Journal of Fluorine Chemistry, 28 (1985) 121–137

INTERACTION OF PERFLUOROBENZOCYCLOALKENES WITH TETRAFLUOROETHYLENE IN THE PRESENCE OF SbF_5

V.M. KARPOV, T.V. MEZHENKOVA, V.E. PLATONOV
and G.G. YAKOBSON

Institute of Organic Chemistry, Novosibirsk, 630090 (U.S.S.R.)

SUMMARY

The reactions of perfluorinated tetralin, indan and benzocyclobutene with tetrafluoroethylene in the presence of SbF_5 led to the formation of the respective perfluoro-1-ethylbenzocycloalkenes transformed further to disubstituted derivatives. In the case of perfluorotetralin, the reaction gave perfluoro-1,4-diethyltetralin. Perfluorobenzocyclobutene gave perfluoro-1,1- and -1,2-diethylbenzocyclobutenes in about equal quantities, and perfluoroindan - practically only perfluoro-1,1-diethylindan. To explain this orientation, the electronic and steric effects are considered, which can influence the reactivity and the relative stability of the intermediate carbocations.

The perfluoro-1-benzocyclobutenyl cation has been generated in the reaction of antimony pentafluoride with perfluorobenzocyclobutene.

INTRODUCTION

Among the chemical transformations of polyfluorobenzocycloalkenes, their reactions with Lewis acids are of interest. These reactions may proceed with substitution of the α-fluorine atoms in the alicyclic fragment of the benzocycloalkene by atoms of other halogens [1-5], by formation of the keto-derivatives of benzocycloalkenes [1-5], by contraction of the six-membered [5] and by expansion of the four-membered fluorinated alicyclic ring [6].

0022-1139/85/$3.30

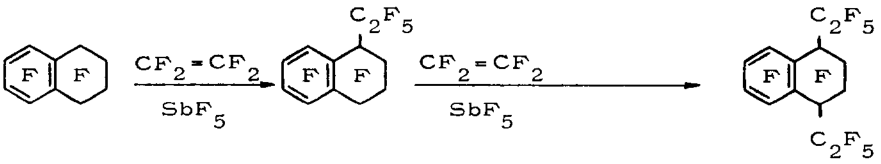
Transformation of the four-membered ring to the five-membered one has been found in the case of perfluoro-1-methylbenzocyclobutene (I) [6]. In order to extend the range of compounds which undergo skeletal rearrangements in reactions with Lewis acids, and to establish the mechanism of the process, it seemed reasonable to study the behaviour of other polyfluorinated 1-alkylbenzocycloalkenes in the presence of Lewis acids. Polyfluoro-1-alkylbenzocycloalkenes have not been described in detail, but the literature contains references to syntheses of alkyl derivatives of perfluorocyclobutene [7] and octafluorotoluene [8] by the reactions of these compounds with fluoroolefins in the presence of SbF_5. Such reactions of polyfluorobenzocycloalkenes have not been investigated. At the same time, it is interesting to study these transformations to examine the reactivity of polyfluorobenzocycloalkenes and the possibility of the synthesis of polyfluorinated alkylbenzocycloalkenes.

In this connection, we have studied the reactions of perfluorinated benzocyclobutene (II), tetralin (III), indan (IV), 4-methylindan (V) and 5-methylindan (VI) with tetrafluoroethylene (TFE) in the presence of SbF_5, and tried to generate perfluorobenzocycloalkenyl cations.

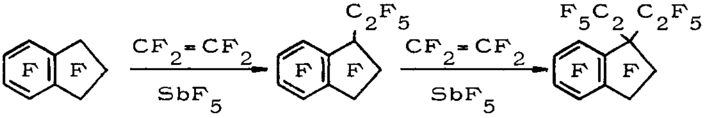
RESULTS AND DISCUSSION

We have found using competing reactions that the rate of the antimony pentafluoride-catalysed reaction of benzocycloalkenes (II)-(IV) with TFE decreases on passing from benzocyclobutene (II) to indan (IV) and tetralin (III). Compound (III) with TFE gave perfluoro-1-ethyltetralin (VII), which was futher transformed to a mixture of about equal amounts of <u>cis</u>- and <u>trans</u>-perfluoro-1,4-diethyltetralins (VIII). The 1,1-isomer has not been detected in the mixture.

