Photoaddition of *cis*-Cyclo-octene to Hexafluorobenzene

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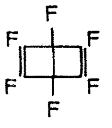
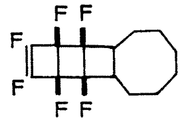
Summary Seven 1 : 1 photoadducts are formed when *cis*-cyclo-octene is irradiated in hexafluorobenzene solution with a medium-pressure mercury lamp.

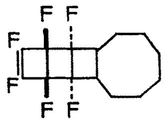
BENZENE and alkylbenzenes undergo several types of photoisomerisation reaction[1] whereas hexafluorobenzene is known only to form perfluorobicyclo[2,2,0]hexa-2,5-diene [the 'Dewar' isomer (I)] on irradiation.[2] Again in contrast with the parent hydrocarbon, the only reports of photoreactions of hexafluorobenzene with other molecules concern an uncharacterised 2 : 2 adduct with butadiene,[3] and solvent derived products from cycloalkane solutions.[4]

We now report that irradiation of a solution of hexafluorobenzene in *cis*-cyclo-octene with a medium-pressure mercury lamp at 15° under nitrogen leads to the rapid formation of seven 1 : 1 adducts (M^+ 296 for each), identified by increasing g.l.c. retention time (Carbowax 20M) as A, B, C, D, and E: D was shown by other procedures to be an unresolved mixture of three adducts. The proportions of the products A, B, C, and E remained constant throughout the irradiation at 8, 16, 32, and 29%, respectively. Pure samples of adducts A, B (m.p. 61—63°), C, and E (m.p. 61·5—63°) were isolated by chromatographic procedures. Adducts A, B, and C isomerised thermally above 200°: A and B each gave the mixture D, and C gave E.

The spectroscopic properties of adducts A and B are those expected for the *cis-endo-* and *cis-exo-*fused isomers (IIa) and (IIb) respectively. The mass spectra of the two adducts are virtually identical and the position of the =C–F stretch band in the i.r. spectrum agrees well with values reported for compound (I)[2] [A, 1750; B, 1755; (I), 1751 (vapour),[2a] and 1760 cm.$^{-1}$].[2b] Only weak end-absorption is observed in the u.v. spectra at wavelengths longer than 200 nm. Each adduct shows only three absorptions of unit intensity in the ^{19}F n.m.r. spectrum (Table) and the chemical shifts of the lowest-field pairs of fluorines are similar to that reported for the vinylic fluorines in (I) and much lower than that reported for a polyfluorinated fused five-membered ring.[5] The ^{1}H n.m.r. spectra show only saturated methine and methylene protons, but permit no conclusion about the stereochemistry of the former.


(I)


(IIa)


(IIb)

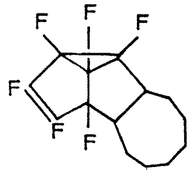
TABLE

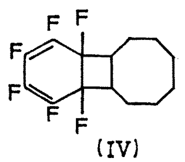
Adduct	Chemical shift in p.p.m. (up field of internal $CFCl_3$ in CCl_4 solution)	Integral
A	121, 170 and 191	1 : 1 : 1
B	123, 160 and 186	1 : 1 : 1
C	145, 147, 170, 198, 222, and 239	1 : 1 : 1 : 1 : 1 : 1
'D' (1 : 1 mixture)	154, 158, 159, 161, 164, and 187·5	1 : 1 : 1 : 1 : 1 : 1
E	141, 146, 148·5, 164·5, 190, and 195·5	1 : 1 : 1 : 1 : 1 : 1

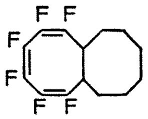
Adduct C, the major product, has six chemically non-equivalent fluorines, and must be unsymmetrical. The ^{1}H n.m.r. spectrum showed the absence of vinylic hydrogen. The two low-field resonances in the ^{19}F n.m.r. spectrum (Table) suggest the presence of olefinic fluorines in a five-membered ring, so the compound is a mono-olefin.[5] All the other fluorines are at saturated carbon atoms, and there is no evidence for a >CFH grouping (in contrast with adduct E). Particularly significant are the two very high-field fluorine absorptions which, by analogy with proton resonances, suggest the presence of a cyclopropane ring: this indication is strongly supported by the catalytic absorption of 2 mol. of hydrogen. A single strong i.r. band at 1720 cm.$^{-1}$ indicates the absence of a conjugated fluorodiene moiety as does the absence of any u.v. absorption maximum above 200 nm.; but here there is a strong end absorption (ϵ_{210} 1900, ϵ_{220} 1000 mole^{-1} l. cm.$^{-1}$ in hexane) reasonably attributable to the vinylcyclopropane chromophore (*cf.* ref. 6). These data are entirely consistent with structure (III) for adduct C.

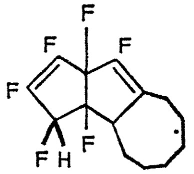
Fraction D has not yet been separated into its pure components, but g.l.c. analysis has indicated the presence of two major adducts (ratio *ca.* 1 : 1), one of which is thermally labile, and at least one minor adduct. The u.v. spectrum of a 1 : 1 mixture of the two main components (in hexane) showed λ_{max} 264 nm. (ϵ *ca.* 1500 mol.$^{-1}$ l. cm.$^{-1}$), consistent with the presence of a cyclic conjugated perfluoro-diene or -triene chromophore. The ^{19}F n.m.r. spectrum of this mixture (Table) was consistent with a 1 : 1 mixture of compounds (IV) and (V). This identification, although tentative, accords with the observed formation of these compounds by thermal rearrangement of adducts (IIa) and (IIb).

