Generation and Some Reactions of Perhalogenated Arenonium Ions

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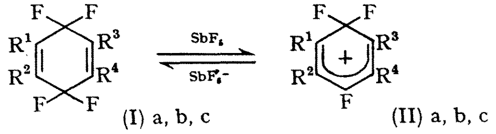
Summary Perhalogenated arenonium ions are formed by elimination of F^- from perhalogenated cyclohexa-1,4-dienes by reaction with SbF_5.

IN previous papers[1–3] on the reaction of electrophiles with aromatic polyfluoro-compounds we have postulated the formation of arenonium ions (σ-complexes) as intermediates, containing CFX groups ($X = NO_2$, SbF_5^-, and SO_3^-) at the sp^3-hybridised centre. We observed the formation of radical-cations when aromatic perfluoro-compounds reacted with such electrophiles as SbF_5 and SO_3. It was suggested that an equilibrium exists between the radical-cations and the polyfluorinated arenonium ions.[3]

We now report the formation and some reactions of a new type of cations, perhalogenated arenonium ions, formed by elimination of F^- from perhalogenated dienes (Ia—c) by reaction with SbF_5.

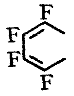
The n.m.r. spectra of the ions (Ia—c) (Figure) are consistent with data in the literature.[4,5] (See Table).



(I) a, b, c (II) a, b, c

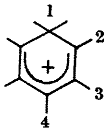
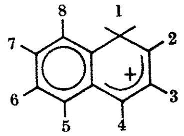
a, $R^1{=}R^2{=}R^3{=}R^4{=}F$; b, $R^1{=}R^2{=}R^3{=}R^4{=}Cl$;

C, $R^1+R^2=$



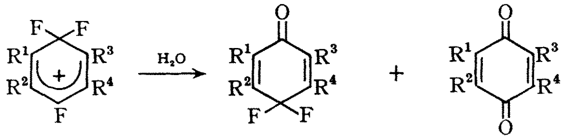
, $R^3{=}R^4{=}F$

TABLE

Ion		δ_F (p.p.m. from external C_6F_6)	J_{FF} (Hz)
	(IIa)	δ_1 −32, δ_2 −108 δ_3 −21 δ_4 −197	J_{12} 23, J_{13} 6, $J_{23} \approx J_{23} \approx$ 6, J_{24} 109, J_{34} 28
	(IIb)	δ_1 −58, δ_4 −200	$J_{14} \leqslant 2$
	(IIc)	δ_1 −50 (or −48), δ_2 −99, δ_4 −170, δ_5 −78, δ_7 −71 δ_3, δ_6, δ_8* −21, −28, −48* (or −50)	J_{24} 100, J_{45} 150

* Not reliably attributable.

When a solution of (IIa) in SbF_5 is diluted with 3 volumes of liquid SO_2, the equilibrium is displaced so that the solute consists almost entirely of the parent diene. Mixtures of halogenated cyclohexadienones (IIIa—c) and quinones (IVa—c) are formed when SbF_5 solutions of (IIa—c) are poured into water.



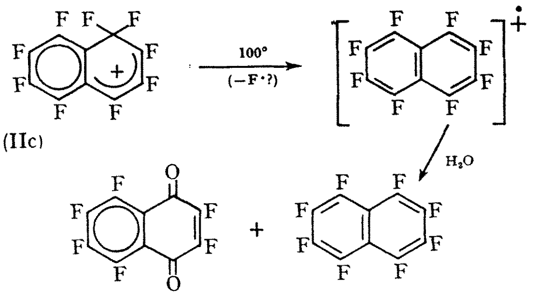
(II a, c) (III a, c) (IVa, c)

When the dark red solution of (IIc) in SbF_5 is heated at 100°, the colour changes to the green typical of octafluoronaphthalene radical-cation.[3] This solution gives an e.s.r. signal, and when it is diluted with dimethyl sulphate the resolved e.s.r. spectrum of $C_{10}F_8^+$ can be observed.[3] The formation of $C_{10}F_8^+$ is confirmed by its conversion into octafluoronaphthalene (V) and into the quinone (IVc) when the green solution is poured into water. The same result was obtained with $C_{10}F_8^+$ produced by the action of SbF_5 on (V).[3] The ratio of (V) to (IVc) is approximately 1 : 1. The process may be due to disproportionation[6]:

$$2C_{10}F_8^+ \rightleftharpoons C_{10}F_8 + C_{10}F_8^{2+}$$

$$C_{10}F_8^{2+} + 2H_2O \rightarrow (IVc) + 2HF + 2H^+.$$

Similarly, the ion (IIa) affords the $C_6F_6^+$ radical-cation on heating to 100°.

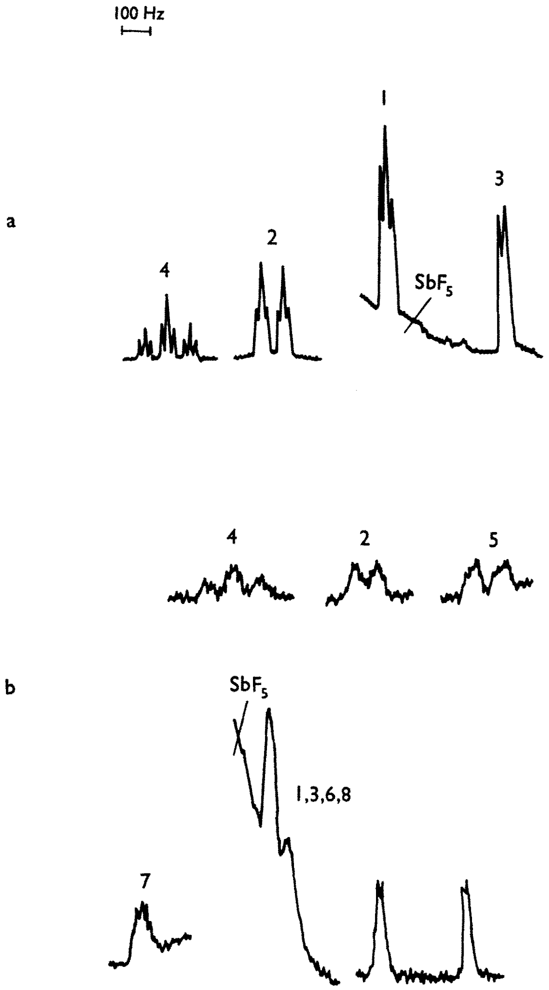


(IIc)

(IVc) (V)

The results reported here are in agreement with previous suggestions concerning the equilibrium between polyfluoroaromatic radical-cations and σ-complexes. A similar equilibrium was observed in the case of some aromatic hydrocarbons.[7] There is probably no difference in principle between the electrophilic reaction mechanisms of fluorinated and nonfluorinated aromatic compounds.

In the light of these results, it will be interesting to see whether radical cations play an important role in electrophilic substitution, addition, and other reactions of aromatic compounds, and whether one-electron transfer is the key stage in these processes.



FIGURE

(a) *Ion* IIa. (b) *Ion* IIc.

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