

## Photoaddition of Ethylenes and Acetylenes to Hexafluorobenzene

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Both *cis*- and *trans*-cyclo-octene undergo stereospecific photoreactions with hexafluorobenzene to give various 1 : 1-cycloadducts which arise *via* 1,2- and 1,3-addition processes and subsequent isomerisations of the initial adducts. No products arising from 1,4-cycloaddition to the aromatic ring have been detected. Effects of irradiation wavelength, temperature, and concentration are discussed in connection with the involvement of free and complexed  $S_1$  hexafluorobenzene.

In contrast, 2,3-dimethylbut-2-ene and hexafluorobenzene gave mainly an acyclic 1 : 1 adduct formed by substitutive addition, and its dehydrofluorination product. Although maleic anhydride and maleimide readily undergo photoaddition to benzene, neither gave photoadducts with hexafluorobenzene.

Propyne and but-2-yne give cyclo-octatetraenes by photoaddition to hexafluorobenzene, and in the case of but-2-yne the precursor 1,2-cycloadduct was isolated as the sole primary product.

In general, the photoadditions to hexafluorobenzene show some points of resemblance to the corresponding processes involving benzene, but various major differences have been noted.

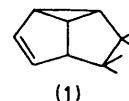
THE photophysical properties of hexafluorobenzene have been investigated in some detail,<sup>1,2</sup> and the absorptions at 254 ( $\epsilon$  175 l mol<sup>-1</sup> cm<sup>-1</sup>), 231 ( $\epsilon$  645), 219 ( $\epsilon$  460), and 194 nm ( $\epsilon$  6 250) have been assigned to states of symmetry  $B_{2u}$ ,  $B_{1u}$ ,  $B_{2u}$ , and  $E_{1u}$  respectively.<sup>2</sup> Excitation at all wavelengths shorter than 280 nm gives rise to two excited singlet states one of which rapidly decays to the fluorescent state while equilibration of the other occurs more slowly. This latter state is considered<sup>1</sup> to be responsible for the highly efficient photoisomerisation to the 'Dewar' isomer, perfluorobicyclo[2.2.0]hexa-2,5-diene.<sup>2,3</sup> (The light-induced formation of other  $C_6F_6$  isomers has been reported in a thesis,<sup>4</sup> but the structural assignments appear highly questionable.<sup>5</sup>)

We now report on our studies of the photoaddition of several ethylenes and acetylenes to hexafluorobenzene and compare the results with those reported for benzene.<sup>6</sup> Preliminary accounts of part of this work have been published.<sup>7,8</sup> Sket and Zupan<sup>9</sup> have recently reported the *cis*-1,2-photoaddition of several ethylenes and acetylenes to hexafluorobenzene. Norbornadiene and the aromatic ethylenes indene and 1,4-dihydronaphthalene gave mainly or exclusively cycloadducts *endo* with respect to the cyclobutane ring, whereas cyclopentene gave mainly a corresponding *exo*-adduct (termed *anti* in ref. 9).

### RESULTS AND DISCUSSION

During the past decade, much research effort has been devoted to the photoaddition reactions of benzene-olefin systems and the modes of addition and mechanisms of the processes are now fairly well established. 1,2-Photoaddition is generally the preferred process with relatively powerful donor and acceptor olefins while for

olefins of ionisation potentials similar to that of benzene, 1,3-addition is preferred, and leads to products of type (1) (see refs. 10 and 11 for exceptions to this). Light-



induced 1,4-cycloaddition to the aromatic ring has been observed with cyclobutene<sup>12</sup> and allenes,<sup>13</sup> and 1,3-dienes yield products which reflect both 1,4-,1'4'- and 1,3-,1'4'-cycloaddition.<sup>14</sup> An 'ene' type 1,4-acyclic addition occurs on irradiation of mixtures of benzene and tetramethylethylene.<sup>8</sup>

*Hexafluorobenzene-cis-Cyclo-octene*.—Irradiation of solutions of hexafluorobenzene and *cis*-cyclo-octene leads to a mixture of five major products which are designated A, B, C, D, and E in order of increasing g.c. retention time (Carbowax 20M). No 'Dewar'-isomer (perfluorobicyclo[2.2.0]hexa-2,5-diene)<sup>2,3</sup> was observed: in a separate experiment, the isomer was found not to react with cyclo-octene under the experimental conditions, so it seems likely that any which had been formed would have survived and been detected.

We reported in a preliminary communication<sup>7</sup> that adducts A, B, C, and E were primary products whose ratio was time invariant: we now know that this is not so. The reason for this apparent discrepancy is that in our earlier work, the use of a relatively high intensity light source (medium-pressure Hg lamp) led to the unusually rapid achievement of a photostationary state. We now report that the ratio of products is, indeed, time dependent, and at very short irradiation times with light from a low-intensity low-pressure mercury arc,

<sup>9</sup> B. Sket and M. Zupan, *J.C.S. Chem. Comm.*, 1976, 1053; 1977, 365; *Tetrahedron Letters*, 1977, 2811.

<sup>10</sup> H. G. Heine and W. Hartmann, *Angew. Chem. Internat. Edn.*, 1975, 708.

<sup>11</sup> M. F. Mirbach, M. J. Mirbach, and A. Saus, *Tetrahedron Letters*, 1977, 959.

<sup>12</sup> R. Srinivasan, *I.B.M.J. Res. Develop.*, 1971, 15, 34; J. Cornelisse and R. Srinivasan, *Chem. Phys. Letters*, 1973, 20, 278.

<sup>13</sup> D. Bryce-Smith, A. Gilbert, and B. E. Foulger, *J.C.S. Chem. Comm.*, 1972, 664.

<sup>14</sup> K. Kraft and G. Koltzenburg, *Tetrahedron Letters*, 1967, 4357 and 4723; N. C. Yang and J. Libman, *ibid.*, 1973, 1409; J. C. Berridge, D. Bryce-Smith, and A. Gilbert, *ibid.*, 1975, 2325.

<sup>1</sup> D. Phillips, *J. Chem. Phys.*, 1967, 46, 4679.

<sup>2</sup> I. Haller, *J. Chem. Phys.*, 1967, 47, 1117.

<sup>3</sup> (a) I. Haller, *J. Amer. Chem. Soc.*, 1966, 88, 2070; (b) G. Camaggi, F. Gozzo, and G. Cevidalli, *J. Chem. Soc.*, (D), 1966, 313; G. Camaggi and F. Gozzo, *J. Chem. Soc.*, (C), 1969, 489; (c) A. Bergomi and F. Gozzo, *Chimicae Industria*, 1968, 50, 745; (d) J. Fajer and D. A. Mackenzie, *J. Phys. Chem.*, 1967, 71, 784.

<sup>4</sup> Y.-C. Wang, *Diss. Abs.*, (B), 1970, 31, (3), 1219, (Ph.D. Thesis, University of New Brunswick, 1969).

<sup>5</sup> D. Bryce-Smith and A. Gilbert, *Tetrahedron*, 1976, 32, 1309.

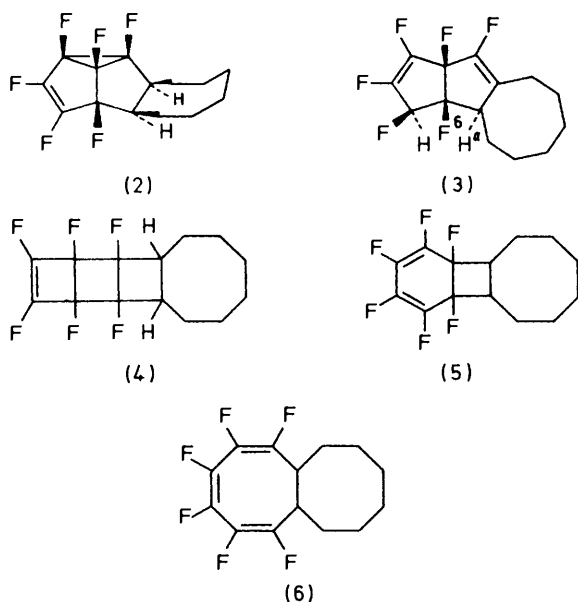
<sup>6</sup> D. Bryce-Smith and A. Gilbert, *Tetrahedron*, 1977, 33, 2459.

<sup>7</sup> D. Bryce-Smith, A. Gilbert, and B. H. Orger, *Chem. Comm.*, 1969, 800.

<sup>8</sup> D. Bryce-Smith, B. E. Foulger, A. Gilbert, and P. J. Twitchett, *Chem. Comm.*, 1971, 794.

products A and B are absent from the product mixture.\* Only the adducts C, D, and E are now considered to be primary photochemical products: A and B result from very efficient secondary light-induced rearrangement of D, and this process is thermally reversible. On the other hand, a typical preparative experiment using medium-pressure lamps gave the components A—E in the approximate proportions 2 : 4 : 8 : 4 : 7 respectively. All these products showed parent ions of  $m/e$  296 by combined g.c.-mass spectrometry, corresponding nominally to 1 : 1 adducts of the starting materials.