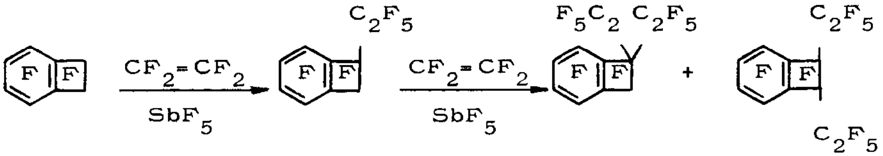
At the same time, in a similar reaction of benzocyclobutene (II), the initially formed perfluoro-1-ethylbenzocyclobutene (IX) gave perfluoro-1,1-diethylbenzocyclobutene (X) and perfluoro-1,2-diethylbenzocyclobutene (XI) in about equal amounts. A separate experiment has shown that compounds (X) and (XI) do not isomerize to each other under the reaction conditions.



(III) (VII) (VIII)

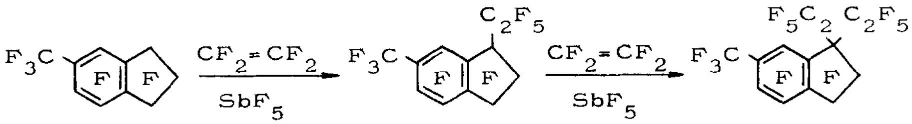


(IV) (XII) (XIII)

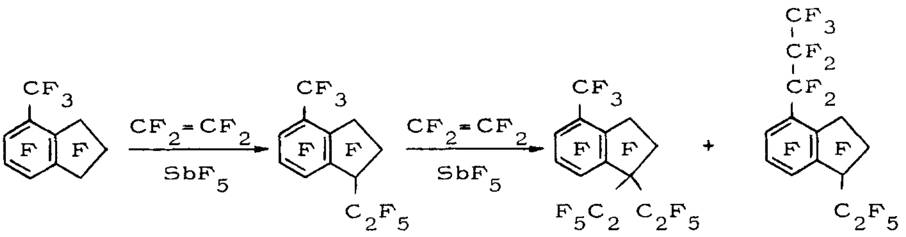


(II) (IX) (X) (XI)

Interaction of indan (IV) with TFE in the presence of SbF_5 led to perfluoro-1-ethylindan (XII), which was transformed to perfluoro-1,1-diethylindan (XIII). Similar reactions were observed with methylindans (V) and (VI). In the products of these reactions, the perfluoroethyl group is situated at the carbon atom of the five-membered ring that is in the meta-position to the trifluoromethyl group. Thus compound (VI) with TFE gave perfluoro-1-ethyl-6-methylindan (XIV), which was further transformed to perfluoro-1,1-diethyl-6-methylindan (XV). Indan (V) gave perfluoro-1-ethyl-4-methylindan (XVI), which reacted further with TFE to form perfluoro-1,1-diethyl-4-methylindan (XVII). Apart from compound (XVII), the reaction gave perfluoro-4-propyl-1-ethylindan (XVIII), the product of interaction of TFE and the CF_3-group of indan (XVI).



(VI) (XIV) (XV)



(V) (XVI) (XVII) (XVIII)

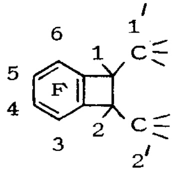
The structures of the products were established by the elemental analysis data and spectral characteristics. Assignment of signals in the ^{19}F NMR spectra of polyfluorobenzocycloalkenes was made on the basis of chemical shifts of the signals, their fine structure and integral intensities, in a similar way as for polyfluoroindanes in ref. [4]. The ^{19}F NMR spectral data for polyfluorinated ethylbenzocyclobutenes and -indanes are given in Tables 1 and 2 respectively.

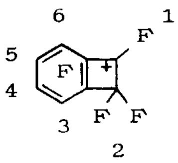
The spectra of 1-ethylbenzocycloalkenes, 1,2-diethylbenzocyclobutene (XI) and 1,4-diethyltetralin (VIII) contain the up-field signals typical of tertiary fluorine atoms [9]. 1,1-Diethylbenzocycloalkenes have no tertiary fluorine atoms, and the signals of difluoromethylene groups of the cycloalkene moiety are at lower field (cf. [10, 11]). Comparison of the $F^{1,2}$ chemical shift value found experimentally for 1,2-diethylbenzocyclobutene (XI) with the values calculated according to the additive scheme for cis- and trans-isomers (Table 1) allows us to make the conclusion that this compound is formed as a cis-isomer. In the calculation, we used increments of the perfluoroethyl group found from comparison of the chemical shifts of the fluorine atoms of benzocyclobutenes (II) and (IX).

