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

V. M. Karpov, T. V. Mezhenkova, and V. E. Platonov

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-1,2,2-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.

Novosibirsk Institute of Organic Chemistry, Siberian Branch, Russian Academy of Sciences, 630090 Novosibirsk. Translated from *Izvestiya Akademii Nauk, Seriya Khimicheskaya*, No. 6, pp. 1419-1424, June, 1992. Original article submitted July 18, 1991.

Cationoid skeletal transformations of polyfluorinated compounds are fairly rare. In the series of polyfluorobenzocyclobutenes such transformations are known for the perfluorinated 1-alkyl [1] and 1,1- and 1,2-dialkyl [2] derivatives in their reactions with aluminum halides [1] and antimony pentafluoride [1,2]. In all cases the alkyl groups are CF_3 and C_2F_5 . In a continuation of these investigations in the present work we studied the behavior of perfluorinated 1-isopropyl (1), 1-methyl-1isopropyl (2), and 1-methyl-2-isopropyl (3) derivatives of benzocyclobutene in antimony pentafluoride.

It was shown that the action of heat on a mixture of compounds 2 and 3 with antimony pentafluoride at 50°C led to the formation of perfluoro- α, β, β, o -tetramethylstyrene (4), i.e., the product from isomerization of compound 2, and not compound 3, as confirmed by a separate experiment with the individual compound 3. At 90°C compound 3 is converted in the presence of antimony pentafluoride into perfluoro-1-isopropylindan (5) (scheme 1).



The formation of compound 4 from compound 2 in the presence of antimony pentafluoride can be represented in the following way. The cation 6 is probably generated from compound 2 (in the limiting version) and isomerizes to an ion of the benzyl type 7. The styrene 4 is produced as a result of the addition of F^- to the ion 7 and migration of the double bond inside the chain. The transformation of the isomer 3 into the indan 5 can be represented in a similar way. The cation 8 generated from 3 is probably converted with ring opening into the ion 9, the cyclization of which leads, after addition of F^- , to the indan 5. A synchronous process is not ruled out here. The milder conditions for the isomerization of compound 2 compared with 3 in the presence of antimony pentafluoride can probably be explained by the greater relative stability of the cation 7 compared with 9 (see [2]).

In the presence of antimony pentafluoride the indan 5 undergoes further transformations (see perfluoro -1-ethylindan [3]). Thus, when heated with antimony pentafluoride at 90°C compound 5 isomerizes to the styrene 4. At 130°C the latter gives a mixture of perfluoro-1,2,2-trimethylindan (10) and perfluoro-2,3-dimethylindene (11) (scheme 2). In this connection compounds 4 and 5 are formed from compound 3 in the presence of antimony pentafluoride at 90°C and compounds 4, 10, and 11 are formed at 130°C.



The isomerization of compound 5 to 4 under the influence of antimony pentafluoride can probably take place in the following way. The perfluoro-1-isopropyl-1-indanyl cation (12) is probably generated from 5 and then isomerizes to the ion 7. The latter undergoes further transformations, leading finally to the styrene 4. The intramolecular cyclization of the cation 13, generated from 4, clearly leads to the indanyl ion 14, from which the indan 10 is produced during the addition of F^- and indene 11 during the elimination of CF_3^+ (see [4, 5]). The transformation of 10 and 11 in antimony pentafluoride probably takes place through the intermediate cation 14 (or through the isomeric perfluoro-2,2,3-trimethyl-1-indanyl cation). Compounds 4, 5, and 10 are not changed at 130°C in the absence of antimony pentafluoride.

The rearrangement of the carbon skeleton in compound 1 by the action of antimony pentafluoride takes place under more drastic conditions than in compounds 2 and 3, perfluoro-1-methylbenzocyclobutene (95° C), and perfluoro-1-ethylbenzocyclobutene (130° C) [1]. Thus, compound 1 is mainly recovered unchanged from the reaction with antimony pentafluoride at 130° C, while heating with antimony pentafluoride at 170° C leads to a mixture containing the unfluorinated 2,2-dimethylindan (15), 2-isobutyltoluene (16), and o-xylene (17) and also the indene (11) and a small amount of perfluoro-2,3-dimethyl-4,5,6,7tetrahydroindene (18). It was shown by separate experiments that the isobutyl derivative 16 is transformed under the reaction conditions into the xylene 17, while the indan 15 is not changed. Compounds 11 and 18 are also not changed under the reaction conditions [3] (scheme 3).