[Although the products are referred to as A—E in the following discussion of properties and spectra-structure relationships, it may be convenient at this stage to note in advance the following conclusions reached: A and B are stereoisomers of (4), probably (9) and (10) respectively; C is the *exo* 1,3-adduct (2); D is an inseparable mixture of (5) and (6); and E is (3).]



The mixture of products A—E distilled essentially unchanged as a colourless oil (b.p. 60—88 °C at 0.4 mmHg) which was stable over a period of several months at 0 °C. As in the case of the benzene-cyclo-octene adducts, the g.c. behaviour of the A—E mixture was sensitive to the injection block temperature. At *ca.* 300 °C, A, B, and C were absent from the eluate, but the proportions of the components D and E had increased correspondingly.

Adducts B (m.p. 61—63 °C) and E (m.p. 61.5—63 °C) were separated from the mixture by column chromatography over silica gel, and preparative g.c. afforded pure samples of A, B, C, and D. The structural assign-

\* See ref. 15 for another example of an aromatic photoaddition reaction (furan plus benzene) which is highly susceptible to the choice of light source and reaction conditions.

† All chemical shifts in the  $^{19}\text{F}$  spectra are upfield from internal  $\text{CFCl}_3$ .

<sup>15</sup> J. C. Berridge, D. Bryce-Smith, and A. Gilbert, *J.C.S. Chem. Comm.*, 1974, 964; T. S. Cantrell, *Tetrahedron Letters*, 1974, 3959; J. C. Berridge, D. Bryce-Smith, A. Gilbert and T. S. Cantrell, *J.C.S. Chem. Comm.*, 1975, 611.

ments for the 1 : 1 hexafluorobenzene-cyclo-octene adducts are largely based on the  $^{19}\text{F}$  n.m.r. spectra, but the paucity of suitable reference data has prevented an assignment of all the fluorines in every case. Many of the observed  $^{19}\text{F}$  resonances were broad and structureless owing no doubt to the many F—F (and HF) couplings possible in such polycyclic systems: further complication arises from the fact that F—F couplings are often significant (>1 Hz) over a distance of more than one intervening C—C bond.<sup>16</sup> Only the major couplings are noted in the resonances where fine structure was discernible, and no detailed analysis of the splitting patterns has been attempted. The basic  $^{19}\text{F}$  n.m.r. spectral data of the separated adducts are presented in the Table. The structures of the primary photoadducts C, D, and E are considered first.

The mass spectrum of C gave little useful information, although it is noteworthy that the parent ion ( $m/e$  296) was more abundant than in the spectra of A, B, or D. It is apparent from the  $^{19}\text{F}$  n.m.r. spectrum that this adduct has an unsymmetrical structure since the six fluorines are chemically non-equivalent. The  $^1\text{H}$  spectrum had two very broad structureless bands at 3.3—2.5 p.p.m. (2 H) and at 2—1 p.p.m. (12 H). A single intense absorption in the CF=CF region (1 720  $\text{cm}^{-1}$ ) in the i.r. spectrum indicates a larger ring fluoro-olefin than is present in hexafluoro-‘Dewar’ benzene (1 751,<sup>3a</sup> 1 760  $\text{cm}^{-1}$ <sup>3b</sup>): the relation between ring size and CF=CF stretching frequency follows the opposite trend to that observed for hydrocarbons.<sup>17</sup> The presence of only two fluorines with chemical shifts in the olefinic region<sup>16</sup> (145 and 147 p.p.m.†) and the single CF—CF i.r. absorption suggests that C is a fluorinated mono-olefin. The 1,3-adduct structure (2) is entirely consistent with these data. The chemical shifts of the CF=CF fluorines agree well with those reported for other 5-membered ring fluorines (see ref. 18, for example), and only C has very high field  $^{19}\text{F}$  resonances (222.5 and 239 p.p.m.) which can be attributable to the shielding effect exerted by the cyclopropane ring in the proposed structure (2). The u.v. spectrum of adduct C has no maximum at wavelengths longer than 200 nm, but its ‘end’ absorption is strong [ $\epsilon(200 \text{ nm}) \sim 2\,600$ ,  $\epsilon(210 \text{ nm}) = 1\,800$ , and  $\epsilon(200 \text{ nm}) = 1\,000 \text{ l mol}^{-1} \text{ cm}^{-1}$  in hexane]. The vinylcyclopropane chromophore is well known to give rise to strong absorption above 200 nm and a maximum is not always observed. The very complex i.r. absorption in C in the C—F stretching region (1 200—1 000  $\text{cm}^{-1}$ ) is not specifically assigned, but demonstrates the presence of several different types of saturated fluorines as in structure (2).

Catalytic hydrogenation of C led to the absorption of 2 mol. equiv. of hydrogen, in conformity with the proposed structure. Adduct C was quantitatively

<sup>16</sup> D. W. Mathieson, ‘Nuclear Magnetic Resonance for Organic Chemists,’ Academic Press, Oxford, 1967, p. 152.

<sup>17</sup> J. K. Brown, *Adv. Fluorine Chem.*, 1965, 4, 253.

<sup>18</sup> (a) R. E. Banks, A. C. Harrison, and R. N. Haszeldine, *J. Chem. Soc. (C)*, 1966, 2101; (b) R. Fields, M. Green, and A. Jones, *J. Chem. Soc. (B)*, 1967, 271.

<sup>19</sup>F N.m.r. spectroscopy data for the photoproducts of hexafluorobenzene and ethylenes

Compound	Chemical shift *	Relative intensity	Appearance	Assignment
(2)	145	1	†	Vinyl fluorine
	147	1	†	Vinyl fluorine
	170	1	m	
	198	1	m	
	222.5	1	complex d $J = 27$ Hz	on a cyclopropane ring Cyclopropyl fluorine
(3)	239	1	m	Cyclopropyl fluorine
	141	1	d $J = 22$ Hz	Vinyl fluorine
	146	1	d $J = 22$ Hz	
	148.5	1	d $J = 17$ Hz	
	164.5	1	†	
	190	1	dd $J = 53$ Hz, and $J' = 22$ Hz	
	195.5	1	d $J = 11$ Hz	
Isomer A of	121.5	1	m	
(4)	191	1	m	
	170	1	d $J = 13$ Hz	
Isomer B of	123	1	m	
(4)	186	1	†	
	160	1	dd $J \approx 23$ Hz, $J' \approx 15$ Hz	
Mixture D	155	1	m	Vinyl fluorine
	159	1	m	
	160	1	br s	
	161.5	1	t $J = 3$ Hz	
	164	1	m	$\geq$ C-F
(13)	187.5	1	†	
	139	1	brd	Vinyl fluorine
	142	1	d $J = 20$ Hz	
	147	1	d with further splitting $J = 20$ Hz	
	164	1	†	
178	1	dt $J = 22$ Hz, $J' = 8$ Hz		
197	1	dd $J = 55$ Hz, $J' = 22$ Hz		

Compound	Chemical shift *	Relative intensity	Appearance	Assignment
(17)	152	2	complex d	<i>o</i> -fluorine
	172	1	$J = 20 \text{ Hz}, J' = 2.5 \text{ Hz}$ t	<i>p</i> -fluorine
	177	2	$J = 20 \text{ Hz}$ td	<i>m</i> -fluorine
(18)	139	2	$J = 20 \text{ Hz}, J' = 7 \text{ Hz}$ complex t	<i>o</i> -fluorine
	150	1	$J = 20 \text{ Hz}, J' = 3.5 \text{ Hz}$ sept t	side-chain fluorine
	165	1	$J = 22 \text{ Hz}, J' = 3.5 \text{ Hz}$ tt	<i>p</i> -fluorine
	170	2	$J = 20 \text{ Hz}, J' = 3.5 \text{ Hz}$ m	<i>m</i> -fluorine

\* In p.p.m. upfield of internal  $\text{CFCl}_3$ . † Broad resonance with no clearly defined splitting.

converted into E at temperatures above 200 °C. On the assumption that this thermal conversion involves a concerted suprafacial 1,5-sigmatropic shift of the type observed with hydrocarbons of structure analogous to *exo* (2), structure (3) is to be expected for E.<sup>19</sup> It must be stressed here, however, that while the C to E conversion is a ready thermal process the ratio of these adducts throughout their formation remains constant, even at the shortest feasible irradiation times, and E is judged to be a primary reaction product. Although the far stronger chromatographic retention properties (g.l.c. and t.l.c.) of E than the other adducts initially suggested that this adduct might be a labile 2:2 adduct not detected in the mass spectrometer, Rast molecular-weight determination established the 1:1 formulation. Consistent with structure (3), adduct E has a CFH group as evidenced by the presence in the <sup>1</sup>H n.m.r. spectrum of a pair of triplets ( $J \approx 6 \text{ Hz}$ ), one at 5.45 and the other at 4.50 p.p.m. Together the triplets represent a single hydrogen which experiences a large coupling of 53 Hz: this can only be attributed to geminal H-F coupling.<sup>16,20</sup> The remainder of the <sup>1</sup>H n.m.r. spectrum consists of a small broad resonance at 2.8–2.4 p.p.m. (1 H) and a strong resonance (12 H) in the 2.4–1.2 p.p.m. region. The <sup>19</sup>F spectrum indicates the presence of six non-equivalent fluorines of which three (141, 146, and 148.5 p.p.m.) are assigned to olefinic fluorines. The large H-F coupling appears in the resonance at 190 p.p.m. ( $J \text{ 53}, J' \text{ 22 Hz}$ ). Both the lowest field resonances are doublets with a coupling constant of 22 Hz, a reasonable value for vicinal F-F coupling.<sup>16</sup> In the i.r. spectrum of E there are two bands in the =C-F region, one at 1 698  $\text{cm}^{-1}$  (m) and the other at 1 745–1 752  $\text{cm}^{-1}$  (s) which is barely resolved into two maxima. Although these bands are very similar to those observed in conjugated fluoro-olefins<sup>17</sup> (also *cf.* adduct D below), the u.v. spectrum of E has no maximum at wavelengths longer than 210 nm: the observed end-absorption is attributed to the fluorinated bridgehead olefinic bond in (3). Thus the 1 698 and *ca.* 1 748  $\text{cm}^{-1}$  absorptions are assigned to the  $\text{>C=C<}_F$  and  $\text{F>C=C<}_F$  moieties in (3) respectively. Consistent with structure (3), adduct E consumed 2

<sup>19</sup> R. Srinivasan, *Tetrahedron Letters*, 1971, 4551.

