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Photocycloadditions of Cyclodienes to Hexafluorobenzene

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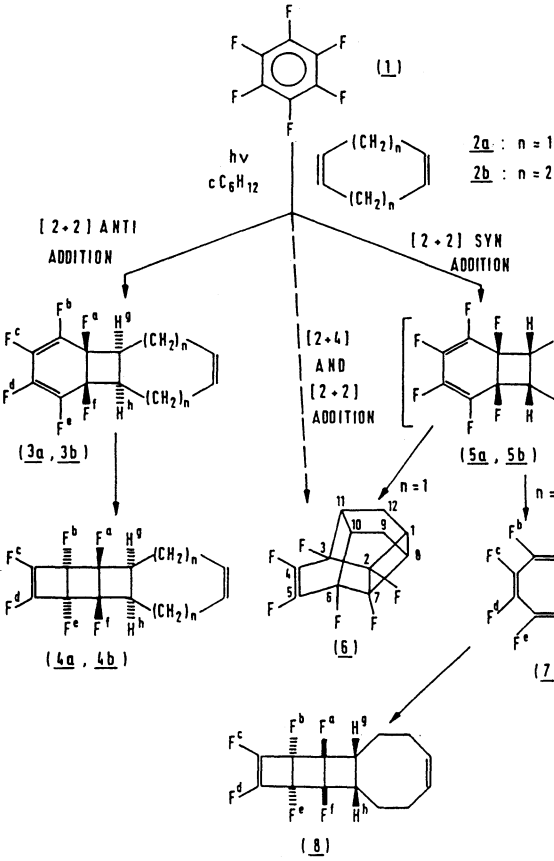
The stereochemistry of photocycloaddition reactions of various cyclodienes to hexafluorobenzene in cyclohexane solution depends on the structure of the cyclodiene and [2+2]cycloadducts are mainly observed. Photoreaction of 1,5-cyclooctadiene with hexafluorobenzene gives nearly equal amounts of syn and anti [2+2]adducts, which are further transformed to tetracyclic systems, contrary to this, the stereochemistry observed by reactions with 1,4-cyclohexadiene depends on the molar ratio of cyclodiene-hexafluorobenzene and 30—54% of syn addition is observed, the syn adduct, however, being further transformed to 2,3,4,5,6,7-hexafluoropentacyclo-$[6.4.0.0^{2,7}.0^{3,11}.0^{6,10}]$dodec-4-ene. Syn selectivity of [2+2]cycloaddition was enhanced when bicyclic dienes were used and it is interesting that in the case of norbornadiene and benzonorbornadiene only exo attack was observed, and no anti attack occurred in the case of benzonorbornene. The quantum yields of [2+2]photocycloaddition reactions depend on the structure of the cyclodiene and the concentrations of hexafluorobenzene and cyclodiene. The quantum yields for norbornadiene and 1,4-cyclohexadiene are nearly the same, while it is two times higher in a photoreaction with 1,5-cyclooctadiene, when equal amounts of hexafluorobenzene and 1,5-cyclooctadiene were irradiated in cyclohexane at λ=253.7 nm.

Aromatic molecules undergo various photochemical transformations, depending on their structure, the reagents and the reaction conditions which initiated wide ranging investigations in the last twenty years.[1] Photocycloaddition reactions of benzene derivatives with alkenes and dienes resulted in 1,2-, 1,3-, or 1,4-cycloaddition products, the course of the reaction depending on the substituent on the phenyl ring and on the structure of the olefin and diene. The advantage of fluorine as a substituent in investigations of phototransformations of organic molecules have been shown in several studies.[2] We have already demonstrated that hexafluorobenzene readily reacted with various cycloalkenes when irradiation was carried out in cyclohexane solution, however, the structure of the olefin played the major role in the stereochemistry of [2+2]cycloaddition reactions: cyclopentene gave predominantly anti products[3] while with indene stereospecific syn addition was observed.[4] We now report investigations of the effect of the structure of the cyclodienes on photocycloaddition reactions to hexafluorobenzene.

