ISOMER CONVERSIONS IN PERFLUORO-1-ETHYLINDANE UNDER THE ACTION OF ANTIMONY PENTAFLUORIDE

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Perfluoro-1-ethylindane on heating with SbF_5 is isomerized to perfluoro-1,1dimethylindane, perfluoro- α,β -o-trimethylstyrene, and perfluoro-1,2-dimethylindane. In the presence of SbF_5 , the latter two products are converted one into the other. In addition, in SbF_5 perfluoro-1,2-dimethylindane is defluorinated to perfluoro-2,3-dimethylindene and fluorinated to perfluoro-2,3-dimethyl-4,5,6,7-tetrahydroindene which is further fluorinated to perfluoro-1,2dimethyl-4,5,6,7-tetrahydroindane and is converted at 200°C to perfluoro-1,7-dimethylindane. The latter is also formed on heating perfluoro- α,β -otrimethylstyrene with SbF_5 at 200°C.

We showed recently that in the presence of SbF_5 the four-membered ring of polyfluorobenzocyclobutene is broken with subsequent recyclization of the polyfluorostyrene which is formed to polyfluoroindane [1]. Conversion of polyfluorindanes under the action of SbF_5 into perfluoro-o-dialkylbenzenes also appears to take place via the intermediate formation of polyfluorostyrenes [2]. In this connection, in order to clarify the general mechanism of skeletal conversions of polyfluorobenzocycloalkenes taking place under the influence of Lewis acids, we have studied, in the present work, the behavior of perfluoro-1-ethylindane (I) in the presence of SbF_5 .

Heating (I) with SbF_5 at 130°C leads to the formation of isomeric perfluoro-1,1-dimethylindane (II), perfluoro-1,2-diemthylindane (III), and perfluoro- α,β -o-trimethylstyrene (IV) (in the absence of SbF_5 (I) is unchanged even at 200°C). In addition, the reaction mixture contains perfluoro-2,3-dimethyl-4,5,6,7-tetrahydroindene (V) and unchanged (I). On prolonged reaction, (I) is practically completely converted into (II)-(V). In this case, the quantity of diene (V) in the mixture increases and that of compounds (III) and (IV) falls. At the same time, the yield of indane (II), calculated on the (I) reacted, is not significantly changed.



Increasing the temperature to 170°C leads to a reduction in the yield of indane (II) and to the practically complete disappearance of products (III) and (IV) from the reaction mixture on one hand, and to the formation of perfluoro-2,3-dimethylindene (VI) and perfluoro-1,2-dimethyl-4,5,6,7-tetrahydroindane (VII) on the other. Under still more vigorous conditions (200°C), in addition to compounds (II) and (V)-(VII), small amounts of perfluoro-1,7-

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It should be noted that indane (II) on heating with SbF_5 is largely unchanged and is not converted into products (III)-(VIII) and likewise indane (II) is not formed from compounds (III)-(VIII) in SbF_5 . Styrene (IV) and indane (III), heated at 130°C for 10 h in the presence of SbF_5 are converted into each other. In addition, under the same conditions indane (III) forms indene (VI) and diene (V) in approximately equal quantities. Successive heating of styrene (IV) with SbF_5 at 130°C and then at 170°C leads to the formation of diene (V) and indene (VI) in the ratio ~2:1 in addition to small quantities of indane (III)



Under more vigorous condition (200°C) styrene (IV) in SbF_5 gives indane (VIII) and olefin (VII) in addition to (V) and (VI). (VIII) and (VII) are also formed by the reaction of diene (V) in SbF_5 at 200°C.

The presence of indene (VI), among the products of the reaction of compounds (I), (III), (IV) with SbF_5 could be taken as evidence of its stability under the reaction conditions. In fact, indene (VI) when reacted with SbF_5 for 16 h at 170°C is fluorinated to diene (V) to only a small extent. The small susceptibility of (VI) to fluorination is probably connected with its almost complete conversion, in the presence of SbF_5 , to a salt of the perfluoro-1,2-dimethylindenyl cation (IX). In fact, the cation (IX) is generated on dissolving indene (VI) in SbF_5 (¹⁹F NMR spectrum) and hydrolysis of this solution yields perfluoro-2,3-dimethylindenone (X) (compare with other polyfluoroindenyl cations [3]).



Hence, from reaction mixtures formed from compounds (I), (III), and (IV) and SbF_5 one obtains ketone (X) by treatment with water and indene (VI) with anhydrous HF. It should be noted that the diene (V) is unchanged on dissolving in SbF_5 (¹⁹F NMR spectrum).