Comparison of the experimentally found chemical shifts of the aromatic fluorine atoms of indanes (XIV) and (XVI) with those calculated according to the additive scheme for these compounds and

TABLE 1

^{19}F NMR spectra of polyfluorobenzocyclobutenes and perfluoro-1-benzocyclobutenyl cation (XXII)





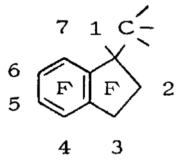
Compound	Chemcal shift, ppm[a]										^JAB (A′B′), Hz
	F-1	F-2		F-3	F-4	F-5	F-6	F-1′,2′		CF_3	
		A	B					A′	B′		
(II)[b]	58.4	58.4	58.4	28.9	21.5	21.5	28.9				
(IX)	2.8	65.9	62.6	28.8	21.8	21.8	30.6	43.3	39.9	81.3	210 (300)
(X)		71.5	71.5	28.0	19.4	21.9	29.9	53.9	53.9	82.4	
(XI)	6.0	6.0		29.9	22.3	22.3	29.9	44.6	39.1	81.6	(293)
	(7.0[c], 10.3[t])	(7.0[c], 10.3[t])									
(XXII)	203.8	86.8		43.8	103.8	43.8	74.6				

[a] Spectra were recorded for solutions of compounds in CCl_4 (concentration 11 mol %). In the case of isomeric compounds (X) and (XI), the spectrum was recorded for their mixture. Shifts are given downfield from C_6F_6 as an internal standard. In the case of cation (XXII), chemical shifts are given relative to C_6F_6 for solution of a salt of this cation in SbF_5-SO_2FCl at -50°C; as an internal standard SO_2FCl was used (262.8 ppm from C_6F_6). [b] The spectrum of compound (II) is given also in ref. [23].

[c,t] In brackets are shifts calculated according to the additive scheme for [c] *cis*- and [t] *trans*-isomers.

TABLE 2

^{19}F NMR spectra of polyfluoroindanes



Compound	Chemical shift, ppm[a]											J_{AB} (A′B′), Hz
	F-1	F-2		F-3		F-4	F-5	F-6	F-7	CF_2CF_3		
		A	B	A′	B′					CF_2	CF_3	
(IV)[b]	55.0	31.7		55.0		24.8	19.5	19.5	24.8			
(V)[b]	54.5	32.0		57.9		105.5 (CF_3)	44.2	17.5	35.8			
(VI)[b]	54.9	31.9		53.9		48.6	105.2 (CF_3)	41.5	23.6			
(XII)	-8.1	40.4	36.1	59.1	52.8	24.4	19.6	19.6	30.6	44.0	82.3	246 (264)
(XIII)		51.4		58.7		24.2	18.7	19.6	35.3	58.7	86.0	

(XIV)	-9.5	41.1	36.2	58.7	51.5	23.8 [23.2][c]	42.0 [41.6]	105.3 (CF_3)	54.7 [54.4]	44.3	82.6	250 (270)
(XV)		51.3		59.3		23.8	40.4	105.4 (CF_3)	56.7	59.3	86.1	
(XVI)	-11.1	41.7	35.7	62.5	56.3	105.6 (CF_3)	44.2 [44.3]	17.7 [17.6]	41.3 [41.6]	44.5	82.8	246 (270)
(XVII)[d]		50.9		61.4		105.8 (CF_3)	43.0	17.6	46.9	59.6	86.5	
(XVIII)[d]	-10.7	47.1	35.3	65.2	56.7	57.7[e] 38.5[f] 82.3[g] or 83.0	45	18	43	45	83.0 or 82.3	250 (290)
(XIX)						[48.8]		[41.6]	[29.4]			
(XX)						[35.4]	[17.6]	[44.3]				