Results and Discussion

Cyclohexane solution of 1,4-cyclohexadiene (1 mmol) and hexafluorobenzene (2 mmol) was irradiated for 1 h at λ=253.7 nm, the solvent evaporated and the crude reaction mixture analyzed by ^{19}F NMR spectroscopy and nine signals, corresponding to three different products in the following relative yields: 61% (**3a**), 16% (**4a**), and 23% (**6**) (Scheme 1), were observed.

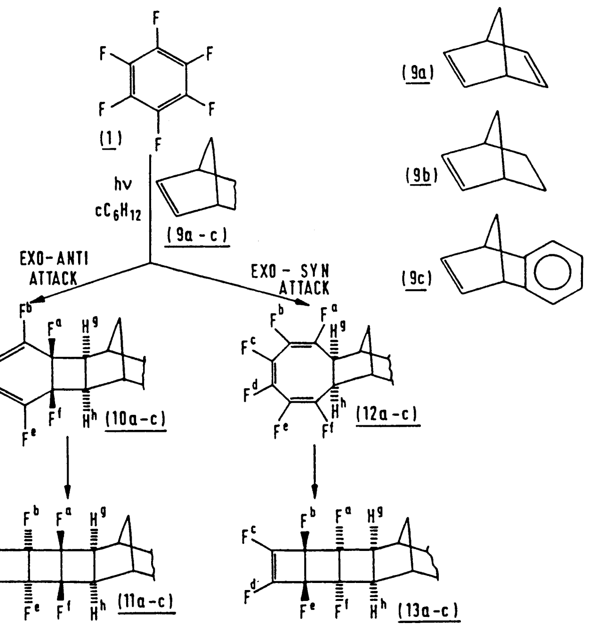
Products were separated by preparative TLC and VPC and the structures of the products determined on the basis of their NMR, MS, and X-ray data. The major product **3a** shows in its ^{19}F NMR the following signals at δ=−169.5, −171.75, and −198.0, while ^{1}H NMR spectrum confirms the presence of olefinic protons, CH_2 group and a signal at δ=3 with a coupling constant $^3J_{FH}$=7.5 Hz. Mass spectrum confirms the presence of 1 : 1-adduct, while irradiation of the pure product **3a** gave exclusively product **4a**, which shows the following three signals in its ^{19}F NMR spectrum at δ=−129.0, −190.5, and −204.25, and in its ^{1}H NMR spectrum olefinic protons at δ=5.9, methylenic protons at δ=2.3 and a signal at δ=3.08 with $^3J_{FH}$=7.5 Hz. The third product formed (**6**) shows a



Scheme 1.

quite different ^{19}F NMR spectrum with a signal at δ=−167.25 (corresponding to fluorine atoms on olefinic carbon atom), and two signals at a much higher field: δ=−216.75 and −217.5, corresponding to fluorine atoms bonded to saturated carbon atoms. ^{1}H NMR spectrum also shows only signals at higher fields: δ=3.2 (2H), 2.64 (2H), and 1.8 (4H). However, mass spectrum (*m/z* 266 (M^+, 24%)) confirms the formation of 1 : 1 adduct, whose structure was finally proven by X-ray analysis.[5] 2,3,4,5,6,7-hexafluoropentacyclo-[6.4.0.0^{2,7}.0^{3,11}.0^{6,10}]dodec-4-ene (**6**) could be formed either by the primary [2+2] syn addition, followed by intramolecular [2+4] or by primary [2+4] addition, followed by [2+2] addition; we were unable to detect the presence of primary formed [2+2] or [2+4] adducts and so the origin of the product **6** formation remains open. However, further studies of the stereochemistry of [2+2]cycloaddition reaction with 1,5-cyclooctadiene (**2b**) where four products were formed (Scheme 1) diminished the possibility of the formation of product **6** via primary [2+4]cycloaddition. The irradiation of cyclohexane solution of 1,5-cyclooctadiene (**2b**) and hexafluorobenzene gave the crude reaction mixture containing four products (**3b**, 41%; **4b**, 9%; **7**, 41%; and **8**, 9%) which were partly separated by preparative TLC. The mixture containing **3b** and **7** was further irradiated for forty hours and the formation of two isomeric tetracyclic products **4b** and **8** was established. On the basis of the spectroscopic data we have found that the formation of the four products corresponds to the exclusively [2+2]cycloaddition process (syn attack 50%). In Scheme 1, the course of photocycloaddition reactions with 1,4-cyclohexadiene and 1,5-cyclooctadiene is presented.

