

# Reactions of Perfluorinated 1-Ethyltetrahydronaphthalene, 1-Ethylindan, and 1,1-Diethylindan with Pentafluorobenzene in Antimony Pentafluoride

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**Abstract**—The reaction of perfluoro(1-ethyltetrahydronaphthalene) with pentafluorobenzene in  $\text{SbF}_5$ , followed by treatment of the reaction mixture with water, afforded a mixture of 1-hydroxyperfluoro(1-phenyl-4-ethyltetrahydronaphthalene) and perfluoro(5-phenyl-8-ethyl-2,6,7,8-tetrahydronaphthalen-2-one). From perfluoro(1,1-diethylindan), 1-hydroxyperfluoro(1,1-diethyl-3-phenylindan) was obtained. Perfluoro(1-ethylindan) reacted with an equimolar amount of pentafluorobenzene in  $\text{SbF}_5$  to give (after hydrolysis) 1-hydroxyperfluoro(3-ethyl-1-phenylindan), 1-hydroxyperfluoro(3-ethyl-1,3-diphenylindan), and perfluoro(1-ethyl-1-phenylindan), while in the reaction with excess pentafluorobenzene, followed by treatment with anhydrous hydrogen fluoride, perfluoro(1-ethyl-3-phenylindan) and perfluoro(1-ethyl-1,3-diphenylindan) were formed.

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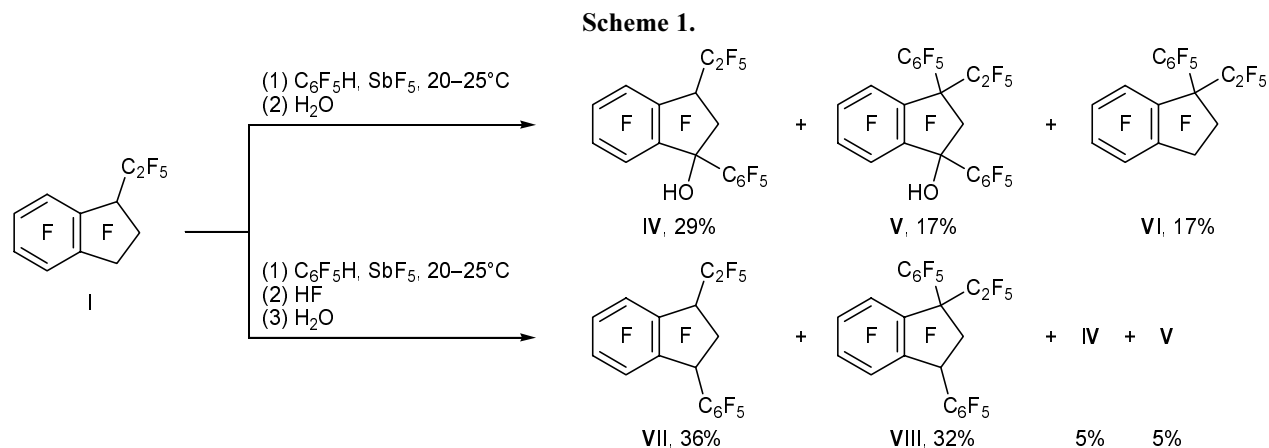
We previously studied reactions of perfluorinated benzocyclobutene, indan, 1,2,3,4-tetrahydronaphthalene [1], and 1-methylbenzocyclobutene [2] with pentafluorobenzene in  $\text{SbF}_5$ , which led to formation of the corresponding perfluoro(phenylbenzocycloalkenes). Reactions of perfluorinated 1-phenylindan, 1-phenyl-1,2,3,4-tetrahydronaphthalene, and 1-arylbenzocyclobutenes with antimony pentafluoride were accompanied by cationoid skeletal rearrangements of polyfluorinated arylbenzocycloalkenes [3].

The present study was aimed at elucidating general relations holding in reactions of polyfluorinated benzocycloalkenes with pentafluorobenzene and obtaining polyfluorinated indans and tetrahydronaphthalenes having both pentafluorophenyl and perfluoroethyl groups. For this purpose, we examined reactions of perfluoro(1-ethylindan) (**I**), perfluoro(1,1-diethylindan) (**II**), and perfluoro(1-ethyl-1,2,3,4-tetrahydronaphthalene) (**III**) with pentafluorobenzene in  $\text{SbF}_5$ .

The reaction of compound **I** with an equimolar amount of pentafluorobenzene in  $\text{SbF}_5$ , followed by hydrolysis of the reaction mixture, gave 1-hydroxyperfluoro(3-ethyl-1-phenylindan) (**IV**), 1-hydroxyperfluoro(3-ethyl-1,3-diphenylindan) (**V**), and perfluoro(1-ethyl-1-phenylindan) (**VI**) in 29, 17, and 17% yield,

respectively (Scheme 1). In addition, the mixture contained unreacted ethylindan **I**. When the reaction was performed with excess pentafluorobenzene, and the mixture was treated first with anhydrous HF and then with water, the major products were perfluoro(1-ethyl-3-phenylindan) (**VII**, 36%) and perfluoro(1-ethyl-1,3-diphenylindan) (**VIII**, 32%). Small amounts (5%) of compounds **IV** and **V** were also formed, while indan **VI** was not detected in the reaction mixture (Scheme 1). By special experiment we showed that individual compound **VII** does not react with  $\text{C}_6\text{F}_5\text{H}$  under analogous conditions. Therefore, diphenylindan **VIII** is formed from compound **VI** rather than from its isomer **VII**.

Presumably, the reaction of ethylindan **I** with pentafluorobenzene involves alkylation of the latter with perfluoro(1-ethylindan-1-yl) and perfluoro(3-ethylindan-1-yl) cations **IX** and **X** generated from **I** by the action of  $\text{SbF}_5$ . As a result, ethylphenylindans **VI** and **VII** are formed, respectively (Scheme 2). Although the concentration of ions **IX** and **X** is too small to detect them by  $^{19}\text{F}$  NMR spectroscopy, it nevertheless is sufficient to ensure reaction with  $\text{C}_6\text{F}_5\text{H}$ . The transformation of phenylindan **VI** into diphenylindan **VIII** is likely to occur in a similar way through perfluoro(3-ethyl-3-phenylindan-1-yl) cation **XI** (Scheme 2).



