

Remarkably Stable Fluorinated Conjugated Cations and a Di-Cation

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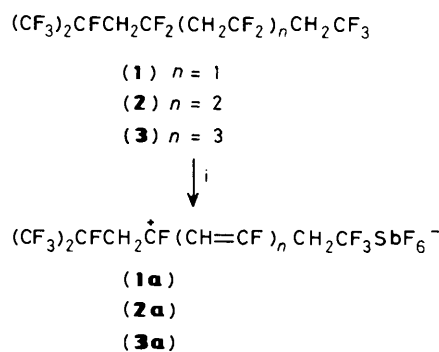
Reactions of hydrofluorocarbons with excess of antimony pentafluoride gives a series of very stable conjugated carbocations; a remarkable contiguous di-allyl, di-cation is described.

In the preceding communication¹ we illustrated the fact that dehydrofluorination of highly fluorinated systems will occur in reactions with antimony pentafluoride. Here we describe the formation of some remarkably stable carbocations, rather than the simple formation of polyenes. Olah and co-workers² have demonstrated that fluorine directly attached to charged sites, *i.e.* +C-F, is stabilising, whereas fluorine atoms at positions adjacent to the charge are massively de-stabilising, *i.e.* +C-C-F, and fluorinated allyl cations have been observed at low temperatures.^{3,4}

We now find that a series of fluorinated cations (**1a**)—(**3a**) can be generated from the precursors (**1**)—(**3**) by simply adding to the latter compounds an excess of antimony pentafluoride at room temperature (Scheme 1). Uniform solutions were obtained which gave n.m.r. spectra which did not change on storage over many weeks. Furthermore, heating (**2a**) and (**3a**) to 120°C gave the same spectra on cooling. In addition, no organic material was transferred when the ions (**1a**)—(**3a**) were exposed to high vacuum for long periods.

That ions are formed is clearly evident from the ¹³C and ¹⁹F n.m.r. spectra, *e.g.* the data for (**1a**) show an unusual range of

chemical shifts, from -182 p.p.m., for the tertiary fluorine, to +58 p.p.m. for the fluorine atoms bonded at the charged sites C-4 and C-6 (Table 1). Thus there is a massive downfield shift for fluorine at the charged sites, compared with fluorine at the more remote positions whose shifts are very similar to those for the neutral precursor (**1**). The same effects are reflected in



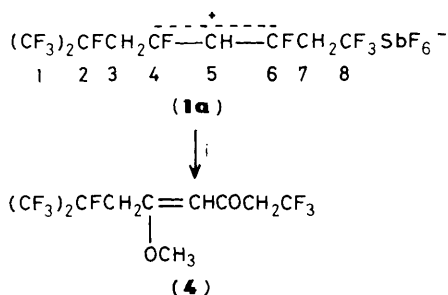
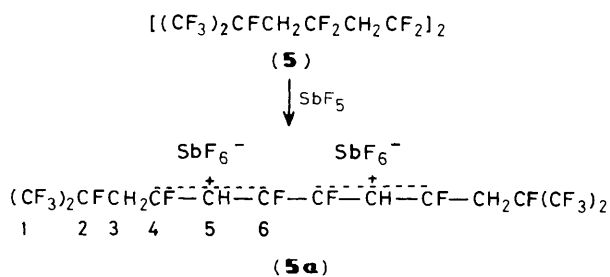
Scheme 1. Reagents and conditions: i, excess SbF₅, room temp.

Table 1. Selected n.m.r. data for (**1a**).

¹⁹ F δ/p.p.m., J/Hz	Rel. int.	Assignment	¹³ C δ, J/Hz	Assignment
-63 m	3	8	36 s	3
-78 d, 6	6	1	42 dq, 36	7
-182 m	1	2	89 dsept., 250, 29	2
+58 m	2	4,6	112 s	5
			117 dq, 26, 287	1
			119 q, 281	8
			209 d, 368	4 or 6
			211 d, 373	4 or 6

Table 2. Selected n.m.r. data for (5a).

^{19}F δ /p.p.m., J/Hz	Rel. int.	Assignment	^{13}C δ , J/Hz	Assignment
+42 m	1	4 or 6	41 s	3
+41 m	1	4 or 6	95 dm, 232	2
-79 d, 6	6	1	122 s	5
-182 m	1	2	123 qd, 287, 26	1
			210 d, 372	4 or 6
			225 dd, 371, 41	4 or 6

**Scheme 2.** Reagents and conditions: i, excess MeOH, -78°C .**Scheme 3**

the ^{13}C n.m.r. data. An upfield trend for the ^{19}F and ^{13}C chemical shifts for the charged sites is observed in comparing data for ions (1a), (2a), and (3a): ^{19}F n.m.r. δ have a range of +8 to 0 p.p.m. for (2a) and -13 to -30 p.p.m. for (3a) and the ^{13}C n.m.r. δ shows peaks at 190 and 195 for (2a) and 179, 184, 186, and 191 for (3a). These trends are, of course, understandable as charge is delocalised over a greater number of atoms.

Further evidence for the formation of carbocations follows from quenching experiments, when for example (1a) gave (4) on addition of anhydrous methanol at low temperature (Scheme 2).

The most remarkable result of all comes from reaction of (5) with antimony pentafluoride (Scheme 3) because the n.m.r. data point clearly to a unique dication (5a) (Table 2). We are unaware of any previous report of dications with adjacent charges of this type. The possibility that (5a) is a monocation which is undergoing rapid exchange is inconsistent with the data because the ^{13}C shifts for the charged sites C-4 and C-6 are even further downfield than in the ion (1a), whereas shifts similar to those observed for (2a) and (3a) would be apparent for a monocation, averaged over six carbon atoms. The coupling to fluorine, associated with the low field signals, is also quite inconsistent with rapid exchange.

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