Further, we have studied the stereochemistry of photocycloaddition reactions with norbornadiene (**9a**) and benzonorbornene (**9c**), where there are four possible [2+2] attacks: exo-syn, exo-anti, endo-syn, and endo-anti. As in the case of norbornene (**9b**),[6] only exo-attack was observed with **9a** and **9c**, while the amount of anti attack was diminished from 20% observed with norbornadiene to the exclusive exo-syn attack, occurring in the case of benzonorbornene. The course of cycloaddition reactions is presented in Scheme 2.



Scheme 2.

Table 1. The Effect of Cyclodiene or Cycloalkene Ring Size on the Stereochemistry of the [2+2]-Photocycloaddition[a] to Hexafluorobenzene

Cyclodiene or ycloalkene	exo-syn		exo-anti
	12	**13**	**11**
9a	47	33	20
9b	57	38	5
9c	72	28	—

a) The relative yields were determined by ^{19}F NMR spectroscopy; concentration of C_6F_6 0.111 mol l^{-1}; concentration of cyclodienes or cycloalkenes 0.055 mol l^{-1}; solvent cyclohexane; 35 °C, λ 253.7 nm.

Table 2. ^{19}F NMR Spectroscopic Data for Photoadducts[a]

	Product	δ_F/ppm		
		$F^{c,d}$	$F^{b,e}$	$F^{a,f}$
2a	**4a**	−129	−204.25	−190.5
2b	**4b**	−125.5	−195	−190
	7	−158.5	−155.2	−165.5
	8	−126	−195	−161.25
9a	**11a**	−123.75	−194.23	−180.8
	12a	−161.25	−159	−168
	13a	−125.25	−180	−164.25
9b	**11b**	−123	−193.5	−177.4
	12b	−159.75	−156	−163.5
	13b	−124.5	−179.25	−158.25
9c	**12c**	−158.3	−156.75	−165
	13c	−124.9	−180	−163

The starting cycloalkenes or cyclodienes were as follows: **2a**; 1,4-cyclohexadiene, **2b**; 1,5-cyclooctadiene, **9a**; norbornadiene, **9b**; norbornene, **9c**; benzonorbornene.

a) All signals correspond to 2F.

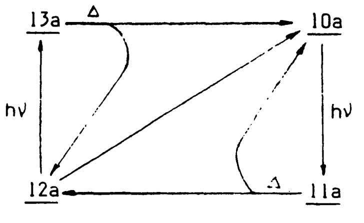
The structures of the products were determined on the basis of their mass spectra, NMR spectra, and X-ray data. Selected NMR data for photoadducts are presented in Table 2, the exact determination of the stereochemistry of the products was, however, enabled by the fact that the structures of **11a**[7] and **13b**[8] were confirmed by X-ray analysis.

In Scheme 3 various thermal and photochemical transformations of [2+2]adducts formed by irradiation of norbornadiene and hexafluorobenzene are presented. Product **12a** is converted stereospecifically to the pentacyclic system **13a** under photochemical conditions, while heating **12a** to 150 °C resulted in the primary formed anti adduct **10a**, which was further transformed under photochemical conditions to the pentacyclic system **11a**. Heating of the pentacyclic

Table 3. The Effect of Cyclodiene or Cycloalkene and Hexafluorobenzene Concentration on Quantum Yield of Photocycloaddition[a)]