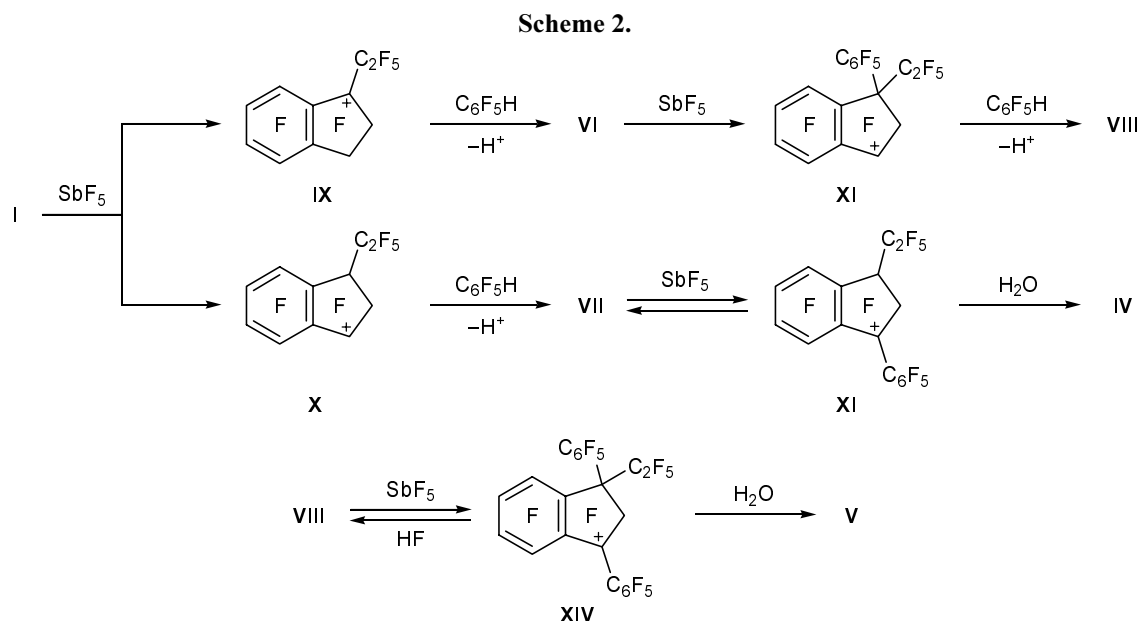
It is known that the action of  $SbF_5$  on perfluoro(1-phenylindan) gives rise to perfluoro(1-phenylindan-1-yl) cation (**XII**) [1]. Therefore, it may be presumed that compounds **VII** and **VIII** in  $SbF_5$  are also converted into perfluoro(3-ethyl-1-phenylindan-1-ylum) (**XIII**) and perfluoro(3-ethyl-1,3-diphenylindan-1-ylum) (**XIV**) salts, respectively. As a result, quenching of the reaction mixture with anhydrous hydrogen fluoride leads to formation of compounds **VII** and **VIII** from ions **XIII** and **XIV**, while hydrolysis of the latter yields alcohols **IV** and **V**.

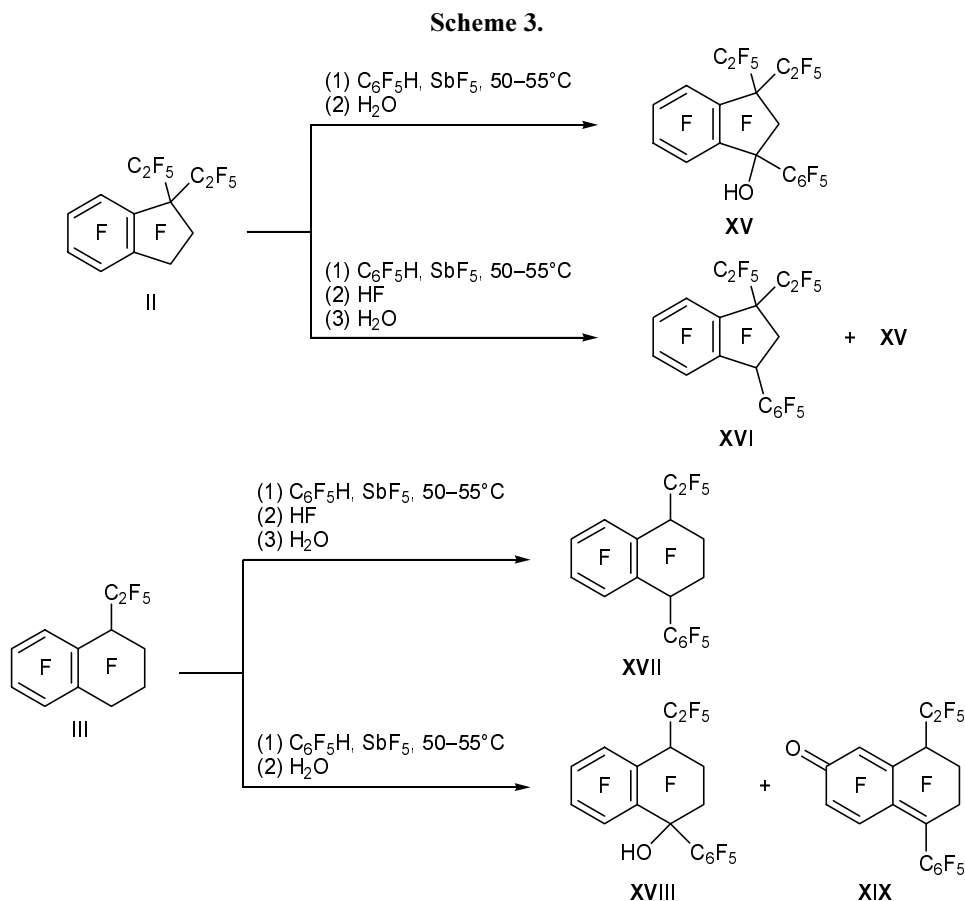
The pentafluorophenyl group on the carbocationic center in ions **XIII** and **XIV**, as well as in **XII** [1], is likely to be turned through a considerable angle with respect to the plane including the tetrafluorobenzene ring, cationic center, and atoms attached thereto. Therefore, the cationic center in **XIII** and **XIV** is

spatially less accessible than that in ions **IX–XI** generated from compounds **I** and **VI**, the reactivity of **VII** and **VIII** toward pentafluorobenzene weakens, as compared to **I** and **VI**, and the reaction is terminated.

