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REGIOSPECIFITY OF ACETYLENE PHOTOCYCLOADDITIONS TO FLUOROSUBSTITUTED BENZENES

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Abstract - Irradiation of a cyclohexane solution of hexafluorobenzene and 1-phenyl-2-alkylsubstituted acetylenes resulted in the formation of bicyclo(4.2.0) octatriene derivatives, the quantum yield of (2+2) photoaddition depending on the structure of the acetylene, the concentration of hexafluorobenzene, and the solvent polarity. Reaction with phenylacetylene resulted in the formation of two isomeric cyclooctatetraene derivatives. Regiospecific (2+2) photoaddition of 1-phenyl-2-tert-butylacetylene to position C-3 and C-4 in alkoxysubstituted pentafluorobenzene derivatives was observed. (2+2) photoaddition of 1-phenylpropyne-1 to alkoxysubstituted pentafluorobenzenes resulted in 3-phenyl-4-methyl-7-alkoxy-1,2,5,6,8-pentafluorobicyclo(4.2.0)octatriene derivatives. Replacement of the fluorine atom in hexafluorobenzene with alkoxy substituents diminished quantum yields of (2+2) photocycloadditions.

Aromatic molecules undergo various photochemical transformations, depending on their structure, the reagents, and the reaction conditions, and their phototransformations have been widely investigated in the last twenty years[1]. The advantage of fluorine as a substituent in phototransformations has been shown in several studies with fluorosubstituted aromatic molecules[2]. Irradiation of benzene solutions of various acetylenes resulted in cyclooctatetraene derivatives and the formation of bicyclo(4.2.0)octatriene derivatives was suggested, while we have previously shown the first example of their isolation in photocycloaddition of phenylsubstituted acetylenes to hexafluorobenzene[3].

Results and Discussion

Irradiation of a cyclohexane solution of 1-phenyl-2-tert-butylacetylene and hexafluorobenzene at λ = 253.7 nm gave 1,2,3,4,5,6-hexafluoro-7-phenyl-8-tert-butylbicyclo(4.2.0)octatriene in high yield. The structure of the product was established by X-ray analysis[4]. Bicyclo(4.2.0)octatriene derivatives were also isolated by photoreaction with phenylpropyne and 1-phenylpentyne, while reaction with phenylacetylene gave two cyclooctatetraene derivatives 3 and 4 (Scheme 1). Heating of bicyclo (4.2.0)octatriene derivatives (2) at T=150°C resulted in ring opening, and 1-phenyl-8-alkyl-2,3,4,5,6,7-hexafluorocycloocta-1,3,5,7-tetraenes were formed.

We further studied the effect of the structure of the acetylene on the quantum yield of photocycloaddition to hexafluorobenzene, and the results are presented in Table 1. In figure the effect of variation of phenylpropyne and hexafluorobenzene concentration is presented, and it is evident that increase of hexafluorobenzene concentration for a constant amount of phenylpropyne increased the quantum yield, while variation of acetylene concentration had no significant effect. The solvent polarity also has an effect on the quantum yield of photocycloaddition, being lower in more polar solvents than in n-hexane, while temperature variation only slightly influences the quantum yield /Table 2/.

Further, we studied the regioselectivity of photocycloaddition reactions of phenyl-substituted acetylenes to alkoxysubstituted pentafluorobenzene derivatives in cyclohexane solution and found that two types of products were formed, depending on the structure of the acetylene (Scheme 2). Reactions with 1-phenyl-2-tert-butylacetylene resulted in each experiment in only one product. The mass spectrum of each of the three products /6, R_3 = Me, Et, i-Pr/ contains the major signals at m/e 158 and m/e 143, observed also with 1,2,3,4,5,6-hexafluoro-7-phenyl-8-tert-butylbicyclo(4.2.0) octatriene /2/, corresponding to phenyl-tert-butylacetylene species and tertbutylacetylene species loosing a methyl group, respectively. On the basis of the spectroscopic data and spin-spin decoupling nmr experiments, we established that (2+2) cycloadditions of phenyl-tert-butylacetylene occurred regiospecifically to C-3 and C-4 positions of the alkoxybenzene ring. Replacement of one fluorine in hexafluorobenzene by an alkoxy group diminished the quantum yield of (2+2)cycloaddition, while the structure of the alkoxy group had little effect /Table 1/.