Cyclodiene or cycloalkene	Concentration[b)]		ϕ/mol Einstein^{-1}			% syn addition	R[c)]
	A	B	ϕ_{syn}	ϕ_{anti}	$\phi_{[2+2]}$		
2a	0.1	0.5	0.049	0.041	0.09	54	1.32
	0.1	0.1	0.030	0.038	0.068	44	1.00
	0.5	0.1	0.043	0.067	0.11	39	1.62
2b	0.1	0.5	0.08	0.07	0.15	53	1.10
	0.1	0.1	0.071	0.065	0.136	52	1.00
	0.5	0.1	0.115	0.105	0.22	52	1.62
9a	0.1	0.4	0.042	0.006	0.048	88	0.70
	0.1	0.1	0.061	0.008	0.069	88	1.00
	0.5	0.1	0.090	0.011	0.101	89	1.46
9b	0.1	0.1	0.051	0.003	0.054	95	1.00

a) Solvent cyclohexane; λ 253.7 nm; T 30 °C; light intensity 2.4×10^{15} photons ml^{-1}s^{-1}. b) Concentration A: C_6F_6 concentration (mol l^{-1}). Concentration B: cyclodiene or cycloalkene concentration (mol l^{-1}). c) R; ratio of [2+2]photocycloaddition quantum yield at the given concentration to [2+2]photocycloaddition quantum yield at concentration of both C_6F_6 and cyclodiene or cycloalkene 0.1 mol l^{-1}.



Scheme 3.

products **11a** and **13a** at 150 °C gave mixtures of **10a** and **12a**.

Photocycloaddition reactions of hexafluorobenzene and norbornadiene at λ=350 nm as well as in the presence of benzophenone as sensitizer did not occur, while photoreaction was completely quenched by 1,3-pentadiene and resulted in a complex mixture of the 1,3-pentadiene-hexafluorobenzene adducts.

The effect of the cyclodiene structure on the quantum yield of photocycloaddition reactions to hexafluorobenzene in cyclohexane solutions is presented in Table 3.

It is evident that the photoreactions of norbornadiene and 1,4-cyclohexadiene with hexafluorobenzene are 30% more efficient than the photoreaction of norbornene, while as much as a 1.5-fold increase of efficiency was observed in the case of [2+2]cycloaddition with 1,5-cyclooctadiene. The effect of the molar ratio of cyclodiene and hexafluorobenzene on photocycloaddition and on the efficiency of syn and anti addition is also presented in Table 1. Variations in the amount of reactants did not play significant role on the efficiency of syn/anti addition in the case of norbornadiene and 88% of syn addition was observed, the increase of the amount of cyclodiene diminished the quantum yield, while an increased amount of hexafluorobenzene increased the quantum yield for 46%. A similar absence of the effect of the reactant concentration on stereochemistry was also observed by 1,5-cyclooctadiene, where only 52% syn addition was observed, however, a variation of the reactant concentration increased the quantum yield, i.e., 10% by changing concentration of cyclodiene from 0.1 to 0.5 mol l^{-1}, and 62% by increasing the hexafluorobenzene concentration from 0.1 to 0.5 mol l^{-1}. The change of the concentration of the reactants influenced in the case of 1,4-cyclohexadiene photoreaction both the stereospecificity and the efficiency of the [2+2]cycloaddition. Irradiation of equal amounts of the reactants hexafluorobenzene and 1,4-cyclohexadiene resulted in 44% of syn attack, an increase of cyclodiene concentration increased the syn addition to 54% and the quantum yield for 32%, while an increase in hexafluorobenzene concentration decreased the syn attack to 39% but increased the efficiency of the photoprocess by 62%.

Experimental

Preparative experiments were carried out with a Rayonet Model RPR 100 with RPR 253.7 nm lamps. IR spectra were recorded using a Perkin Elmer 727B spectrometer and ^{1}H and ^{19}F NMR spectra by JEOL JNM-PS-100 spectrometer from $CDCl_3$ or CCl_4 solutions with $(CH_3)_4Si$, or CCl_3F as internal reference. Mass spectra and high resolution measurements were taken on a CEC 21-110 spectrometer. TLC was carried out on Merck PSC Fertigplatten F 254, and GLC on Varian Aerograph, Model 1800.

Materials: Hexafluorobenzene, 1,4-cyclohexadiene, 1,5-cyclooctadiene, norbornadiene, were commercially available and distilled before use, while benzonorbornene was synthesized. Cyclohexane was purified and distilled before use. It had been demonstrated in a separate experiment that the presence of oxygen had no significant effect on product distribution and quantum yields and thus no special attention was paid to air exclusion.

