

**SKELETAL REACTIONS OF PERFLUOROMETHYLETHYL- AND
PERFLUORODIETHYLBENZOCYCLOBUTENES WITH 1,1- AND 1,2-
ALKYL GROUPS IN SbF_5 ***

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Taking perfluoro-1,1-dialkylbenzocyclobutenes as examples, it has been shown to be possible to enlarge the four-membered ring in polyfluorobenzocyclobutenes to five-membered in the presence of SbF_5 , by cleavage of the four-membered ring followed by cyclization of the resulting polyfluorostyrene to the polyfluoroindane, which then undergoes further reactions. Perfluoro-1-methyl-1-ethylbenzocyclobutene isomerizes at 50°C in the presence of SbF_5 to perfluoro- α,β -o-trimethylstyrene, which is reversibly converted at 130°C into perfluoro-1,2-dimethylindane. Perfluoro-1,1-diethylbenzocyclobutene isomerizes at 130°C in the presence of SbF_5 to give perfluoro- α -ethyl- β ,o-dimethylstyrene, which at 170°C gives perfluoro-2-methyl-3-ethylindene- and perfluoro-2-methyl-3-ethyl-4,5,6,7-tetrahydroindene. The last two compounds, together with perfluoro-o-dipropylbenzene, are obtained from perfluoro-1,2-diethylbenzocyclobutene with SbF_5 at 170°C. From perfluoro-1-methyl-2-ethylbenzocyclobutene with SbF_5 at 95°C there is obtained perfluoro-1-ethylindane, while at 130°C, in addition to the latter compound, there are obtained perfluorinated 1,1-dimethylindane, 1,2-dimethylindane, α,β -o-trimethylstyrene, 2,3-dimethylindene, and 2,3-dimethyl-4,5,6,7-tetrahydroindene.

We have recently observed the conversion of perfluoro-1-methyl- and perfluoro-1-ethylbenzocyclobutene into polyfluoroindanes on treatment with Lewis acids. The mechanism of the reaction was not examined in detail, but it was shown that the enlargement of the four-membered ring to five-membered in these reactions proceeds differently than in the nonfluorinated compounds [2]. In order to extend the range of compounds undergoing these reactions, and to identify the reaction sequence, we have now examined the behavior of perfluoro-1-methyl-1-ethyl- (I) and perfluoro-1-methyl-2-ethylbenzocyclobutene (II), and of perfluoro-1,1-diethyl- (III) and perfluoro-1,2-diethylbenzocyclobutene (IV) on treatment with SbF_5 .

It has been shown that on heating mixtures of (I) and (II) with SbF_5 at 50°C, the (I) isomerizes to perfluoro- α,β -o-trimethylstyrene (V), but (II) remained unchanged. In the presence of SbF_5 at 130°C, the styrene (V) cyclizes to perfluoro-1,2-dimethylindane (VI) (Scheme 1).

The conversion of (I) into (V) and (VI) in the presence of SbF_5 may be represented as in Scheme 1, involving the intermediate formation of carbocations (crypto-ions). Thus, (I) probably gives rise to the ion (VII), which isomerizes to the benzyl cation (VIII). Subsequently, addition and removal of fluoride ion results in a shift of the double bond (cf. [3]) to give the styrene (V). It appears that the ions (IX) generated from (V) cyclizes, giving, after addition of F^- , the indane (VI). In the presence of SbF_5 at 130°C, the latter reversibly isomerizes to the styrene (V), as well as undergoing fluorination and defluorination [4].

*For previous communication, see [1].