The formation of compounds 15-17 from compound 1 in the presence of antimony pentafluoride can be represented as shown in scheme 3 (path 1). The cation (crypto-ion) 19 generated from 1 isomerizes to the ion 20, the cyclization of which followed by the addition of F^- gives the indan 15. The fluorination of the styrene 21 under the reaction conditions probably

Compound	Mol. mass* Found/Cal- culated	Molecular formula	∨, cm ⁻¹	$\lambda_{\text{max}}, \text{nm}$ (log ε)
4 5	447.9762 447.9744 447.9767 447.9744	C12F16 C12F16	1489, 1530, 1623(w) 1641 (w), 1667 (w) 1519, 1644 (w)	$\begin{vmatrix} 272(3.44), \\ 297(2.34, sh) \\ 266(3.03, sh), \\ 272(3.08), \\ 304(2.12) \end{vmatrix}$
10	<u>447.9744</u> 447.9744	C12F18	1523	262(3.00, sh), 268(3.08)
13	<u>397.9798</u> 397.9776	CtiF14	1525, 1647 (w)	262(2.94, sh), 267(3.00)
16	435.9756 435.9744	C11F16	1476, 1532, 1630	275 (3.36)

TABLE 1. Elemental Analyses and IR and UV Spectra of Compounds 4, 5, 10, 15, and 16

*Determined by high-resolution mass spectrometry.

Compound	wt.,g	SbF ₅ , g	T. °C (t.h)	Yield of mix- ture, g	Content (yield) ^a of reac- tion products in mixture, (GLC, ¹⁹ F_NMR) %
\$ 10	1.34 2.03	3.66 ^b 7.75	130(9) 170(5.5)	1.1 1.63	$\begin{bmatrix} 1 & -79 \\ 1 & -28(22.5), 11 & -20(17.8), \\ 15 & -13(10.4), 16 & -17(12.5) \end{bmatrix}$
3	1.92	7.32	170(10)	1.49	17 - 7(7.8) 1 - 8(6.2), 11 - 30(25.7), 15 - 19(14.7), 16 - 11(7.8), 17 - 16(17.3), 18 - 2(1.4)
3 C	1.5	3.63 ^b	90(54.5)	1,23	3 - 17, 4 - 27, 5 - 50
3 C	1.16	3.94	130(5)	0.85	4 - 66, 10 - 9, 11 - 7
3 C	1.37	4.64	130(15)	1.08	4 - 18, 10 - 33, 11 - 29
3 C	1.33	4.51	130(45)	1.06	4 - 4, $10 - 30$, $11 - 47$
3C	1.48	5.01	130(90)	0.99	4 - 2, 10 - 21, 11 - 55
3	1.01	3.43	90(60)	0.79	4 - 37, 5 - 47
16	0.61	2.31d	170(30)	0.27	17 - 67
15+16	0.61+0.35	3.78	170(30)	0.61	15 - 66. 17 - 7

TABLE 2. Reaction of Compounds 1-3, 5, 15, and 16 with Antimony Pentafluoride (SbF₅:substrate molar ratio 7)

a) mole/mole of substrate.

b, d) SbF₅:substrate molar ratio 5 (b), 7.6 (d).

c) The product containing 5% of compound 2 and 3% of compound 4 was used.

leads to compound 16 (see [2, 4]), while the elimination of $CF_3CF=CF_2$ from the intermediate cation 22, generated from 16 by the action of antimony pentafluoride, leads to compound 17.

It can be supposed that the transformation of compound 1 into compounds 11 and 18 in antimony pentafluoride takes place according to path 2. The cation 23 probably first isomerizes to the ion 24 as a result of a 1,2-shift of the CF₃ group. The ion 24 then either gives perfluoro-1,2-dimethylindan (25) itself as a result of recyclization, as reflected in the scheme, or perfluoro-1-methyl-1-ethylbenzocyclobutene is obtained from it initially after addition of F^- and is transformed, as shown earlier [2], into compound 25. Under the reaction conditions the indan 25 gives compounds 11 and 18 (see [3]).

Attention is drawn to the fact that compound 11 is formed from 1 in significantly larger amounts than compound 18, whereas the opposite situation is observed in the case of compound 25 [3]. Such a difference in the ratio of 11 and 18 is probably due to the fact that the role of acceptors of fluorine atoms in the reaction of compound 1 with antimony pentafluoride during the defluorination of compound 25 is mainly played by the styrene 21, while in the case of [3] it was played by another molecule of compound 25. It should be noted that a 1,2-shift of the CF_3 group in the cations was proposed during the isomerization of perfluoro-1,1-dimethylindan by the action of antimony pentafluoride [3].

The structures of compounds 4, 5, 10, 15, and 16 were established by elemental analysis and spectral characteristics. The relationships observed in the ¹⁹F NMR spectra of these products agreed with those for similar compounds in [2,3]. The ¹⁹F NMR spectra of the products 11, 17, and 18 were identical with the spectra of these compounds described in [3,6].