<sup>20</sup> E. F. Mooney, 'An Introduction to <sup>19</sup>F N.m.r. Spectroscopy,' Heyden/Sadtler, 1970.

mol. equiv. of hydrogen on catalytic hydrogenation. To account for the apparent formation of E as a 'primary' product, it seems necessary to propose the formation of a vibrationally excited ('hot') form of adduct C which rearranges to E before collisional deactivation occurs.

Primary adduct D was isolated from the mixture by preparative g.c. Close inspection by both analytical g.c. and t.l.c. showed that D isolated in this way was a 1:1 mixture of two components ( $D_1$  and  $D_2$ ). In the irradiated solution, however, although D gives a chromatogram with the same two components, the approximate ratio is here 1:6 at low (<200 °C) injection and 1:1 at high (>250 °C) injection block temperature. From practical considerations it was found most convenient to work with the 1:1 mixture of the adducts as all attempts to obtain pure samples of  $D_1$  and  $D_2$  by chromatographic procedures resulted in some decomposition and only slight enrichment of the mixture in one or other of the adducts. The 1:1 adduct mixture D had u.v. absorption maximum at 264 nm [ $\epsilon(\text{hexane}) = \text{ca. } 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$ ] which is in the absorption region for cyclohexa-1,3-diene and cyclo-octa-1,3,5-triene, and is very similar to the value reported for a perfluoro-bicyclo[4.3.0]nona-1,3,7-triene.<sup>18a</sup> This datum along with the three i.r. bands shown by D in the 1 700–1 740  $\text{cm}^{-1}$  region (1 742s, 1 738sh, and 1 693m  $\text{cm}^{-1}$ ) strongly indicates the presence of a conjugated fluoro-olefin system. Attempts to trap out a compound with such a structural moiety with donor and acceptor olefins (including tetracyanoethylene, maleic anhydride, vinylene carbonate, and ethyl vinyl ether) failed under conditions which did not cause decomposition of the fluorocarbon. Likewise crystalline derivatives were not obtained following irradiation of D with either duroquinone<sup>21</sup> or with pentacarbonyliron,<sup>22</sup> and treatment of the mixture with tetrakis(triphenylphosphine)platinum in refluxing benzene<sup>23</sup> also resulted in the recovery of starting materials only.

It has transpired however that identification of  $D_1$

<sup>21</sup> G. Koltzenburg, K. Kraft, and G. O. Schenck, *Tetrahedron Letters*, 1965, 303.

<sup>22</sup> R. L. Hunt, D. M. Roundhill, and G. Wilkinson, *J. Chem. Soc. (A)*, 1967, 982.

<sup>23</sup> M. Green, R. B. L. Osborn, A. J. Rest, and F. G. A. Stone, *J. Chem. Soc. (A)*, 1968, 2525; B. L. Booth, R. N. Haszeldine, and N. I. Tucker, *J. Organometallic Chem.*, 1968, 11, 5.

and  $D_2$  could be achieved without resolution of the mixture. Thus the  $^{19}\text{F}$  n.m.r. spectrum of the ( $D_1 + D_2$ ) mixture has six resonances all of approximately unit intensity: five of these resonances are close to that of hexafluorobenzene. The remaining high-field resonance is undoubtedly due to tertiary aliphatic fluorine. The spectrum may be nicely explained on the basis of a 1 : 1 mixture of  $D_1$  and  $D_2$  in which each component gives rise to three fluorine resonances corresponding to three pairs of equivalent fluorines in each compound. One component then has four vinylic fluorines and two tertiary aliphatic fluorines, whereas all the fluorine atoms in the other component are vinylic. Both  $D_1$  and  $D_2$  must accordingly be symmetrical as far as the fluorine substitution is concerned. It was observed that irradiation of the mixture D at 254 nm led to the rapid quantitative conversion to a mixture of A and B, the proportions of which were exactly the same as those from direct irradiation of hexafluorobenzene and cyclooctene. This photoprocess was thermally reversible. As discussed below, A and B are stereoisomers of the tetracyclic structure (4). This information, taken in conjunction with the spectral data, suggests that the two components of D have structures (5) and (6). We have no information on the stereochemistry of (5). The most obvious allowed thermal isomerisation of (4) (A and B) involves ring opening of the bicyclohexene moiety to the cyclohexadiene (5). The analogous isomerisation of perfluorocyclobutene is known.<sup>24</sup> Structure (5) would account for two of the low-field and the high-field  $^{19}\text{F}$  resonances, and is fully consistent with the i.r. and u.v. spectra. The three remaining low-field  $^{19}\text{F}$  resonances in D are accounted for by structure (6). Isomerisations of the types (5) to (6) and (6) to (5) have numerous literature precedents.

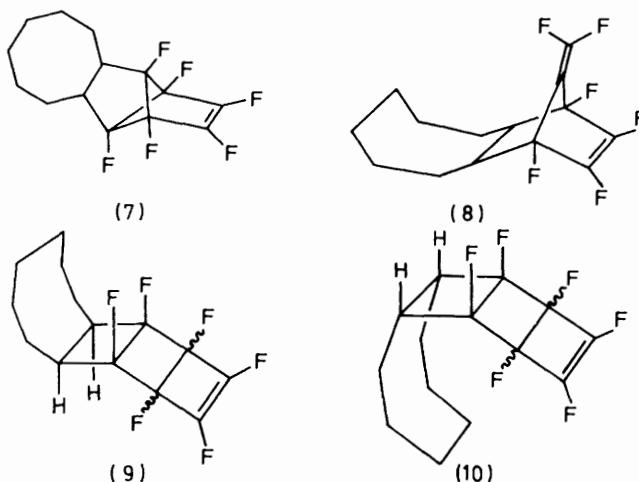
As outlined earlier, A and B result from a photo-reaction of the mixture D, and their structures are therefore highly relevant to the structural assignment of the components of D.

The mass spectra of A and B are virtually indistinguishable, and indicate closely related structures. Both compounds have only three  $^{19}\text{F}$  resonances, each of unit intensity: three pairs of equivalent fluorine atoms are, therefore, present in each. The lack of any significant u.v. absorptions above 200 nm in hexane [ $\epsilon(205) \approx 300 \text{ l mol}^{-1} \text{ cm}^{-1}$ ] excludes structures having conjugated diene moieties, and the intense i.r. absorption around  $1750 \text{ cm}^{-1}$  [A,  $1750$ ; B,  $1755 \text{ cm}^{-1}$  ( $\text{CCl}_4$  solution)] is characteristic of the  $\text{CF}=\text{CF}$  group: these values are very similar to those reported for perfluoro-‘Dewar’ benzene ( $1752$ ,<sup>3a</sup>  $1760 \text{ cm}^{-1}$ <sup>3b</sup>). Similarly the lowest field  $^{19}\text{F}$  resonances in A and B are almost identical with that ( $121$ ,<sup>3a</sup>  $123$ <sup>3b</sup>) reported for this ‘Dewar’ isomer, and approximate to the values reported for other bicyclo[2.2.0]hex-2-ene derivatives.<sup>25</sup> The small splitting observed in both adducts ( $J_{\text{max}} \approx 10 \text{ Hz}$ ) for the

<sup>24</sup> R. N. Haszeldine and J. E. Osborne, *J. Chem. Soc.*, 1955, 3880.