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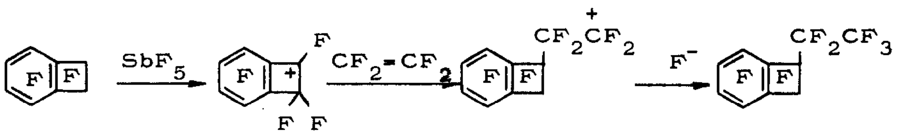
[a] Spectra were recorded for solutions of compounds in CCl_4 (concentration 11 mol %). Shifts are given down-field from C_6F_6 as an internal standard. [b] Spectra of indanes (IV)-(VI) are in agreement with those reported in ref. [11]. [c] Shifts in square brackets were calculated according to the additive scheme. [d] In the case of isomeric compounds (XVII) and (XVIII), the spectrum was recorded for their mixture. [e] $\underline{CF_2}CF_2CF_3$, [f] $CF_2\underline{CF_2}CF_3$, [g] $CF_2CF_2\underline{CF_3}$.

also for perfluoro-1-ethyl-5-methylindan (XIX) and perfluoro-1-ethyl-7-methylindan (XX) (Table 2) allows us to exclude the structures of the latter compounds. In the calculation we used increments of the perfluoroethyl group found from comparison of fluorine chemical shifts of indanes (IV) and (XII).

The spectrum of compound (VIII) contains two high-field signals (-5.5 and -8.7 ppm) of the tertiary fluorine atoms, which do not come closer to each other and are not broadened when the temperature is raised from 40 to 120°C. This indicates that the signals are from fluorine atoms of two compounds; that is, tetralin (VIII) is a mixture of cis- and trans-isomers. The comparative analysis of chemical shifts in the ^{19}F NMR spectra of 2-chloroperfluorotetralin (XXI) [3], tetralins (III), (VII) and (VIII) and of perfluorinated cyclohexane, chloro- and methyl-cyclohexanes [12] allows to us unambiguously ascribe to compounds (VII) and (VIII) the structures of 1- and 1,4-derivatives. For example, the spectrum of 1-ethyltetralin (VII) has two signals at δ 68.4 and 54.4 ppm, which belong to the fluorine atoms (F^4) of one CF_2-group (δ average 61.4 ppm; a similar δ value for compound (III) 56.5 ppm). At the same time, in the case of isomeric 2-ethyltetralin, the signals of each of the two difluoromethylene groups ($F^{1,4}$) should have an average chemical shift at $\delta > 56.5$ ppm (the same has been observed, for example, for tetralin (XXI) [3]).

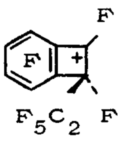
Interaction of perfluorobenzocycloalkenes with TFE possibly proceeds via the intermediate formation of 1-benzocycloalkenyl cations (crypto-ions). Thus the reaction of compound (II) with TFE may be represented as follows. The intermediate perfluoro-1-benzocyclobutenyl cation (XXII) (its generation will be discussed below) attacks TFE giving the perfluoro-2-(benzocyclobutenyl-1)-ethyl cation. The latter adds the fluorine anion to form benzocyclobutene (IX).



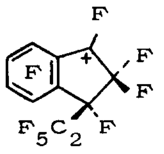
(II) (XXII) (IX)

Let us consider next the influence of electronic factors on orientation in the reactions of perfluorinated 1-ethylbenzocycloalkenes with TFE. In the case of benzocyclobutene (IX), formation of the

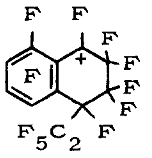
1,2-isomer (XI) may be represented as involving the benzocyclobutenyl cation A_1, and of the 1,1-isomer (X) - cation B_1. In view of the difference in the effect of the perfluoroethyl group and the fluorine atom on the relative stability of carbocations [13, 14], cation A_1 may be expected to be more stable than cation B_1. A similar supposition was used to explain the results of hydrolysis of the product of the interaction of compound (I) with SbF_5 [1]. Due to its lower stability, cation B_1 should be more reactive (the positive charge is higher) than ion A_1. Therefore it is difficult to predict the relative rates of formation of 1,1- and 1,2-diethyl-derivatives.



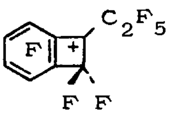
A_1



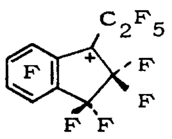
A_2



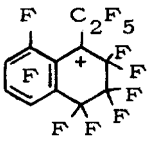
A_3



B_1



B_2



B_3

In the pairs of indanyl cations A_2 and B_2 and the tetralinyl ones A_3 and B_3, each ion will differ from the respective benzocyclobutenyl cation by the $-CF_2-$ or $-C_2F_4-$ group in the cycloalkenyl part of the ion. Therefore the stability ratio of cations A and B within each pair may be thought to vary insignificantly. The same applies to the ratio of their reactivities. Thus, influence of electronic factors on the orientation in the reactions of 1-ethylbenzocycloalkenes with TFE should be about the same.

