

Photochemistry of Organo-halogenic Molecules. Part 20. The Effect of Cycloalkene Structure on the [2 + 2] Photocycloaddition to Hexafluorobenzene

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The stereochemistry of photocycloaddition reactions of various cycloalkenes to hexafluorobenzene in cyclohexane solution depends on the structure of the cycloalkene, and [2 + 2] cycloadducts are mainly observed. [1,3]-Photocycloaddition is observed only when a large excess of the cycloalkene is used (hexafluorobenzene:cyclopentene, 1:8) and at higher concentrations. Photoreactions with indene and 1,2-dihydronaphthalene occur stereospecifically *syn*, and a *cis-syn-cis* [2 + 2] cycloadduct is isolated. The photocycloaddition reaction with norbornene proceed exclusively *exo*, with preferential *syn* addition accompanied by 5% *anti*-addition. The stereochemistry of the [2 + 2]-photocycloaddition reactions is changed completely in the case of cyclopentene, where 85% *anti* addition is observed. The course of *anti*-photocycloaddition diminishes with increasing ring size of the cycloalkene until in the case of cyclooctene, it is reduced to 53%. The quantum yields of [2 + 2]-photocycloadditions, depend on the structure of the cycloalkene and on the concentration of hexafluorobenzene, the greatest effect being observed during [2 + 2]-cycloaddition with indene.

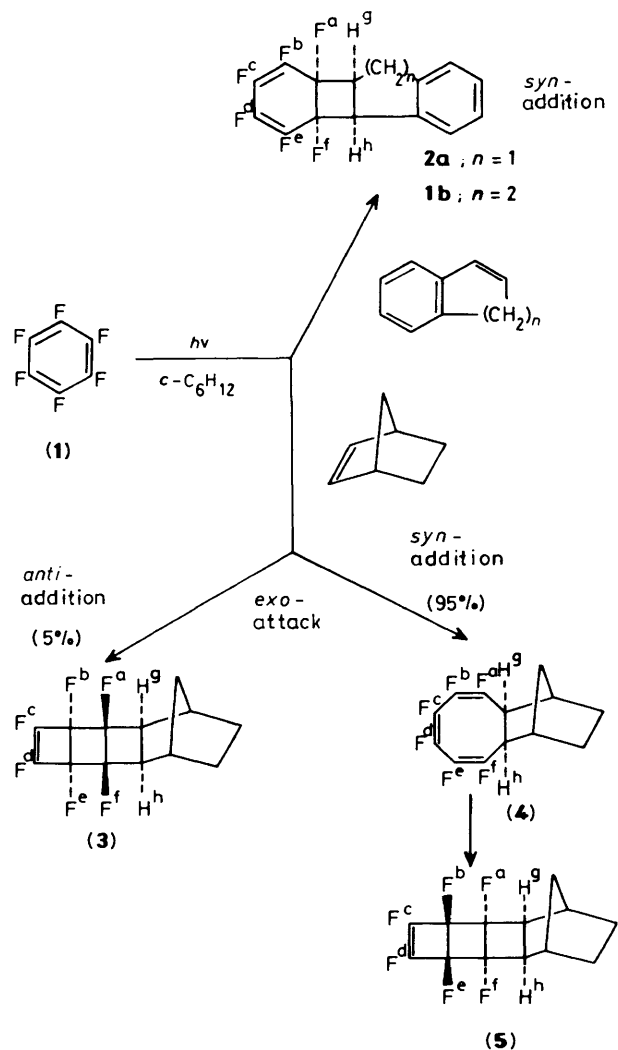
Aromatic molecules undergo various photochemical transformations, which depend on their structure, the reagents, and the reaction conditions, and which have initiated wide ranging investigations during the last 20 years.¹ Photocycloaddition reactions of benzene derivatives with alkenes have resulted in 1,2-, 1,3-, or 1,4-cycloaddition products, the course of the reaction depending on the substituents on the benzene ring and on the structure of the alkene.¹ The advantage of having fluorine as a substituent for the investigation of phototransformations of organic molecules has been demonstrated in several studies.² Bryce-Smith and co-workers³ established the formation of six 1:1 photoadducts by irradiation of *Z*-cyclooctene in hexafluorobenzene solution and formulated several pathways to account for the products. In contrast, we found⁴ that photoreaction of indene or 1,2-dihydronaphthalene with hexafluorobenzene in cyclohexane solution resulted in only one [2 + 2]-photoadduct, the reaction occurring stereospecifically *syn*, while in the case of cyclopentene it proceeded in a predominantly *anti* fashion.⁵ Bryce-Smith and co-workers⁶ did complete their investigations,³ but nevertheless [1,3]-cycloaddition predominated over [1,2]-cycloaddition. It would seem that at least two points must be taken into account to explain the difference in results, (a) the effect of ring size of the cycloalkene and (b) the effect of the solvent and/or concentration of the reactants.