The formation of (VI) in the reactions under consideration by defluorination of (III) on the walls of the nickel reactor seems unlikely since (VI) is also obtained on reacting (I) with SbF_5 at 170°C in a vessel constructed from Fluoroplast-4. In view of this, a more probable route to the formation of (VI) and (V) is the disproportionation of indane (III) under the conditions of the reaction (compare with the disproportionation of polyfluorinated cyclohexadienes in the presence of SbF_5 into the corresponding aromatic compounds and cyclohexenes [4, 5]). Furthermore, diene (V) is also obtained by fluorination of indane (III)

by SbF_5 (compare [4]). Evidence of the fluorination of (III) is provided by the formation of (V), in many cases in much larger quantity than indene (VI), in the reaction of (I) with SbF_5 [(VI) under similar conditions undergoes insignificant change].

From this point of view we also have an explanation of the fact that indane (III), converted to a small extent under the action of SbF_5 (130°C, 10 h), gives compounds (V) and (VI) in approximately equal quantities whereas indane (I) under similar conditions yields diene (V) and practically no (VI).

It can be supposed that disproportionation of (III) to (V) and (VI) is a process which is second order in indane (III) and its fluorination to (V) is first order. In passing from (III) to (I) in their reactions with SbF_5 at 130°C the concentration of (III) will fall markedly. Consequently, in the case of (I) the rate of disproportionation of (III) will slow down to a greater extent than the rate of fluorination to (V).

Diene (V) under more vigorous conditions (200°C) probably also undergoes disproportionation to olefin (VII) and indane (III). The latter in its turn (by virtue of low concentration) is largely fluorinated to (V) and reversibly converted into the styrene (IV) which apparently cyclizes to indane (VIII). Furthermore, it is not possible to show unequivocally whether olefin (VII) is formed by fluorination of diene (V) by SbF_5 , and likewise concerning the formation of (VII) at 170°C by fluorination or (and) disproportionation of (V). Thus, the overall transformations of products (I)-(VIII) observed in SbF_5 can be expressed by the following scheme:

The fluorination of aromatic compounds under the influence of SbF_5 has been described in the literature [2, 6]. In this connection, one notes that the aromatic ring of indane (III) is readily fluorinated in comparison with (II) and other polyfluoroindanes [2]. The difference in the behavior of (III) and, for example, (II) can be understood if one supposes that in the presence of SbF_5 the triene (XI) exists in equilibrium with (III) and its fluorination by SbF_5 must occur more easily than that of the aromatic ring of (III) [4-6].



In fact, the relative concentration of (XI) in equilibrium with (III) must be higher than that of trienes (XII) in equilibrium with (II) since the fluorine atoms located at the multiple bond have a destabilizing influence on the olefins [7]. One cannot exclude the possibility that disproportionation of (III) under the influence of SbF_5 into (V) and (VI) also takes place via the triene (XI), just as occurs in the case of polyfluorinated cyclohexadienes [4, 5].

Isomerization of (I) under the influence of SbF_5 into compounds (II)-(IV) can be represented by the following scheme (compare with the skeletal transformations of other polyfluoroindanes [2])



It seems that the perfluoro-1-ethyl-1-indanyl cation (XIII) is first generated from (I) and this is isomerized into a benzyl type ion. A shift of the double bonds within the chain takes place, evidently by addition-separation of fluoride ions, as a result of which styrene (IV) is obtained. Intramolecular cyclization of the cation (XIV) generated there-from leads to indane (III) which is reversibly converted to styrene (IV). The formation of (II) from (I) by the action of SbF₅ can be represented, for example, by the isomerization of the ion (XIII) into cation (XV) by 1,2-shift of a CF₃ group and subsequent addition of fluoride ion to (XV).

It could be supposed that the conversion of styrene (IV) to indane (VIII) under the influence of SbF_5 takes place in the following manner. The ion (XVI) is evidently formed from (IV) and this ion undergoes intramolecular cyclization, proceeding, for example, thus



TABLE 1. Elemental Composition, IR, and UV Spectra of Compounds (II), (V)-(VIII), and (X)

Com-	Found*	Empiri-	IR spectra, v, cm ⁻¹		
pound	Calc.	cal for- mula	C=C (C=0)	fluorinated aromatic ring	$(\log \epsilon)$
(11)	<u>397,9772</u> 397,9776	C11F14		1520	263 sh (2,93), 267 (2,99)
(V)	435,9745 435,9744	C ₁₁ F ₁₆	1685		270 (3,34)
(VI)	359,9816 359,9808	C ₁₁ F ₁₂	1658	1513	299 (3.61), 308 (3,63), 320 sh (3,46)
(VII)	473,9710 473,9712	C11F18			
(VIII)	<u>397,9756</u> <u>397,9776</u>	C ₁₁ F ₁₄		1520, 1500	274 (3,11), 2,87 (3,09)
(X)	337,9795 337,9789	C ₁₁ F ₁₀ O	(1740) 1638	1500	354 (3,49)

*Mol. wt. from high resolution mass spectra.