<sup>25</sup> M. G. Barlow, R. B. Haszeldine, and R. Hubbard, *J. Chem. Soc. (C)*, 1971, 90.

vicinal  $\text{CF}=\text{CF}$  coupling (normally 30–60 Hz) has been shown to be characteristic of the fluorinated cyclobutene system.<sup>26</sup> Two possible structures (7) and (8) for these



adducts can be discounted both from the above data and the lack of  $^{19}\text{F}$  resonances attributable to vinylic fluorines in a 5-membered ring<sup>18</sup> and in a  $\text{C}=\text{CF}_2$  group:<sup>27</sup> this latter group would also have a distinctive i.r. absorption in the  $1800 \text{ cm}^{-1}$  region,<sup>27</sup> and this was not observed in spectra of either A or B. All the data presented so far are consistent with isomers of structure (4), viz. (9) and (10), for the present two adducts, but an unambiguous assignment of the absolute stereochemistry of each adduct is difficult. From comparison with the  $^{19}\text{F}$  data for systems similar to (4),<sup>25</sup> we assign the highest field resonances in A and B (191 and 186 p.p.m. respectively) to fluorine in the allylic positions, and the resonances at intermediate field (170 and 160 p.p.m. respectively) to the  $\beta$ -fluorines. Such assignments can explain features in the  $^1\text{H}$  n.m.r. spectra. The  $^1\text{H}$  spectrum of A has a small very broad resonance at 2.75 p.p.m. (2 H), and two broad resonances at 1.8 and 1.5 p.p.m. (12 H). In the spectrum of B, the lowest field resonance is split into two broad peaks at 3.2 p.p.m. (1 H) and 2.8 p.p.m. (1 H) corresponding to a chemical-shift difference or coupling of ca. 23 Hz. The remaining protons give rise to two strong absorptions at 1.9 (4 H) and 1.5 p.p.m. (8 H). The largest splitting observed in the  $^{19}\text{F}$  spectrum of B is in the resonance at 160 p.p.m. which is a poorly resolved double doublet ( $J \approx 23 \text{ Hz}$ ,  $J' \approx 15 \text{ Hz}$ ). If the 23 Hz splitting observed in both the  $^1\text{H}$  and  $^{19}\text{F}$  spectra of B arise from H–F coupling, then the value of 23 Hz is reasonable for a vicinal coupling where the dihedral angle is almost zero.<sup>28</sup> This fact serves to define the relative stereochemistry of the cyclo-octane ring and is further evidence for the assignment of the absorption at 160 p.p.m. to the  $\beta$ -fluorines in (4). There are several stereoisomers of

<sup>26</sup> L. Cavalli, *J. Chem. Soc. (B)*, 1967, 384.

<sup>27</sup> R. E. Banks, W. R. Deem, R. N. Haszeldine, and D. R. Taylor, *J. Chem. Soc. (C)*, 1966, 2051.

<sup>28</sup> K. L. Williamson, Y.-F. Li, F. H. Hall, and S. Swager, *J. Amer. Chem. Soc.*, 1967, **89**, 5678.

such a structure as (4) and on the basis of the available data it is not possible to assign A and B to particular isomers. It is, however, considered that the partial stereochemical structures (9) and (10) may reasonably be assigned to A and B respectively. Chemical support for these assignments is, of course, provided by the expected thermal conversion to, and photochemical formation from, D.

Thus *cis*-cyclo-octene undergoes both 1,2- and 1,3-photocycloaddition to hexafluorobenzene, as it does to benzene.<sup>6</sup> It has been reported that the relative efficiencies of the 1,2- and 1,3-modes of cycloaddition of olefins to benzene depend upon the electron donor or acceptor power of the olefin relative to the aromatic, and ionisation potentials of the reactants have been used as a measure of this property.<sup>29</sup> In the present case, there is a significant difference in ionisation potential between the aromatic and the olefin (I.P. *ca.* 10.4 and 8.75 eV respectively), so it is not surprising that some 1,2-cycloaddition products are formed. The quantum yield ratio (1,2-/1,3) was 0.60 (*cf.* 0.24 for the corresponding additions to benzene<sup>29</sup>). In the light of the data for benzene additions,<sup>29</sup> we should, however, have expected a somewhat higher value of this ratio, and the failure to observe 1,3-cycloaddition to cyclopentene (I.P. 9.02 eV) is surprising.<sup>9</sup> It may well be that electron affinities can provide a better correlation than ionisation potentials with the photochemical behaviour in these systems.<sup>11</sup> The total quantum yield for all 1:1 products from irradiation of equimolar mixtures of the reactants was 0.51, but with light of wavelength 231 nm this was increased to 0.74 although there is little change in the ratios of products (0.57: *cf.* 0.60 above). At both these wavelengths, C<sub>6</sub>F<sub>6</sub> is the only absorbing species in the system, but at the shorter wavelength the S<sub>0</sub>→S<sub>2</sub> transition is involved to a greater extent. The S<sub>0</sub>→S<sub>1</sub> and S<sub>0</sub>→S<sub>2</sub> bands in hexafluorobenzene overlap to a considerable extent, unlike those in benzene, and irradiation of hexafluorobenzene at wavelengths shorter than 280 nm leads to some population of both the S<sub>1</sub> and S<sub>2</sub> states.<sup>1</sup> We doubt, however, whether the higher quantum yield at the shorter wavelength results from direct addition to the S<sub>2</sub> state since orbital symmetry considerations suggest that the higher quantum yield would have been associated with marked changes in the product ratios.<sup>5,30</sup> It seems more likely that addition occurs more readily at the higher vibrational levels of the S<sub>1</sub> state which would be populated at the shorter wavelength. In contrast, the photoisomerisations of hexafluorobenzene and benzene to their

'Dewar' forms appear to occur directly from the S<sub>2</sub> state, in accordance with orbital symmetry considerations.<sup>5,6,30</sup>

Investigations into the question of singlet or triplet intermediates have been complicated by the lability of common organic triplet quenchers in this system. But since oxygen has no apparent effect on the efficiency or course of the reaction, and naphthalene is ineffective as a sensitizer,\* we consider that the products arise from S<sub>1</sub> hexafluorobenzene, analogously to photoadditions of alkenes to benzene.<sup>6</sup> 1,3-Photoaddition of olefins to benzenoid rings is an allowed concerted process from the <sup>1</sup>B<sub>2u</sub> (S<sub>1</sub>) state of the aromatic whereas 1,2-attack requires either the S<sub>2</sub> or T<sub>1</sub> states for a concerted addition, or a degree of charge-transfer.<sup>30</sup> The relative quantum yields of 1,2-, 1,3-, and 1,4-photoaddition of simple olefins to benzene are independent of concentration, and from this it has been suggested that all three modes of reaction arise from the same precursor, probably the S<sub>1</sub> benzene-S<sub>0</sub> olefin exciplex:<sup>33,34</sup> it is also reported that the best way of obtaining the 1,2-adduct in practice is to irradiate mixtures containing high proportions of the olefin.<sup>33</sup> We have carried out similar concentration studies with the hexafluorobenzene-*cis*-cyclo-octene system using 254 nm radiation and the results are in marked contrast with those obtained for the benzene system. Thus while the quantum yields of the products (2) and (3) remain approximately constant over the range 10–90 mol % of C<sub>6</sub>F<sub>6</sub>, the yield of 1,2-adducts increases by 50% from 10 to 50 mol % C<sub>6</sub>F<sub>6</sub>, and more than doubles in passing from 50 to 90 mol % C<sub>6</sub>F<sub>6</sub>. These results tend to suggest that 'dark' complexation between the cyclo-octene and hexafluorobenzene may be more important in 1,2- than in 1,3-cycloaddition. It is true that the absorption spectrum of a mixture shows no sign of a charge-transfer band, but neither does the spectrum of a mixture of benzene and hexafluorobenzene despite the fact that a crystalline 1:1 molecular complex between these can readily be isolated.<sup>35</sup> Thus the idea of complexation between cyclo-octene and hexafluorobenzene seems intrinsically reasonable. Since any complex formed is non-absorbing, the results indicate that 1,3-cycloaddition<sup>36</sup> can occur with similar efficiency by excitation of either 'free' or 'complexed' hexafluorobenzene. On the other hand, the observation that 1,2-cycloaddition is favoured by increased proportions of hexafluorobenzene implies that the 1,2-process occurs more readily by excitation of 'free' hexafluorobenzene and/or that a complex containing more than 1 mol.

<sup>30</sup> D. Bryce-Smith, *Chem. Comm.*, 1969, 806.

<sup>31</sup> D. Bryce-Smith, A. Gilbert, and P. J. Twitchett, *J.C.S. Chem. Comm.*, 1973, 457.

<sup>32</sup> R. B. Cundall and D. A. Robinson, *J.C.S. Faraday II*, 1972, 1691.

<sup>33</sup> K. E. Wilzbach and L. Kaplan, *J. Amer. Chem. Soc.*, 1971, **93**, 2073.

<sup>34</sup> R. C. Dougherty, *J. Amer. Chem. Soc.*, 1971, **93**, 7187.

<sup>35</sup> See for example M. E. Baur, C. M. Knobler, D. A. Horsma, and P. Perez, *J. Phys. Chem.*, 1970, **74**, 4594; R. J. Powell and F. L. Swinton, *J. Chem. Thermodynamics*, 1970, **2**, 87, 95, and 105; P. R. Hammond, *J. Chem. Soc. (A)*, 1968, 145.

<sup>36</sup> D. Bryce-Smith, *Pure and Appl. Chem.* 1973, **34**, 193.