Photoreactions of alkoxysubstituted pentafluorobenzenes with 1-phenylpropyne resulted in one product in each experiment, the nmr spectrum and mass spectra being very different from those observed for products 2 or 6. On the basis of the spectroscopic

SCHEME 1

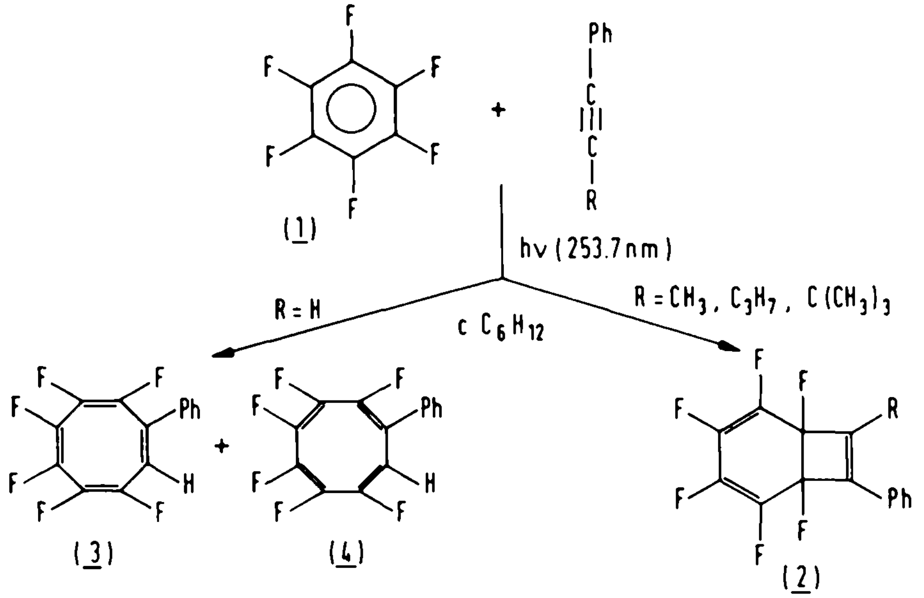
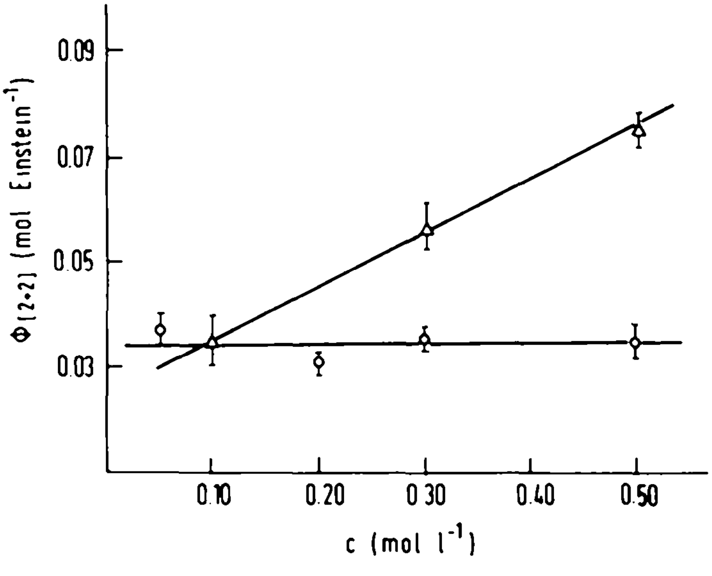