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Wt. (I)	T, °C	Yield of		Content (3	/ield)* of r	eaction pro	ducts, % (GLC,	, ¹⁹ F NMR)		
used, g	(time, h)	mixture, g	(1)	(11)	(III)	(IV)	(A)	(VI) + (X)	(111)	(1111)
2,12	130 (15)	1,82	36 (30,7)	22(18,8) +	19(16,2) †	8(6,8) +	10(7,8) +			
1,99	130 (35)	1,81	3(2,7)	27 (24,6)	9(8,2)	4 (3,6)	48 (39,9)	° V		
2,29	170 (15)	1,92		18(15,1)			52 (39,8)	19(17,6)	2(1,4)	
2,28	170 (30)	2,10		18(16,6)			55 (46,2)	15 (15,3)	5 (3,9)	
2,11	170 (45)	1,85		16(14,0)			46 (36,8)	17 (16,5)	10 (7,4)	
3,42	200(3,5)	3,18		14(13,0)			52 (44,1)	16(16,4)	4(3,1)	
3,22	200(8)	2,57		16(12,8)			36 (26,2)	16(14,1)	15(10,1)	
3,41	200(30)	3,11		14(12,8)			12 (10,0)	13(13,1)	27 (20,7)	7 (6,4)
3,01	200 (63)	2,61		13(11,3)			9(7,1)	13(12,5)	34 (24,8)	8(6,9)
1,6 ⁽¹ ‡)	170(30)	0,92		15 (8,4)			52 (26,6)	10(6,2)	12 (5,7)	

(1 = 7)Conversions of Perfluoro-1-ethvlindane (I) in ShF. (mole ShF./mo TABLE 2.

*Mole/mole (I). †Yield on (I) reacted amounted to 27.3% (II), 23.6% (III), 9.9% (IV), 11.3% (V). ‡Reacted in Fluoroplast-4 vessel.

Products (III) and (IV) were identified in the reaction mixture by means of GLC and their ¹⁹F NMR spectra which coincided with the spectra of authentic samples [1]. The structure of compounds (II), (V)-(VIII) was supported by their elemental composition and their spectral characteristics. Thus, evidence for the structure of compound (V) was provided by the absence of upfield signals, characteristic of tertiary fluorine [2, 8, 9], from its ¹⁹F NMR spectrum. The existence of signals of CF_3 groups at ~90 ppm in the spectrum of compound (VII) corresponds to the location of these groups at the saturated carbon atom [2, 9] and not at the double bond of the five-membered ring (compare with (V), (VI) [10]). These results, taken with the presence of signals from two tertiary fluorine atoms (-8.0 and -23.1 ppm) repudiate structures other than (VII) for the distribution of the double bonds.

EXPERIMENTAL

A Varian A56/60A instrument (56.4 MHz) was used to obtain the ¹⁹F NMR spectra of the reaction mixtures without a solvent and of solutions of the products in CC_4 relative to C_6F_6 . IR spectra of solutions in CCl_4 were run on a UR-20 instrument and UV spectra in heptane on a Specord UV-VIS. Elemental compositions were determined by high resolution mass spectrometry on a Finnigan MAT 8200. An LKhM-72 chromatograph was used for GLC: 50-270°C, 4000 × 4 mm SKTFT-50, E-301 on Chromatone N, 15:100, He 60 ml/min. Compounds (II), and (V)-(VIII) were separated from the mixture by preparative GLC (125°C, SKTFT-50 on Celite, N₂). Data for the elemental compositions are given in Table 1 and the spectra in Table 2 and in the experimental section which follows.

 $\frac{^{19}\text{F NMR Spectra of Compounds (\delta ppm, J Hz).}{(II): 99.0 (2CF_3), 56.6 (2F^3) 43.9 (2F^2), 30.6 (1F^7), 24.7 (1F^4), 19.8 (1F^6), 8.2 1F^5). (V): 104.0 (CF_3), 101.3 (CF_3), 49.8 (2F), 47.6 (2F), 34.5 (2F), 29.3 (2F), 28.4 (2F). (VI): 104.3 (CF_3^2), 98.2 (CF_3^3), 43.7 (2F^1), 29.6 (1F^4), 24.2 (1F^7), 16.9 and 15.8 (2F^{5,6}); J_{12} = 6, J_{23} = 11, J_{34} = 27. (VII) (no solvent): 89.3 (CF_3), 88.4 (CF_3), -8.0 (1F^1), -23.1 (1F^2); the remaining signals were in the 63-21 ppm region. (VIII): 105.6 (CF_3^7), 87.2 (CF_3^1), 60.7 (1FA^3), 51.1 (1FB^3, JAB = 268), 46.2 (1F^6), 42.0 (1FA^2), 31.3 (1FB^2, JAB = 247), 35.7 (1F^4), 17.6 (1F^5), -11.3 (1F^1); J_{67} = 20, J_{CF_3}^7 - F^{1=} 41, J_{CF_3} - CF_3 = 10, J_{45} ~ J_{46} ~ J_{56} ~ 19.$ The parameters of the spectrum of (VIII) were found to be in accordance with those of related compounds [9, 11]. (X): 103.9 (CF_3^2), 98.8 (CF_3^3), 32.1 (1F^4), 28.8 (1F^7), 20.8 (1F^5), 17.1 (1F^6); J_{23} = 12, J_{34} = 29.