\* We have previously observed that naphthalene can photosensitise the reaction of hexafluorobenzene with benzene.<sup>31</sup> The only exothermic energy process available appears to involve naphthalene (S<sub>1</sub>) and C<sub>6</sub>F<sub>6</sub>(T<sub>1</sub>). This suggests the novel phenomenon whereby an exciplex of naphthalene (S<sub>1</sub>) and C<sub>6</sub>F<sub>6</sub>(S<sub>0</sub>) decays to naphthalene (S<sub>0</sub>) and C<sub>6</sub>F<sub>6</sub>(T<sub>1</sub>) possibly aided by spin-orbit perturbation induced by the combined effects of six fluorine atoms. Such a suggestion recalls Cundall and Robinson's proposal that the benzene excimer dissociates to S<sub>0</sub> plus T<sub>1</sub> benzene.<sup>32</sup>

<sup>29</sup> D. Bryce-Smith, A. Gilbert, B. H. Orger, and H. M. Tyrrell, *Chem. Comm.*, 1974, 334.

equiv. of hexafluorobenzene per mol. equiv. of cyclo-octene is involved.

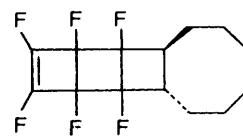
The photoaddition of *cis*-cyclo-octene to hexafluorobenzene at 254 nm exhibits an interesting temperature dependence (which is not observed in the corresponding photoaddition to benzene<sup>37</sup>). Thus although the quantum yield for 1,3-addition [formation of (2) + (3)] is independent of temperature over the range 16–75 °C, the quantum yield of the 1,2-adduct and derived products is almost doubled at the higher temperature, *i.e.* increased from 0.19 to *ca.* 0.36. Effects of increased temperature will be associated with an increased rate of some thermal component of the overall process. The observed temperature effect on 1,2-addition implies a thermal activation energy of *ca.* 8 kJ mol<sup>-1</sup>. This would be consistent with the formation of a weak molecular complex by the electronically excited species in an essentially second-order process, *e.g.* an exciplex, which then transforms with a lower activation energy into the 1,2-adduct. The essential absence of a temperature effect in the corresponding 1,3-addition implies a zero thermal activation energy for transformation *via* any quasi-second-order process; in other words, increased translational, as distinct from vibrational, energy of this order promotes the 1,2-addition, but not the 1,3-addition.

Passing to the effects of wavelength on these processes, we may first note that the quantal energy at 231 nm is some 50 kJ mol<sup>-1</sup> greater than that at 254 nm, *i.e.* approximately six-fold greater than the collisional activation energy for 1,2-addition. In contrast with the above thermal activation, reducing the wavelength of excitation tends selectively to populate higher vibrational levels, so it may be concluded that both 1,2- and 1,3-addition occur more readily from these in quasi-unimolecular processes prior to normalisation of the energy distribution. Complexation may well occur *en route* to the adducts, but if it does it is not rate-determining: we may suppose that it is the vibrational energy level of the excited species which determines the rate or quantum yield. On the other hand, the 1,2-addition is evidently promoted by increase in temperature because of the 8 kJ mol<sup>-1</sup> activation energy for formation of a necessary precursor complex: the 1,3-addition has no significant activation energy for any complex formation which may be involved, but occurs more readily from the higher vibrational levels of the electronically excited species, probably S<sub>1</sub> hexafluorobenzene, as is already known for similar 1,3-photoadditions to benzene.

Some ethylenic compounds other than *cis*-cyclo-octene have been employed in order to investigate the possibility that the reaction mode may depend on the electron donor character of the ethylene (*cf.* benzene<sup>6</sup>).

*Hexafluorobenzene-trans-Cyclo-octene.*—Irradiation of mixtures of C<sub>6</sub>F<sub>6</sub> and *trans*-cyclo-octene under conditions similar to those employed for the *cis*-isomer gave at least seven 1 : 1 adducts (*M*<sup>+</sup> 296) of the starting materials, together with hydrogen fluoride, brown polymeric

material, and a white polymer having the empirical formula C<sub>4</sub>H<sub>7</sub>.<sup>\*</sup> Only three of the adducts were found to be primary products, although the remainder were formed very rapidly. The <sup>19</sup>F n.m.r. spectrum of the mixture had 36 resonances from 116 to 232 p.p.m. upfield of internal CFCl<sub>3</sub>. Chemical and chromatographic separation of the adduct mixture proved extremely difficult and only two of the products were obtained sufficiently pure for spectroscopic examination to be meaningful. One of these was a secondary product and from its i.r., u.v., and n.m.r. spectra and a comparison with those of (9) and (10) from *cis*-cyclo-octene-C<sub>6</sub>F<sub>6</sub>, this adduct is assigned structure (11). We have no evidence on the stereochemistry of (11) except at the point of fusion with



(11)

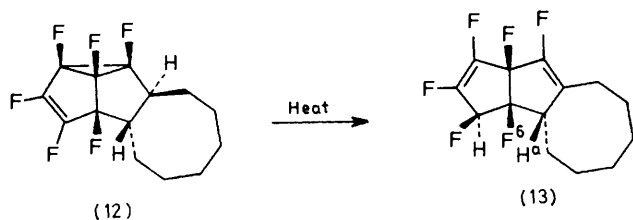
the cyclo-octane ring and for the two adjacent fluorine atoms. Resonances at 120 and 186 p.p.m. in the <sup>19</sup>F spectrum are assigned to the olefinic and allylic fluorines in (11) respectively. The <sup>19</sup>F resonances of the two fluorine atoms immediately adjacent to the C<sub>8</sub> ring appear as two separate one-fluorine signals at 153 and 184 p.p.m. These fluorines in (11) are sufficiently close to the unsymmetrical position of *trans*-fusion of the cyclo-octane ring for their nuclear environments to be significantly different, so two signals are to be expected, provided that the two fluorine atoms are *cis* with respect to each other.

The other adduct isolated in a pure state was apparently a primary product and had the longest g.c. retention time of all: in this respect, and in the <sup>19</sup>F n.m.r. spectrum (see Table), it is reminiscent of (3) from *cis*-cyclo-octene. It is believed to arise *via* the 1,3-adduct (12), and is assigned structure (13) from the following evidence. The <sup>1</sup>H n.m.r. spectrum of (13) exhibits two resonances, *viz.* a broad absorption at 3.0–1.0 p.p.m. (13 H) and a doublet centred at 5.0 p.p.m. (1 H). The doublet splitting of 55 Hz is typical for a geminal CHF coupling.<sup>20</sup> The i.r. and u.v. spectra of (13) and (3) are closely similar. As we have previously discussed, the formation of (3) is considered to arise *via* a thermally allowed suprafacial 1,5-hydrogen shift in a vibrationally 'hot' molecule of the 1,3-adduct. The

\* This polymer [*M* = *ca.* 1700 (Rast)] has been shown to arise *via* a rather surprising *thermal* reaction between hexafluorobenzene and *trans*-cyclo-octene which even occurs slowly under nitrogen or air at 20 °C. Although it contains no fluorine or aromatic groups, it does not form in the absence of hexafluorobenzene. The n.m.r. spectrum shows a single broad structureless band centred at 1.4 p.p.m. The polymer decomposes above 80 °C to give mainly a *ca.* 1 : 1 mixture of *cis*- and *trans*-cyclo-octenes. It is soluble in chloroform, slightly soluble in cyclohexane, and essentially insoluble in methanol and carbon tetrachloride.

<sup>37</sup> B. H. Orger, Ph.D. Thesis, Reading University, 1969.

stereochemical structure of product (13) may be inferred on the reasonable assumption that the genesis of this compound is similar to that of (3). Two modes of 1,3-addition of *trans*-cyclo-octene to hexafluorobenzene can occur in which olefin stereochemistry is preserved:<sup>6</sup> only one of these adducts [*i.e.* (12)] is able to undergo a suprafacial thermal 1,5-prototropic rearrangement to (13). Compounds (13) and (3) differ only in the stereochemistry of the bridgehead hydrogen ( $H^a$ ) so only  $F^6$  has a significantly different environment in the two products. Further the  $H^a-F^6$  coupling in (13) would be



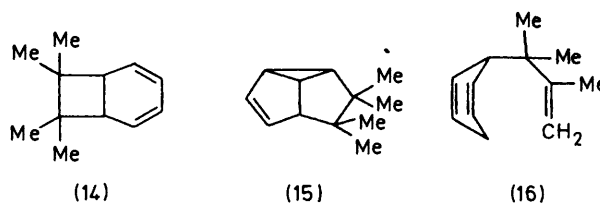
expected to be stronger than that in (3) where models indicate that the dihedral angle  $H-C-C-F$  approaches  $90^\circ$ .<sup>28</sup> This consideration allows assignment of  $F^6$  to the 178 p.p.m. resonance in (13) and to the 195.5 p.p.m. resonance in (3). The assignments of fluorine resonances are summarised in the Table.

Although meaningful structural data for the other 1:1 adducts from *trans*-cyclo-octene could not be obtained, two further points may be made. First, none of the products from the *cis*- and *trans*-cyclo-octenes was common to both photo-processes. This fact provides a further strong indication that the stereochemistry of the cycloalkene is retained in both processes and that the various reactions occur by concerted or quasi-concerted processes.

