

SKELETAL REARRANGEMENTS IN THE REACTIONS
OF PERFLUORO-1-METHYL- AND -1-ETHYL-
BENZOCYCLOBUTENES WITH LEWIS ACIDS

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SUMMARY

The reactions of perfluoro-1-methyl- and -1-ethyl-benzocyclobutenes with Lewis acids (SbF_5 , AlCl_3 , AlBr_3) have been studied. A four-membered ring expansion, unknown earlier in the halogenated series, has been found. The mechanism of the process differs from that for non-fluorinated analogues.

INTRODUCTION

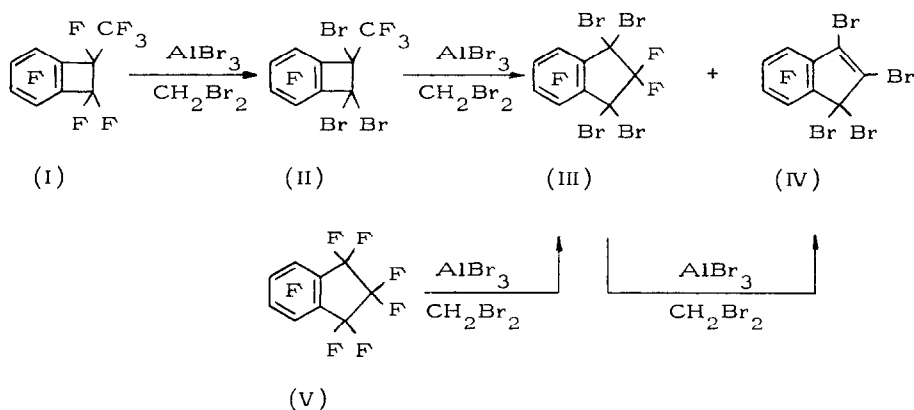
In earlier work, Prof. G.G.Yakobson and his co-workers have shown that the reaction of 2-halopolyfluorotetralins with antimony pentafluoride proceeds with contraction of the alicyclic ring of the tetralins giving 1-methylindanes [1]. Ring expansion for polyfluorinated benzocycloalkenes has not been reported in the literature. At the same time, for non-fluorinated benzocyclobutenes, a cationoid expansion of the alicyclic fragment of the molecules is known [2]. Arising from this, it was interesting to study the reactions of polyfluorinated 1-alkylbenzocyclobutenes with Lewis acids to see whether four-membered ring expansion occurred in these reactions.

RESULTS AND DISCUSSION

At the initial stage of the reaction of perfluoro-1-methylbenzocyclobutene (I) with aluminium bromide, there occurs substitution of fluorine

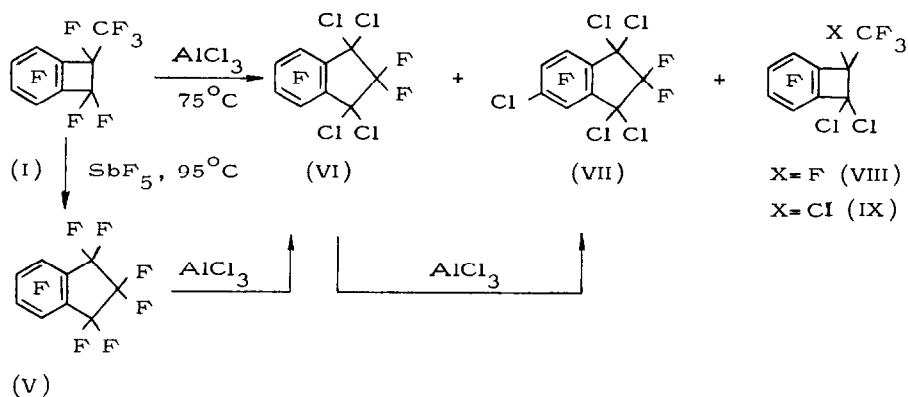
atoms by bromine in positions 1,2 of compound (I). The resulting 1,2,2-tribromoperfluoro-1-methylbenzocyclobutene (II) reacts with aluminium bromide with expansion of the four-membered ring.

Thus the reaction of benzocyclobutene (I) and AlBr_3 in the ratio 1:1.25 gave a mixture of 1,1,3,3-tetrabromohexafluoroindan (III), 1,1,2,3-tetrabromotetrafluoroindene (IV) and compound (II) in the ratio 2:1:4. With an excess of aluminium bromide, the main product was indene (IV). An alternative synthesis of compounds (III) and (IV) from indan (V) and AlBr_3 [3] supports the structures of these compounds.

