161.06 (CO), 54.32, 54.68, 54.04 (CH₃O), 128.71, 122.80, 117.25, 111.56 (CF₃). ¹⁹F NMR spectrum (acetone-d₆, δ , ppm, *J*, Hz): -0.44 q (CF₃, *J*_{F-F} = 5), -2.2 s (CF₃), -3.38 s (CF₃), -3.53 q (CF₃, *J*_{F-F} = 5). IR spectrum (ν , cm⁻¹): 1780 (C=O), 1856 (C=O), 1058 (CO), 1022 (CO). Raman spectrum (ν , cm⁻¹): 1778 (C=O), 1857 (C=O). Found %: C 30.52; H 2.09; F 36.52. C₈H₆F₆O₆. Calculated %: C 30.76; H 1.92; F 36.53.

B. A mixture of 6.24 g of keto ester 1 and 5.52 g of potassium carbonate in 30 ml of methanol was heated at 80-90°C for 15 h. After fractional distillation we obtained 4.3 g (70.3%) of compound 5; bp 57°C (1 mm Hg), n_D^{20} 1.3642. PMR spectrum (acetone-d₆, δ , ppm): 3.55 s (3H, OCH₃), 3.62 s (3H, OCH₃), 3.94 s (3H, OCH₃), 3.97 s (3H, OCH₃). ¹⁹F NMR spectrum (acetone-d₆, δ , ppm, J, Hz): -0.46 q (CF₃, $J_{F-F} = 5$), -2.3 s (CF₃), -3.38 s (CF₃), -3.56 q (CF₃).

LITERATURE CITED

- 1. A. F. Sanzen, P. F. Rodesiler, and C. J. Willis, Chem. Commun., No. 19-24, 673 (1966).
- 2. R. V. Middleton and J. R. Lindsey, J. Am. Chem. Soc., 86, No. 22, 4948 (1964).
- 3. C. L. Frye, R. M. Salingrer, and J. R. Patin, J. Am. Chem. Soc., 88, No. 9-10, 2343 (1966).
- 4. I. L. Knunyants, N. P. Gambaryan, and V. V. Tyuleneva, Izv. Akad. Nauk, Ser. Khim., No. 12, 2662 (1967).
- 5. V. A. Soloshonok, I. I. Gerus, Yu. L. Yagupol'skii, and V. P. Kukhar', Zh. Org. Khim., 23, No. 7, 1441 (1987).

FLUOROINDENES. 13.* TRANSFORMATIONS OF POLYFLUORINATED INDENES AND 1-ALKYLIDENEINDANS IN THE H₂O₂-HF-SbF₅ SYSTEM

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UDC 547.665'161:547.814.1

The reaction of perfluorinated indene, 3-methylindene, and 1-methylene- and 1-ethylideneindans with hydrogen peroxide in the hydrogen fluoride—antimony pentafluoride medium takes place at the multiple bond of the substrate and leads to the oxo derivatives of indan. The process probably takes place through the electrophilic addition of HO^+ . The C=C bond in perfluoro-3-methylindenone is not affected. In this compound and also in perfluoro-2-indanone and perfluoro-1-methyl-2-indanone the carbonyl group is involved in reaction with hydrogen peroxide in the $HF-SbF_5$ system, and six-membered oxygen-containing heterocyclic compounds are formed.

Keywords: Polyfluorinated indenes, alkylideneindans, electrophilic hydroxyfluorination, polyfluorinated ketones, Baeyer–Villiger reaction.

It is known that the reaction of perfluoroindene (1) with nitric acid most probably takes place by an electrophilic path, while the reaction of perfluorinated 3-methylindene (2), 1-methyleneindan (3), and 1-ethylideneindan (4) takes place by a radical path [2]. In order to investigate further the reactions of compounds 1-4 taking place with potential electrophilic reagents at the multiple bond of the substrate, in the present work we studied the transformations of compounds 1-4 in the $H_2O_2-HF-SbF_5$ system [3].