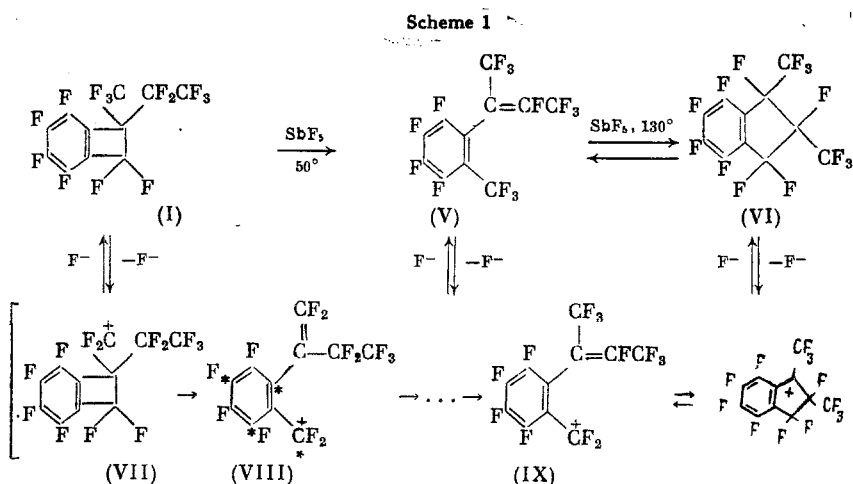
†Deceased.

TABLE 1. Elemental Composition, IR and UV Spectra of (V), (VI), and (XVI)-(XIX)

Compound	Mol. mass, [†] Found/Calculated	Empirical formula	IR spectrum ν , cm^{-1}		UV spectrum, λ_{max} , nm (log ϵ)
			C=C	fluorinated aromatic ring	
trans-(V)	$\frac{397.9795}{397.9776}$	$\text{C}_{11}\text{F}_{14}$	1713 w	1530, 1490	272(3,32)
cis-(V) [‡]	$\frac{397.9795}{397.9776}$	$\text{C}_{11}\text{F}_{14}$			
(VI)	$\frac{397.9784}{397.9776}$	$\text{C}_{11}\text{F}_{14}$		1522	268(3,08)
(XVI)	$\frac{447.9734}{447.9744}$	$\text{C}_{12}\text{F}_{16}$	1700 w	1533, 1485	272(3,30)
(XVII)	$\frac{485.9712}{485.9712}$	$\text{C}_{12}\text{F}_{18}$		1628, 1525, 1470	276(3,40)
(XVIII)	$\frac{485.9712}{485.9712}$	$\text{C}_{12}\text{F}_{18}$	1677 w 1642 w		269(3,35)
(XIX)	$\frac{409.9775}{409.9776}$	$\text{C}_{12}\text{F}_{14}$	1645	1520, 1509	303(3,66), 311(3,66), 323 sh (3,50)

[†]Found by high resolution mass spectrometry.

[‡]Mixture of cis-(V):(II), ~1.5:1.

