

Preliminary note

Contraction of the six-membered alicyclic ring of perfluorinated ethyl- and diethyl-tetralins to five- and four-membered ones under the action of antimony pentafluoride

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Abstract

Interaction of perfluoro-1-ethyltetralin (**2**) with SbF_5 leads to the formation of perfluorinated 5-ethyltetralin (**5**), 3-methyl-4-ethylindan (**6**) and 1,3,4-trimethylindan (**4**). Perfluoro-1,4-diethyltetralin (**3**) under the action of SbF_5 gives perfluorinated 5,8-diethyltetralin (**8**), 1-methyl-4,7-diethylindan (**9**) and 1,1-dimethyl-3,6-diethylbenzocyclobutene (**10**).

Keywords: Alicyclic contraction; Perfluorinated ethyltetralins; Perfluorinated diethyltetralins; Antimony pentafluoride; NMR spectroscopy

In the hydrocarbon series cationoid rearrangements are widespread, whereas in the series of polyfluorinated compounds they occur very rarely. We have previously reported the reactions of alicyclic ring cleavage, contraction and expansion of perfluorinated benzocycloalkenes by antimony pentafluoride [1–5]. For example, we have shown, that perfluorotetralin (**1**) heated with SbF_5 at 200 °C undergoes contraction of the alicyclic ring giving perfluoro-1-methylindan [2].

Here we report analogous transformations of perfluoro-1-ethyltetralin (**2**) and perfluoro-1,4-diethyltetralin (**3**) in their reactions with antimony pentafluoride. We have found that the ethyltetralin **2** when heated with SbF_5 at 200 °C unexpectedly transformed to perfluoro-1,3,4-trimethylindan (**4**). Under milder conditions, tetralin **2** reacted with SbF_5 giving isomeric perfluoro-5-ethyltetralin (**5**) together with perfluoro-3-methyl-4-ethylindan (**6**).

Isomerization of tetralin **2** to tetralin **5** seems to proceed by elimination–addition of fluoride ion, leading to removal of the double bonds from one ring to another. Indan **6** was formed from tetralin **5** by SbF_5 -catalyzed contraction of the six-membered ring to the five-membered one. It should be noted that this contraction proceeds under milder conditions as compared with tetralin **1**. Indeed, on heating a mixture of tetralins **1** and **5** with SbF_5 at 170 °C, compound **5** was

converted to indanes **4** and **6**, whereas compound **1** remained unchanged.