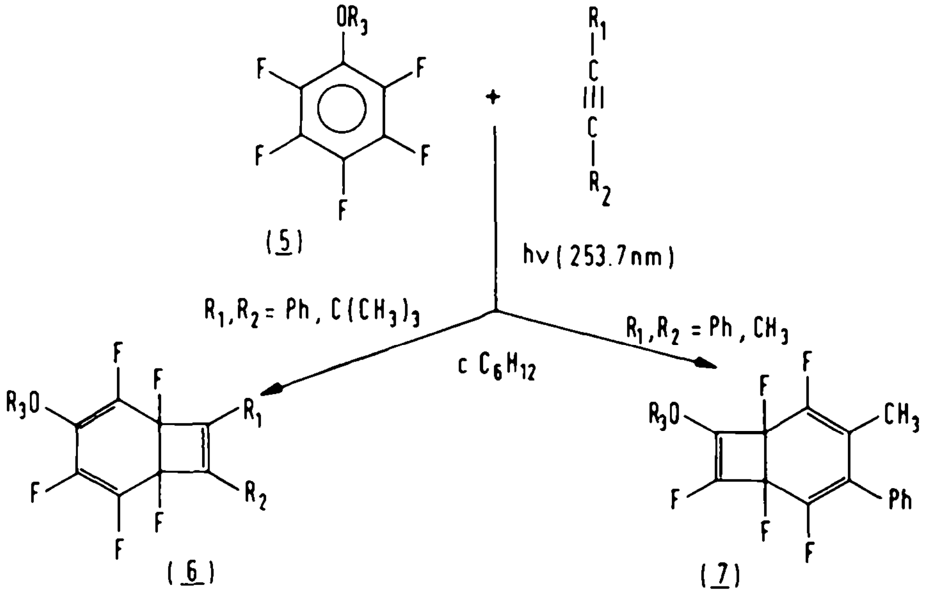
FIGURE DEPENDENCE OF QUANTUM YIELD OF C_6F_6 – PHENYLPROPYNE [2+2] PHOTOADDITION ON C_6F_6 AND PHENYLPROPYNE CONCENTRATION IN CYCLOHEXANE, T = 30°C, λ = 253.7 nm, LIGHT INTENSITY 3.2×10^{15} PHOTONS ML^{-1} S^{-1}

○ VARIATION OF PHENYLPROPYNE CONC., AT CONSTANT C_6F_6 CONC. (0.1 MOL/L)

△ VARIATION OF C_6F_6 CONC., AT CONSTANT PHENYPROPYNE CONC. (0.1 MOL/L)



SCHEME 2



data and spin-spin decoupling nmr experiments, we established that 3-phenyl-4-methyl-7-alkoxy-1,2,5,6,8-pentafluoro-bicyclo(4.2.0)cyclooctatrienes were formed. The quantum yields of (2+2) photocycloadditions are presented in Table 1 and diminishment is again observed when fluorine is replaced by alkoxy group. In order to detect primarily formed (2+2) adducts between alkoxy substituted pentafluorobenzenes and 1-phenylpropyne, we reduced the irradiation time, but we were unable to detect any signals in the ^{19}F nmr spectra of crude reaction mixture which would give evidence for initial formation of adducts similar to compounds 6, transforming further to products 7.

Experimental Section

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 727 B spectrometer and ^{1}H and ^{19}F nmr spectra by Jeol JNM-PS-100 spectrometer from $CDCl_3$ or CCl_4 solutions 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 a Varian Aerograph, Model 1800.