Like perfluoro(1-ethylindan) (**I**), diethylindan **II** reacts with pentafluorobenzene in the presence of  $SbF_5$ , but more severe conditions are required for the conversion of **II** to be complete. Hydrolysis of the reaction mixture yields 1-hydroxyperfluoro(3,3-diethyl-1-phenylindan) (**XV**), while treatment first with anhydrous HF and then with water leads to formation of perfluoro(1,1-diethyl-3-phenylindan) (**XVI**) together with hydroxy derivative **XV** (Scheme 3).

Unlike ethylindan **I**, the reaction of perfluoro(1-ethyl-1,2,3,4-tetrahydronaphthalene) (**III**) with pentafluorobenzene in  $SbF_5$  is selective. After treatment of the reaction mixture with anhydrous hydrogen

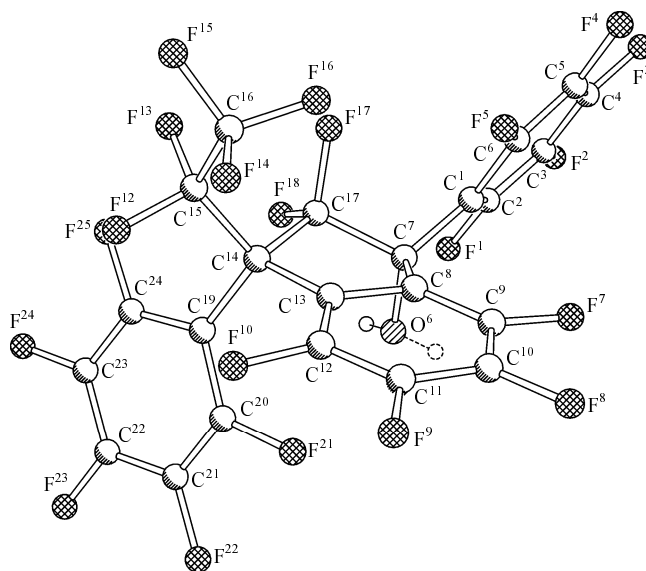




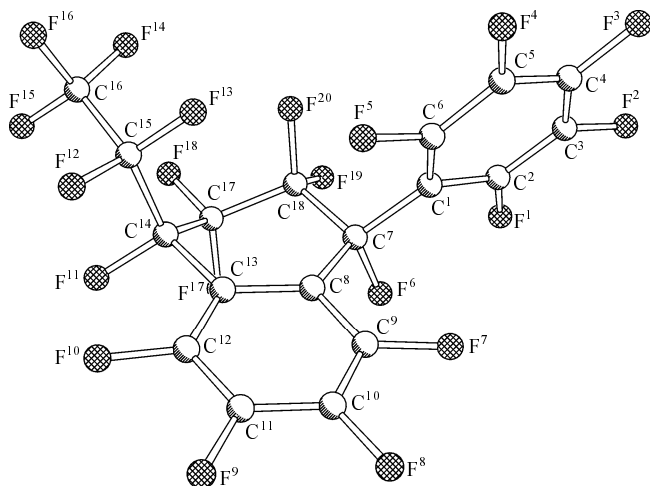
fluoride, followed by hydrolysis, we isolated perfluoro-(1-ethyl-4-phenyltetrahydronaphthalene) (**XVII**), while isomeric 1-phenyl-1-ethyl derivative was not detected. Hydrolysis of the reaction mixture (without preliminary treatment with anhydrous HF) gave a mixture of 1-hydroxyperfluoro(4-ethyl-1-phenyl-1,2,3,4-tetrahydronaphthalene) (**XVIII**) and perfluoro(5-phenyl-8-ethyl-2,6,7,8-tetrahydronaphthalen-2-one) (**XIX**) (Scheme 3). Presumably, ketone **XIX** is formed due to hindered approach of water molecule to the C<sup>1</sup> atom in perfluoro(4-ethyl-1-phenyl-1,2,3,4-tetrahydronaphthalen-1-yl) cation derived from compound **XVII** in SbF<sub>5</sub>, which is shielded by the pentafluorophenyl group. We previously rationalized in a similar way the formation of 3-chloro-7-pentafluorophenyldecafluorobicyclo-[4.4.0]deca-1,4,6-triene in the reaction of 1-hydroxyperfluoro(1-phenyltetrahydronaphthalene) with SOCl<sub>2</sub> [1]. It should be noted that the observed difference in the reagent orientation in reactions of compounds **I** and **III** with C<sub>6</sub>F<sub>5</sub>H does not contradict our previous data on the reactions of the same compounds with tetrafluoroethylene in the presence of SbF<sub>5</sub> [4].