EXPERIMENTAL

The ¹⁹F NMR spectra of the reaction mixtures without a solvent were recorded on a Varian A-56/60A instrument at 56.4 MHz with reference to hexafluorobenzene as external standard. The ¹⁹F NMR spectra of solutions of the individual compounds in deuterochloroform (concentrations ≤ 10 mole %) were recorded on a Bruker WP-200SY instrument at 188.3 MHz with reference to hexafluorobenzene as internal standard. The IR spectra of solutions in carbon tetrachloride were recorded on a UR-20 instrument. The UV spectra of solutions in heptane were recorded on a Specord UV-Vis instrument. The elemental composition of the substances was determined by high-resolution mass spectrometry on a Finnigan MAT 8200 instrument. Analysis by GLC was conducted on an LKhM-72 chromatograph (50-270°C, 4000 × 4 mm, SKTFT-50 on Chromaton N, 15(25):100, helium, 60 ml/min). The individual compounds were isolated by PGLC (115°C, 125°C, SKTFT-50 on Chromaton, nitrogen). The elemental analyses and spectral characteristics of the obtained compounds are given in Table 1.

The ¹⁹F NMR Spectra of the Compounds (δ , ppm, J, Hz). 4: 105.3 (CF₃⁰); 102.6, 102.5, 102.3 (3CF₃); 27.5, 27.2, 16.5, 15.3 (aromatic F atoms). 5: 90.8, 91.5 (2CF₃); 58.5 (F_A³), 57.0 (F_B³, J_{AB} = 264), 43.1 (F_A²), 41.6 (F_B², J_{AB} = 253); 32.6 (F⁷); 24.2 (F⁴); 19.9 (F^{5,6}); 4.1 (F¹); -13.8 (CF(CF₃)₂, J_{CF-F⁷} = 68). 10: 102.8, 101.9 (2CF₃²); 86.9 (CF₃¹); 77.6 (F_A³); 66.6 (F_B³, J_{AB} = 272); 27.2 (F⁷); 23.3 (F⁴); 19.9, 19.5 (F^{5,6}); -6.4 (F¹). 15: 100.4 (2CF₃); 71.9 (2CF₂); 23.7 (F^{4,7}); 20.2 (F^{5,6}). 16: 108.9 (CF₃¹); 89.6 (2CF₃²); 69.4 (CF₂); 34.4 (F³); 31.7 (F⁶); 18.0, 17.1 (F^{4,5}); -18.1 (CF).

Isomerization of Compound 2 to Compound 4 in the Presence of Antimony Pentafluoride a. A 7.97-g sample of a mixture containing 4% of 2, 80% of 3, 6% of 4, and 6% of perfluoro-1-methylbenzocyclobutene (26) was heated in a sealed tube with 7.98 g of antimony pentafluoride at 50°C for 8.5 h. The mixture was then kept at 20-25°C for 60 h, treated with \sim 5 ml of anhydrous HF, and poured onto ice. The organic layer was dried with magnesium sulfate. We obtained 7.14 g of a mixture containing (GLC and ¹⁹F NMR) 80% of compound 3, 10% of compound 4, and 3% of compound 26.

b. Similarly to [7] from a mixture of 6.53 g of compound 26, 4.93 g of hexafluoropropylene, and 2.85 g of antimony pentafluoride in a sealed tube after 154 h at 20-25°C we obtained 9.1 g of a mixture containing (GLC and ¹⁹F NMR) 4% of compound 2, 74% of compound 3, 4% of compound 4, and 15% of compound 26.

The other reactions of the compounds with antimony pentafluoride were conducted in a nickel bomb (10 ml). At the end of the holding period the mixture was cooled to $\sim -10^{\circ}$ C, and 2-4 ml of anhydrous hydrogen fluoride was added. The mixture was stirred, transferred to crushed ice, cooled with liquid nitrogen, and the organic layer was separated and dried with magnesium sulfate. The results are given in Table 2.

LITERATURE CITED

- 1. V. M. Karpov, T. V. Mezhenkova, V. E. Platonov, and G. G. Yakobson, J. Fluor. Chem., 28, 115 (1985).
- 2. V. M. Karpov, T. V. Mezhenkova, V. E. Platonov, and G. G. Yakobson, Izv. Akad. Nauk, Ser. Khim., No. 5, 1114 (1990).
- 3. V. M. Karpov, T. V. Mezhenkova, and V. E. Platonov, Izv. Akad. Nauk, Ser. Khim., No. 3, 645 (1990).
- 4. V. M. Karpov, T. V. Mezhenkova, V. E. Platonov, and G. G. Yakobson, Bull. Soc. Chim. France, 980 (1986).
- 5. V. A. Petrov, V. K. Kunanets, B. A. Kvasov, M. V. Galakhov, K. N. Makarov, and L. S. German, *Izv. Akad. Nauk, Ser. Khim.*, No. 1, 122 (1989).
- 6. F. Ayanbadejo, Spectrosc. Acta, 25A, No. 5, 1009 (1969).
- 7. V. M. Karpov, T. V. Mezhenkova, V. E. Platonov, and G. G. Yakobson, *Izv. Akad. Nauk, Ser. Khim.*, No. 10, 2315 (1985).