Table 1:

The Effect of Substituents on the Quantum Yield of |2+2| Photocycloaddition in Cyclohexane[a)]

Benzene derivative	Acetylene	$\Phi_{/2+2/}$ /mol Einstein^{-1}/
C_6F_6	$Ph-C\equiv C-CH_3$	0.035 ± 0.005
C_6F_6	$Ph-C\equiv C-CH_2CH_2CH_3$	0.053 ± 0.001
C_6F_6	$Ph-C\equiv C-C(CH_3)_3$	0.133 ± 0.001
$C_6F_5OCH_3$	$Ph-C\equiv C-C(CH_3)_3$	0.028 ± 0.004
$C_6F_5OCH_2CH_3$	$Ph-C\equiv C-C(CH_3)_3$	0.027 ± 0.002
$C_6F_5OCH(CH_3)_2$	$Ph-C\equiv C-C(CH_3)_3$	0.026 ± 0.002
$C_6F_5OCH_3$	$Ph-C\equiv C-CH_3$	0.028 ± 0.002

a) Concentration of benzene derivative: 0.1 mol l^{-1}, concentration of acetylene: 0.1 mol l^{-1}, λ = 253.7 nm, T = 30°C, light intensity: 3.2×10^{15} photons $ml^{-1}s^{-1}$.

Table 2:

Solvent Effect on the Quantum Yield of Hexafluorobenzene-1-Phenyl Propyne |2+2| Photocycloadditions[a)]

Solvent	$\Phi_{/2+2/}$/mol Einstein^{-1}/
$n-C_6H_{14}$	0.039 ± 0.002
$c-C_6H_{12}$	0.035 ± 0.005
$(CH_3)_2CO$	0.024 ± 0.001
CH_3CN	0.025 ± 0.002

a) Concentration of C_6F_6: 0.1 mol l^{-1}, concentration of 1-phenyl propyne: 0.1 mol l^{-1}, T = 30°C, λ = 253,7 nm, light intensity: 3.2×10^{15} photons $ml^{-1}s^{-1}$.

Table 3:

The Effect of Xe and O_2 on the Quantum Yield of Hexafluorobenzene - 1-Phenyl-2-tert-Butyl Acetylene |2+2| Photocycloadditions in Cyclohexane[a)]

Condition	$\Phi_{/2+2/}$/mol Einstein^{-1}/
presence of air	0.133 ± 0.001
degassed	0.134 ± 0.004
O_2-saturated	0.130 ± 0.006
Xe-saturated	0.131 ± 0.001

a) Concentration of C_6F_6: 0.1 mol l^{-1}, concentration of 1-phenyl-2-tert-butyl acetylene: 0.1 mol l^{-1}, T = 30°C, λ = 253.7 nm, light intensity: 3.2×10^{15} photons $ml^{-1}s^{-1}$.

Materials:

Hexafluorobenzene, pentafluroanisole, phenylacetylene, phenylpropyne-1, and phenylpentyne-1 were commercially available and distilled before use. Ethoxypentafluorobenzene, isopropoxypentafluorobenzene, and 1-phenyl-2-tert-butylacetylene were synthesized. Solvents were purified and distilled before use.

A. Reactions of Hexafluorobenzene with Acetylenes

1 mmol of 1-phenyl-2-alkylacetylene and 2 mmols of hexafluorobenzene were dissolved in 18 ml of cyclohexane, the solution was irradiated for 60 hours at λ = 253.7 nm, the solvent was evaporated in vacuo, the crude reaction mixture was analyzed by ^{19}F nmr, and the products were purified.