^{*}For Communication 12, see [1].

Novosibirsk Institute of Organic Chemistry, Siberian Branch, Russian Academy of Sciences, 630090 Novosibirsk. Translated from *Izvestiya Akademii Nauk, Seriya Khimicheskaya*, No. 6, pp. 1412-1419, June, 1992. Original article submitted March 11, 1991.

It was shown that perfluoro-1-acetylindan (5) is formed in the reaction of compound 4 with hydrogen peroxide in $HF-SbF_5$. Here part of the initial compound 4 remains unchanged. Under analogous conditions methyleneindan 3 undergoes full transformation in a shorter time than compound 4. As a result, after treatment of the reaction mass with water perfluoroindan-1-carboxylic acid (6) is obtained in addition to a small amount of the indene 2 and perfluoro-1-methyl-2-indanone (7). The latter is clearly the product from hydroxyfluorination—dehydrofluorination of the indene 2, while compound 2 is the product from isomerization of compound 3 under the reaction conditions. Compound 3 is not changed by the action of hydrogen peroxide in hydrogen fluoride in the absence of antimony pentafluoride.



1-Hydroxyperfluoro-1-methylindan (8), which is the product corresponding to the orientation opposite that observed during the hydroxyfluorination of compound 3, was not detected. At the same time it was shown by separate experiment that the indan 8 is not changed under the reaction conditions. $\dot{\tau}$

The process can be represented in the following way. The reaction of the substrate with the HO⁺ cation generated from the H₂O₂ (see [3]) probably leads to the intermediate formation of an ion of the benzyl type 9 (as the limiting form), which gives the reaction product as a result of addition of F⁻ and elimination of HF. The direction of addition of HO⁺ here probably agrees with the relative stability of the intermediate cation 9 (see [4]).

The direction probably also agrees with the relative stability of the intermediate cation during the reaction of HO⁺ with the multiple bond of the indene 2. Thus, the alcohol 8 is not formed in the reaction of 2 with hydrogen peroxide in the $HF-SbF_5$ medium, but a mixture containing the indanone 7, perfluoro-4-methyl-3,4-dihydroisocoumarin (10), 2-(1-carboxytetra-fluoroethyl)tetrafluorobenzoic acid (11), and a small amount of perfluoro-4-methylcoumarin (12) is obtained together with the initial compound 2.



When the reaction time was reduced from 8 to ~ 1.5 h, the product 10 was hardly formed at all, in contrast to the other compounds. It was shown by a separate experiment that the ketone 7 under the conditions of the reaction of compound 2 with hydrogen peroxide gives a mixture of dihydroisocoumarin 10 and the acid 11. In view of the fact that in the reaction of the indene 2 with H₂O₂ in HF-SbF₅ compound 10 is formed later than compound 11, it can be supposed that the transformation of the ketone 7 into the products 10 and 11 takes place according to the following scheme:



 $[\]dagger$ Obtained in addition to other compounds during the reaction of compound 3 with nitric acid (or NO₂BF₄) in HF; this will be examined in a separate article.