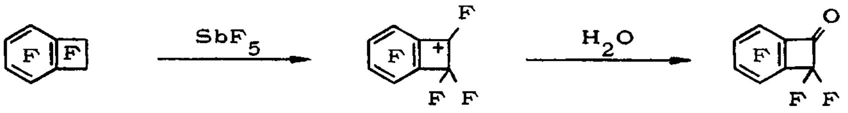
Let us consider the steric effects in these reactions. In the cycloalkenyl moiety of benzocyclobutene (IX) and indan (XII) the fluorine atoms, or the fluorine atom and the C_2F_5-group situated in neighbouring positions are extensively eclipsed. In the case of compound (IX), there is one F-F interaction and one $F-C_2F_5$, which disappear in both cations A_1 and B_1. In indan (XII), there are three

F-F interactions and one F-C_2F_5. When cation A_2 is formed, two F-F interactions disappear; in the case of cation B_2 these are interactions F-F and F-C_2F_5. The stability of cation B_2, where there is no interaction between the fluorine atom and the bulky perfluoroethyl group, seems to increase in comparison with A_2. Therefore, by contrast with the similar reaction of benzocyclobutene (IX), among the diethyl-derivatives of indan, compound (XIII) formed with participation of cation B_2 should prevail.

In the cycloalkenyl moiety of the tetralin molecule, which has a non-planar structure, atoms and groups situated in neighbouring positions are staggered [15,16]. Therefore passing from tetralin (VII) to cations A_3 and B_3 should not be very energetically favourable as a result of the disappearance of interactions between groups in neighbouring positions. But on the other hand, in these cations there is peri-interaction between a substituent at the cationic centre and the fluorine atom of the aromatic ring (cf. [17,18]). In the case of benzocyclobutenyl and indanyl cations, such interactions should be insignificant [17,19]. Due to the fact that the perfluoroethyl group is more bulky than the fluorine atom, peri-interaction in cation B_3 should be stronger than in ion A_3, which should lead to a decrease of its stability in comparison with cation A_3. In this connection, compound (VIII) formed with participation of cation A_3 may be expected to prevail among the diethyl-derivatives of tetralin, in contrast to the similar reaction of benzocyclobutene (IX). Similar steric factors were used in the literature to explain kinetic data on S_N1-solvolysis of the derivatives of cyclobutane, -pentane, -hexane [20] and also to explain the higher reactivity of 1-chloroindan in comparison with 1-chlorotetralin in S_N1-solvolysis of these compounds [21].

As mentioned above, in compounds (XIV) and (XVI) (the products of the reactions of indanes (VI) and (V) with TFE) the C_2F_5-group is at the carbon atom of the five-membered ring in the meta-position relative to the trifluoromethyl group. Since in the para- or ortho-position to the arising carbocationic centre the CF_3-group shows higher electron accepting ability than in the meta-position [13], the observed orientation seems to be in agreement with the relative stabilities of the intermediate cations.

The stabilities of the cations may also be used to explain the relative rates of the reactions of compounds (II)-(IV) with TFE. Perfluoro-1-benzocyclobutenyl cation (XXII) was generated by dissolution of benzocyclobutene (II) in SbF_5 or in the system SbF_5 - SO_2FCl. Perfluorinated 1-indanyl (XXIII) and 1-tetralinyl (XXIV) cations were not detected under similar conditions by the ^{19}F NMR method. The structure of cation (XXII) was established by its ^{19}F NMR spectrum (Table 1) and confirmed by reference to the structure of the product of its hydrolysis. Pouring the solution of the cation salt into water led to perfluorobenzocyclobutenone (XXV). Formation of the ketone (XXV), together with other compounds, by treatment of the product of the reaction of benzocyclobutene (II) and a larger excess of SbF_5 with water has been reported earlier in ref. [2].



(II) (XXII) (XXV)

Assignment of signals in the spectrum of cation (XXII) has been made in a similar way as for polyfluorobenzyl cations [13]. As compared with the precursor, the fluorine signals of the cation are shifted down-field. The largest shifts were noted for the signals of fluorine atoms in positions 1,4,6. The observed values J_{FF} ($J_{14} \sim 40$, $J_{34} \sim J_{45} \sim 20$, $J_{46} \sim 55$ Hz) and $\Delta\delta$ are in agreement with those for the polyfluorobenzyl cations [13].