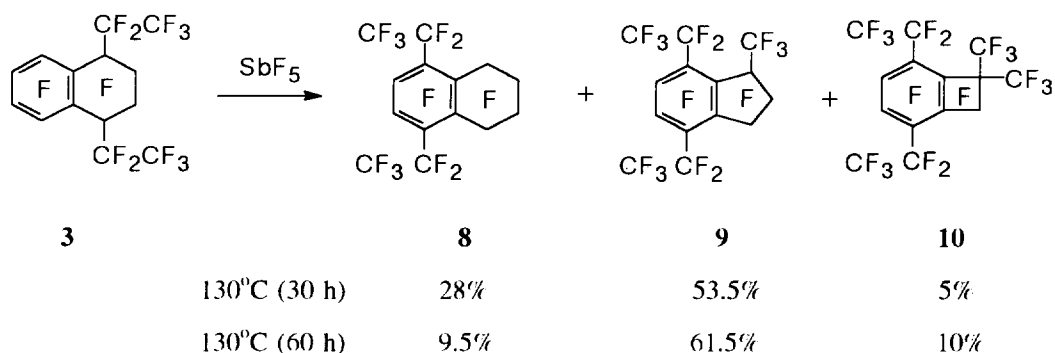
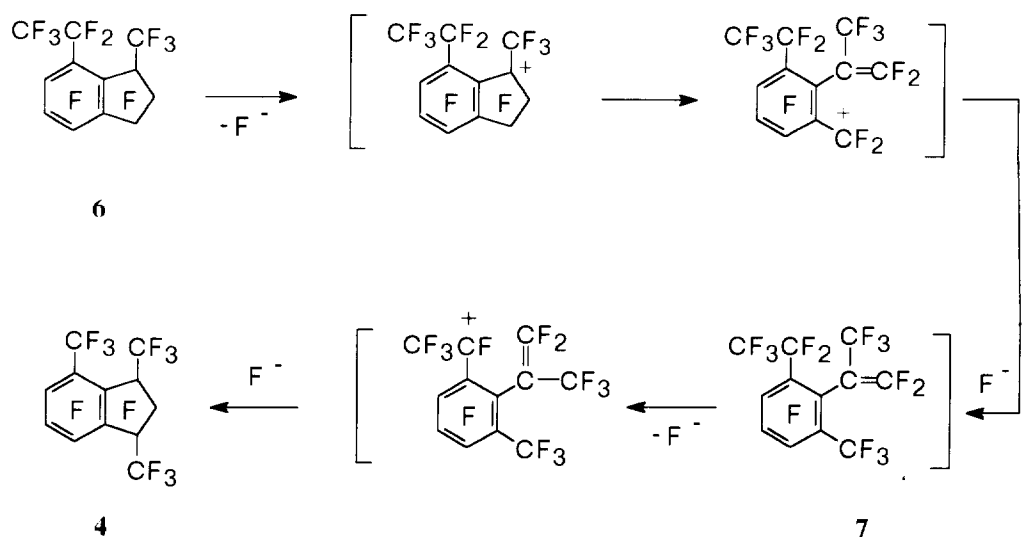
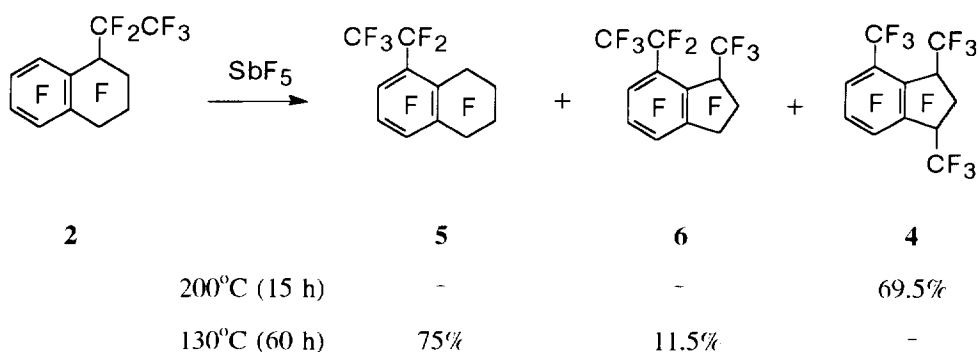
Indan **4** is possibly formed from indan **6** under the action of SbF_5 . This isomerization can proceed by cleavage of the five-membered ring of indan **6** leading to compound **7**, which is then converted to indan **4** (cf. Ref. [3]):

In the reaction of diethyltetralin **3** with SbF_5 , as well as in the case of ethyltetralin **2**, removal of the double bonds from one ring to another occurs giving perfluoro-5,8-diethyltetralin (**8**). The latter then undergoes contraction of the alicyclic ring. This process occurs more readily than in the case of tetralin **5**. Indeed, tetralin **3** when heated with SbF_5 at 130 °C gave tetralin **8** together with perfluoro-1-methyl-4,7-diethylindan (**9**) and a small amount of perfluoro-1,1-dimethyl-3,6-diethylbenzocyclobutene (**10**). When the reaction time was increased, the yield of tetralin **8** decreases, whereas the yields of compounds **9** and **10** increased.

Benzocyclobutene **10** is possibly formed from indan **9**. It should be noted that any examples of cationoid contraction of the five- or six-membered ring to the four-membered one are unknown in the series of polyfluorinated compounds.