	Found/ Calculated, % (mol. wt.)	Molecular formula	IR spe	ctrum,	ν, cm ^{-1.a}	UV spectrum, λ_{max} , nm; (log ε) ^b	
Compound	C H F		fluor- inated aroma- tic ring	C=0	other bands		
5	$\left(\frac{375.9756}{375.9757}\right)$	C11F12O	1519	1778	1413	270(3.05)	
6	<u>37.06</u> 0.29 52.92 37.06 0.31 52.76	- C10HF9O2	1522	1758	2600-3400 (O-H), 1411	269(2.98)	
7	$\left(\frac{325.9761}{325.9789}\right)$	C10F10O	1519	1811	1408	266 (2.98)	
7a	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	- C10H2F10O2	1518		3570 (O-H) 1410	268 (2.89)	
10	$\left(\frac{341.9747}{341.9738}\right)$	C10F10O2	1525, 1505	1810	1632, 1400	236(3.93), 240(3.88), 286(3.47), 293(3.47)	
11	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	C10H2F8O4	1537. 1484	1759, 1738	1645, 1630, 1436	270 (3.19)	
12	$\left(\frac{303.9784}{303.9771}\right)$	C10F8O2	1531, 1492	1781	1652	$\begin{array}{c} 249 (3.72), \ 276 (4.00), \\ 283 (4.02), \ 294 {\rm sh} (3.88) \\ 321 {\rm sh} (3.26) \end{array}$	
17	$\left(\frac{-287.9833}{-287.9821}\right)$	$C_{10}F_8O$	1505	1764	1690, 1387	318(3.43), 331(3.51), 346(3.36), 374(2.85)	
18	$\left(\frac{275.9808}{275.9821}\right)$	C ₉ F ₈ O	1525, 1514	1812	1409	340 (3.30), 314 (2.00)	
1 8a	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\frac{4}{8} C_9 H_2 F_8 O_2$	1527		3580 (O-H), 1411	269(2.97)	
20	$\left(\frac{291.9771}{291.9771}\right)$	C ₉ F ₈ O ₂	1527, 1505	1804	1632, 1403	$ \begin{bmatrix} 234(3.93), 240(3.89), \\ 286(3.47), 293(3.48) \end{bmatrix} $	
Zic					walking of the second se	244(4.00), 252(4.01), 293(3.48)	

TABLE 1. Elemental Composition and IR and UV Spectra of Compounds 5-7a, 10-12, 17-18a, 20-21

a) For solutions in carbon tetrachloride, for 11 in potassium bromide.

b) For solutions in heptane, for 6 and 11 in alcohol.

c) Obtained by the method in [11].



Perfluoro-4-methylisochroman-3-one (13) is probably formed initially as a result of a reaction of the Baeyer-Villiger type. Compound 13 probably isomerizes in the acidic system to the difluoride of the acid 11, the cyclization of which leads to the dihydroisocoumarin 10, while hydrolysis leads to the acid 11. The proposed scheme is not contradicted by the behavior of the perfluoro-1-indanone (14) under analogous conditions [5] or by data on the ring-chain isomerism of dicarboxylic acid halides [6]. In terms of the presented scheme the migration of the CFCF₃ group in the cation 15 to the O⁺ atom must be hindered in comparison with the CF₂ group, since at the developing carbonium center in the corresponding transition state instead of the F atom there will be a CF₃ group, which destabilizes it (see [2]).

The formation of the product 12 in the reaction of the indene 2 with $H_2O_2-HF-SbF_5$ may include the acid-catalyzed substitution of the F atom at position 1 of compound 2 by the OOH group. The product obtained here probably undergoes further transformations, including migration of the aryl group to the oxygen atom with the final formation of the coumarin 12. Under the reaction conditions the latter most likely exists in the protonated form, i.e., in the form of a 2-hydroxyperfluoro-4-methyl-1-benzopyrylium salt (16).



Come	ó, ppm										
pound	F	F	2	1	7 3	F4	R5_6	E,	CP.	Ци	n 3'(AB
		А	В	A	В				C. S		JA'I
5*	-0.3	42.4	39.8	63.2	53.0	24.9	20.2; 20.7	27.2	86.8	:	262 (250)
6**	5.4	39.9	38.2	60.6 66.7	53,1	23.9	18.3	25.4	96.3	10.61	263(246)
7a *	-6.0			56.3	54.9	22.5	17.0	27.1	87.1	4.08	254
17**		35	.1			25.6	21.4(F ⁵)	31.0	98.9		
18 **	61.7			61	.7	25.7	20.7	25.7			
18a **	53.9			53	.9	23.2	17.0	23.2		3.94	

*For solutions in deuterochloroform.