By contrast with benzocyclobutene (II), perfluoro-o-xylene does not give the cation in a concentration sufficient for detection by the ^{19}F NMR technique [13]. The higher relative stability of ion (XXII) in comparison with the perfluoro-o-methylbenzyl, indanyl (XXIII) and tetralinyl (XXIV) cations may result from homoaromatic stabilisation of the cationic centre in it (cf. [7,22]). The factors destabilising the tetralinyl cation (XXIV) in comparison with the indanyl ion (XXIII) have been discussed above.

EXPERIMENTAL

^{19}F NMR spectra were recorded on a Varian A-56/60A at 56.4 MHz for reaction mixtures without a solvent and for CCl_4 solutions of compounds (11 mol%). Chemical shifts are given in δ ppm down-field from C_6F_6 as an internal standard. IR spectra were recorded on a UR-20 spectrometer for solutions in CCl_4. UV spectra were recorded on a Specord UV-VIS for solutions in heptane, 10^{-4}-10^{-3} mol/l. Mass spectra were recorded on an AEI-MS 902. Elemental analysis data, IR and UV spectra of novel compounds are presented in Table 3.

Perfluoro-1,1-diethylbenzocyclobutene (X) (nc) and perfluoro-1,2-diethylbenzocyclobutene (XI) (nc)

(a) 3 g of $CF_2=CF_2$ was passed for 2 h through a stirred mixture of 3.0 g of benzocyclobutene (II) and 0.5 g of SbF_5 at 25-40°C. The mixture was treated with water, distilled with steam and dried over $MgSO_4$ to give 4.4 g of a mixture containing (GLC) 93% of compounds (X) and (XI) in the ratio 1:1.1 (^{19}F NMR spectrum). Vacuum distillation yielded 3 g of a mixture of benzocyclobutenes (X) and (XI) in the same ratio, b.p. 75-77°C (21 mm/Hg). The preparative GLC (100°C, SKTFT-50 on celite, N_2) was used to obtain fractions enriched by compound (X) or (XI).

(b) 3.92 g of a mixture of isomers (X) and (XI) (1.2:1 respectively) was stirred with 0.38 g of SbF_5 at 35-40°C for 4 h, then treated with water to give 3.72 g of the starting compounds.
From 2.9 g of a mixture of benzocyclobutenes (X) and (XI) (1:2) and 0.32 g of SbF_5 in a similar manner, 2.83 g of the starting compounds were obtained. In both experiments the ratio of isomers (X) and (XI) was not changed.

Reaction of perfluoroindan (IV) with tetrafluoroethylene

15 g of $CF_2=CF_2$ was passed for 8 h through a stirred mixture of 36.2 g of indan (IV) and 2.6 g of SbF_5 at 20-26°C. The mixture was treated with water, distilled with steam and dried over $MgSO_4$ to give 47.8 g of a mixture containing (GLC, ^{19}F NMR spectrum) 19% of the starting compound (IV), 39% of indan (XII) (nc) and 33% of indan (XIII) (nc). Individual compounds were isolated by preparative GLC.

A mixture (373 g) containing 39% of compound (IV), 36% of indan (XII) and 17% of indan (XIII) was distilled in vacuum on a rectification

TABLE 3

Elemental analysis data, IR and UV spectra of compounds

Compound	Found, %		Required, %		IR spectrum (cm^{-1}), fluorinated arom. ring			UV spectrum λ_{max}, nm (lg ε)
	C	F	C	F				
$C_{12}F_{16}$[a] (VII)					1644	1540	1500	275 (3.28)
$C_{14}F_{20}$[a] (VIII)					1637	1535	1488	279 (3.40)
$C_{10}F_{12}$[a,b] (IX)						1535	1498	256 (2.58), 263 (2.48, sh.)
$C_{12}F_{16}$ (X) + (XI)	32.2	67.8	32.2	67.8		1533	1497	258 (2.60), 263 (2.53, sh.)
$C_{11}F_{14}$ (XII)	33.3	67.1	33.2	66.8	1645	1519		264 (3.02, sh.), 270 (3.08)
$C_{13}F_{18}$ (XIII)	30.9	68.9	31.3	68.7	1641	1526		264 (3.07, sh.), 269 (3.13)
$C_{12}F_{16}$[a] (XIV)					1658	1517		277 (3.39, sh.), 282 (3.44)
$C_{14}F_{20}$[a] (XV)					1653	1514		275 (3.49), 282 (3.54)
$C_{12}F_{16}$[a] (XVI)					1638	1533	1485	261 (2.71), 267 (2.60, sh.)
$C_{14}F_{20}$[a] (XVII) + (XVIII)					1632	1522	1489	263 (2.73), 267 (2.66, sh.)