We now report investigations of the effect of the structure of the cycloalkene on the photocycloaddition reactions to hexafluorobenzene.

Results and Discussion

Irradiation of a cyclohexane solution of indene or 1,2-dihydronaphthalene and hexafluorobenzene at λ 253.7 nm gave

† All crude reaction mixtures were analysed by ¹⁹F n.m.r. spectroscopy and in no case was there any reaction between hexafluorobenzene and cyclohexane observed. In contrast to this in the paper by Bryce-Smith *et al.*, *Chem. Ind. (London)*, 1966, 855, reactions of hexafluorobenzene with cycloalkanes are presented, but we believe that these reactions could be ascribed to the relatively high intensity light source and long reaction times. However, we have found that hexafluorobenzene reacted very quickly with cyclohexane or methanol in the presence of benzophenone, M. Zupan, B. Šket, B. Pahor, *Tetrahedron Lett.*, 1977, 4541; *J. Org. Chem.*, 1978, 43, 2297.



the [2 + 2]-photocycloadduct (**2a**) or (**2b**) (Scheme 1) in high yield, in which only a *syn*-[2 + 2]-cycloaddition occurred.†

Further, we investigated photoreaction of hexafluorobenzene

Table 1. The effect of cycloalkene ring size on the stereochemistry of the [2 + 2]-photocycloaddition^a to hexafluorobenzene

Cycloalkene	Product distribution				% <i>anti</i> -Addition
	(7)	(8)	(10)	(11)	
Cyclopentene	59	26	15		85
Cyclohexene	51	31		18	82
Cycloheptene	60	15	20	5	75
Cyclo-octene	35	18	31	16	53

^a The relative yields were determined by ¹⁹F n.m.r. spectroscopy; concentration of C₆F₆ 0.111 mol l⁻¹; concentration of cycloalkene 0.055 mol l⁻¹; solvent cyclohexane; 35 °C; λ 253.7 nm.

Table 2. ¹⁹F N.m.r. spectroscopic data for photoadducts.* The starting alkenes were as follows: **a**; cyclopentene, **b**; cyclohexene, **c**; cycloheptene **d**; cyclo-octene, and (3), (4), and (5); norbornene

	δ _F /p.p.m.		
	F ^{c,d}	F ^{b,e}	F ^{a,f}
(7) a ;	-165 (br s)	-161.5 (m)	-189.75 (m)
b ;	-159 (br s)	-156 (m)	-180.75 (m)
c ;	-159 (br s)	-157.5 (m)	-182.25 (m)
d ;	-158.25 (br s)	-162.75 (m)	-185.25 (m)
(8) a ;	-124.5 (d)	-196.5 (dd)	-183.75 (dd)
b ;	-120.75 (br s)	-190.5 (m)	-175.5 (m)
c ;	-129.75 (br s)	-205.5 (m)	-192.0 (m)
d ;	-129.0 (br s)	-204.0 (m)	-192.0 (m)
(3)	-123.0 (br s)	-193.5 (m)	-177.0 (m)
(10) a ;	-160.5 (br s)	-158.3 (m)	-167.3 (m)
b ;			
c ;	-158.25 (br s)	-154.13 (m)	-162.75 (m)
d ;	-156.75 (br s)	-153.75 (m)	-159.75 (m)
(4)	-159.75 (br s)	-156.0 (d)	-163.5 (dd)
(11) a ;	-126.5 (br s)	-190.5 (m)	-163.5 (m)
b ;	-122.6 (br s)	-188.25 (m)	-161.5 (m)
c ;	-132.0 (br s)	-201.0 (m)	-172.5 (m)
d ;	-130.0 (br s)	-199.0 (m)	-170.0 (m)
(5)	-124.5 (br s)	-179.25 (d)	-158.25 (dd)