**For solutions in carbon tetrachloride.

Occurrence of the reaction through the intermediate formation of perfluoro-3-methylindenone (17) seems less likely, since the compound was not found in the reaction mixture in appreciable quantities. At the same time it was shown by a separate experiment that, although it gives the coumarin 12 under the conditions of the reaction of the indene 2 with hydrogen peroxide in HF-SbF₅, the indenone 17 is largely recovered from the process unchanged. The last transformation can probably be represented by the following scheme:



The indenone 17 was produced by hydrolysis of a solution of the indene 2 in antimony pentafluoride.

From the indene 1 in its reaction with H_2O_2 in HF-SbF₅ the perfluoro-2-indanone (18) is obtained with a high yield together with a small amount of hexafluorohomophthalic acid (19) as impurity. Perfluoro-1-indanone (14) and its possible transformation products [5] were not found in the reaction mixture.



Compound 18 then reacts with H_2O_2 in HF-SbF₅ to give the acid 19 and perfluoro-3,4-dihydroisocoumarin (20). The transformations of compounds 1 and 18 in the H_2O_2 -HF-SbF₅ system probably take place similarly to the transformations for compounds 2 and 7, respectively. Here the higher reactivity of compound 1 compared with compound 2 makes it possible to obtain the indanone 18 with a higher yield than compound 7, since compound 18 does not surpass compound 7 in reactivity. It should be noted that hydroxylation of the aromatic ring occurs in 1- and 2-indanones under similar conditions, while the products corresponding to the Baeyer-Villiger reaction were not detected [7].

Compounds 7 and 18 are very hygroscopic and are isolated from the reaction mixtures (partly for compound 7 and completely for compound 18) in the form of 2,2-dihydroxyperfluoro-1-methylindan (7a) and 2,2-dihydroxyperfluoroindan (18a), respectively. The anhydrous ketones 7 and 18 were obtained from the hydrates 7a and 18a by the action of phosphorus pent-oxide. At the same time the hydrate 7a partly loses water during purification. Its analytical sample was therefore prepared from the ketone 7 and the stoichiometric amount of water.



Com-		δ, ppm					
pound	F3	F+	F ⁵	F ⁶	F'	F ⁸	SSCC, Hz
10	88.7 (A) 73.1 (B)	85.7 (CF ₃) -27.2	28.4	24.0	18.0	33.0	$J_{AB} = 155, J_{45} = 40, J_{CE_{1}E^{2}} = 10$
12 20	47.1 73.1	103.3 (CF ₃) 47.9	27.1 26.7	4.3 24.1	14.1 18.5	6.8 33.5	$J_{34} = 40, \ J_{45} = 44 J_{45} = 25$

*For solutions in deuterochloroform.

TABLE 4. Reaction of Polyfluorinated Indenes, Alkylideneindans, and Indanones with H_2O_2 -HF-SbF₅ (substrate: H_2O_2 :SbF₅ molar ratios 1:1:3)

Expt. No.	Initial com- pound, g	τ, °C	Holding time, h	Yield of mixture, g*	Reaction products, molar ratio according to ¹⁹ F NMR spectrum
1	2: 2.21	-10	1 h 40 min	1.78 (a)	2:7:7a:12=35:45:18:3
2	2: 1.96	- 10	8	0.50 (b) 1.47 (a)	7a:11=1:1 2:7:7a:10:12=17:37:17:24:5
3 4 5 ** 6 7	1; 10.86 3; 1.31 3; 1.31 4; 2 7; 0.77	-30 -10 -10 -10 -10	2.5 1 h 40 min 1 h 40 min 8 8	0.44 (b) 11.7 (b) 1.23 (a) 1.28 (a) 2.00 (a) 0.42 (a)	7a: 11=58: 42 18a: 19=97: 3 2: 6: 7a=7: 85: 8 3 4: 5=40: 60 7: 7a: 13=17: 11: 72
8 9	17; 0.55 18; 2	- 10 - 10	8 8	+ 0.25 (b) 0.54 (a) 0.87 (a) +	7: 11=22: 78 $12: 17=1: 2$ $18a: 20=1: 1$ $18a: 40=87: 42$

*The mixtures were obtained by extraction of the reaction mass with methylene chloride (a), ether (b), or with methylene chloride and ether in succession.