Adduct E is assigned structure (VI) on the basis of the following spectroscopic properties. The i.r. spectrum shows bands at 1698 and 1745—1752 cm.$^{-1}$ (the latter split into a doublet) in the FC=CF region. The u.v. spectrum shows only end-absorption. There are six nonequivalent fluorines, as indicated by ^{19}F n.m.r., three of which occur in the olefinic region (141, 146, and 148·5 p.p.m.). The absorptions at 141 and 146 p.p.m. both show a doublet splitting of 22 Hz., which is in the range expected for J_{vic} in a *cis*-fluoro-olefin. In the ^{1}H n.m.r. spectrum, the most characteristic feature is a doublet (J 53 Hz.) of broad triplets (J' 6 Hz.) centred at τ 4·98, which corresponds to a single proton. The remaining protons give rise to broad absorptions in the range τ 7·0—8·8. The large splitting of 53 Hz. is attributed to a geminal H–F coupling and the fluorine involved is observed as a double doublet (J 53 Hz., J' *ca.* 23 Hz) at 190 p.p.m. The formation of adduct (VI) from adduct (III) at 200° by a 1,5-hydrogen shift is exactly paralleled in the case of the corresponding hydrocarbons.[7]


(III)


(IV)


(V)


(VI)

Since the relative proportions of adducts (IIa), (IIb), (III), and (VI) are independent of the time of irradiation, these compounds appear to be primary photochemical products—a surprising conclusion in the case of adduct (VI). The observed formation of this latter from adduct (III) at 200° should involve a suprafacial 1,5-hydrogen shift: any analagous photoisomerisation would need to proceed by the sterically unattractive antarafacial pathway. Possibly compound (VI) is formed from vibrationally 'hot' adduct (III).

Irradiation of pure liquid hexafluorobenzene under the above conditions gives small amounts of the Dewar-isomer (I). Addition of *cis*-cyclo-octene, followed by continued irradiation, produces the adducts described above, but there is no appreciable change in the concentration of the Dewar-isomer (I). Since no detectable amounts of this isomer are formed when hexafluorobenzene is irradiated in excess of *cis*-cyclo-octene, it appears that the Dewar-isomer (I) is not itself a precursor of any of the photoadducts, but that one or more of its precursors is capable of being intercepted by *cis*-cyclo-octene, very feasibly in formation of adducts (IIa) and (IIb). Although no confirmed examples of this type of addition are known in benzene photochemistry (*cf.* Srinivasan, quoted in ref. 8), the symmetry considerations previously applied to benzene apply also to hexafluorobenzene.[4b,9,10] They suggest that any direct concerted formation of adducts of type (IIa), (IIb), and (IV) should involve excited species of B_{1u} symmetry, whereas adducts of type (III) should be formed *via* species of B_{2u} symmetry. Both types of excited species could well have been generated since the chosen irradiation conditions would have led to population of the first three excited singlet states of hexafluorobenzene (λ_{max} 254, 231, and 219 nm.).

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[1] H. J. F. Angus, J. M. Blair, and D. Bryce-Smith, *J. Chem. Soc.*, **1960**, 2003; K. E. Wilzbach, J. S. Ritscher and L. Kaplan, *J. Amer. Chem. Soc.*, 1967, **89**, 1031; K. E. Wilzbach and L. Kaplan, *ibid.*, 1965, **87**, 4004; H. R. Ward and J. S. Wishnok, *ibid.*, 1968, **90**, 1085.

[2] (a) I. Haller, *J. Amer. Chem. Soc.*, 1966, **88**, 2070; (b) G. Camaggi, F. Gozzo, and C. Cevidalli, *Chem. Comm.*, 1966, 313.

[3] G. Koltzenburg and K. Kraft, *Tetrahedron Letters*, 1966, 389.

[4] (a) D. Bryce-Smith, B. E. Connett, A. Gilbert, and T. E. Kendrick, *Chem. and Ind.*, 1966, 855; (*b*) I. Haller, *J. Chem. Phys.*, 1967, **47**, 1117.

[5] R. Fields, M. Green, and A. Jones, *J. Chem. Soc.* (*B*), 1967, 270.

[6] D. Bryce-Smith, A. Gilbert, and B. H. Orger, *Chem. Comm.*, 1966, 512.

[7] D. Bryce-Smith, A. Gilbert, and B. H. Orger, Abstracts of papers presented at the Symposium on Organic and Physical Aspects of Photochemistry (Chem. Soc.–R.I.C. Joint Annual Meeting), Nottingham, April 1969, 5. 19.

[8] D. Bryce-Smith, *Pure Appl. Chem.*, 1968, **16**, 47.

[9] D. Bryce-Smith and H C. Longuet-Higgins, *Chem. Comm.*, 1966, 593.

[10] D. Bryce-Smith, *Chem. Comm.*, 1969, 806.