Compounds **V** and **VIII** were isolated as a single stereoisomer, while products **IV**, **VII**, **XVII**, and

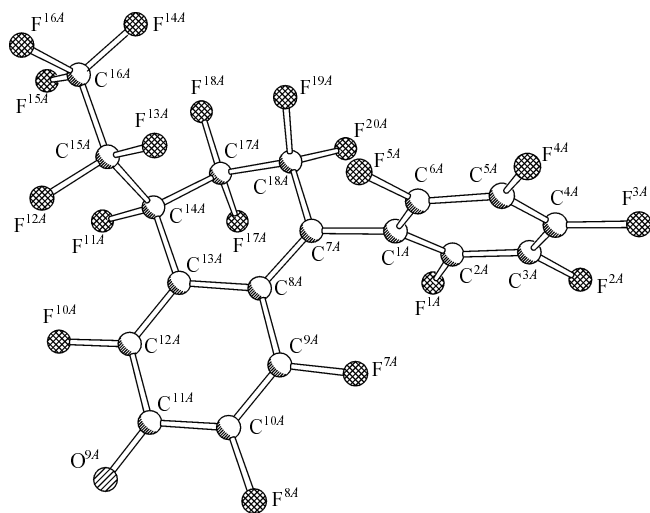
**XVIII** were mixtures of two stereoisomers, the major isomer being characterized by *cis* orientation of the pentafluoroethyl and pentafluorophenyl groups with



**Fig. 1.** Structure of the molecule of *trans*-2,2,4,4,5,6,7-hexafluoro-1-hydroxy-3-(pentafluoroethyl)-1,3-bis(pentafluorophenyl)indane (**V**) according to the X-ray diffraction data.



**Fig. 2.** Structure of the molecule of *cis*-2,2,3,3,5,6,7,8-octafluoro-1-pentafluoroethyl-4-pentafluorophenyl-1,2,3,4-tetrahydronaphthalene (**XVII**) according to the X-ray diffraction data.



**Fig. 3.** Structure of the molecule of 1,3,4,6,6,7,7,8-octafluoro-8-pentafluoroethyl-5-pentafluorophenyl-2,6,7,8-tetrahydronaphthalen-2-one (**XIXA**) according to the X-ray diffraction data.

respect to each other. The structure of **IV–VIII**, **XV–XIX** was determined on the basis of their analytical and spectral data. In addition, the structure of ketone **XIX** and configurations of isomers *Z-IV*, *trans-V*, *trans-VIII*, *cis-XVII*, and *Z-XVIII* were proved by X-ray analysis.

Signals in the  $^{19}\text{F}$  NMR spectra were assigned on the basis of their position, fine structure, and intensity (Table 1). In the spectra of the *E* and *Z* isomers of alcohol **IV**, the 6-F signal was located at  $\delta_{\text{F}}$   $-5.9$  and  $5.2$  ppm, respectively. Therefore, *trans* configuration was assigned to that perfluoro(ethylphenylindan) **VII**

isomer whose 6-F atom resonated at  $\delta_{\text{F}}$   $-7.6$  ppm, while the signal observed at  $\delta_{\text{F}}$   $1.8$  ppm was assigned to the *cis*-isomer.

According to the X-ray diffraction data, crystallographically independent part of a unit cell of compounds *Z-IV*, *Z-XVIII*, and **XIX** contains two molecules *A* and *B*. The five-membered ring in polyfluoroindans *Z-IV*, *trans-V*, and *trans-VIII* in crystal adopts an *envelope* conformation with pseudoequatorial 1- $\text{C}_6\text{F}_5$  and 3- $\text{C}_2\text{F}_5$  groups (Fig. 1). The  $\text{C}^{17}$  atom deviates from the plane formed by the other atoms of the five-membered ring by  $0.421(7)$  (**IVA**),  $0.450(7)$  (**IVB**),  $0.447(3)$  (**V**), and  $0.415(3)$  Å (**VIII**). An analogous conformation was found previously for the five-membered ring in 2-nitroindan-1,3-diol (deviation  $0.466$  Å) [5].

Polyfluorinated tetrahydronaphthalenes *cis-XVII* and *Z-XVIII* (Fig. 2), as well as ketone **XIX** (Fig. 3), are characterized by a *sofa*-like conformation of the saturated fragment, where the  $\text{C}^{17}$  atom deviates from the plane formed by the remaining five ring atoms by  $0.595(4)$ ,  $0.47(1)$  (*A*),  $0.48(1)$  (*B*), and  $0.60(1)$  (*A*), and  $0.60(1)$  Å (*B*), respectively. An analogous *sofa* conformation (deviation of the sixth atom is  $0.625$  Å) was observed for structurally related (+)-isoolivil [6]. The orientations of the 1- $\text{C}_6\text{F}_5$  group in *Z-IV*, *trans-V*, *trans-VIII*, *cis-XVII*, *Z-XVIII* are alike: the torsion angle  $\text{C}^6\text{C}^1\text{C}^7\text{C}^8$  varies from  $-29.7(3)$  to  $-40.8(3)^\circ$  (Table 2). The  $\text{C}^{20}$  atom in the pseudoaxial 3- $\text{C}_6\text{F}_5$  group in *trans-V* and *trans-VIII* is eclipsed by  $\text{C}^{13}$ , the torsion angle  $\text{C}^{13}\text{C}^{14}\text{C}^{19}\text{C}^{20}$  being  $10.0(3)$  and  $9.9(3)^\circ$ , respectively. A similar orientation is inherent to the phenyl group in *cis*-1,3,4,5,6,7-tetrachloro-1-silylmethyl-3-(2,3,4,5-tetrachlorophenyl)indan (the corresponding torsion angle is  $18.4^\circ$ ) [7]. Presumably, the 3- $\text{C}_6\text{F}_5$  group affects orientation of the  $\text{C}_2\text{F}_5$  group, for its orientation approaches eclipsed conformation only in molecules *trans-V* and *trans-VIII*: the torsion angle  $\text{C}^{13}\text{C}^{14}\text{C}^{15}\text{C}^{16}$  is  $25.4(3)$  and  $26.1(3)^\circ$ , respectively. The disordered  $\text{C}_2\text{F}_5$  group in *Z-XVIII* adopts a *transoid* orientation which is characterized by torsion angles  $\text{C}^{13}\text{C}^{14}\text{C}^{15}\text{C}^{16}$  of  $-177.9(9)$  and  $-141(1)^\circ$  (molecule *A*) and  $-177.3(9)$  and  $-139(1)^\circ$  (molecule *B*). The corresponding torsion angles in molecules **IV** and **XIX** range from  $171.8(5)$  to  $177.2(9)^\circ$ .

