Mass Spectrometry of Carbonium Ion Salts: 3-Halogeno-1,2,3-triphenylcyclopropanes

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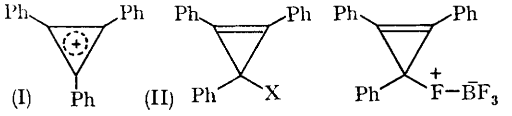
IN extending our studies of rearrangements of tetra-arylcyclopropenes to rearrangements induced by electron impact[2] it became essential to generate the triphenylcyclopropenyl cation (*a*, *m/e* 267) in the mass spectrometer in a relatively unambiguous manner. High on the list of possible cyclopropene precursors to *a* are the triphenylcyclopropenyl salts themselves, although one might have assumed that they would not be amenable to mass spectral studies because of their ionic character. We now report that triphenylcyclopropenyl bromide (Ia),[3] chloride (Ib) and, more surprisingly, fluoroborate (Ic) are volatilized into a mass spectrometer without difficulty at temperatures below their melting points to give well resolved spectra that afford useful information on the fragmentation of 3-halogeno-1,2,3-triphenylcyclopropenes and formation of cation *a* on electron bombardment.



(I) (II) (IIc)

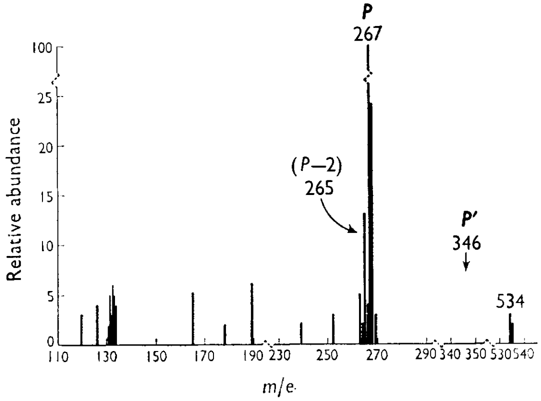
a; X=Br b; X=Cl
c; X=Br_4 d; X=F

From their physical properties, (Ia) (m.p. 269—271°), and (Ic) (m.p. 325—328°), are clearly ionic whereas the lower melting chloride (Ib)† (m.p. 141—143°) may to some extent be covalent.† The mass spectra‡ obtained for (Ia–c) are shown in the Figure. The base peak in the spectrum of (Ia) occurs at *m/e* 267 corresponding to the hydrocarbon ion $C_{21}H_{15}^+$ while the molecular ion (*m/e* 346) was not seen at either 70 or 20 ev. The $C_{21}H_{15}^+$ species shows only very little fragmentation indicative of a very stable even-electron ion to which we assign the triphenylcyclopropenyl cation structure, *a*. A molecular ion of low intensity was observed for the chloride (Ib) at *m/e* 302 although the most intense peak appeared at *m/e* 267 corresponding to loss of chloride radical, a process characterized by the appropriate metastable peak. With the exception of the weak molecular ion peaks (*m/e* 302 and 304) the spectrum of (Ib) is essentially superimposable on that of (Ia).

The mass spectrum of fluoroborate (Ic) (Figure c) is markedly different from those of (Ia) and (Ib). Fragmentation is clearly more extensive, and the base peak is found at *m/e* 286 rather than *m/e* 267, although the latter is only slightly less intense. In addition a completely new and fairly intense peak is observed at *m/e* 209. In view of the fact that loss of 19 and 77 mass units from *m/e* 286 would give rise respectively to the two most abundant fragment ions (*m/e* 267 and 209) we formulate the *m/e* 286 ion as 1,2,3-triphenylcyclopropenyl fluoride(IId) which, as a result of the strength of the C–F bond, may lose either a fluoride radical to give ion *a* or C_6H_5 to form fluorodiphenylcyclopropenyl cation (*b*, *m/e* 209) (see Scheme).

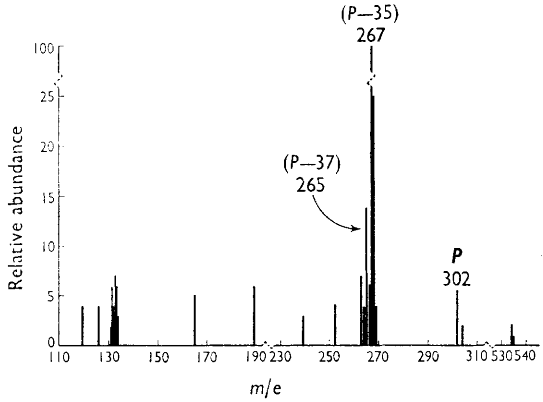
Formation of fluoride (IId) in the ion chamber may occur either thermally by decomposition of