Secondly, whereas product (13) constitutes 50% of the entire product mixture from the *trans*-cycloalkene, the corresponding product (3) from *cis*-cyclo-octene constitutes only 29%. Since it is obviously difficult to conceive fully concerted pathways for the formation of (3) and (13) by direct photoadditions of the cycloalkenes to hexafluorobenzene, we assume for (13)—as was shown for (3)—the prior formation of a 1,3-adduct. Although this adduct (12) could not be isolated, its presence in the product mixture is suggested by the observation of  $^{19}F$  resonances up to 232 p.p.m. [ $F$  on a cyclopropane ring: *cf.* 198, 222, and 239 p.p.m. for (2)].

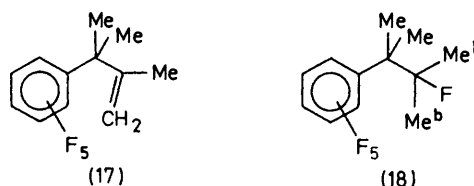
**Experiments with Donor and Acceptor Ethylenes.**—Irradiation of benzene with the electron donor 2,3-dimethylbut-2-ene gave three photoproducts (14), (15), and (16).<sup>8</sup> The 'ene-type' adduct (16) is unique in benzene photochemistry (although Dr. R. J. Forrester has obtained a similar product from 2-methylbut-2-ene, but not from *cis*- or *trans*-but-2-ene<sup>38</sup>) and prompted a similar investigation with hexafluorobenzene. Likewise, the behaviour of the acceptors maleic anhydride and maleimide has been studied in view of the well known photoreactions of these compounds with benzene.<sup>6</sup>

**Hexafluorobenzene and 2,3-Dimethylbut-2-ene.**—Irradiation of an equimolar mixture of the above compounds led to the formation of hydrogen fluoride and two



products assigned the structures (17) and (18), the relative proportions (1:7 respectively) of which were time invariant. These products constituted approximately 80% of the total reaction mixture: several minor components were present, and from m.s.-g.c. at least two of these were evidently 1:1 adducts of the starting materials. It proved only practical, however, to investigate the products (17) and (18).

The minor product (17) had a molecular weight ( $m/e$  250) corresponding to a 1:1 adduct of the starting materials minus HF, whereas that of the major component (18) was 270 corresponding to a 1:1 adduct of  $C_6F_6$  and 2,3-dimethylbut-2-ene.



The  $^{19}F$  n.m.r. spectrum of (17) (see the Table) is typical for a pentafluorophenyl derivative, but with some long-range coupling of the *ortho*-fluorines to protons on a side chain. The coupling constants are in accord with literature values for pentafluorophenyl systems,<sup>39</sup> but the range of chemical shifts extends beyond that generally quoted (132—174 p.p.m.).<sup>20</sup> The shifts do, however, increase in the order *ortho* < *para* < *meta*, a rule to which there are few known exceptions in the literature. The  $^1H$  n.m.r. spectrum is consistent with the presence of three methyl groups [1.73 (3 H, t) and 1.61 p.p.m. (6 H, t)], two of which are identical, and one =CH<sub>2</sub> group [4.9 p.p.m. (2 H, partially resolved quartet)]. Structure (17) is fully consistent with these n.m.r. data, and is supported by the i.r., u.v., and mass spectra (see Experimental section).

The  $^{19}F$  n.m.r. spectrum (see the Table) of the adduct (18) is again consistent with the presence of a pentafluorophenyl group. The regular septuplet at 150 p.p.m. suggests the structural moiety  $Me_2CF$ , and the coupling constant of 22 Hz is comparable with the three-bond

<sup>38</sup> J. Forrester, Ph.D. Thesis, Reading University, 1977.

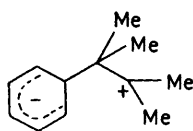
<sup>39</sup> R. Fields, J. Lee, and D. J. Mowthorpe, *J. Chem. Soc. (B)*, 1968, 308.



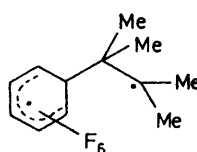
H-F coupling in  $\text{Me}_3\text{CF}$  of 20.4 Hz.<sup>40</sup> The chemical shift is not within the usual range for open-chain tertiary fluorines, but the proximity of a pentafluorophenyl group could account for this. The  $^1\text{H}$  n.m.r. spectrum shows only the presence of two different types of methyl group. The observed 22 Hz coupling on the methyl groups b is certainly due to the tertiary aliphatic fluorine atom, and it is suggested that the 3.5 Hz triplet at 1.65 p.p.m. in the  $^1\text{H}$  n.m.r. spectrum results from coupling with the *ortho*-fluorines. The septuplet at 150 p.p.m. in the  $^{19}\text{F}$  spectrum also has a 3.5 Hz triplet coupling, and this may arise from a 5-bond or 'through-space' interaction with the *ortho*-fluorines. The complexity of the later signal may be accounted for by these side-chain couplings, although the *meta*-signal is also not first order. Again the i.r., u.v., and mass spectra substantiate the structural assignment.

Both (17) and (18) appear to be primary photochemical products in that the ratio is invariant with time down to the shortest feasible irradiation periods. This is a surprising conclusion in the case of (17). Adduct (18) may be expected to undergo ready thermal elimination of HF, and indeed at high injection block g.c. temperatures ( $>200^\circ\text{C}$ ), the proportion of (17) increases at the expense of (18). As with compounds (3) and (13), product (17) could, in principle, arise from a thermally non-equilibrated precursor, in this case (18).

In the photoreaction of 2,3-dimethylbut-2-ene with benzene, the major product has structure (16), and this is known to be formed *via* a non-concerted proton-catalysed 'ene'-reaction involving a polar intermediate, possibly (19).<sup>8</sup> In contrast, the presence of traces of



(19)



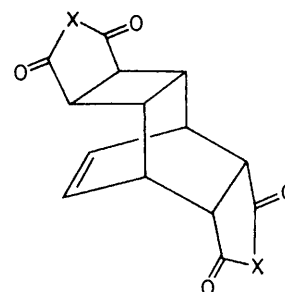
(20)

trifluoroacetic acid or of methanol has little effect on the present reaction, so it seems unlikely that an intermediate analogous to (19) is involved. A 1,3-fluorine shift in the diradical (20) could however provide an attractive route to product (18), and loss of HF from this diradical offers a further feasible mechanism for the formation of (17). Since hexafluorobenzene forms cycloadducts with both *cis*- and *trans*-cyclo-octenes, the failure to detect any corresponding adducts as major products in the present system is surprising. It is possible that some of the minor reaction products which were not isolated may be such adducts, but the considerable preponderance of (18) remains indisputable.

\* The irradiations described in refs. 9 and 45 were carried out with cyclohexane solutions, so it is a little surprising that the authors do not mention the formation of cyclohexylpentafluorobenzene and related products which are readily obtained by irradiation of cyclohexane and hexafluorobenzene alone.<sup>46</sup>

<sup>40</sup> J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution N.M.R.', Pergamon, Oxford, 1966, vol II, p. 880.

*The System Hexafluorobenzene-Maleimide and Hexafluorobenzene-Maleic Anhydride.*—Maleic anhydride and maleimide give 2:1-photoadducts of structure (21) with benzene, the former by charge-transfer excitation, and the latter by direct excitation of maleimide.<sup>6</sup> Since solutions of maleic anhydride or maleimide in hexafluorobenzene show no charge-transfer absorption, the failure of maleic anhydride to form a photoadduct is not



(21) X = O or NR

unduly surprising, but the similar failure of maleimide to add following direct excitation of the imide is less readily explained. The only products isolated were the known *anti*-cyclobutane dimers of the ethylenes.<sup>41</sup> We have not so far investigated whether non-absorbing molecular complexes are formed in these systems.

*Photoreactions of Hexafluorobenzene with Acetylenes.*—The photoaddition of various acetylenes to benzene has been previously shown to give cyclo-octatetraenes.<sup>6</sup> The photoaddition of non-conjugated acetylenes is generally inefficient ( $\Phi < 0.001$ ) but with conjugated acetylenes, the reaction proceeds readily and in the case of methyl phenylpropiolate at least, it has been shown that it is excitation of the acetylene which leads to reaction.<sup>42</sup> Only one case of apparent 1,3-cycloaddition of an acetylene to benzene has been reported,<sup>43</sup> and this almost certainly results from a secondary reaction.<sup>44</sup> Sket and Zupan have obtained bicyclo[4.2.0]octatrienes in high yields by irradiation of hexafluorobenzene with various phenyl-substituted acetylenes in cyclohexane solution.<sup>45,\*</sup>

Preliminary experiments on the irradiation of hexafluorobenzene with dimethyl acetylenedicarboxylate led to an intractable mixture of products. Propyne and but-2-yne have proved experimentally more convenient.