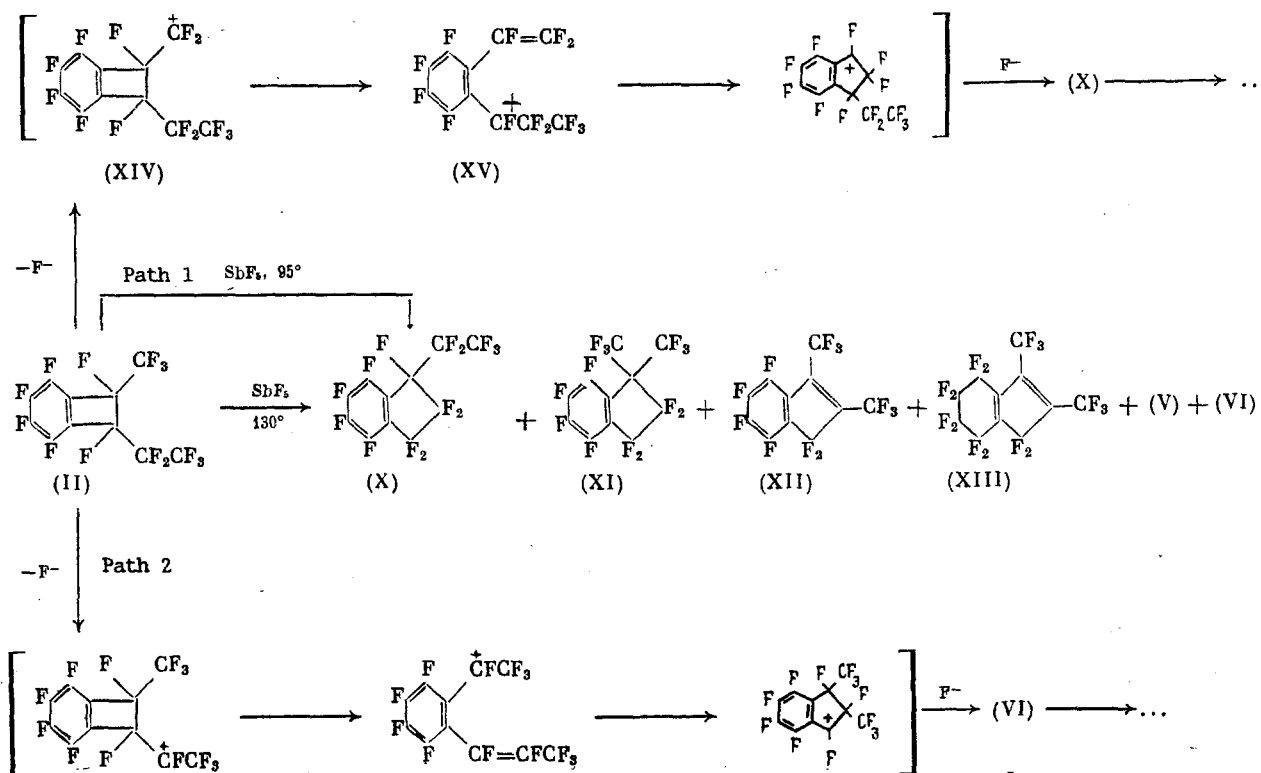


Skeletal reactions of (II), catalyzed by SbF_5 , require more severe conditions than the isomer (I). In SbF_5 at 95°C , (II) isomerizes to perfluoro-1-ethylindane (X), while at 130°C it gives, in addition to (X), a mixture of (V), (VI), perfluoro-1,1-dimethylindane (XI), perfluoro-2,3-dimethylindene (XII), and perfluoro-2,3-dimethyl-4,5,6,7-tetrahydroindene (XIII) (Scheme 2).

The isomerization of (II) to (X) in the presence of SbF_5 may be represented as follows. Apparently the ion (XIV), generated from (II), is converted into the cation (XV), cyclization of which gives, after addition of F^- , the indane (X) (path 1). The reaction could also be synchronous. The more facile isomerization of (I) than of (II) could for example be due to the greater relative stability of the cation (VIII) as compared with (XV). In fact, although in the cation (VIII) the perfluoroethyl group is located in a nonresonance position (resonance positions are marked *), in the ion (XV) it is located at the carbonium center, which should result in the destabilization of (XV) (cf. [5]).