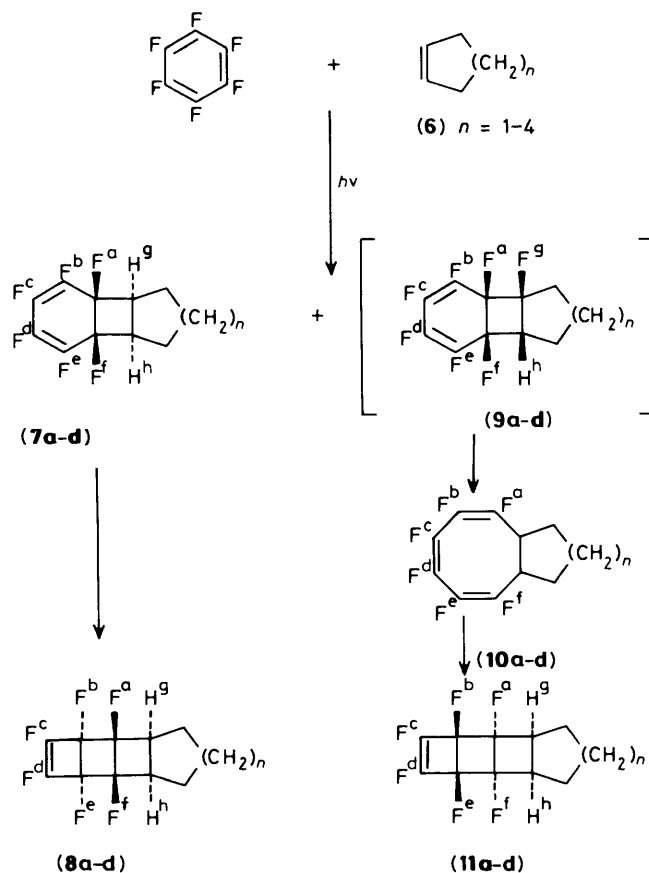
* All signals correspond to 2F.

in cyclohexane solution with norbornene and found that three products [(3) (5%), (4) (57), and (5) (38)] were formed. Products (4) and (5) were isolated by preparative t.l.c., and the pure product (4) was converted into product (5) by further irradiation. On the basis of spectroscopic data we ascertained that product (4) was a cyclo-octatriene derivative, which was converted to a pentacyclic product (5), with the stereochemistry outlined in Scheme 1. The structure of product (5) was also established spectroscopically (¹H and ¹⁹F n.m.r., i.r., and mass spectra). However, the correct stereochemical assignment was possible only by an X-ray analysis.⁷ The minor product (3) present in the crude reaction mixture, which was not isolated, showed in its ¹⁹F n.m.r. spectrum signals very similar to those observed for the product formed after an *anti*-[2 + 2] addition of norbornadiene to hexafluorobenzene,⁸ *exo*-attack whose exact structure was also established by X-ray analysis.⁹ From the above-mentioned data it was evident that only [2 + 2] photocycloaddition occurred, with exclusively *exo* attack of norbornene on hexafluorobenzene, while predominant *syn* addition was also accompanied by *anti* addition.

We then studied the effect of ring size of the cycloalkene on the course of photocycloaddition with hexafluorobenzene. All irradiations were carried out under the same conditions: 1 mmol of cycloalkene and 2 mmols of hexafluorobenzene, dissolved in 18 ml of cyclohexane. These were irradiated at λ 253.7 nm for 1

h. The crude reaction mixtures were analysed by ¹⁹F n.m.r. spectroscopy and the formation of up to four products, which were isolated by preparative g.l.c. or t.l.c. was established. The relative yields of the products are presented in Table 1. The structure of the products were established on the basis of their n.m.r., mass, and i.r. spectra, and by comparison with the spectroscopic data of the isomeric pentacyclic systems, where exact structures were determined by X-ray analysis. The ¹⁹F n.m.r. data of the [2 + 2]-*anti*-adducts (7a–d), cyclo-octatriene derivatives (10a–d), and isomeric tetracyclic systems (8a–d) and (11a–d) are presented in Table 2.