As mentioned above, the presence of the accepting perfluoroethyl groups in the aromatic ring of polyfluorotetralins **5** and **8** makes contraction of the alicyclic ring easier as compared with tetralin **1**. This suggests that the mechanism of the reactions of tetralins **1**, **5** and **8** with SbF_5 possibly differs from that proposed for the contraction of the alicyclic ring in 2-halopolyfluorotetralins [6]. This problem will be discussed in detail in a subsequent article.

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^{19}F NMR spectra were recorded on a Bruker WP-200SY instrument (188.3 MHz) for CDCl_3 solutions of the individual compounds (≤ 10 mol%). Chemical shifts are given in δ ppm downfield from C_6F_6 as internal standard. Compounds 4–6 and 8–10 were isolated by preparative GLC. The elemental compositions of these compounds were determined

by means of high-resolution mass spectrometry on a Finnigan Mat 8200 instrument.

A typical experimental procedure was as follows. Tetralin 2 (3.1 g, 6.7 mmol) and SbF_5 (10.2 g, 47 mmol) were heated at 200 °C in a 10 ml nickel bomb for 45 h. The reaction mixture was poured on to ice, cooled with liquid N_2 , and the

organic layer separated and dried over MgSO_4 to give 2.91 g of a mixture containing (GLC, ^{19}F NMR spectrum) 74% of indan **4** (yield 69.5%).

The ^{19}F NMR spectra of the compounds prepared are listed below.

Compound **4**: 105.5 (CF_3 -4); 89.4 (CF_3 -1); 87.1 (CF_3 -3); 46.4 (F-5); 42.1 (F-7); 42.2 (F_A -2), 37.7 (F_B -2, J_{AB} = 265 Hz); 18.2 (F-6); 3.0 (F-1); -12.2 [F-3, $J(\text{F-3}, \text{CF}_3$ -4) = 42 Hz] (cf. Ref. [3]) ppm.

Compound **5**: 79.8 (CF_3); 61.4 (F-4,4); 58.4 (CF_3CF_2); 57.6 (F-1,1); 49.8 (F-6); 41.1 (F-8); 27.4, 26.9 (F-2,2, F-3,3); 17.5 (F-7) ppm.

Compound **6**: 82.3 (CF_3 -3); 78.3 (CF_3CF_2); 59.8 (F_A -1), 52.0 (F_B -1, J_{AB} = 270 Hz); 53.6 (F_A), 52.0 (F_B , CF_3CF_2 , J_{AB} = 290 Hz); 49.2 (F-5); 41.3 (F_A -2), 30.8 (F_B -2, J_{AB} = 245 Hz); 36.7 (F-7); 18.3 (F-6); -13.9 (F-3) ppm.

Compound **8**: 80.6 (2CF_3); 63.8 (F-1,1,4,4); 58.5 ($2\text{CF}_3\text{CF}_2$); 51.5 (F-6,7); 27.1 (F-2,2,3,3) ppm.

Compound **9**: 88.4 (CF_3 -1); 78.9, 78.4 ($2\text{CF}_3\text{CF}_2$); 63.9 (F_A -3), 56.7 (F_B -3, J_{AB} = 270 Hz); 54.8, 53.3 (A-components of two AB-systems), 51.4, 51.3 (B-components of two AB-systems, $2\text{CF}_3\text{CF}_2$, J_{AB} = 285 Hz); 48.7, 47.2 (F-5, F-6); 41.2 (F_A -2), 29.4 (F_B -2, J_{AB} = 240 Hz); 14.7 (F-1) ppm.

Compound **10**: 96.4 (2CF_3 -1); 78.4, 77.6 ($2\text{CF}_3\text{CF}_2$); 64.3 (F-2,2); 49.8, 48.5 ($2\text{CF}_3\text{CF}_2$); 46.1, 41.5 (F-4, F-5) ppm.

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