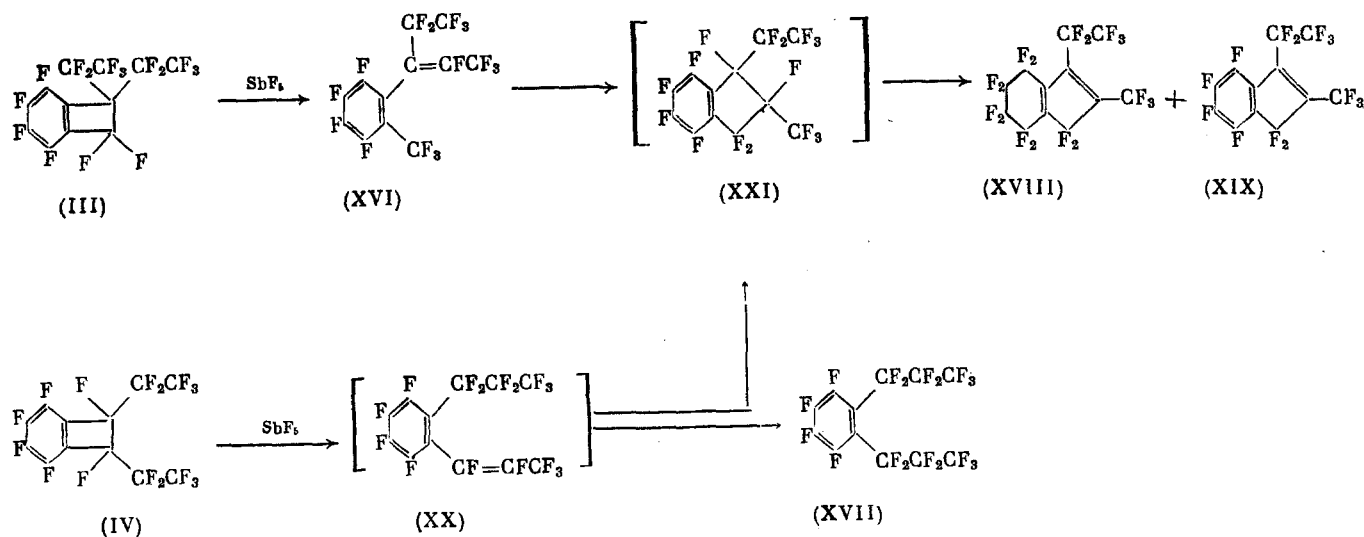
The indane (X), formed initially on reaction of (II) with SbF_5 at 130°C (path 1) may undergo further reactions to give (V), (VI), and (XI-XIII) [4]. In this case, the reaction probably follows path 2, since under similar conditions perfluoro-1-ethylbenzocyclobutene is known to isomerize to perfluoro-2-methylindane [2]. In fact, the proportion of (XI) in the reaction products of (II) in SbF_5 is considerably smaller than when (X) reacts with SbF_5 at 130°C [4]. Consequently, at 130°C the reaction of (II) with SbF_5 follows another path, such as path 2, in addition to path 1.

Scheme 2



Reconstruction of the carbon skeleton of the diethyl compounds (III) and (IV) in the presence of SbF_5 requires more severe conditions than for (I) and (II) [2]. At 130°C, a mixture of (III) and (IV) affords perfluoro- α -ethyl- β , α -dimethylstyrene (XVI), in addition to small amounts of perfluoro- α -dipropylbenzene (XVII) and perfluoro-2-methyl-3-ethyl-4,5,6,7-tetrahydroindene (XVIII). However, most of the (IV) remains unreacted. At 170°C, mixtures of (III) and (IV) in SbF_5 afford perfluoro-2-methyl-3-ethylindene (XIX), in addition to (XVII) and (XVIII). It was shown in a separate experiment that (IV) alone on treatment with SbF_5 at 170°C affords (XVII)-(XIX), while the styrene (XVI) gives (XVIII) and (XIX), but no (XVII) (Scheme 3).

Scheme 3



The reactions of (III) and (IV) in the presence of SbF_5 may be represented by Scheme 3, which is analogous to that for (I) and (II). It appears that (IV) gives the intermediate styrene (XX), which is then fluorinated to the benzene (XVII). Intramolecular cyclization of (XX), and of (XVI), should afford perfluoro-1-ethyl-2-methylindane (XXI), fluorination and defluorination of which also probably leads to the formation of (XVIII) and (XIX), as with (VI) [4].