**The reaction was conducted in the absence of SbF5.

The structure of the compounds was confirmed by elemental analysis and spectral characteristics. Thus, the absence of spin-spin coupling constants $J_{CF2}1_{-F}$ s in the ¹⁹F NMR spectra of the dihydroisocoumarins **10** and **20** makes it possible to reject the isomeric structures containing the C=O group at position 3. In addition, the similarity in the UV spectra of these compounds and the spectra of the perfluorinated 1-indanones [8] and 1-tetralone (21) favors structures **10** and **20**. Comparison of the ¹⁹F NMR spectra of perfluoro-4-methylisocoumarin [9] and coumarin **12** made it possible to determine the structure of the latter unambiguously. The acid **19** was identified by means of the ¹⁹F NMR spectrum, which coincides with the spectrum of an authentic sample [10].

EXPERIMENTAL

The ¹⁹F and ¹H NMR spectra were recorded on Varian A-56/60A and Bruker AC-200 instruments. The concentrations of the solutions of the individual compounds were ≤ 11 mole %. The shifts are given downfield from C₆F₆ and TMS, and C₆F₆ and HMDS (0.04 ppm from TMS) were used as internal standards. The IR spectra were recorded on a UR-20 instrument. The

UV spectra were obtained on a Specord UV-VIS instrument. The mass spectra were obtained on a Finnigan MAT 8200 instrument. The elemental analyses and IR UV spectra of the compounds are given in Table 1, and the ¹⁹F and ¹H NMR spectra are given in Tables 2 and 3.

Anhydrous hydrogen fluoride was used in the reactions, and the experiments were conducted in Teflon apparatus.

Perfluoro-3-methylindenone (17). A mixture of 5.5 g of SbF₅, 3 ml of SO₂FCl, and 1.37 g of perfluoro-3-methylindene (2) was kept in a sealed tube at 20°C for 3 h, cooled to -40° C, poured into iced water, and extracted with methylene chloride. The extract was dried with magnesium sulfate, and the solvent was distilled. From the residue (1.25 g) after purification on a column of silica gel with pentane as eluant and vacuum sublimation (90°C, 50 mm Hg) we obtained 0.63 g of the indenone 17; mp 54.5-55.5°C.

Reaction of Perfluoro-3-methylindene (2) with H_2O_2 -HF-SbF₅. To a solution of 4.63 g (0.021 mole) of antimony pentafluoride in 20 ml of hydrogen fluoride, stirred at -30°C, we added dropwise 0.27 g (0.007 mole) of 90% hydrogen peroxide and then 2.21 g (0.007 mole) of the indene 2. The mixture was stirred at -12 to -8°C for 1 h 40 min, poured into iced water, and extracted with methylene chloride and then with ether. The extract was dried with magnesium sulfate, and the solvent was distilled. From the methylene chloride extract (a) we obtained 1.78 g of a mixture of the initial indene 2, perfluoro-1-methyl-2indanone (7), 2,2-dihydroxyperfluoro-1-methylindan (7a), and perfluoro-4-methoxycoumarin (12) in ratios of 35:45:18:3 (¹⁹F NMR spectrum). From the ether extract (b) we obtained 0.50 g of a mixture of the hydrate 7a and 2-(1-carboxytetrafluoroethyl)tetrafluorobenzoic acid (11) in a ratio of 1:1.

The reactions of the other compounds with hydrogen peroxide in the $HF-SbF_5$ system were conducted similarly to the reaction described above for indene 2, and the results are given in Table 4.