Photocycloaddition Reactions of Hexafluorobenzene with Cyclodienes. 1 mmol of cyclodiene and 2 mmol of hexafluorobenzene were dissolved in 18 ml of cyclohexane, the solution irradiated for various times (1—60 h) at λ=253.7 nm, the solvent evaporated in vacuo, the crude reaction mixture analyzed by ^{19}F NMR and the products separated by preparative TLC or GLC.

Reaction with 1,4-Cyclohexadiene (2a). After 1 h irradiation, the reaction mixture was separated by preparative TLC (SiO_2, petroleum ether), and 23% of oily product **3a**, 7% of white crystalline product **4a**, mp=56—58 °C, and 10% of white crystalline product **6**, mp=137—139 °C, was obtained.

Spectroscopic Data for 3a: NMR δ_F −169.5 (m, 2F), −171.75 (broad s, 2F), −198 (m, 2F), δ_H 2.2 (m, 4H), 3.0 (m, 2H), 5.8 (m, 2H), $^3J_{FH}$=7.5 Hz; MS: Calcd for $C_{12}H_8F_6$: M, 266.0931. Found: *m/z* 266.0930; *m/z* 266 (M^+, 5%), 212 (20), 186 (30), 169 (20), 133 (35), 109 (25), 93 (20), 80 (80), 79 (95), 54 (55), 51 (60), 39 (100), 30 (40).

Spectroscopic Data for Product 4a: NMR (numbering of fluorine atoms is evident from Scheme 1): $\delta_{F^{c,d}}$ −129.0 (d, 2F), $\delta_{F^{b,e}}$ −204.25 (m, 2F), $\delta_{F^{a,f}}$ −190.5 (m, 2F, $^3J_{FH}$=7.5 Hz); δ_H 2.3 (m, 4H), 3.08 (m, 2H), 5.9 (m, 2H); MS: Calcd for $C_{12}H_8F_6$: M, 266.05301. Found: *m/z* 266.05272; *m/z* 266 (M+, 4%), 169 (31), 133 (43), 109 (37), 80 (100), 79 (98), 77 (43), 54 (63), 39 (64).

Spectroscopic Data for Product 6: NMR δ_F −167.25 (m, 2F), −216.75 (m, 2F), −217.5 (m, 2F); δ_H 1.88 (m, 4H), 2.64 (dm, 2H), 3.2 (m, 2H); MS: Calcd for $C_{12}H_8F_6$: M, 266.0530. Found: *m/z* 266.0530; *m/z* 266 (M^+, 24%), 164 (30), 134 (31), 133 (100), 115 (40), 80 (36), 79 (76).

Reaction with 1,5-Cyclooctadiene (2b). After 1 h irradiation, the reaction mixture was separated by preparative TLC (SiO_2, petroleum ether), and 36% of mixture of **3b** and **7** and 9% of mixture of **4b** and **8** was isolated. All attempts to separate the products were unsuccessful, however, when 80 mg of mixture of **3b** and **7** was dissolved in 5 ml of cyclohexane and irradiated at λ=253.7 nm for 40 h the formation of isomeric tetracyclic products **4b** and **8** was established.

NMR Data for Product 3b: δ_F −150.75 (m, 2F), −157.0 (broad s, 2F), −204 (m, 2F).

NMR Data for Product 7 (numbering of fluorine atoms is evident from Scheme 1): $\delta_{F^{c,d}}$ −158.5 (m, 2F), $\delta_{F^{b,e}}$ −155.2 (m, 2F), $\delta_{F^{a,f}}$ −165.5 (broad s, 2F), mass spectrum of mixture of **3b** and **7**: Calcd for $C_{14}H_{12}F_6$: M, 294.0844. Found: *m/z* 294.0841.

NMR Data for Product 4b (numbering of fluorine atoms is evident from Scheme 1): $\delta_{F^{c,a}}$ −125.5 (m, 2F), $\delta_{F^{b,e}}$ −195.0 (m, 2F), $\delta_{F^{a,f}}$ −190.0 (m, 2F).