Additionally, we found that under photochemical conditions, the pure [2 + 2] photoadducts (7) were transformed into tetracyclic products (8), while the cyclo-octatriene derivatives (10) were converted into isomeric tetracyclic products (11) (the stereochemistry is outlined in Scheme 2). Under the above-

**Scheme 2.**

mentioned conditions, we did not observe formation of any 1,3-cycloadduct. The ring size of the cycloalkene influenced only the stereochemistry of [2 + 2]-photocycloaddition; in the case of cyclopentene, *anti*-addition was predominant, while with an increase in ring size, the *anti*-selectivity diminished and only 53% *anti*-addition was observed in the reaction with cyclo-octene (Table 1). Primary products (7) resulting from an *anti*-[2 + 2] attack, were stable enough to be isolated. However, they were stereospecifically converted to the tetracyclic products (8), with the stereochemistry outlined in Scheme 2. On the other hand, *syn*-[2 + 2]-adducts were unstable at room temperature, undergoing a ring opening process, thus forming cyclo-octatriene derivatives (10), which were also stereospecifically converted to tetracyclic systems (11).

The effect of the cycloalkene structure on the quantum yield of photocycloaddition to hexafluorobenzene in cyclohexane

Table 3. The effect of cycloalkene structure on the quantum yield of the [2 + 2]-photocycloaddition to hexafluorobenzene^a

Cycloalkene	$\Phi_{[2+2]}$ (mol Einstein ⁻¹)
Indene	0.075 ± 0.004
1,2-Dihydronaphthalene	0.097 ± 0.004
Cyclopentene	0.080 ± 0.005
Cycloheptene	0.050 ± 0.002
Norbornene	0.054 ± 0.003

^a Concentration of C₆F₆ 0.1 mol l⁻¹; concentration of cycloalkene 0.1 mol l⁻¹, solvent cyclohexane; λ 253.7 nm; light intensity 3.2×10^{15} photons ml⁻¹ s⁻¹; 30 °C.

Table 4. The effect of hexafluorobenzene-cyclopentene concentration on product distribution of photocycloaddition

C ₆ F ₆ / mmol ^b	C ₅ H ₈ / mmol ^b	Product distribution ^a				<i>anti</i> - [2 + 2]- Addition
		(7a)	(8a)	(10a)	(11a)	
8	1	56	30	14		86
4	1	47	41	12		88
4	4	45	32	23		77
1	4 ^c	21	56	15	10	75
1	8 ^d	16	53	14	17	69

^a The relative yields were determined by ¹⁹F n.m.r. spectroscopy.

^b Dissolved in cyclohexane (4 ml); 5 h irradiation. ^c Trace amount of a 1,3-adduct was formed. ^d Two 1,3 adducts were formed (20%).

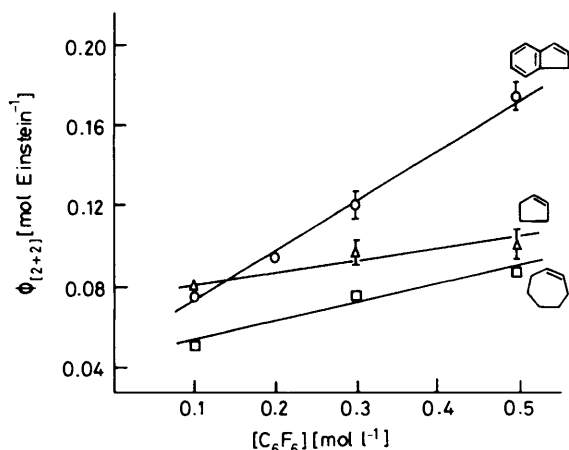


Figure. Dependence of quantum yield of [2 + 2] photoaddition on C₆F₆ concentration in cyclohexane. $\lambda = 253.7$ nm; light intensity 3.2×10^{15} photons ml⁻¹ s⁻¹; 30 °C; cycloalkene concentration 0.1 mol l⁻¹

solution is presented in Table 3. In the Figure the effect of variation in the hexafluorobenzene concentration on the quantum yield with various cycloalkenes is also presented. As is evident from the Figure, the quantum yields of [2 + 2]-cycloadditions increase with increased hexafluorobenzene concentration, the degree of increase depending on cycloalkene structure, while variation of cycloalkene (cyclopentene, cycloheptene, and indene) concentration in concentration range 0.1–0.5 mol l⁻¹ caused no significant effect.

