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A Fluorinated Long-lived Allyl Cation

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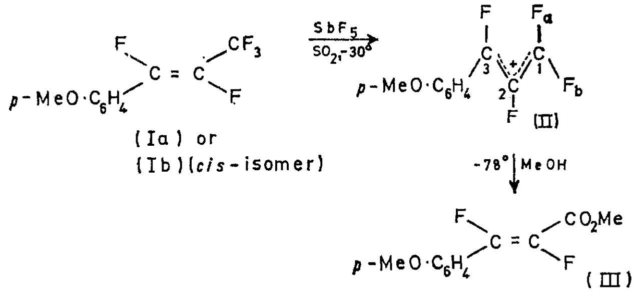
Summary A long-lived cation is observed on reaction of *trans*- or *cis*-1-*p*-methoxyphenylpentafluoropropene with antimony pentafluoride; hexafluoropropene under similar conditions gives a dimer.

STRIKING examples of the ambiguous nature of the electronic effects of fluorine in fluorocarbon systems have now emerged, *e.g.* in some circumstances fluorine, relative to hydrogen, actually raises the energy of an attached carbanion[1] through electron-pair repulsions offsetting inductive electron withdrawal $(\overset{\longleftrightarrow}{\bar{C} \longrightarrow \ddot{F}})$. Furthermore, there are now examples of long-lived carbocations with attached fluorine,[2,3] where a stabilising interaction of the electron pairs can occur $(> \overset{+}{C}\text{–}\ddot{F} \leftrightarrow > C{=}\overset{+}{F})$. Clearly, in delocalised carbocations the opportunity for this type of interaction occurs over a number of positions.

We now report, for the first time, a long-lived highly fluorinated allyl cation (II), produced by use of a technique developed by Olah and his co-workers,[2] involving reaction of antimony pentafluoride with *trans*-1-*p*-methoxyphenylpentafluoropropene (Ia) in sulphur dioxide at $-30°$. Four distinct fluorine resonances were observed as indicated in



(Ia) or
(Ib)(*cis*-isomer)
(II)
(III)

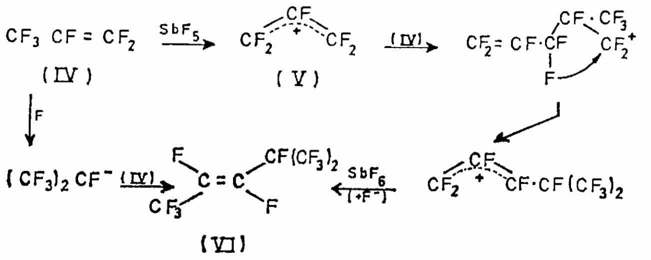
the Table, each of integral intensity one. The assignments were made on the basis of observed coupling constants, the largest value being attributed to a geminal F–F coupling, $J_{1a,1b}$. Likewise, the F-2 signal was identified by the large couplings with F-1a and -1b. Also, the relatively large value of $J_{1a,3}$ indicates that these fluorine atoms are in a *cis* arrangement and is consistent with values of *peri*-F–F

^{19}F *N.m.r. data for the ion* (II)

Chemical shift (p.p.m. from CFCl$_3$)	+64·8(F-1a);	+68·6(F-1b);	+180·6(F-2); [+6·3][a]	+53·1(F-3) [−94·7][a]		
J/Hz	$J_{1a,1b}$ 105·5	$J_{1a,2}$ 97·5	$J_{1b,2}$ 70·5	$J_{1a,3}$ 59	$J_{1b,3}$ 3	$J_{2,3}$ 22

[a] Figures in brackets represent shifts from the values for (Ia) in SO$_2$.

coupling which have been observed in bicyclic aromatic systems.[4] The *trans* relationship of F-2 and F-3 was confirmed by quenching the ion (II) with methanol at −78°, which gave exclusively the *trans*-ester (III) in 62% yield.



Further proof of ionisation came from the production of the same ion (II) from the *cis*-olefin (Ib), and subsequent quenching also gave the ester (III).

There is a difference of over 100 p.p.m. between the chemical shifts for the fluorine atoms at positions 1 and 3 and that for F-2; also, while the F-3 signal moves downfield by 94 p.p.m. from its position in the spectrum of the olefin (Ia) on ionisation, F-2 experiences a 6 p.p.m. upfield shift. This is a clear demonstration that charge is concentrated mainly at positions 1 and 3. While this is an established concept for allyl ions, there is relatively little direct experimental proof apart from recent ^{13}C n.m.r. data on some methylallyl systems.

Hexafluoropropene (IV) reacted with antimony pentafluoride under similar conditions but the perfluoroallyl cation (V) was not observed. Instead a dimer (VI) was produced. This reaction is more likely to be an electrophilic dimerisation, as observed with 1,1,1-trifluoropropene,[5] than a fluoride-ion induced process,[6] under these conditions.

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