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CONVERSION OF RADICAL CATIONS OF POLYFLUOROAROMATIC COMPOUNDS INTO DIHYDROAROMATIC PRODUCTS IN THE PRESENCE OF FLUORIDE AND CHLORIDE ANIONS

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SUMMARY. Octafluoronaphthalene radical cations generated by oxidation of octafluoronaphthalene by SbF_5 or by electrochemical oxidation react with fluoride and chloride anions giving perfluoro-1,4-dihydronaphthalene and 1,4-dichlorooctafluoro-1,4-dihydronaphthalene, respectively.

Reactions of aromatic radical cations with a number of nucleophilic agents have been reported [1 - 3].Though the reactions of radical cations with halogen anions were considered doubtful by some authors [4,5], arguments in favour of these reactions were given in [6 - 8].We have obtained experimental data on the reactions of the fluoride and chloride anions with polyfluoroaromatic radical cations.

A solution of 1.8 g of octafluoronaphthalene (I) in 20 g of SbF_5 +) was poured into 100 ml of 40% HF solution in methanol at -20 ÷ 20°C.The mixture was stirred and poured onto ice, the usual work-up gave 2.1 g of the product containing 59% of naphthalene (I), 8% of perfluoro-1,4-dihydronaphthalene II and 14% of 1-oxooctafluoro-1,4-dihydronaphthalene III.Reactions of naphthalene I solution in antimony pentafluoride with 70% HF solution in pyridine, 30% HF solution in ether or 30% CsF solution in methanol [9] also afforded dihydronaphthalene II.A similar treatment of the solution of decafluorodiphenyl in SbF_5 with 50% HF solution in methanol gave the product containing decafluorodiphenyl and perfluoro-1-phenyl-1,4-cyclohexadiene.

The cyclic voltammetry measurements have shown that octafluoronaphthalene in acetonitrile, in the presence of $Et_4NF\cdot 2HF$, undergoes reversible oxidation on platinum at $E_{1/2} = +1.83$ V (relative to 0.1 M Ag/Ag^+ in acetonitrile).The preparative electrolysis of 1.35 g of naphthalene I on the

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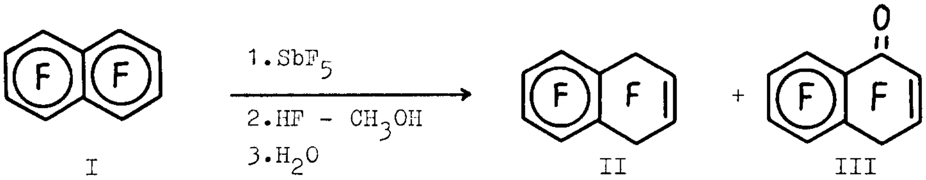
+) Octafluoronaphthalene treated with SbF_5 is almost quantitatively converted into the corresponding radical cation [3].We have found, using the Faraday method, that the extents of conversion of naphthalene I and decafluorodiphenyl in SbF_5 are ~100% and ~40%, respectively.

platinum electrode at the controlled potential +2.0 V, in the solution of 4 g of $Et_4NF \cdot 2HF$ in 30 ml of dry acetonitrile, in argon, gave dihydro - naphthalene II and dihydronaphthalene III, in 13 and 70% yields, respectively (naphthalene I conversion 72%).



Since the solution of octafluoronaphthalene radical cation in SbF_5 is stable for at least 7 days (as shown by the UV data and the results of the Faraday measurements), and the octafluoronaphthalene dication is much more reactive (cf. [10]), formation of products II and III in the reaction of octafluoronaphthalene radical cation generated by chemical or electrochemical oxidation, with various souces of fluoride anions, is believed to indicate the ability of polyfluoroaromatic radical cations to react with F^-.

Oxodihydronaphthalene III is supposed to be the product of the hydrolysis of intermediate perfluoronaphthalenonium cation (cf. [11]).

We also managed to perform the reaction of octafluoronaphthalene radical cation with the chlorine anion: a solution of naphthalene I in SbF_5 is mixed with HCl - methanol mixture at -20 ÷ 20°C to give 1,4-dichlorooctafluoro - 1,4-dihydronaphthalene and naphthalene I.

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