It can be seen that different photochemical behaviour of hexafluorobenzene observed by Bryce-Smith and co-workers^{3,6} compared to the reactions in cyclohexane solution studied by us, can be explained by the effect of the solvent, for which reason we studied the effect of the molar ratio of cyclopentene to

hexafluorobenzene at higher concentrations and the results are presented in Table 4. It is evident that the concentration of cyclopentene and the ratio to hexafluorobenzene had two different effects. By increasing the proportion of cyclopentene to hexafluorobenzene, in the molar ratio 1 : 8 the *anti*-specificity of photoaddition was diminished and besides the expected [2 + 2]-photoadducts, the formation of two [1,3]-photoadducts was also observed. It can be concluded that cyclohexane, as the solvent, plays a very important role in the course of photocycloaddition reactions between hexafluorobenzene and a cycloalkene. However, the effect of the structure of the cycloalkene on the stereochemistry of [2 + 2]-photocycloaddition reaction still remains open.

Experimental

Preparative experiments were carried out with a Rayonet Model RPR 100 with RPR 253.7 nm lamps. I.r. spectra were recorded on a Perkin-Elmer 727 B spectrometer and ¹H and ¹⁹F n.m.r. spectra on a JEOL JNM-PS-100 spectrometer in CDCl₃ or CCl₄ solutions with Me₄Si or CCl₃F as an internal reference. Mass spectra and high resolution measurements were taken on a CEC 21-110 spectrometer. T.l.c. was carried out on Merck PSC Fertigplatten F 254, and g.l.c. on a Varian Aerograph, Model 1800.

Materials.—Hexafluorobenzene, indene, cyclopentene, cyclohexene, cycloheptene, and cyclo-octene were commercially available and were distilled before use. 1,2-Dihydronaphthalene was synthesized. Cyclohexane was purified and distilled before use. In a separate experiment it was demonstrated that the presence of oxygen had no significant effect on product distribution or quantum yields, and for this reason, no special attention was paid to air exclusion.

Photocycloaddition Reactions of Hexafluorobenzene with Cycloalkenes: General Procedure.—The alkene (1 mmol) and hexafluorobenzene (2 mmol) were dissolved in cyclohexane (18 ml). The solution was then irradiated for various times (1–60 h) at λ 253.7 nm, evaporated under reduced pressure, and the crude residue was analysed by ¹⁹F n.m.r. spectroscopy. The products were then separated by preparative t.l.c. or g.l.c.

Reaction with indene. After irradiation for 60 h, product (2a) was purified by t.l.c. (SiO₂-petroleum), and crystallized from methanol, to give the tetracycle (2a) (35%), m.p. 88–90 °C, δ_F –156.4 (ddd, F^f), –156.4 (m, F^e), –157.5 (br s, F^d), –158.6 (m, F^b), –162.4 (br s, F^c), and –178.5 p.p.m. (ddd, F^a); δ_H 4.05 (ddd, H^b) and 3.7 (m, H^g); ³J_{f,h} = ³J_{a,g} 25 Hz, ³J_{a,f} 50 Hz, ³J_{g,h} 12 Hz, and ⁴J_{a,h} 4 Hz (Found: *M*⁺, 302.0524. Calc. for C₁₅H₈F₆: *M*, 302.0530; *m/z* 302 (*M*⁺, 2%), 224 (24), 223 (98), 222 (100), 221 (55), 186 (10), 118 (15), 117 (35), 116 (97), 115 (68), and 104 (14).