Crystallographically independent molecules *A* and *B* of compound *Z-IV* in crystal give rise to infinite chains along the *a* axis via intermolecular interactions  $\text{O}^{6A}\text{--H}\cdots\text{O}^{6B}$  [ $\text{H}\cdots\text{O}$   $2.26(4)$  Å,  $\angle\text{O--H}\cdots\text{O}$   $129(4)^\circ$ ] and  $\text{O}^{6B}\text{--H}\cdots\text{F}^{8A}$  [ $2.40(6)$  Å,  $122(5)^\circ$ ]. However,



**Table 2.** Selected bond lengths and torsion angles in the molecules of compounds *Z-IV*, *trans-V*, *trans-VIII*, *cis-XVII*, *Z-XVIII*, and *XIX*<sup>a</sup>

Bond or angle	IV	V	VIII	XVII	XVIII	XIX
C <sup>1</sup> –C <sup>7</sup>	1.515(6) 1.535(6)	1.519(3)	1.517(3)	1.529(3)	1.558(8) 1.560(9)	1.50(1) 1.47(1)
O <sup>6</sup> –C <sup>7</sup> [F <sup>6</sup> –C <sup>7</sup> ]	1.398(5) 1.415(5)	1.417(2)	[1.387(2)]	[1.384(3)]	1.421(7) 1.411(7)	–
C <sup>7</sup> –C <sup>8</sup>	1.509(6) 1.518(6)	1.518(3)	1.499(3)	1.528(3)	1.533(8) 1.537(8)	1.34(1) 1.336(9)
C <sup>7</sup> –C <sup>17</sup> [C <sup>7</sup> –C <sup>18</sup> ]	1.549(6) 1.542(7)	1.550(3)	1.549(3)	[1.555(3)]	[1.543(9)] [1.544(8)]	[1.51(1)] [1.52(1)]
C <sup>13</sup> –C <sup>14</sup>	1.507(6) 1.517(7)	1.530(3)	1.529(3)	1.520(3)	1.521(9) 1.511(9)	1.53(1) 1.52(1)
C <sup>14</sup> –C <sup>15</sup>	1.546(7) 1.550(7)	1.579(3)	1.587(3)	1.570(3)	1.58(1) 1.565(9)	1.55(1) 1.53(1)
C <sup>14</sup> –C <sup>17</sup>	1.558(6) 1.559(6)	1.571(3)	1.572(3)	1.544(4)	1.55(1) 1.560(9)	1.54(1) 1.55(1)
C <sup>14</sup> –F <sup>11</sup> [C <sup>14</sup> –C <sup>19</sup> ]	1.380(5) 1.369(5)	[1.547(3)]	[1.549(3)]	1.375(3)	1.382(7) 1.390(7)	1.388(8) 1.378(7)
C <sup>6</sup> C <sup>1</sup> C <sup>7</sup> C <sup>8</sup>	–29.9(5) –32.5(5)	–31.4(3)	–29.7(3)	–40.8(3)	–35.3(8) –35.2(8)	–87.5(9) –86.0(9)
C <sup>8</sup> C <sup>13</sup> C <sup>14</sup> C <sup>17</sup>	–13.2(5) –14.6(5)	–10.2(2)	–10.6(2)	26.6(3)	26.1(8) 22.8(8)	34(1) 38.9(9)
C <sup>13</sup> C <sup>8</sup> C <sup>7</sup> C <sup>17</sup> [C <sup>13</sup> C <sup>8</sup> C <sup>7</sup> C <sup>18</sup> ]	18.9(5) 19.9(5)	23.5(2)	20.9(2)	[4.6(3)]	[14.5(9)] [10.8(9)]	[–6(1)] [–3(1)]
C <sup>13</sup> C <sup>14</sup> C <sup>15</sup> C <sup>16</sup>	175.4(4) 171.8(5)	25.4(3)	26.1(3)	175.2(2)	<sup>b</sup> <sup>c</sup>	177.2(9) 172.9(7)
C <sup>13</sup> C <sup>14</sup> C <sup>19</sup> C <sup>20</sup>	–	–10.0(3)	–9.9(3)	–	–	–

<sup>a</sup> For compounds **IV**, **XVIII**, and **XIX**, the data for two crystallographically independent molecules *A* and *B* are given (upper and lower string, respectively)

<sup>b</sup> –177.9(9) and –141(1)°.

<sup>c</sup> –177.3(9) and –139(1)°.

replacement of the fluorine atom in position 3 by C<sub>6</sub>F<sub>5</sub> group (in going from compound **IV** to **V**) changes the supramolecular motif to centrosymmetric dimer pairs formed via intermolecular hydrogen bonds O<sup>6</sup>–H···O<sup>6</sup> [2.19(8) Å, 158(7)°]. Analogous but not centrosymmetric dimers are observed in the crystalline structure of *Z-XVIII*: O<sup>6</sup>–H···O<sup>6</sup> [2.07 (*A*), 2.15 Å (*B*); 170 (*A*), 148° (*B*)]. Crystals of the other compounds are characterized by weaker intermolecular interactions. For example, molecules of *trans-VIII* in crystal are linked through apex–face-like F···π interactions between the pentafluorobenzene rings C<sup>1</sup>–C<sup>6</sup> and C<sup>19</sup>–C<sup>24</sup> with the F···C distance ranging from 3.09 (F<sup>25</sup>···C<sup>4</sup>) to 3.64 Å (F<sup>25</sup>···C<sup>1</sup>). These values are close to that optimized for an analogous complex consisting of two hexafluorobenzene molecules (3.15 Å) [8].

Similar interactions in the crystalline structure of **XIX** are weaker, and the corresponding distances are extended by about 0.3 Å.