NMR Data for Product 8 (numbering of fluorine atoms is evident from Scheme 1): $\delta_{F^{c,d}}$ −126 (m, 2F), $\delta_{F^{b,e}}$ −195 (m, 2F), $\delta_{F^{a,f}}$ −161.25 (m, 2F); MS of mixture of **4b** and **8**: Calcd for $C_{14}H_{12}F_6$: M, 294.0844. Found: *m/z* 294.0844.

Reaction with Norbornadiene (9a). After 3 h irradiation the reaction mixture was separated by preparative TLC (SiO_2, petroleum ether) and 2% of white crystalline product **10a**, mp=83—85 °C, and 9% of white crystalline product **12a**, mp=85—87 °C was isolated.

Spectroscopic Data for Product 10a: NMR δ_F −162.3 (m, 2F), −163.9 (broad s, 2F), −188.62 (m, 2F); δ_H 6.12 (broad s, 2H), 3.36 (broad s, 2H), 2.34 (m, 2H), 1.35 (m, 2H), $^3J_{FH}$=7.5 Hz; MS: Calcd for $C_{13}H_8F_6$: M, 278.0530. Found: *m/z* 278.0535; *m/z* 278 (M^+, 6%), 232 (43), 186 (71), 117 (50), 92 (83), 91 (100).

Spectroscopic Data for Product 12a: NMR (numbering of fluorine atoms is evident from Scheme 2): $\delta_{F^{c,d}}$ −161.25 (broad s, 2F), $\delta_{F^{b,e}}$ −159.0 (m, 2F), $\delta_{F^{a,f}}$ −168.0 (m, 2F); δ_H 6.2 (broad s, 2H), 3.09 (broad s, 2H), 2.7 (m, 2H), 1.5 (m, 2H), $^3J_{FH}$=26 Hz, $^3J_{F^bF^a}$=13 Hz; MS: Calcd for $C_{13}H_8F_6$: M, 278.0530. Found: *m/z* 278.0518; *m/z* 278 (M^+, 9%), 232 (16), 97 (22), 92 (32), 91 (40), 66 (100).

After 60 h irradiation, the reaction mixture was separated by preparative TLC, and 27% of solid **12a** and 29% of mixture of **11a** and **13a** was isolated. Isomeric pentacyclic products **11a** and **13a** were separated by preparative VPC (FFAP 30%, Chrom A AW, *T*=120 °C) and 7% of white crystalline product **11a**, mp=92—94 °C, and 50% of white crystalline product **13a**, mp =98—100 °C, was isolated.

Spectroscopic Data for Product 11a: NMR (numbering of fluorine atoms is evident from Scheme 2): $\delta_{F^{c,d}}$ −123.75 (d, 2F), $\delta_{F^{b,e}}$ −194.25 (dd, 2F), $\delta_{F^{a,f}}$ −180.75 (dd, 2F); δ_H 6.33 (s, 2H), 3.24 (s, 2H), 2.55 (d, 2H), 1.74 (broad s, 2H), $^3J_{FH}$=7.5 Hz, $^3J_{F^bF^a}$=15 Hz, $^3J_{F^cF^b}$=9 Hz; MS: Calcd for $C_{13}H_8F_6$: M, 278.0530. Found: *m/z* 278.0550; *m/z* 278 (M^+, 10%), 237 (19), 232 (7), 109 (21), 93 (24), 92 (14), 91 (42), 79 (43), 67 (44), 66 (100).

Spectroscopic Data for Product 13a (numbering of fluorine atoms is evident from Scheme 2): $\delta_{F^{c,d}}$ −125.25 (broad s, 2F), $\delta_{F^{b,e}}$ −180 (d, 2F), $\delta_{F^{a,f}}$ −164.25 (d, 2F); δ_H 6.24 (d, 2H), 3.18 (s, 2H), 2.7 (d, 2H), 1.53 (broad s, 2H), $^3J_{FH}$=24 Hz, $^3J_{F^bF^a}$=15 Hz, $^3J_{F^cF^b}$=4.5 Hz; MS: Calcd for $C_{13}H_8F_6$: M, 278.0530. Found: *m/z* 278.0545; *m/z* 278 (M^+, 6%), 237 (5), 232 (18), 97 (20), 92 (25), 91 (44), 79 (20), 67 (14), 66 (100).