Isolation of the Individual Compounds from the Mixtures given in Table 4. 2-(1-Carboxytetrafluoroethyl)tetrafluorobenzoic acid (11): From the extract (b) of expt. 1 by sublimation at 70°C (5 mm Hg) we separated 0.22 g of the hydrate 7a, and then at 140°C (1 mm Hg) we obtained 0.22 g of the acid 11; mp 160-161.5°C (from a mixture of ether and carbon tetrachloride). The NMR spectra of a solution of the acid 11 in acetone-d₆ (δ , ppm). ¹H: 9.15. ¹⁹F: 87.6 (CF₃); 29.3; 22.4; 13.4; 9.8 (F atoms of aromatic ring); -2.9 (C_{tert}-F).

2,2-Dihydroxyperfluoro-1-methylindan (7a) and perfluoro-1-methyl-2-indanone (7): From 1 g of the extract (a) of expt. 1 on a column of silica gel with methylene chloride as eluant we isolated 0.33 g of the indene 2, with ether we eluted 0.60 g of the hydrate 7a, and by vacuum sublimation of the latter (70°C, 25 mm Hg) we obtained a mixture of compounds 7 and 7a in a ratio of 1:1. We heated 1.4 g of the mixture and 3 g of phosphorus pentoxide in a sealed V-shaped tube at 130°C for 5 min, and we then distilled the product while cooling the other end of the tube with liquid nitrogen. We obtained 1 g of the indanone 7 (a liquid). A mixture of 0.089 g of the indanone 7 and 0.0049 g of water was kept in a sealed tube at \sim 20°C for 24 h. According to the IR and ¹⁹F and ¹H NMR spectra, the hydrate 7a was obtained (a liquid). The molecular mass, determined by vapor-phase osmometry (in chloroform), was 345; calculated 344.

Perfluoro-2-indanone (18) and 2,2-dihydroxyperfluoroindan (18a): By sublimation of the mixture from expt. 3 (100°C, 25 mm Hg) we obtained 9.88 g of hydrate 18a; mp 73-74.5°C (from a mixture of methylene chloride and pentane). By a method similar to that described above for compound 7 from 1.62 g of the hydrate 18a and 3 g of phosphorus pentoxide we obtained 1.41 g of the indanone 18 (a liquid).

Perfluoroindan-1-carboxylic acid (6): The mixture from expt. 4 was dissolved in aqueous sodium bicarbonate, washed with carbon tetrachloride, acidified with hydrochloric acid, and extracted with methylene chloride. The extract was dried with magnesium sulfate, and the solvent was distilled. We obtained 0.97 g of the acid 6; mp 99.5-101°C (from a mixture of methylene chloride and carbon tetrachloride).

Perfluoro-1-acetylindan (5): From 1.57 g of the mixture from expt. 6 on a column of silica gel with pentane as eluant we isolated 0.49 g of perfluoro-1-ethylideneindan (4). With ether we eluted 0.79 g of the ketone 5 (a liquid), which we purified further by vacuum sublimation (70°C, 25 mm Hg).

Perfluoro-4-methyl-3,4-dihydroisocoumarin (10): From the extract (a) of expt. 7 on a column of silica gel with methylene chloride as eluant we isolated 0.24 g of compound 10 (a liquid), which we purified further by vacuum sublimation (70°C, 25 mm Hg). With ether we eluted 0.16 g of the hydrate (7a).

Perfluoro-3,4-dihydroisocoumarin (20): From the extract (a) of expt. 9 on a column of silica gel with methylene chloride as eluant we isolated 0.37 g of compound 20 (a liquid), which we purified further by vacuum sublimation (70°C, 25 mm Hg). With ether we eluted 0.35 g of the hydrate 18a.

Perfluoro-4-methylcoumarin (12): Without separating the mixture obtained in expt. 8 we repeated its reaction with $H_2O_2-HF-SbF_5$. We obtained 0.50 g of a mixture of compounds 12 and 17 in a ratio of 53:47, from which we isolated the product 12 by fractional crystallization from a mixture of methylene chloride and hexane; mp 73.5-74.5°C.