(a) Irradiation at  $20^\circ\text{C}$  of hexafluorobenzene saturated with propyne gave one major product, a 1:1 adduct. The proton n.m.r. spectrum had two resonances at 1.9 (3 H, triplet,  $J$  4 Hz) and 6.05 p.p.m. (1 H, doublet of triplets,  $J$  13, 4 Hz) consistent with the presence

<sup>41</sup> G. O. Schenck, W. Hartmann, S. P. Mannsfeld, W. Metzner, and C. H. Krauch, *Chem. Ber.*, 1962, **95**, 1642.

<sup>42</sup> D. Bryce-Smith, A. Gilbert, and J. Grzonka, *Chem. Comm.*, 1970, 498.

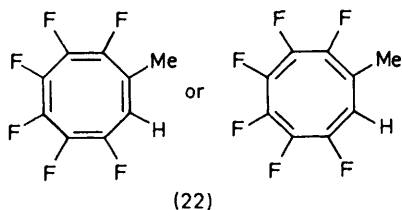
<sup>43</sup> R. S. H. Liu and C. G. Krespan, *J. Org. Chem.*, 1969, **34**, 1271.

<sup>44</sup> 'Photochemistry,' Chemical Society Specialist Periodical Report, The Chemical Society, London, vol. 2, p. 500.

<sup>45</sup> B. Sket and M. Zupan, *J. Amer. Chem. Soc.*, 1977, **99**, 3504.

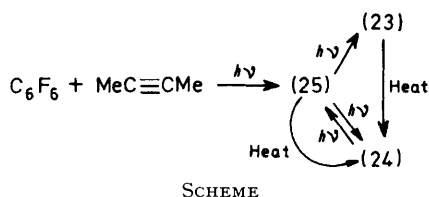
<sup>46</sup> D. Bryce-Smith, B. E. Connett, A. Gilbert, and E. Kendrick, *Chem. and Ind.*, 1966, 855.

of the  $\text{CH}_3\text{C}=\text{C}$  and  $\text{HC}=\text{C}$  moieties. The lack of spin-coupling greater than 20 Hz in the proton spectrum indicated the absence of a geminal  $\text{>CFH}$  group. The  $^{19}\text{F}$  n.m.r. spectrum had six distinct resonances in the 105.9–125.5 p.p.m. region offset upfield of  $\text{CFCl}_3$ . These data are consistent with the adduct(s) being the cyclo-octatetraenes (22), and discount other



simple 1 : 1 adduct structures such as 1,3- or 1,4-cycloadducts, or fluorinated styrene derivatives. The i.r. spectrum had three strong bands and a shoulder in the olefinic region, and agrees with this assignment. On the other hand, the adduct was colourless whereas unfluorinated cyclo-octatetraenes are generally yellow as the ring inversion allows coplanarity and hence some conjugation of the ethylenic bonds for a brief period. Neither the u.v.-visible spectrum nor the  $^1\text{H}$  n.m.r. spectrum was changed on heating the sample to temperatures of 160 and 90 °C respectively and all attempts to prepare derivatives of the cyclo-octatetraene system with tetracyanoethylene and other dienophiles proved unsuccessful.

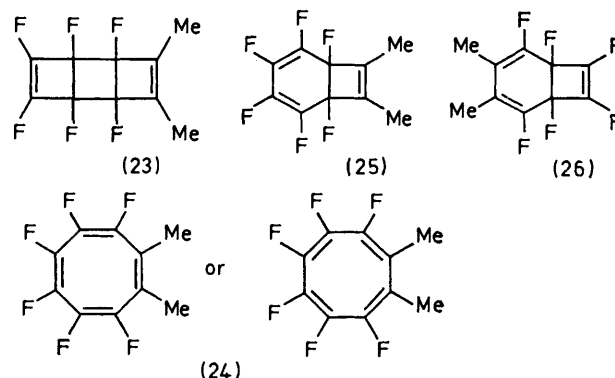
(b) Irradiation of but-2-yne in hexafluorobenzene resulted in a mixture of three 1 : 1 adducts (m.s.-g.c.) designated (23), (24), and (25) in order of increasing g.c.



retention time. The ratios of these were dependent upon the irradiation time and the temperature involved in the work-up and analysis procedures, and the relationships are shown in the Scheme: it will be noted that (25) is the sole primary product. Products (24) and (25) were liquids at room temperature, whereas (23) was obtained as colourless tabular crystals, m.p. 29–32 °C. Compounds (24) and (25) had identical mass spectra, and that of (23) differed only from these in that the molecular-ion peak was less pronounced. Comparison of the i.r. and  $^{19}\text{F}$  n.m.r. spectra with those of compounds (10) and (11), leads to assignment of the tricyclo-[4.2.0.0<sup>2,5</sup>]octadiene structure (23), although it is not possible to decide between the *syn*- and *anti*-isomers of this structure. The  $^{19}\text{F}$  n.m.r. spectrum of adduct (24) had only three signals in the ratio 1 : 1 : 1: these are in the region associated with  $=\text{CF}$  resonances. The splitting of the  $^{19}\text{F}$  resonances is not first order, a feature

which suggests that even though the six fluorines are related in pairs by symmetry, the two halves of each pair are magnetically non-equivalent. All the spectra ( $^{19}\text{F}$  n.m.r., i.r., and u.v.) of (24) were remarkably similar to those of the  $\text{C}_6\text{F}_6$ -propyne adduct (22). Structure (25) assigned to the third adduct must be regarded as rather less well supported. It has proved difficult to obtain this compound in an adequate state of purity. However, all the spectral data for the product isolated by preparative g.c. and containing this third adduct as the major product strongly indicate structure (25) (cf. ref. 45). There are indications that the major impurity in such isolated samples has the isomerised structure (26).

Thus on the irradiation of simple alkynes in  $\text{C}_6\text{F}_6$ , 1,2-cycloaddition appears to be the major, if not the exclusive, mode of reaction. Irradiation of mixtures of  $\text{C}_6\text{F}_6$  and but-2-yne at wavelengths  $>300$  nm also rather surprisingly led to the formation of adduct (25).



No evidence for charge-transfer absorption was obtained using a thin-film technique,<sup>47</sup> but the absorption spectrum of pure but-2-yne unexpectedly showed the presence of a very weak absorption ( $\lambda_{\text{max}}$ , 265 nm,  $\epsilon < 1$ ) which extended to 310 nm. The present results are therefore consistent with the previous proposal<sup>32</sup> and demonstration<sup>42</sup> that excitation of the acetylene rather than the arene is involved in these 1,2-cycloadditions.

#### EXPERIMENTAL

N.m.r. spectra were recorded on a Perkin-Elmer R10 spectrometer at 33 °C and at 60.00 and 56.46 MHz for proton and fluorine spectra respectively. Preparative scale photolyses were carried out using either (a) a 300-ml immersion cell illuminated by a water-cooled 100 W medium-pressure mercury arc, or (b) a fused silica tube of capacity 65 ml illuminated by a 15 W low-pressure spiral mercury arc. The latter apparatus was cooled by means of a fan. Small scale irradiations were performed using the lamp described in (b) and fused silica tubes of capacity 1.5 ml mounted in a holder which was rotated at ca. 15 rev.  $\text{min}^{-1}$ . All solutions were flushed with nitrogen for 30 min prior to the reaction: more rigorous deoxygenation was shown not to be necessary, the addition reactions being rather insensitive to the presence of oxygen.

<sup>47</sup> D. Bryce-Smith, B. E. Connett, and A. Gilbert, *J. Chem. Soc. (C)*, 1968, 816.

*Irradiation of Hexafluorobenzene and cis-Cyclo-octene.*—A solution of hexafluorobenzene (50 ml, 0.44 mol) and *cis*-cyclo-octene (150 ml, 1.2 mol) was irradiated in reactor (a) for 45 h. The brown polymer deposited on the outer surface of the lampwell was periodically removed. G.l.c. analysis (Carbowax 20M 8% on HMDS Chromosorb W, 80–100 mesh) revealed the presence of five 1:1 adducts A, B, C, D, and E. Small-scale irradiations of this system using the apparatus (b) revealed that only C, D, and E were primary photochemical products and that A and B arose from a secondary photochemical reaction of D. The irradiated solution was examined for the presence of perfluoro-‘Dewar’ benzene by g.l.c. on a 15% dinonyl phthalate-HMDS Chromosorb W (80–100 mesh) column at 30 °C. Under such conditions this valence-bond isomer has a retention time relative to hexafluorobenzene of 0.16;<sup>48</sup> but no trace could be detected. The starting materials were removed from the irradiated solution by rotary evaporation at water-pump pressure and the remaining greenish black oil (ca. 15 ml) was distilled at 80–88 °C and 0.4 mmHg to give 12.8 g of a colourless oil which comprised the adducts A–E. By the use of silica-gel packed column (24 in × 3/4 in) and light petroleum (60–80 °C) as eluant, pure samples of adducts B and E were obtained from the mixture. All the adducts were separated by the use of preparative g.l.c. (8% Carbowax 20 M on Chromosorb P).

Irradiation of neat hexafluorobenzene gave a solution of the ‘Dewar’ isomer. Irradiation of this solution with cyclo-octene caused no consumption of the Dewar isomer and did not result in any increased rate of formation of the adducts A–E. This experiment appears to rule out the ‘Dewar’ isomer as a precursor of any of the photoadducts.