## EXPERIMENTAL

The <sup>19</sup>F NMR spectra of the reaction mixtures and individual compounds (in CHCl<sub>3</sub>) were recorded on a Bruker WP-200SY spectrometer at 188.3 MHz. The spectrum of a 2:1 mixture of *cis*- and *trans-XVII* was obtained on a Bruker AM-400 spectrometer at a frequency of 376.4 MHz. Hexafluorobenzene was used as internal reference. The elemental compositions were determined from the high-resolution mass spectra which were measured on a Finnigan MAT 8200 mass spectrometer. GLC analysis was performed using

an LKhM-72 chromatograph (oven temperature 50–270°C; 4000×4-mm column packed with SKTFT-50 or E-301 on Chromosorb W; carrier gas helium, flow rate 60 ml/min). GC–MS analysis was performed on a Hewlett–Packard G1081A GC–MS system consisting of an HP 5890 Series II gas chromatograph coupled with an HP 5971 mass-selective detector (electron impact, 70 eV); HP-5 capillary column, 30 m×0.25 mm×0.25 μm (5% of biphenyl, 95% of dimethylsiloxane); carrier gas helium, flow rate 1 ml/min.

X-Ray diffraction data were acquired on Bruker P4 and Syntex P2<sub>1</sub> diffractometers. Single crystals of **XIX** were grown at 30°C in a sealed evacuated (2 mm) ampule, and single crystals of *Z-IV*, *cis-XVII*, and *Z-XVIII* were obtained by slow evaporation of the solvent from hexane solution. Crystals of *trans-V* and *trans-VIII* were obtained by recrystallization from chloroform and acetone, respectively. The crystallographic data and parameters of X-ray diffraction experiments are given in Table 3. The structures were solved by the direct method using SHELXS-97 software and were refined by the least-squares procedure in anisotropic–isotropic approximation using SHELXL-97 software. Independent part of a unit cell of *Z-IV*, *Z-XVIII*, and **XIX** contained two crystallographically independent molecules (*A* and *B*). The positions of hydrogen atoms in the hydroxy groups were determined by the difference synthesis of electron density. The hydroxy hydrogen atom in *trans-V* was disordered by two positions at a ratio of 42(7):58(7). The pentafluoroethyl group in molecule *Z-XVIII* was also disordered by two positions at a ratio of 66(1):34(1) (*A*) and 57(1):43(1) (*B*). The structures of molecules *trans-V*, *cis-XVII*, and **XIX** are shown in Figs. 1–3.

#### Reaction of perfluoro(1-ethylindan) (**I**) with pentafluorobenzene in antimony pentafluoride.

*a.* Pentafluorobenzene, 1.75 g (10.42 mmol), was added dropwise over a period of 10 min to a mixture of 4.16 g (10.45 mmol) of compound **I**, 6.79 g (31.33 mmol) of SbF<sub>5</sub>, and 4 ml of hexafluorobenzene under stirring at 20–25°C. The mixture was stirred for 4 h at ~25°C and was treated with water at 0–10°C. The organic phase was separated, dried over MgSO<sub>4</sub>, and filtered from the drying agent and solid product. The solid material was dissolved in chloroform, and the solvent was distilled off to obtain 0.51 g of a mixture containing alcohols **IV** (5%) and **V** (90%) and compound **VI** (3%; hereinafter, given are the product compositions determined from the GLC and <sup>19</sup>F NMR data). Hexafluorobenzene was distilled off from the

filtrate, 1 ml of hexane was added to the residue, and the mixture was kept for 24 h at 5°C. The precipitate was filtered off to isolate 0.65 g of alcohol **V** with a purity of 94%, mp 156–157°C (from acetone). The filtrate was evaporated to leave 3.55 g of a mixture containing 8% of **I**, 45% of **IV** (*Z:E* ≈ 10:1), 4% of **V**, and 27% of **VI**. The overall yields of compounds formed in these reactions are given in Scheme 1. The latter mixture was subjected to column chromatography on silica gel using carbon tetrachloride to isolate 0.4 g of compound **VI** [a viscous liquid; it was additionally purified by vacuum “sublimation” at 115°C (5 mm)] and several fractions (total of 0.71 g) containing 70–80% of **VI**. The subsequent elution with CHCl<sub>3</sub> gave 0.07 g of a mixture of *E-IV* (68%) and **V** (29%), 0.5 g of *Z-IV* (mp 65.5–66.5°C, from hexane), and several fractions (0.4 g) containing isomers *E-IV* and *Z-IV* at various ratios.

Isomer *Z-IV*. Found, %: C 36.97; H 0.11; F 59.23. C<sub>17</sub>HF<sub>17</sub>O. Calculated, %: C 37.52; H 0.19; F 59.35.

Mixture *E-IV/V*. Found for *E-IV*: *M*<sup>+</sup> 543.9749. C<sub>17</sub>HF<sub>17</sub>O. Calculated: *M* 543.9756.

Compound **V**. Found, %: C 40.03; H 0.28; F 57.46. C<sub>23</sub>HF<sub>21</sub>O. Calculated, %: C 39.91; H 0.15; F 57.64.

Compound **VI**. Found, %: C 37.57; F 62.70. C<sub>17</sub>F<sub>18</sub>. Calculated, %: C 37.39; F 62.61.