The products (X)-(XIII) were identified in the reaction mixtures by GLC and the ^{19}F NMR spectra, which were in agreement with the spectra of authentic samples [4]. The structures of (V), (VI), and (XVI)-(XIX) were confirmed by their elemental composition and spectral data. For example, the presence in the ^{19}F NMR spectrum of the indane (VI) of two $J_{\text{CF}_3-\text{F}}$ constants of ~ 20 -24 Hz for each CF_3 group is evidence of the trans configuration of (VI) [6]. The doublet splitting with $J_{\text{CF}_3-\text{F}}^{\text{gem}} = 7$ Hz (the doublet components were broadened) of the CF_3 group in the β -position of the styrenes (V) and (XVI) corresponds to the trans disposition of the perfluoroalkyl groups at the double bond in these compounds. In the case of (V), in addition to the trans isomer small amounts of the cis-isomer (V) admixed with (II) were isolated, for which the signal for the analogous CF_3 group is seen as a quartet with $J_{\text{CF}_3-\text{CF}_3}^{\text{cis}} = 11$ Hz of doublets with $J_{\text{CF}_3-\text{F}}^{\text{gem}} = 7$ Hz (see the analogous constants for polyfluoropropenes [7]). It is noteworthy that no isomers with cis-oriented perfluoroalkyl groups were obtained from the indane (VI) and the styrene (XVI), although they may possibly be formed in small amounts.

EXPERIMENTAL

The ^{19}F NMR spectra were obtained on a Varian A-56/60A (56.4 MHz) for the reaction mixtures in the absence of a solvent, and for solutions of the compounds (11 mole %) in CCl_4 relative to C_6F_6 as internal standard. The IR spectra of solutions in CCl_4 were obtained on a UR-20, and UV spectra in heptane on a Specord UV-VIS. The elemental compositions of the compounds were determined by high resolution mass spectrometry on a Finnigan MAT 8200. GLC analyses were carried out on an LKhM-72 chromatograph (50-270°C, 4000 \times 4 mm, SKTFT-50, E-301 on Chromatone N, 15(25): 100, He, 60 ml/min). Compounds (V), (VI), and (XVI)-(XIX) were isolated from the mixtures by preparative GLC (80, 110°C, SKTFT-50 on celite, nitrogen). The elemental compositions of the compounds are shown in Table 1, and their spectral characteristics, in the text of the Experimental section and in Table 1.

Perfluoro- α,β,o -trimethylstyrene (V). A mixture containing (I) and (II) in a ratio of 1:1:1 (1.68 g) was heated with 2.86 g of SbF_5 in a sealed ampul for 13 h at 50°C. The reaction mixture was added dropwise to water, the organic layer separated, and dried over MgSO_4 to give 1.51 g of a mixture containing (GLC, ^{19}F NMR spectrum) 45% of trans-(V), 7% cis-(V), and 45% of (II). Pure trans-(V) and (II) were isolated by preparative GLC. There was also obtained a mixture containing 57% of cis-(V) and 41% of (II).

Perfluoro-1,2-dimethylindane (VI). In a nickel bomb (10 ml) was placed a solution of 2.8 g of (V) in 13.6 g of SbF_5 , and the mixture heated for 19 h at 130°C. The reaction mixture was transferred to 20 ml of anhydrous HF, and cooled to 0°C. Dichloromethane (8 ml) was then added, and the mixture poured into an ice-water mixture. The organic layer was separated, and the aqueous layer extracted with dichloromethane. The dichloromethane solutions were combined, washed with aqueous potassium carbonate, dried over MgSO_4 , and the solvent distilled off to give 2.2 g of a mixture containing (GLC, ^{19}F NMR spectrum) 19% (V), 59% (VI), 3% (XII), 3% (XIII).

Reactions of Perfluoro-1-methyl-2-ethylbenzocyclobutene (II) in the Presence of SbF_5 . a) A solution of 1 g of (II) in 3 g of SbF_5 was heated in a sealed ampul for 8.5 h at 95°C. The reaction mixture was transferred to a vessel of Fluoroplast-4, treated with anhydrous HF (3 ml), transferred to water, and the organic layer separated and dried over MgSO_4 to give 0.73 g of a mixture containing (GLC, ^{19}F NMR spectrum) 78% of (II) and 18% of (X).

b) A mixture of 0.71 g of (II) and 2.71 g of SbF_5 was heated in a nickel bomb for 36.5 h at 130°C. It was then cooled to -10°C, ~ 1 ml of anhydrous HF added, and transferred to water and ice. The organic layer was separated, and dried over MgSO_4 to give 0.59 g of a mixture containing (GLC, ^{19}F NMR spectrum) 5% (V), 17% (VI), 6% (X), 13% (XI), 3% (XII), 38% (XIII).