*Attempted Chemical Separation of the Components of the Mixture D.*—Adducts A–E were unstable when heated for prolonged periods, and in each of the experiments designed to separate the components of mixture D, it was found prudent to include a ‘blank’ reaction.

(i) *Addition of ethylenes.* Solutions of maleic anhydride, tetracyanoethylene, ethyl vinyl ether, and vinylene carbonate (0.1 g) in benzene (5.0 ml) were heated for 4 h under reflux or in a sealed tube at 100 °C with 0.1 ml of the adduct mixture A–E. No change in the concentration of any adduct was detected.

(ii) *Duroquinone.* Adducts A–D (0.1 ml) were photolysed with a solution of duroquinone (0.1 g) in acetone (20 ml) using a medium-pressure mercury arc with a Pyrex filter. After photolysis for 12 h the yellow colour of the duroquinone had faded and g.l.c. analysis showed some depletion of adduct D. No product could be isolated, but it seemed probable that some photosensitised ring-closure of D to A and B had occurred.

(iii) *Pentacarbonyliron.* A mixture of adducts A–D (0.5 ml) was placed in a Pyrex test tube and pentacarbonyliron (0.5 ml) was added. The whole was flushed with nitrogen and irradiated using a medium-pressure mercury arc. No change in the fluorocarbon concentration was detected.

(iv) *Tetrakis(triphenylphosphine)platinum.* A solution of the adduct mixture A–D (0.1 g) in benzene (10 ml) was shaken with tetrakis(triphenylphosphine)platinum (0.1 g). No reaction occurred and the mixture was refluxed under nitrogen for 3 h. Again no change in composition was detected. Evaporation of the mixture under vacuum yielded only starting materials.

*Irradiation of Hexafluorobenzene and trans-Cyclo-octene.*—

A mixture of hexafluorobenzene (220 ml) and *trans*-cyclo-octene (20 ml) was irradiated under nitrogen for 60 h using cell (a). It was necessary to clean the lampwell at intervals to remove opaque brown polymeric deposits. The pale yellow solution was filtered to give a white solid (0.25 g): this was separately shown to arise from a thermal reaction of the starting materials. Unchanged starting materials were removed by rotary evaporation at water pump pressure to yield a pale yellow oil (15 ml). Analysis by g.l.c. under the conditions previously specified revealed the presence of at least seven 1:1 adducts of the starting materials (m.s.–g.l.c.). Irradiation of hexafluorobenzene and *trans*-cyclo-octene using low-pressure lamps showed that only three of these adducts were primary products. Attempts to separate the mixture using column chromatography (silica gel–light petroleum b.p. 40–60 °C) were unsuccessful and preparative g.l.c. (Carbowax 20M on Chromosorb P) was only capable of separating adducts (11) and (13) in acceptable states of purity.

*Irradiation of Hexafluorobenzene and 2,3-Dimethylbut-2-ene.*—Hexafluorobenzene (18.6 g) and 2,3-dimethylbut-2-ene (8.4 g) were irradiated in a fused silica tube using a low-pressure mercury arc for 60 h. The solution had turned pale yellow and some HF vapours were evident. G.l.c. analysis showed the presence of two compounds which constituted 80% of the product mixture. Removal of the starting materials by rotary evaporation at water-pump pressure gave a yellow oil (5 ml). The oil was distilled at 60–65 °C and 0.5 mmHg. The relative retention times on g.l.c. of (17) and (18) on 8% Apiezon L–Chromosorb W were ca. 0.4 to 1.0 respectively. The two products were separated by preparative g.l.c. on 15% Apiezon L–Chromosorb P columns. The i.r. absorption bands assigned in (17) were 3 110w (=C–H str.); 1 650, 1 530s (C<sub>6</sub>H<sub>5</sub><sup>–</sup>, C=C str.); 1 490s (C–F str.); 1 370–1 395m (3 bands) (CMe<sub>2</sub>, C–H bend); and 990s cm<sup>–1</sup> (=CH<sub>2</sub>, C–H str.). The mass spectrum of (17) (*M*<sup>+</sup> 250) shows major fragmentation to *m/e* 235 (*M* – CH<sub>3</sub>) and to *m/e* 181, which may represent (C<sub>7</sub>F<sub>5</sub>H<sub>2</sub>)<sup>+</sup>, the analogue of the tropylium ion which is common in the mass spectra of alkylbenzenes. The u.v. spectrum of (17) λ<sub>max</sub>(EtOH) 262 nm, (ε 300 l mol<sup>–1</sup> cm<sup>–1</sup>) shows no fine structure.

The spectral data for (18) are as follows: the u.v. spectrum had λ<sub>max</sub>(EtOH) 262 nm (ε 610 l mol<sup>–1</sup> cm<sup>–1</sup>). The i.r. spectrum is very similar to that of (17) but lacks the =CH<sub>2</sub> absorption at 900 cm<sup>–1</sup>. In the mass spectrum of (18), significant fragmentation is observed to *m/e* 255 (*M* – CH<sub>3</sub>), 250 (*M* – HF), 235 [*M* – (CH<sub>3</sub> + HF)], 209 (C<sub>6</sub>F<sub>5</sub>CMe<sub>2</sub><sup>+</sup>), 181 (C<sub>7</sub>F<sub>5</sub>H<sub>2</sub><sup>+</sup>–tropylium ion analogue), and 61 (Me<sub>2</sub>CF<sup>+</sup>).

*Irradiation of Hexafluorobenzene and Maleic Anhydride.*—Hexafluorobenzene (5.0 ml) and maleic anhydride (5.5 g) were dissolved in acetone (10 ml) and irradiated for 10 h with light from a medium-pressure mercury arc. Filtration of the irradiated solution gave a white solid and red filtrate. The solid product, m.p. 285 °C (decomp.), was found to be insoluble in chloroform, carbon tetrachloride, and ether. This product was identified by its spectroscopic properties as the reported cyclobutane dimer of maleic anhydride.<sup>41</sup> Evaporation of the red filtrate gave an oil from which only maleic acid was induced to crystallise.

<sup>48</sup> E. Ratajczak and A. F. Trotman-Dickenson, *J. Chem. Soc. (A)*, 1968, 509.

*Irradiation of Hexafluorobenzene and Maleimide.*—Hexafluorobenzene (6.0 ml) and maleimide (4.9 g) were dissolved in acetone (15 ml) and irradiated for 12 h as above. The irradiated solution was filtered to give a cream coloured solid, m.p. 345 °C (decomp.), which was soluble only in dimethyl sulphoxide and concentrated sulphuric acid. Spectral data for the solid indicated that it was a cyclobutane dimer of maleimide.

*Irradiation of Hexafluorobenzene and Propyne.*—Hexafluorobenzene (28 ml) was saturated with propyne (a volume increase of 5% was noted) and the solution was irradiated with a low-pressure mercury arc for 50 h. To maintain saturation, further quantities of propyne were bubbled through the solution at intervals during the irradiation. The resulting pale yellow liquid was analysed by g.l.c. (8% Carbowax 20M or Apiezon L on Chromosorb W) and found to contain one major product. Unchanged hexafluorobenzene was removed by rotary evaporation at water pump pressure to give 1.8 g of a residual oil. The oil was distilled at 30 °C and 0.9 mmHg, and this yielded a colourless liquid ( $n_D^{20}$  1.4318): relevant spectroscopic data are given in the text. Catalytic hydrogenation of the adduct(s) (22) with 10% Pd-C led to consumption of hydrogen equivalent to 4.05 ethylenic bonds. G.l.c. analysis of the solution however indicated the presence of five major and three minor hydrogenation products.

*Irradiation of Hexafluorobenzene and But-2-yne.*—A

mixture of hexafluorobenzene (40 ml) and but-2-yne (4 ml) was irradiated for 100 h with a low-pressure mercury arc. Hydrogen fluoride was formed during the irradiation. The clear pale yellow solution was rotary evaporated at water-pump pressure to give 12 ml of a pale yellow mobile liquid. The liquid was stored at 0 °C since it decomposed with evolution of HF when set aside at room temperature. G.l.c. analysis (8% Carbowax 20M–Chromosorb W) indicated the presence of three components (23), (24), and (25). The products were separated by preparative g.l.c. on Carbowax 20M. As noted in the text, the adducts were thermally and photochemically interconvertible.

*Irradiation of Hexafluorobenzene with But-2-yne at Wavelengths greater than 300 nm.*—A mixture of hexafluorobenzene (0.5 ml), but-2-yne (0.05 ml), and acetone (0.5 ml) was irradiated for 30 min in a Pyrex tube using a Pyrex-sheathed 100 W medium-pressure mercury arc. A similar tube containing only hexafluorobenzene and but-2-yne was irradiated alongside the first. The contents of the tubes were analysed by g.l.c. (5% tricresyl phosphate on Chromosorb W) and the adduct (25) was found to be present in each solution. The chemical yield from the acetone-sensitized reaction was approximately three times that obtained in the absence of acetone.

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