*b.* A mixture of 2.9 g (7.29 mmol) of compound **I**, 7.91 g (36.5 mmol) of SbF<sub>5</sub>, and 3.68 g (21.9 mmol) of pentafluorobenzene was stirred for 25 h at 20–25°C in a Teflon vessel. Hexafluorobenzene, 3 ml, and anhydrous hydrogen fluoride, 15 ml, were then added in succession, the mixture was poured into an ice–water mixture, 5 ml of methylene chloride was added, and the organic phase was separated, washed with water, and dried over MgSO<sub>4</sub>. The solution was kept for 24 h at 5°C, and the precipitate, 0.53 g, was filtered off. It contained 14% of alcohol **V** and 86% of compound **VIII**. The solvent and volatile substances were distilled off from the filtrate, 1 ml of hexane was added to the residue, the mixture was kept for 24 h at 5°C, and the precipitate, 1.0 g, was filtered off. It contained 17% of alcohol **V** and 79% of **VIII**. The product was subjected to column chromatography on silica gel using carbon tetrachloride as eluent to isolate 0.4 g of compound **VIII** with mp 147–148°C (from acetone). The solvent was distilled off from the filtrate to obtain 2.14 g of a mixture containing 9% of **IV**, 67% of **VII**, and 17% of **VIII**. The overall yields of the products formed in this reaction are given in Scheme 1. The mixture was chromatographed on a column charged

**Table 3.** Crystallographic data for compounds **Z-IV**, *trans*-**V**, *trans*-**VIII**, *cis*-**XVII**, **Z-XVIII**, and **XIX** and parameters of X-ray diffraction experiments

Parameter	<b>Z-IV</b>	<i>trans</i> - <b>V</b>	<i>trans</i> - <b>VIII</b>	<i>cis</i> - <b>XVII</b>	<b>Z-XVIII</b>	<b>XIX</b>
Formula	C <sub>17</sub> HF <sub>17</sub> O	C <sub>23</sub> HF <sub>21</sub> O	C <sub>23</sub> F <sub>22</sub>	C <sub>18</sub> F <sub>20</sub>	C <sub>18</sub> HF <sub>19</sub> O	C <sub>18</sub> F <sub>18</sub> O
Molecular weight	544.18	692.24	694.23	596.18	594.19	574.18
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 1	<i>P</i> 2 <sub>1</sub> / <i>c</i>
Instrument	Syntex P2 <sub>1</sub>	Bruker P4	Bruker P4	Syntex P2 <sub>1</sub>	Syntex P2 <sub>1</sub>	Bruker P4
Irradiation source	CuK <sub>α</sub>	MoK <sub>α</sub>	MoK <sub>α</sub>	CuK <sub>α</sub>	CuK <sub>α</sub>	MoK <sub>α</sub>
Scan range θ, deg	2.53–71.01	2.07–24.99	2.28–25.00	4.00–69.94	4.58–69.93	1.77–20.00
Unit cell parameters						
<i>a</i> , Å	9.438(2)	10.9515(6)	7.5552(4)	12.852(3)	10.062(2)	25.027(3)
<i>b</i> , Å	10.973(3)	11.1830(7)	9.3287(5)	9.766(2)	10.226(2)	6.4956(8)
<i>c</i> , Å	17.691(4)	11.5089(7)	16.6437(9)	15.343(3)	10.441(2)	24.164(3)
α, deg	98.41(2)	117.988(4)	104.906(4)		67.38(3)	
β, deg	90.78(2)	106.135(4)	98.710(4)	105.32(3)	75.97(3)	99.157(9)
γ, deg	102.62(2)	99.498(5)	94.448(4)		76.80(3)	
Unit cell volume, Å <sup>3</sup>	1766.7(8)	1120.8(1)	1112.1(1)	1857.3(7)	951.1(3)	3878.1(8)
<i>Z</i> , <i>d</i> , g/cm <sup>3</sup> (calcd.)	4, 2.046	2, 2.051	2, 2.073	4, 2.132	2, 2.075	8, 1.967
μ, mm <sup>-1</sup>	2.332	0.246	0.251	2.494	2.394	0.241
Crystal habit, mm	0.60 × 0.35 × 0.20	0.70 × 0.40 × 0.16	0.60 × 0.40 × 0.24	1.00 × 0.32 × 0.22	0.65 × 0.60 × 0.10	1.20 × 0.35 × 0.06
Number of reflections, total/independent	7324/6733	3850/3633	4071/3750	3769/3509	3723/3609	3746/3618
Correction for absorption	–	–	By facet	By facet	Empirical	By facet
Transmission	–	–	0.88–0.94	0.36–0.66	0.46–0.97	0.92–0.99
Number of reflections with <i>I</i> > 2σ( <i>I</i> )	3921	2979	3093	2848	3091	1979
Number of refined parameters	640	416	407	344	736	668
<i>R</i> <sub>1</sub> for [ <i>F</i> > 4σ( <i>F</i> )]	0.0749	0.0346	0.0380	0.0437	0.0504	0.0516
<i>wR</i> <sub>2</sub> for all reflections	0.2586	0.0989	0.1043	0.1232	0.1423	0.1713
GOOF	0.994	0.997	1.033	1.057	1.057	1.044
Extinction coefficient	0.0052(7)	0.014(2)	0.013 (2)	0.0100(5)	0.019(2)	0.0011(5)

with silica gel using hexane as eluent to isolate 0.78 g of **VII** (*cis:trans* ≈ 6 : 1) and several fractions (0.78 g) containing compounds **VII** and **VIII** at different ratios.

Compound **VII** (*cis:trans* ≈ 6 : 1). Found, %: C 37.04; F 62.71. C<sub>17</sub>F<sub>18</sub>. Calculated, %: C 37.39; F 62.61.

Compound **VIII**. Found, %: C 40.18; F 60.12. C<sub>23</sub>F<sub>22</sub>. Calculated, %: C 39.77; F 60.12.