1,2,3,4,5,6-Hexafluoro-7-Phenyl-8-tert-Butylbicyclo|4.2.0|octatriene

The crude product was crystallized from methanol and 280 mg /86%/ of white crystalline product, mp 98-99°C, was obtained. Nmr: δ_{F_1} -154.9(dd), δ_{F_2} -153.4(ddddd), δ_{F_3,F_4} -161.6, -162.75 (m), δ_{F_5} -150.75(ddddd), δ_{F_6} -159(dd) δ_{CH_3} 1.4 (s,9H), $\delta_{C_6H_5}$ 7.22(s,5H), $^3J_{F_1F_2} = {}^3J_{F_5F_6}$ = 30Hz, $^4J_{F_1F_5} = {}^4J_{F_2F_6} = {}^5J_{F_2F_5}$ = 15 Hz, $^4J_{F_2F_4} = {}^4J_{F_3F_5} = {}^3J_{F_2F_3} = {}^3F_4F_5$ = 7.5 Hz. Mass spectrum: calcd. for $C_{18}H_{14}F_6$ m/e 344.1000, found m/e 344,1001, m/e: 345 (M^+ + 1,18%), 344 (M^+,80), 329 (19), 283 (30), 186 (32), 159 (19), 158 (82), 144 (41), 143 (100), 141 (15), 129 (55), 128 (22), 115 (31), 91 (14), 77 (25), 57 (64), 41 (35).

1,2,3,4,5,6-Hexafluoro-7-Phenyl-8-n-Propylbicyclo|4.2.0|octatriene

Product was purified by preparative tlc and 215 mg /65%/ of crystalline compound, mp 40-42°C, was isolated. Nmr: δ_{F_1} -159 (ddt), δ_{F_2} -155(ddddd), $\delta F_3,F_4$-162 (m), δ_{F_5} -150.5 (ddddd), δ_{F_6} -158.3 (dd), δ_H2.6 (m,2H), 1.8 (m,2H), 1.0(t,3H), 7.4(s,5H), $^3J_{F_1F_2} = {}^3J_{F_5F_6}$ = 30 Hz, $^4J_{F_1F_5} = {}^4J_{F_2F_6} = {}^5F_2F_5$ = 15 Hz, $^4J_{F_2F_4} = {}^4J_{F_5F_3} = {}^3F_2F_3 = {}^3F_4F_5$ = 7.5 Hz, $^4J_{F_1CH_2}$ = 3 Hz. Mass spectrum: calcd. for $C_{17}H_{12}F_6$ m/e 330.0843, found m/e 330.0850, m/e: 331 (M^+ +1,20%), 330 (M^+,100), 301 (41), 288 (31), 287 (39), 281 (34), 269 (18), 268 (19), 261 (17), 237 (22), 144 (19), 129 (27), 121 (19), 120 (21), 119 (60), 117 (61), 115 (28).

1,2,3,4,5,6-Hexafluoro-7-Phenyl-8-Methylbicyclo|4.2.0|octatriene

The product was purified by preparative glc /FFAP 30% Chrom A/AW, T = 210°C/ and 181 mg /60%/ of white crystalline compound, mp 70-71°C, was isolated. Nmr: δ_{F_1} -160 (ddq), δ_{F_2} - 156.4 (ddddd), δ_{F_3,F_4} -162.0, -162.3 (m), δ_{F_5} -150.4 (ddddd), δ_{F_6} -161.25 (dd), δ_{CH_3} 2.1(d,3H), $\delta_{C_6H_5}$ 7.4(m,5H), $^3J_{F_1F_2} = {}^3J_{F_5F_6} = 30$ Hz, $^4J_{F_1F_5} = {}^4J_{F_2F_6} = {}^5J_{F_2F_5} = 15$ Hz, $^4J_{F_5F_3} = {}^4J_{F_5F_3} = {}^4J_{F_2F_4} = {}^3J_{F_2F_3} = {}^3J_{F_4F_5} = 7.5$ Hz, $^4J_{F_1CH_3} = 3$ Hz. Mass spectrum: calcd. for $C_{15}H_8F_6$ 302.0530, found 302.0525, m/e: 302 (M^+,100), 300(23), 287(31), 283(18), 282(12), 281(13), 237(26), 186(27), 120(48), 117(33), 116(96), 115(83).