Reaction with 1,2-dihydronaphthalene. After irradiation for 60 h, the product was purified by preparative t.l.c. (SiO₂-light petroleum) and was crystallized from methanol, to give the tetracycle (2b) (45%), m.p. 63–65 °C, δ_F –157.5 (m, F^e), –159.0 (m, F^b), –160.5 (ddd, F^f), –161.4 (br s, F^d), –162.4 (br s, F^c), and –171.0 p.p.m. (ddd, F^a); δ_H 4.05 (ddd, H^b) and 3.18 (m, H^g); ³J_{f,h} = ³J_{a,g} 25, ³J_{a,f} 50, ³J_{g,h} 12, and ⁴J_{a,h} 4 Hz (Found: *M*⁺, 316.0699. Calc. for C₁₆H₁₀F₆: *M*, 316.0687; *m/z* 316 (*M*⁺, 5%), 186 (64), 131 (73), 130 (100) 129 (93), 128 (77), 127 (61), 117 (40), 115 (83), and 102 (28).

Reaction with norbornene. After irradiation for 60 h, the reaction mixture was separated by preparative t.l.c. (SiO₂-light petroleum) to give crystalline product (5) (25%), m.p. 83–84 °C (from methanol), and the crystalline product (4) (38%), m.p. 54–56 °C (from methanol). The ¹⁹F n.m.r. data for both compounds are given in Table 2. Compound (4) showed: δ_H 2.85 (2 H, m), 2.5 (2 H, s) and 1.5 (6 H, m); ³J_{a,b,e,f} 15 and ³J_{a,g,f,h} 24

Hz (Found: M^+ , 280.0670. Calc. for $C_{13}H_{10}F_6$: M^+ , 280.0686); m/z 280 (M^+ , 5%), 239 (11), 212 (31), 204 (32), 169 (13), 91 (21), 89 (18), 68 (100), 67 (58), and 66 (68).

Compound (**5**) showed: δ_H 2.73 p.p.m. (2 H, d), 2.5 (2 H, s), and 1.5 (6 H, m); $^3J_{a,b,c,f}$ 15 Hz, $^3J_{a,g,f,h}$ 24 Hz (Found: M^+ , 280.0692); m/z 280 (M^+ , 7%), 238 (21), 212 (58), 194 (56), 169 (21), 99 (16), 81 (34), 80 (14), 79 (25), 68 (100), 67 (81), and 66 (84).

Reaction with cyclopentene. After irradiation for 3 h, the crude reaction mixture was separated by preparative t.l.c. (SiO_2 -light petroleum) and the following products were isolated: (**7a**) (oil; 33%) (**8a**) (17%), m.p. 35–35.5 °C, and (**10a**) (oil; 8%). Irradiation for 6 h gave a reaction mixture which was separated first by preparative g.l.c. (110–150 °C; FFAP 30% Chromosorb A AW) and subsequently by preparative t.l.c. (SiO_2 -light petroleum) to give compounds (**8a**) (52%), (**11a**) (oil; 8.8%), and (**10a**) (6.0%).

Compound (**7a**) (0.5 mmol) was dissolved in cyclohexane (9 ml) and irradiated for 60 h at λ 253.7 nm. The crude reaction mixture was purified by preparative t.l.c. to afford the product (**8a**) (75%).

Compound (**10a**) (0.5 mmol) was dissolved in cyclohexane (9 ml) and irradiated for 60 h at λ 253.7 nm. The crude reaction mixture was purified by preparative t.l.c. and the product (**11a**) (68%) was isolated.

Compound (**8a**) (0.5 mmol) was heated in a sealed tube for 10 min at 150 °C, and the resulting mixture was analysed by ^{19}F n.m.r. spectroscopy, and was shown to contain compound (**7a**) (81.5%) and (**10a**) (18.5%).

Compound (**7a**) showed: δ_F as given in Table 2; δ_H 3.1 (2 H, m) and 2.0 (6 H, m); $^3J_{a,g,f,h}$ 7.5 Hz (Found: M^+ , 254.0533. Calc. for $C_{11}H_8F_6$: M , 254.0530); m/z 254 (M^+ , 14%), 212 (20), 187 (36), 186 (54), 181 (24), 169 (28), 163 (22), 143 (26), 138 (17), 117 (43), 99 (68), 93 (40), 86 (31), 83 (26), 81 (24), 79 (22), 77 (27), 68 (100), 67 (80), and 66 (49).