Under similar conditions, a parallel experiment using 0.76 g of (X) and 2.93 g of SbF_5 gave 0.63 g of a mixture containing 3% (V), 9% (VI), 3% (X), 31% (XI), <2% (XII), 43% (XIII) (cf. [4]).

Perfluoro- α -ethyl- β,o -dimethylstyrene (XVI). A mixture of (III) and (IV) in a ratio of 1:1:1 (4.57 g) was dissolved in 6.64 g of SbF_5 , and heated in a nickel bomb for 17 h at 130°C. The mixture was worked up as in the synthesis of (V), to give 3.93 g of a mixture containing (GLC, ^{19}F NMR spectrum) 38% (IV), 33% (XVI), 5% (XVII), 9% (XVIII).

Reactions of (III), (IV) and (XVI) with SbF_5 at 170°C . The reactions were carried out as for (II), at 130°C .

a) From 0.94 g of (XVI) and 4.07 g of SbF_5 there was obtained after 15.5 h 0.77 g of a mixture containing (GLC, ^{19}F NMR spectrum) 4% (XVI), 53% (XVIII), 19% (XIX).

b) From 1.66 g of (IV) and 6.89 g of SbF_5 there was obtained after 15 h 1.5 g of a mixture containing 30% (XVII), 24% (XVIII), 8% (XIX).

c) From 3.17 g of a mixture of (III) and (IV) and 10.75 g of SbF_5 there was obtained after 20 h 2.78 g of a mixture containing 19% (XVII), 35% (XVIII), 16% (XIX).

^{19}F NMR Spectra, δ , ppm (J, Hz): cis-(V): 104.9 (CF_3^α), 104.6 (CF_3^α), 93.5 (CF_3^β), 59.1 (F^β), 28.5, 27.8, 15.8, 14.5 (aromatic F atoms); trans-(V): 105.8 (CF_3^α), 101.4 (CF_3^α), 93.0 (CF_3^β), 55.5 (F^β), 29.4, 27.6, 15.8, 15.1 (aromatic F atoms); (VI): 89.2 four d (CF_3 , 24, 21, 8, 4 Hz), 86.4 four d (CF_3 , ~21, ~21, ~8, ~8), 70.3 (1F_A^3), 62.2 (1F_B^3 , $J_{AB} = 271$), 28.4 (1F), 24.0 (1F), 20.2 (2F) (aromatic F atoms), -8.7 (1F^1), -23.8 (1F^2); (XVI): 106.0 (CF_3^α), 93.6 (CF_3^β), 78.5 (3F), 50.7 (2F) (CF_3CF_2), 60.0 (F^β), 30.5 (1F), 27.9 (1F), 15.5 (2F) (aromatic F atoms); (XVII): 81.7, 63.7, 40.6, 35.5, 18.0 with an intensity ratio of 6:4:4:2:2 respectively; (XVIII): 103.9 (CF_3^2), 80.7 (CF_3), 52.8 (2F), 50.8 (2F), 47.0 (2F), 34.0 (2F), 28.7 (2F), 27.7 (2F); (XIX): 105.0 (CF_3^2), 79.8 (CF_3^3), 50.3 (CF_2^3), 43.5 (2F^1), 33.6 (1F^4), 23.7 (1F^7), 17.3 and 15.8 ($2\text{F}^{5,6}$). $J_{\text{CF}_2^3-\text{F}^4} = 46$, $J_{\text{CF}_2^3-\text{CF}_3^2} = 16$, $J_{\text{CF}_3^3-\text{F}^4} = 17$ Hz.

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