<u>Perfluoro-2,3-dimethylindenone (X).</u> (VI) (0.89 g) was dissolved in 3.64 g SbF₅ at ~20°C. According to the ¹⁹F NMR results, cation (IX) was generated (C_6F_6 int. std, δ ppm): 179.0 (1F), 106.7 (1F), 101.8 (CF₃), 96.4 (CF₃), 82.2 (1F), 69.2 (1F), 27.3 (1F), cf. [3]. Poured onto ice, extracted with CH₂Cl₂, dried over MgSO₄, solvent distilled off to yield 0.76 g of a product containing ~80% (X) which was purified on a silica gel column with hexane as eluent and sublimed (120°C/90 mm), mp 67-68.5°C.

<u>Reaction of Perfluoro-1-ethylindane (I) with SbF_5 . Method A</u>. Into a 10 ml nickel autoclave was placed a solution of 2.29 g (I) in 8.75 g SbF_5 and heated 15 h at 170°C. Cooled to ~-10°C, 3-4 ml anhyd. HF added, stirred, transferred to crushed ice, cooled in liquid N₂. From GLC and ¹⁹F NMR results, the 1.92-g mixture obtained (dried MgSO₄) contained 18% (II), 52% (V), 14% (VI), 2% (VII), and 5% (X). Other experiments with (I) and SbF₅ were carried out in a similar way. The concentration of (X) in the mixtures did not exceed 3%. The results of the experiments are set out in Table 2.

<u>Method B.</u> The reaction mixture was transferred to ice without preliminary treatment with HF. From 2.92 g (I) and 11.15 g SbF_5 ($SbF_5/(I) = 7$) over 15 h at 170°C there was formed 2.64 g of a mixture containing (from GLC and ¹⁹F NMR) 16% (II), 57% (V), 2% (VII), and 16% (X).

Conversion of Compounds (II)-(VI) on Heating in SbF_5 . Perfluoro-2,3-dimethylindene (VI). Heating 0.49 g (VI) and 2.1 g SbF_5 ($SbF_5/(VI) = 7$) for 16 h at 170°C gave (method A) 0.27 g of a mixture containing (GLC and ¹⁹F NMR) 7% (V), 62% (VI), and 11% (X).

<u>Perfluoro-1,1-dimethylindane (II)</u>. Heating 1.3 g (II) and 4.97 g SbF_5 ($SbF_5/(II) = 7$) for 59 h at 200°C gave (method A) 1.05 g product containing 74% (II).

<u>Perfluoro-1,2-dimethylindane (III)</u>. Heating 0.4 g (III) and 2.19 g SbF₅ (SbF₅/(III) = 10) for 10 h at 130°C gave (method A) 0.18 g of a mixture containing 45% (III), 18% (IV), and 8% (VI).

 $\frac{\text{Perfluoro-}\alpha-\beta-\text{o-trimethylstyrene (IV).}}{(\text{SbF}_5/(\text{IV}) = 9.7) \text{ for 10 h at 130°C gave (method A) 0.45 g of a mixture containing 57% (III), 23% (IV), 4% (V), and <2% (VI).}$

b) Heating 1.52 g (IV) and 7.45 g SbF_5 ($SbF_5/(IV) = 9$) for 20 h at 130°C and then 10 h at 170°C gave (method A) 1.15 g of a mixture containing 6% (III), 2% (IV), 55% (V), and 25% (VI).

c) Heating 1.57 g (IV) and 5.99 g SbF_5 ($SbF_5/(IV) = 7$) for 60 h at 200°C gave (method B) 1.37 g of a mixture containing 15% (V), 37% (VII), 12% (VIII), and 9% (X).

<u>Perfluoro-2,3-dimethyl-4,5,6,7-tetrahydroindene (V)</u>. Heating 2.6 g (V) and 9.05 g SbF₅ (SbF₅/(V) = 7) for 60 h at 200°C gave (method B) 1.82 g of a mixture containing 12% (V), 58% (VII), and 6% (VIII).

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