Compound (**8a**) showed: δ_F as given in Table 2; δ_H 3.2 (2 H, m) and 1.6–2.4 (6 H, m); $^3J_{b,c,d,e}$ 9, $^3J_{a,b,c,f}$ 18 Hz, and $^3J_{a,g,f,h}$ 7.5 Hz (Found: M^+ , 254.0535); m/z 254 (M^+ 3%), 226 (3), 213 (15), 199 (22), 169 (12), 163 (12), 121 (28), 99 (33), 85 (17), 81 (22), 68 (100), and 67 (28).

Compound (**10a**) showed: δ_F as given in Table 2; δ_H 3.5 (2 H, m) and 2 (6 H, m); $^3J_{a,b,c,f}$ 12, $^3J_{a,g,f,h}$ 27.0 Hz (Found: M^+ , 254.0530); m/z 254 (M^+ , 22%), 212 (40), 211 (27), 99 (33), 68 (75), 67 (58), 58 (40), 43 (73), and 42 (100).

Compound (**11a**) showed: δ_F as in Table 2; δ_H 3.4 (2 H, m), 1.6–2.4 (6 H, m); $^3J_{a,b,c,f}$ 18 and $^3J_{a,g,f,h}$ 24 Hz (Found: M^+ , 254.0533); m/z 254 (M^+ , 6%), 226 (6), 213 (14), 199 (20), 169 (14), 163 (12), 121 (26), 99 (33), 85 (31), 81 (23), 68 (100), and 67 (40).

Reaction with cyclohexene. After irradiation for 1 h, the products were separated by preparative g.l.c. (FFAP 30%; Chromosorb A AW; 135–180 °C) to give (**8b**) (oil; 15%), (**11b**) (liquid, 9%), and (**7b**) (liquid; 23%).

Compound (**7b**) (0.25 mmol) was dissolved in cyclohexane (5 ml) and the solution was irradiated for 20 h at λ 253.7 nm. The solvent was evaporated under reduced pressure and the crude reaction mixture was analysed by ^{19}F n.m.r. spectroscopy, and only the presence of compound (**8b**) was established. Pure (**8b**) (56%) was obtained by preparative g.l.c. (FFAP 30%; Chromosorb A AW; 140 °C).

Compound (**7b**) showed: δ_F as shown in Table 2; δ_H 3.05 (2 H, m) and 2.0 (8 H, m); $^3J_{a,g,f,h}$ 7 Hz (Found: M^+ , 268.0690. Calc. for $C_{12}H_{10}F_6$: M , 268.0687); m/z 268 (M^+ , 1%), 194 (13), 186 (14), 83 (31), 82 (88), 81 (49), 67 (100), 55 (30), 54 (56), 41 (50), and 39 (33).

Compound (**8b**) showed: δ_F as shown in Table 2; δ_H 3.1 (2 H, m) and 2.0 (8 H, m); $^3J_{a,g,f,h}$ 7 Hz (Found: M^+ , 268.0691); m/z

268 (M^+ , 1%), 82 (49), 67 (60), 58 (27), 54 (37), 43 (100), 41 (25), and 39 (19).

Compound (**11b**) showed: δ_F as given in Table 2; δ_H 3.3 (2 H, d) and 2.0 (8 H, m); $^3J_{a,g,f,h}$ 24 Hz (Found: M^+ , 268.0690); m/z 268 (M^+ , 1%), 82 (37), 67 (80), 58 (44), 54 (30), 43 (100), 41 (67), and 39 (28).

Reaction with Cycloheptene. After irradiation for 1 h, the products were separated by preparative g.l.c. (FFAP 30%; Chromosorb A AW; 135–175 °C), and the following compounds were isolated: a mixture of (**7c**) and (**10c**) (41%), (**8c**) (white crystalline material; 9%), m.p. 62–64 °C, and (**11c**) (liquid; 6.5%).