0.5 mmol of product **12a** dissolved in 9 ml of cyclohexane, was irradiated at λ=253.7 nm for 60 h, the solvent evaporated in vacuo and the crude reaction mixture, containing only pentacyclic product **13a**, was isolated. 0.5 mmol of product **10a**, dissolved in 9 ml of cyclohexane, was irradiated at λ=253.7 nm for 60 h, the solvent evaporated in vacuo and the reaction mixture, containing only pentacyclic product **11a**, was isolated.

0.5 mmol of pentacyclic product **13a** was heated for 5 min at 150 °C in a sealed glass tube. The crude reaction mixture contained 65% of **10a** and 35% of **12a**. Similar heating of 0.5 mmol of isomeric pentacyclic product **11a** gave a mixture, containing 67% of **10a** and 33% of **12a**.

0.5 mmol of product **12a** was heated for 5 min in a sealed glass tube. The crude reaction mixture contained 30% of the starting material and 70% of **10a**.

After 60 h irradiation of mixture of hexafluorobenzene and norbornadiene at λ=350 nm no products were formed.

Reaction of Benzonorbornene (9c). After 60 h irradiation the reaction mixture was separated by preparative TLC (SiO_2, petroleum ether), 15% of white crystalline product **13c**, mp=132—134 °C and 37% of white crystalline product **12c**, mp=141—143 °C, was isolated.

Spectroscopic Data for Product 12c: NMR (numbering of fluorine atoms is evident from Scheme 2): $\delta_{F^{c,d}}$ −158.3 (broad s, 2F), $\delta_{F^{b,e}}$ −165.75 (d, 2F), $\delta_{F^{a,f}}$ −165 (dd, 2F); δ_H 7.2 (m, 4H), 3.6 (s, 2H), 2.85 (m, 2H), 1.89 (m, 2H), $^3J_{F^bF^a}$=15 Hz, $^3J_{FH}$=25 Hz; MS: *m/z* 328 (M^+, 13%), 282 (19), 186 (57), 181 (20), 147 (40), 143 (27), 142 (100), 141 (81), 129 (68), 128 (25), 116 (77), 115 (76); Calcd for $C_{17}H_{12}F_6$: C, 61.8; H, 3.6%. Found: C, 61.2; H, 3.4%.

Spectroscopic Data for Product 13c: NMR (numbering of fluorine atoms is evident from Scheme 2): $\delta_{F^{c,d}}$ −124.9 (broad s, 2F), $\delta_{F^{b,e}}$ −180 (d, 2F), $\delta_{F^{a,f}}$ −163 (dd, 2F); δ_H 7.2 (m, 4H), 3.66 (s, 2H), 2.85 (d, 2H), 1.89 (m, 2H), $^3J_{F^bF^a}$=15 Hz, $^3J_{FH}$=24 Hz; MS: *m/z* 328 (M^+, 7%), 142 (13), 141 (16), 129 (23), 128 (16), 117 (45), 116 (100), 115 (64); Calcd for $C_{17}H_{12}F_6$: C, 61.8; H, 3.6%. Found: C, 61.8; H, 3.4%.

Determination of Quantum Yields. Quantum yields were measured by using a trioxalatoferrate(III) actinometer and in each experiment the amount of transmitted light was measured. Quartz cuvettes (12 ml) were filled with 10 ml of a cyclohexane solution of hexafluorobenzene and cyclodiene and thermostated by external cooling and the temperature of the solution measured. The light source was an RPR 253.7 nm lamp without filters. In a separate experiment with filters only 2—3% difference was found. The products were analyzed using ^{19}F NMR spectroscopy with $CF_3C_6H_5$ or octafluoronaphthalene as the 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, together with the data on concentrations of reagents, light intensity, and temperatures.

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