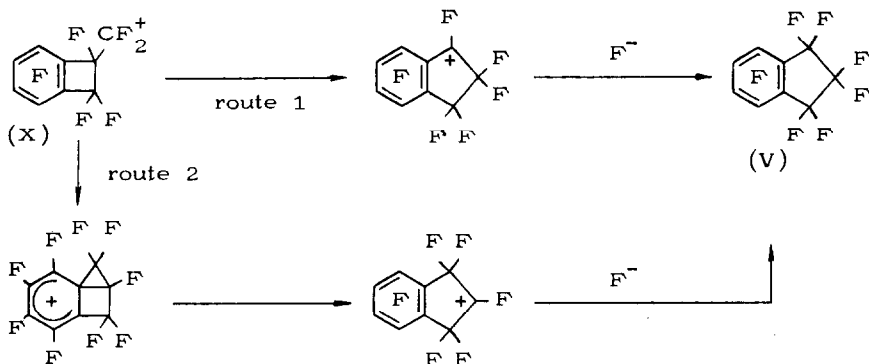


Since in this reaction of benzocyclobutene (I) with aluminium bromide we found expansion of the four-membered ring, hitherto unknown in the halogenated series, it was interesting to study the behaviour of compound (I) with other Lewis acids. In this connection we have studied the reaction of benzocyclobutene (I) with AlCl_3 and SbF_5 in more defined conditions than in ref. [4]. These reactions also proceed with expansion of the four-membered ring.

Thus treatment of benzocyclobutene (I) with an excess of AlCl_3 at 75°C gave mainly 1,1,3,3-tetrachlorohexafluoroindan (VI) together with 1,1,3,3,5-pentachloropentafluoroindan (VII). In addition to these products, the reaction mixture contained also small amounts of 2,2-dichloroperfluoro-1-methylbenzocyclobutene (VIII) and 1,2,2-trichloroperfluoro-1-methylbenzocyclobutene (IX). An alternative synthesis of compounds (VI) and (VII) from indan (V) and AlCl_3 [5] supports the structures of these compounds.

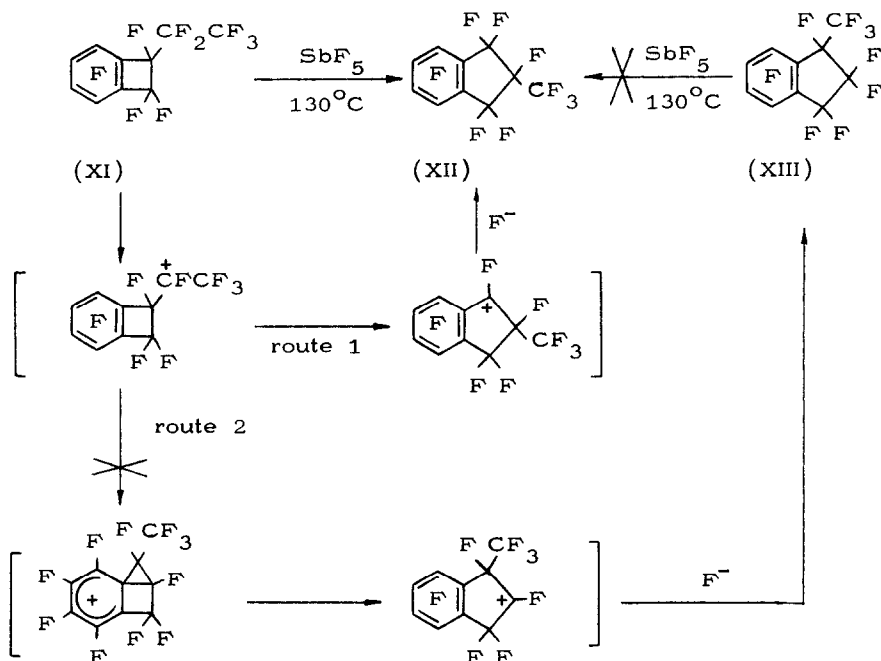


Benzocyclobutene (I) reacted with antimony pentafluoride to give perfluoroindan (V). Ring expansion in this reaction may be represented as proceeding via the intermediate perfluorobenzocyclobutenyl-1-methyl cation (X). Formally, transformation of the latter to indan (V) may proceed by migration of the alkyl (route 1) or aryl (route 2) group according to the scheme:



The products of the reactions of compound (I) with AlCl_3 and AlBr_3 did not contain the indanes having chlorine or bromine atoms in position 2. This result is in agreement with route 1 of the expansion of the chlorinated or brominated four-membered ring but contradicts route 2. By contrast, in the hydrocarbon series, expansion of the four-membered ring proceeds by a route of type 2 [2]. It was suggested that, as in the case of aluminium halogenides, route 1 will take place in the reaction of benzocyclobutene (I) with SbF_5 , although route 2 cannot be excluded.

To test this suggestion, we studied the reaction of perfluoro-1-ethylbenzocyclobutene (XI) with antimony pentafluoride. At 95°C the reaction practically did not proceed, and at 130°C it gave perfluoro-2-methylindan (XII). Perfluoro-1-methylindan (XIII) was not detected in the reaction mixture.