The mixture of (**7c**) and (**10c**) (0.5 mmol) was dissolved in cyclohexane (9 ml) and the solution was irradiated for 20 h at λ 253.7 nm. The solvent was evaporated under reduced pressure, and the crude reaction mixture was analysed by ^{19}F n.m.r. spectroscopy, which showed only the presence of compounds (**8c**) and (**11c**). The pure products (**8c**) (48%) and (**11c**) (17%) were isolated by preparative g.l.c. (FFAP 30%; Chromosorb A AW; 135 °C).

Compound (**7c**) and (**10c**) showed: δ_F as given in Table 2 (Found: M^+ (mixture), 282.0850. Calc. for $C_{13}H_{12}F_6$: M , 282.0843).

Compound (**8c**) showed δ_F as given in Table 2; δ_H 2.68 (2 H, m) and 1.0–2.1 (10 H, m); $^3J_{a,g,f,h}$ 7.5 Hz (Found: M^+ , 282.0848); m/z 282 (M^+ , 2%), 181 (20), 169 (22), 163 (22), 96 (59), 81 (99), 77 (41), 68 (57), 67 (85), 55 (95), 54 (54), 51 (34), 41 (100), and 39 (80).

Compound (**11c**) showed: δ_F as given in Table 2; δ_H 2.7 (2 H, d) and 1.5 (10 H, m); $^3J_{a,g,f,h}$ 27 Hz (Found: M^+ , 282.0841); m/z 282 (M^+ , 2%), 181 (10), 169 (12), 163 (12), 151 (10), 96 (37), 83 (70), 81 (81), 68 (39), 67 (72), 55 (100), 54 (42), 51 (23), 41 (96), and 39 (61).

Reaction with cyclo-octene. After irradiation for 1 h, the products were separated by preparative g.l.c. (FFAP 30%; Chromosorb A AW; 125 °C) and the following were isolated: a mixture of compounds (**7d**) and (**10d**) (32%), (**11d**) (liquid; 6%), and (**8d**) (liquid; 8%). A mixture of compounds (**7d**) and (**10d**) (0.5 mmol) was dissolved in cyclohexane (9 ml) and the solution was irradiated for 40 h at λ 253.7 nm. The solvent was then evaporated under reduced pressure and the crude reaction mixture was analysed by ^{19}F n.m.r. spectroscopy, which revealed only the presence of compounds (**8d**) and (**11d**). The pure products (**8d**) (30%) and (**11d**) (24%) were isolated by preparative g.l.c. (FFAP 30%; Chromosorb A AW; 125 °C).

Compounds (**7d**) and (**10d**) showed: δ_F as given in Table 2 [Found: M^+ (mixture), 296.0994. Calc. for $C_{14}H_{14}F_6$: M^+ , 296.0999].

Compound (**8d**) showed: δ_F as given in Table 2; δ_H 2.2 (2 H, d) and 1.1 (12 H, m); $^3J_{a,g,f,h}$ 7.5 Hz (Found: M^+ , 296.0995); m/z 296 (M^+ , 2%), 82 (69), 81 (43), 67 (65), 55 (42), 54 (56), 41 (100), and 39 (54).

Compound (**11d**) showed: δ_F as given in Table 2; δ_H 2.8 (2 H, m) and 1.6 (12 H, m), $^3J_{a,g,f,h}$ 25 Hz (Found: M^+ , 296.0998); m/z 296 (M^+ , 2%), 110 (41), 82 (100), 81 (57), and 67 (82).

Determination of Quantum Yields.—Quantum yields were measured using a ferrioxalate actinometer and in each experiment the amount of transmitted light was measured. Quartz cuvettes (12 ml) were filled with a cyclohexane solution of hexafluorobenzene and the alkene (10 ml), and thermostatted by external cooling prior to the measurement of the temperature of the solution. The light source was a RPR 253.7 nm lamp without filters. In a separate experiment with filters, we found only 2–3% difference. The products were analysed using ^{19}F n.m.r. spectroscopy with $PhCF_3$ or octafluoronaphthalene as an internal standard, which was added after solvent

evaporation. Irradiation times were chosen so that conversion of hexafluorobenzene did not exceed 5—7% of its initial amount. Each quantum yield determination was repeated at least three times and the average data are presented in Table 3 and in the Figure, together with the data on concentration of reagents, light intensity, and temperatures.

References

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