[a] Elemental composition of compounds was determined by means of high-resolution mass spectrometry.

[b] B.p. 74-75°C (51 mm/Hg).

TABLE 4

Interaction of perfluorobenzocycloalkenes with tetrafluoroethylene

Benzocycloalkene, g	CF_2=CF_2, g	SbF_5, g	Temperature, °C (Time, h)	Yield of mixture, g	Content of main products in mixture, %*
(II) - 15	4.7	0.6	5 - 10 (2)	18.2	(II) - 17, (IX) - 73, (X) - 4, (XI) - 5
(II) + (IV) - 2 + 2.4	0.8	0.35	20 - 25 (1)	4.5	(II) - 18, (IV) - 49, (IX) - 25, (X) + (XI) - 3, (XII) - <1
(III) + (IV) - 1.7 + 2	0.6	0.25	20 - 25 (1)	3.8	(III) - 49, (IV) - 20, (VII) - <1, (XII) - 16, (XIII) - 11
(III) - 20	4.2	6.1	20 - 25 (4)	20.3	(III) - 62, (VII) - 31, (VIII) - 4
(V) - 7	4.2	1.9	32 - 34 (4)	7.9	(V) - 17, (XVI) - 49, (XVII) - ~ 20, (XVIII) - ~ 7
(VI) - 6.3	5.6	0.8	22 - 26 (7)	6.5	(VI) - 54, (XIV) - 26, (XV) - 10

* According to GLC and ^{19}F NMR spectroscopy data; (VII) to (XVIII) are new compounds.

column to give 105 g of compound (IV), b.p. 140-141°C (760 mm/Hg), 96 g of indan (XII), b.p. 97-97.5°C (54 mm/Hg) and 46 g of compound (XIII), b.p. 116-116.5°C (52 mm/Hg).

Other reactions of perfluorobenzocycloalkenes with TFE

These were carried out in a similar manner (Table 4). The individual compounds (for isomers (XVII) and (XVIII) only their mixture) were isolated by preparative GLC.

Generation of perfluoro-1-benzocyclobutenyl cation (XXII)

(a) In SbF_5

Benzocyclobutene (II) (0.28 g) was dissolved at 20°C in 1.4 g of SbF_5, and the ^{19}F NMR spectra were recorded (+40...-40°C). The solution was then poured into water to give 0.12 g of a mixture (dried over $MgSO_4$) containing 19% of benzocyclobutenone (XXV) and 74% of precursor (II) (GLC, ^{19}F NMR spectrum).

(b) In SbF_5-SO_2FCl

Compound (II) (0.07 g) was dissolved in 0.51 g of SbF_5, the solution was diluted with SO_2FCl at -50°C and its spectrum was recorded (Table 1). The ^{19}F NMR spectra of the solution of benzocyclobutene (II) in SbF_5 and in the system SbF_5-SO_2FCl contained signals of the cation (XXII) and the precursor (II).

^{19}F NMR spectra of tetralins (III), (VII), (VIII)

Ethyltetralin (VII): 82.9 (CF_3), 68.4 (F^4_A), 54.4 (F^4_B), J^{AB}_{FF} = 295 Hz, 48.3 ($\underline{CF_2}CF_3$), 44.8 (F^2_A), 30.3 (F^2_B), J^{AB}_{FF} = 280 Hz, 39.0 (F^3_A), 25.1 (F^3_B), J^{AB}_{FF} = 270 Hz, 32.3 (F^8), 28.8 (F^5), 18.3 ($F^{6,7}$), -16.6 (F^1). The J^{AB}_{FF} values are in agreement with those for chlorine-containing polyfluorotetralins [3]. Product (VIII): 83.3 (CF_3), 18.6 ($F^{6,7}$), -5.5 and -8.7 ($F^{1,4}$), the signals of other fluorine atoms are at 57 - 30 ppm. Tetralin (III): 56.5 ($F^{1,4}$), 27.3 ($F^{2,3,5,8}$), 18.1 ($F^{6,7}$), cf. [5].

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