A separate experiment has shown that compound (XIII) does not isomerize to indan (XII) under the conditions of the reaction of benzocyclobutene (XI) with antimony pentafluoride. This suggests that the reaction of compound (XI) with SbF₅ also proceeds by route 1.

EXPERIMENTAL

¹⁹F NMR spectra were recorded on a Varian A-56/60A at 56.4 MHz. IR spectra were recorded on a UR-20 spectrometer for CCl₄ solutions. UV spectra were recorded on a Specord UV-VIS for heptane solutions.

Interaction of perfluoro-1-methylbenzocyclobutene (I) with AlBr_3

(a) (I): AlBr_3 = 1:1.05

A solution of 1.08 g of AlBr_3 in 2 ml of CH_2Br_2 was added dropwise for 15 min to a mixture of 1.15 g of compound (I) and 1 ml of CH_2Br_2 stirred at 0°C . The mixture was then stirred at 25°C for 1 h. After that, 10 ml of 5% HCl was added to it. The organic layer was separated and dried over MgSO_4 . CH_2Br_2 was distilled off to give 1.8 g of 1,2,2-tribromoperfluoro-1-methylbenzocyclobutene (II) (n.c.). The sample for analysis was obtained by molecular distillation in vacuum (95°C , 15 mm/Hg). Found (%): C 22.6; Br 50.2; F 27.7. $\text{C}_9\text{Br}_3\text{F}_7$ requires (%): C 22.5; Br 49.9; F 27.7. ^{19}F NMR spectrum (11 mol.% solution in CCl_4 ; ppm downfield from C_6F_6 as an internal standard): 94.3 (CF_3); 24.6 (1F); 22.6 (1F); 18.5 (2F). IR spectrum (cm^{-1}): 1530, 1490 (fluorinated aromatic ring). UV spectrum, λ_{max} , nm ($\lg \epsilon$): 207 (4.41), 262 (3.10, sh.), 276 (2.95, sh.).

(b) (I): AlBr_3 = 1:1.25

Similar treatment of 1 g of benzocyclobutene (I) with 1.13 g of AlBr_3 gave 1.65 g of a mixture containing compounds (II), (III), (IV) in the ratio of 4:2:1 (^{19}F NMR spectrum).

(c) (I): AlBr_3 = 1:4

A solution of 1.1 g of AlBr_3 in 2 ml of CH_2Br_2 was added dropwise for 20 min to a mixture of 0.3 g of benzocyclobutene (I) and 0.3 ml of CH_2Br_2 stirred at -20°C . The mixture was stirred at 0°C for 20 min and at 25°C for 2 h. Then it was treated as in experiment (a) to yield 0.46 g of solid product containing indene (IV) and benzocyclobutene (II) in the ratio of 9:1 (^{19}F NMR spectrum). The ^{19}F NMR spectra of compounds (III) and (IV) obtained in experiments (b) and (c) coincide with those of the authentic samples synthesized by us from perfluoroindan (V) and AlBr_3 [3].

Reaction of benzocyclobutene (I) with AlCl_3

Compound (I), 0.3 g, was heated in a sealed tube with 0.7 g of AlCl_3 ((I): AlCl_3 = 1:5) at 50°C for 14 h and then at 75°C for 26 h. The reaction mixture was treated with water, extracted with CH_2Cl_2

and dried over MgSO_4 . The solvent was distilled off to give 0.3 g of a mixture containing (GLC, ^{19}F NMR spectrum) 70% of indan (VI), 12% of indan (VII) and benzocyclobutenes (VIII) and (IX) - 7% of each. The ^{19}F NMR spectra of compounds (VI)-(IX) coincide with those of the authentic samples [4, 5].

Interaction of benzocyclobutene (I) with SbF_5

A solution of 0.3 g of compound (I) in 1.22 g SbF_5 ((I): SbF_5 = 1:5.5) was heated at 95°C for 8.5 h. The reaction mixture was poured onto ice cooled with liquid N_2 . This gave 0.17 g of a mixture containing (GLC, ^{19}F NMR spectrum) 78% of indan (V).

Reaction of perfluoro-1-ethylbenzocyclobutene (XI) with SbF_5

A solution of 0.4 g of compound (XI) in 1.26 g of SbF_5 ((XI): SbF_5 = 1:5) was heated at 130°C for 4.5 h. The reaction mixture was dissolved at -40°C in liquid SO_2 and poured into water containing ice. This gave 0.28 g of the product (dried over MgSO_4) containing 78% of indan (XII) and 10% of the initial compound (GLC and ^{19}F NMR spectrum). The ^{19}F NMR spectrum of indan (XII) coincides with that of the authentic sample [6].

A similar treatment of 0.14 g of indan (XIII) with 0.66 g of SbF_5 ((XIII): SbF_5 = 1:7.6) gave 0.1 g of the product, the ^{19}F NMR spectrum of which did not contain the signals of indan (XII).

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