction is of no use (for example, the isomeric composition of the products of the reaction of alkene **3a** with CsF in diglyme at 190 °C is virtually the same after 8 h and 100 h; see Table 1). For monohydroperfluoroalkenes with ≥5 carbon atoms, the complete migration of the double bond along the whole carbon chain cannot be accomplished.

The degree of migration of the double bond depends on the reaction conditions. Under conditions of kinetic control, the major (sometimes the only) products of isomerization of monohydroperfluoro-1-alkenes are ω-H-perfluoro-2-alkenes. For example, the action of catalytic amounts of SbF_5 on ω-H-perfluoro-1-alkenes (≥6 carbon atoms) at ~10—20 °C results in the formation of ω-H-perfluoro-2-alkenes, predominantly (>80 %) as *trans*-isomers, in almost quantitative yields (Scheme 4).

Scheme 4

$$H(CF_2)_nCF{=}CF_2 \xrightarrow{SbF_5} H(CF_2)_{n-1}CF{=}CFCF_3$$

3a (*n* = 4)	**3e** (*n* = 4)
4a (*n* = 5)	**4f** (*n* = 5)
6a (*n* = 6)	**6b** (*n* = 6)
7a (*n* = 8)	**7b** (*n* = 8)

However, under the conditions of thermodynamic control, the double bond shifts further, and, of course, the more symmetrical 3- and 4-alkenes predominate in the equilibrium mixture.

Experimental

^{19}F and ^1H NMR spectra were recorded on Tesla BS-567A (94.1 and 100 MHz, respectively) and Tesla BS-587A (75.3 and 80 MHz, respectively) spectrometers, the chemical shifts are given in ppm, relative to $CFCl_3$ or TMS (internal standards), and are taken to be positive when the field increases (for ^{19}F). The ^1H NMR spectra of alkenes **1c**, **2b—2d**, and **3b—3e** were recorded without a solvent, those of alkenes **4b—4e** were recorded in acetone-d_6. GLC analysis was carried out on a LKhM-72 MD chromatograph using a katharometer as the detector, helium as the carrier gas, and steel columns (6500 × 4 mm) with 15 % SKTFT-100 on Chromosorb W and 20 % FS-1265 on Chromosorb W. The ratios between isomers were determined from GLC and NMR spectroscopic data.

ω-H-Perfluoro-1-alkenes 1a—4a, 6a, and 7a were prepared by pyrolysis of sodium ω-H-perfluoroalkanoates *in vacuo*.[13] The yields and physicochemical characteristics of **1a—4a**, **6a**, and **7a** are given in Table 6. The data of elemental analysis are in satisfactory agreement with the calculated values for all of the compounds synthesized. IR, ν(C=C)/cm^{-1}: 1790 (**1a—4a**, **6a**, **7a**); 1740 (**1c**); 1720 (**3e**, **4f**, **6b**, **7b**).

Table 6. Yields and boiling points of alkenes **1a—4a**, **6a**, **7a**, **1c**, **3e**, **4f**, **6b**, and **7b**

Compound	Yield (%)	B.p. /°C	Compound	Yield (%)	B.p. /°C
1a	81	20—21	**1c**	95	18
2a	92	48—49			
3a	90	74—75	**3e**	92	66—67
4a	89	98—99	**4f**	90	89—91
6a	82	120—122	**6b**	94	111—112
7a	84	162—163	**7b**	88	152—154

Isomerization of alkenes (1a—4a) through the action of CsF in diglyme (general procedure). ***A.*** A mixture of ω-H-perfluoro-1-alkene and a catalytic amount of freshly calcined CsF in diglyme (distilled over $LiAlH_4$) was stirred for several hours, then filtered and distilled.

B. A mixture of ω-H-perfluoro-1-alkene and a catalytic amount of CsF in diglyme was heated in a sealed tube on a bath with Wood's alloy, then filtered and distilled.

Isomerization of heptene 4a through the action of KHF_2 in DMF. A mixture of 1.4 g of alkene **4a** and 0.4 g of KHF_2 in 2 mL of DMF was heated in a sealed tube on a bath with Wood's alloy, then filtered and distilled to give 1.2 g of a mixture of products. The reaction conditions and the isomeric composition of the resulting alkenes are given in Table 1.