**Reaction of perfluoro(1,1-diethylindan) (II) with pentafluorobenzene in SbF<sub>5</sub>.** *a.* Pentafluorobenzene,

0.78 g (4.64 mmol), was added dropwise over a period of 5 min to a mixture of 2.1 g (4.22 mol) of compound **II**, 2.74 g (12.64 mmol) of SbF<sub>5</sub>, and 1.5 ml of C<sub>6</sub>F<sub>6</sub> under stirring at ~20°C. The mixture was stirred for 4 h at ~20°C and was treated with water at 0–10°C. The organic phase was separated and dried over MgSO<sub>4</sub>, and C<sub>6</sub>F<sub>6</sub> was distilled off to obtain 2.02 g of a mixture containing 71% of alcohol **XV** (yield 52%) and 25% of initial compound **II**.



b. Following an analogous procedure, from 2.36 g (4.74 mmol) of compound **II**, 0.88 g (5.24 mmol) of pentafluorobenzene, 3.08 g (14.21 mmol) of  $\text{SbF}_5$ , and 1.5 ml of hexafluorobenzene (50–55°C, 4 h), we obtained 2.5 g of a mixture containing 82% of alcohol **XV** (yield 67%) and 14% of compound **II**.

c. A mixture of 2.2 g (4.42 mmol) of compound **II**, 4.78 g (22.05 mmol) of  $\text{SbF}_5$ , and 0.82 g (4.88 mmol) of pentafluorobenzene was stirred for 6 h at 50–55°C. Hexafluorobenzene, 2 ml, was then added, and the mixture was treated as described above in *a*. We isolated 2.45 g of compound **XV** with a purity of 95%, which was subjected to column chromatography on silica gel using chloroform as eluent. Yield of **XV** 2.3 g (81%), viscous liquid. Found:  $M^+$  643.9724.  $\text{C}_{19}\text{HF}_{21}\text{O}$ . Calculated:  $M$  643.9692.

d. A mixture of 3.04 g (6.1 mmol) of compound **II**, 6.62 g (30.54 mmol) of  $\text{SbF}_5$ , and 1.03 g (6.13 mmol) of pentafluorobenzene was stirred for 6 h at 50–55°C in a Teflon vessel. Hexafluorobenzene, 3 ml, and anhydrous hydrogen fluoride, 12 ml, were added in succession, and the mixture was poured into an ice–water mixture. The organic phase was separated, washed with water, and dried over  $\text{MgSO}_4$ , and hexafluorobenzene was distilled off to obtain 3.13 g of a mixture containing 21% of alcohol **XV** and 73% of **XVI**. This mixture was chromatographed on a column charged with silica gel using carbon tetrachloride as eluent to isolate 2.18 g (55%) of compound **XVI** as a viscous liquid. Found, %: C 35.54; F 64.58.  $\text{C}_{19}\text{F}_{22}$ . Calculated, %: C 35.32; F 64.68.

#### Reaction of perfluoro(1-ethyl-1,2,3,4-tetrahydronaphthalene) (**III**) with pentafluorobenzene in $\text{SbF}_5$ .

*a*. A mixture of 1.38 g (3.08 mmol) of compound **III**, 3.35 g (15.46 mmol) of  $\text{SbF}_5$ , and 0.57 g (3.39 mmol) of pentafluorobenzene was stirred for 6 h at 50–55°C, 2.5 ml of hexafluorobenzene was added, and the mixture was treated with water at 0–10°C and extracted with chloroform. The extract was dried over  $\text{MgSO}_4$ , and the solvent and hexafluorobenzene were distilled off to obtain 1.68 g of a mixture containing 82% of alcohol **XVIII** ( $Z:E \approx 10:1$ , yield 75%) and 12% of ketone **XIX** (yield 11%). Hexane, 2 ml, was added, and the mixture was kept for 12 h at –18°C. The precipitate, 1.02 g (95% of **Z-XVIII**), was filtered off, sublimed at 110–140°C (5 mm), and recrystallized from hexane to isolate isomer **Z-XVIII** with mp 85.5–88°C. The filtrate, 0.57 g, contained 45% of **XVIII** ( $Z:E \approx 3:1$ ) and 35% of ketone **XIX**; it was chromatographed on a column charged with silica gel using

chloroform as eluent to isolate 0.11 g of **XIX**, mp 54–56°C [after recrystallization from hexane and sublimation at 30–40°C (1–2 mm)], 0.13 g of **Z-XVIII**, and 0.05 g of **E-XVIII** (purity 90%, viscous liquid).

Isomer **Z-XVIII**. Found:  $M^+$  593.9734.  $\text{C}_{18}\text{HF}_{19}\text{O}$ . Calculated:  $M$  593.9724.

Isomer **E-XVIII**. Found:  $M^+$  593.9745.  $\text{C}_{18}\text{HF}_{19}\text{O}$ . Calculated:  $M$  593.9724.

Ketone **XIX**. Found:  $M^+$  573.9668.  $\text{C}_{18}\text{F}_{18}\text{O}$ . Calculated:  $M$  573.9662.

*b*. A mixture of 2.95 g (6.58 mmol) of compound **III**, 7.14 g (32.94 mmol) of  $\text{SbF}_5$ , and 1.22 g (7.26 mmol) of pentafluorobenzene was stirred for 6 h at 50–55°C in a Teflon vessel. Hexafluorobenzene, 3.5 ml, and anhydrous hydrogen fluoride, 15 ml, were added in succession, and the mixture was poured into an ice–water mixture and extracted with chloroform. The organic phase was separated, washed with water, and dried over  $\text{MgSO}_4$ , and the solvent and  $\text{C}_6\text{F}_6$  were distilled off to obtain 3.55 g of a solid material containing 86% of *cis-XVII* and 9% of *trans-XVII* (yield 86%). This material was recrystallized from hexane to isolate *cis-XVII* with mp 72–72.5°C. The mother liquor was evaporated, and the residue, 0.89 g, containing 58% of *cis-XVII* and 28% of *trans-XVII* was chromatographed on a column charged with silica gel using hexane as eluent. We thus isolated 0.65 g of **XVII** as a mixture of 66% of the *cis* isomer and 33% of the *trans* isomer (according to the GC–MS and  $^{19}\text{F}$  NMR data).

Isomer *cis-XVII*. Found, %: C 36.22; F 63.69.  $\text{C}_{18}\text{F}_{20}$ . Calculated, %: C 36.26; F 63.74.

Mixture *cis-XVII/trans-XVII*. Found:  $M^+$  595.9702.  $\text{C}_{18}\text{F}_{20}$ . Calculated:  $M$  595.9680.

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