1,2,3-Triphenycyclopropenyl bromide



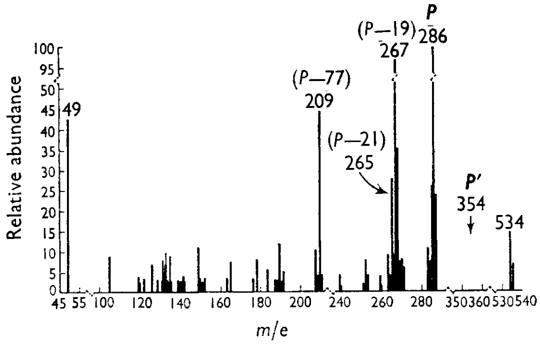
(a)

3-Chloro-1,2,3-triphenylcyclopropene



(b)

1,2,3-Triphenycyclopropenyl fluoroborate
(3-Fluoro-1,2,3-triphenylcyclopropene)



(c)

FIGURE. *Mass spectra of* 3-*halogeno*-1,2,3-*triphenylcyclopropenes*

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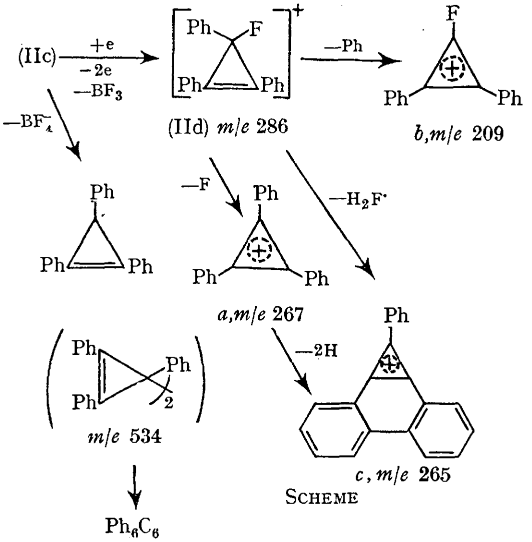
† Prepared quantitatively by reaction of triphenylcyclopropene with triphenylmethyl chloride in liquid sulphur dioxide at its boiling point, (Ib) is a colourless solid, slightly soluble in non-polar solvents such as ether and hexane, which rapidly turns yellow and otherwise decomposes on exposure to the atmosphere.

‡ The mass spectra were recorded on a Hitachi Perkin–Elmer RMU-6E instrument.

(Ic) in the insert (200°, 10^{-6} torr) or by electron bombardment of the molecular fluoroborate species (IIc) which may be regarded as slightly polarized boron trifluoride–triphenylcyclopropenyl fluoride donor–acceptor complex. We prefer the latter explanation since it was found that (Ic) sublimed unchanged above 200° at pressures less than 10^{-2} torr. In any event salts (Ia–c) serve as convenient sources of the corresponding covalent halides (IIa), (IIb), and (IId) in the mass spectrometer and the relative abundances (0, 5, and 100%) of the halogenocyclopropene ions, as well as their subsequent fragmentations, are very readily rationalized in terms of the relative ease of breaking of the carbon–halogen bond.



SCHEME

Two additional features of the spectra should be noted. The fragmentation at *m/e* 265 is presumed due to the aromatic cyclopropa-[*l*]phenanthrene ion *c*, formed by *ortho*-coupling of two phenyl rings in *a* followed by elimination of hydrogen (see Scheme).[4] A metastable peak is observed for this process in all three spectra, but it is interesting that the relative abundance of the 265 peaks is greatest in the spectrum of (Ic) where loss of H_2F from (IId) can be established by its metastable peak. The ion at *m/e* 207 in this same spectrum may be similarly accounted for by the loss of hydrogen from cyclopropenyl cation *b*. The high molecular weight species at *m/e* 534 (a dimer of *m/e* 267) is thought to be due to hexaphenylbenzene (identical fragmentation pattern to that of an authentic sample in the 300—500 mass region) which is known to arise when (Ia) is photolyzed.[5] At 20 ev, where competing fragmentation processes are diminished, the amounts of dimer produced were (Ia) 2·8, (Ib) 3·6, and (Ic) 4·7% of total ionization suggesting that dimer formation may be a function of the electron affinity of the respective carbon-bound halogens. Thus formation of hexaphenylbenzene may arise by resonance dissociative capture of an electron by the covalent halogenocyclopropene followed by coupling of two triphenylcyclopropenyl radicals to give bis(triphenylcyclopropenyl), which should instantly rearrange to Ph_6C_6 under the conditions employed (see Scheme).

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[1] M. A. Battiste, B. Halton, and R. H. Grubbs, *Chem. Comm.*, 1967, 907.

[2] M. A. Battiste and B. Halton, "Mass Spectrometry in the Tetra-arylcyclopropene Series", in preparation.

[3] R. Breslow and C. Yuan, *J. Amer. Chem. Soc.*, 1958, **80**, 5991.

[4] *Cf.* J. H. D. Eland, and C. J. Danby, *J. Chem. Soc.*, 1965, 3935; D. H. Williams, R. S. Ward, and R. G. Cooks, *J. Amer. Chem. Soc.*, 1968, **90**, 966.

[5] E. E. van Tamelen, T. M. Cole, R. Greeley, and H. Schumacher, *J. Amer. Chem. Soc.*, 1968, **90**, 1372.