Isomerization of monohydroperfluoroalkenes through the action of SbF_5 (general procedure). ***A.*** A catalytic amount of SbF_5 was added to an ω-H-perfluoro-1-alkene (**3a**, **4a**, **6a**, or **7a**), and the mixture was kept for ~1 h at 10—20 °C and poured into ice water. The lower layer was separated and distilled over conc. H_2SO_4 (or dried with $MgSO_4$ and distilled). Yields and physicochemical characteristics of the ω-H-perfluoro-2-alkenes prepared are given in Table 6.

B. A mixture of an alkene (**2a—4a**) and a catalytic amount of SbF_5 (or SbF_5 on graphite) was placed into a glass tube (at 0 °C), and the tube was sealed and heated in a bath containing Wood's alloy. The products were poured into ice water, and the lower layer was separated and distilled over H_2SO_4 (or dried with $MgSO_4$ and distilled).

C. An alkene (**2a**, **3a**) was added dropwise to a solution of a catalytic amount of SbF_5 in perfluorotributylamine, the mixture was stirred with a reflux condenser, and the products were isolated by distillation. The reaction conditions and isomeric composition of the products are given in Table 1.

The reaction of 5-H-perfluoro-1-pentene 2a with TFE. A mixture of 232 g of pentene **2a**, 35 g of TFE, and 15 mL of SbF_5 was kept in a rocking steel autoclave (250 mL) for 6 h at 50 °C, then 35 g of TFE was added and the mixture was kept for 6 h at 50 °C. This operation was repeated two more times (the overall amount of TFE charged in the autoclave was 140 g). After opening the autoclave, the liquid part of the reaction mixture was separated and fractionated to give 294 g (88.6 %) of a mixture of 3-H-perfluoro-2-heptene **5a** and 3-H-perfluoro-3-heptene **5b** (44:56); the individual components of the mixture were identical to the authentic samples.[14]

References

1. W. T. Miller, J. H. Fried, and H. C. Goldwhite, *J. Am. Chem. Soc.*, 1960, **82**, 3091.
2. J. A. Young, *Fluor. Chem. Rev.*, 1967, **1**, 359.
3. *Uspekhi khimii ftora* [*Advances in Fluorine Chemistry*], Ed. M. Steisi, Khimiya, Moscow, 1970, 280 (Russ. Transl.).
4. G. G. Belen'kii, G. I. Savicheva, E. P. Lur'e, and L. S. German, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, 1640 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1978, **27**, 1432 (Engl. Transl.)].
5. T. I. Filyakova, M. I. Kodess, N. V. Peschanskii, A. Ya. Zapevalov, and I. P. Kolenko, *Zh. Org. Khim.*, 1987, **23**, 1858 [*J. Ogr. Chem. USSR*, 1987, **23** (Engl. Transl.)].
6. C.-M. Hu, H. Liu, and Z.-O. Xu, *J. Fluor. Chem.*, 1990, **46**, 491.
7. T. I. Filyakova, G. G. Belen'kii, E. P. Lur'e, A. Ya. Zapevalov, I. P. Kolenko, and L. S. German, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 681 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1979, **28**, 635 (Engl. Transl.)].
8. T. I. Filyakova, A. Ya. Zapevalov, I. P. Kolenko, and L. S. German, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 2789 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1979, **28**, 2597 (Engl. Transl.)].
9. US Pat. 2918501; *Chem. Abstrs.*, 1960, **20**, 20875f.
10. A. Zhunke, *Yadernyi magnitnyi rezonans v organicheskoi khimii* [*Nuclear Magnetic Resonance in Organic Chemistry*], Mir, Moscow, 1974 (Russ. Transl.).
11. V. A. Petrov, Ph. D. Thesis, Moscow, 1983.
12. T. A. Sinitsina, L. V. Saloutina, and A. Ya. Zapevalov, *Zh. Prikl. Spektrosk.*, 1990, **53**, 939 [*J. Appl. Spectrosc.*, 1990, **53** (Engl. Transl.)].
13. A. Ya. Zapevalov, V. S. Plashkin, I. P. Kolenko, and P. G. Neifel'd, *Zh. Org. Khim.*, 1977, **13**, 2504 [*J. Ogr. Chem. USSR*, 1977, **13** (Engl. Transl.)].
14. V. A. Petrov, G. G. Belen'kii, and L. S. German, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 1591 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1982, **31**, 1414 (Engl. Transl.)].

Received June 6, 1994