LITERATURE CITED

- 1. I. P. Chuikov, V. M. Karpov, and V. E. Platonov, Izv. Akad. Nauk, Ser. Khim., No. 8, 1856 (1990).
- 2. I. P. Chuikov, V. M. Karpov, and V. E. Platonov, Izv. Akad. Nauk, Ser. Khim., No. 4, 837 (1990).
- K. O. Christie, W. W. Wilson, and E. C. Curtis, *Inorg. Chem.*, 18, No. 9, 2578 (1979); L. S. German, G. G. Belen'kii, and I. L. Knunyants, *Dokl. Akad. Nauk SSSR*, 171, No. 6, 1333 (1966).
- 4. V. A. Koptyug, Arenonium Ions. Structure and Reactivity [in Russian], Nauka, Novosibirsk (1983), p. 235.
- 5. I. P. Chuikov, V. M. Karpov, and V. E. Platonov, Izv. Akad. Nauk, Ser. Khim., No. 10, 2463 (1990).
- C. Thomas, Anhydrous Aluminum Chloride in Organic Chemistry [Russian translation], IL, Moscow (1949), pp. 236, 520;
 L. M. Yagupol'skii, I. I. Burmakov, L. A. Alekseeva, and B. V. Kunshenko, Zh. Org. Khim., 9, No. 4, 689 (1973).
- 7. J. P. Gesson, J. C. Jacquesy, M. P. Jouannetaud, and G. Morellet, Tetrahedron Lett., 24, No. 30, 3095 (1983).
- 8. V. M. Karpov, L. S. Klimenko, V. E. Platonov, and G. G. Yakobson, Zh. Org. Khim., 11, No. 11, 2372 (1975).
- 9. V. M. Karpov, T. V. Mezhenkova, V. E. Platonov, and G. G. Yakobson, Izv. Akad. Nauk, Ser. Khim., No. 3, 753 (1991).
- 10. V. M. Karpov, V. E. Platonov, and G. G. Yakobson, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk,* No. 4 (2), 124 (1974).
- 11. V. V. Bardin, G. G. Furin, and G. G. Yakobson, J. Fluor. Chem., 14, No. 6, 455 (1979).

REARRANGEMENT OF THE CARBON SKELETON OF PERFLUORINATED 1-ISOPROPYL-, 1-METHYL-1-ISOPROPYL-, AND 1-METHYL-2-ISOPROPYLBENZOCYCLOBUTENES BY THE ACTION OF ANTIMONY PENTAFLUORIDE

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UDC 542.97:542.952.1:547.539.1+547.513:547.665

Perfluorinated 1-isopropyl-, 1-methyl-1-isopropyl-, and 1-methyl-2-isopropylbenzocyclobutenes isomerize under the influence of antimony pentafluoride to perfluorinated alkylstyrenes and alkylindans. The process may be accompanied by dealkylation and also by fluorination and defluorination of the products. With antimony pentafluoride at 50° C perfluoro-1-methyl-1-isopropylbenzocyclobutene gives perfluoro- α,β,β,o -tetramethylstyrene, which isomerizes under the influence of antimony pentafluoride at 130° C into perfluoro- $1,\beta,\beta,o$ -tetramethylstyrene, which isomerizes under the influence of antimony pentafluoride at 130° C into perfluoro-1,2,2-trimethylindan, and the latter forms perfluoro-2,3-dimethylindene under the reaction conditions. Perfluoro-1-methyl-2-isopropylbenzocyclobutene is not changed in the presence of antimony pentafluoride at 50° C but isomerizes to perfluoro-1-isopropylindan at 90° C. The latter is transformed under these conditions into the above-mentioned tetramethylstyrene. Perfluoro-1-isopropylbenzocyclobutene 2,2-dimethylindan, 2,3-dimethylindene, 2,3-dimethyl-4,5,6,7-tetrahydroindene, and 2-isobutyltoluene, which is converted into perfluoro-o-xylene under the reaction conditions.

Keywords: Perfluoroalkylbenzocyclobutenes, perfluoroalkylstyrenes, perfluoroalkylindans, antimony pentafluoride, cationoid skeletal transformations.

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