1-Phenyl-3,4,5,6,7,8-Hexafluorocycloocta-1,3,5,7-Tetraene (3)

From the reaction mixture obtained by irradiation of hexafluorobenzene and phenylacetylene, 3 was isolated by preparative tlc, and 115 mg /40%/ of oily product was obtained. Nmr spectrum: δ_F-107.25 (m,1F),-111.75(m,2F), -129.4(m,3F), δ_H6,1 (broad s,1H). Mass spectrum: calcd.for $C_{14}H_6F_6$ 288,0374, found 288,0370, m/e: 289 (M^++1,17%), 288 (M^+,88), 287(18), 270(35), 237(40), 220(18), 219(26), 186(22), 120(26), 102(100).

1-Phenyl-2,3,4,5,6,7-Hexafluorocycloocta-1,3,5,7-Tetraene (4)

From the reaction mixture obtained by irradiation of hexafluorobenzene and phenylacetylene, 4 was isolated by preparative tlc and 62 mg /21.5%/ of liquid product was obtained. Nmr spectrum: δ_F-123.75 (m,2F), -125.25 (m,1F), -127.5 (dd,1F); -129 (m,1F), -135.75 (m,1F), δ_H6.3 (d), $^3J_{FH} = 24$ Hz. Mass spectrum: calcd. for $C_{14}H_6F_6$ 288.0374, found 288.0380, m/e: 289 (M^++1,18%), 288(M^+,100), 287(28), 270(29), 269(22), 238(18), 237(32), 219 (30),120(42), 102(22).

B. Reactions of Alkoxypentafluorobenzenes with 1-Phenyl-2-tert-Butylacetylene

8 mmols of alkoxypentafluorobenzene and 8 mmols of phenyl-tert-butylacetylene were dissolved in 144 ml of cyclohexane and irradiated for 70 hours /R_3=CH_3, C_2H_5/ or 30 hours /R_3=C_3H_7/ at λ = 253.7 nm. The solvent was evaporated in vacuo, the crude reaction mixture was analyzed by ^{19}F nmr and the products were purified.

3-Methoxy-7-Phenyl-8-tert-Butyl-1,2,4,5,6-Pentafluorobicyclo|4.2.0|octatriene

The product was isolated by preparative tlc /Al_2O_3, chloroform: petrol ether 5:95/, crystallized from methanol and 574 mg /20.1%/ of crystalline product, mp 50-51°C, was obtained. Nmr spectrum: δ_{F_1} -155.25(dd), δ_{F_2} -153.75(ddd), δ_{F_4} -156.75(m), δ_{F_5} -153(dddd), δ_{F_6} -157.5(dd), $\delta_{C(CH_3)_3}$ 1.2 (broad s,9H), δ_{OCH_3} 3.9(broad s,3H), $\delta_{C_6H_5}$ 7.2(m,5H), ${}^3J_{F_1F_2}$ = 33 Hz, ${}^3J_{F_5F_6}$ = 30 Hz, ${}^4J_{F_1F_5}$ = ${}^4J_{F_2F_6}$ = 15 Hz, ${}^5J_{F_2F_5}$ =21 Hz, ${}^3J_{F_4F_5}$ = 7.5 Hz. Mass spectrum calcd. for $C_{19}H_{17}F_5O$ 356.1199, found 356.1212, m/e: 357 (M^++1,11%), 356 (M^+,52), 341 (23), 336 (15), 321 (13), 316 (16), 303 (15), 301 (10), 299 (18), 295 (34), 281 (10), 280 (33), 238 (11), 237 (26), 183 (15), 158 (52), 144 (25), 143 (100), 128 (46), 127 (27), 115 (28), 103(15), 91 (20), 77 (25), 73(16), 61 (13),57 (56), 51 (16).

3-Ethoxy-7-Phenyl-8-tert-Butyl-1,2,4,5,6-Pentafluorobicyclo|4.2.0|octatriene

The product was isolated by preparative tlc /Al_2O_3, petrol ether: chloroform 95:5/, crystallized from methanol and 390 mg /13.2%/ of crystalline product, mp 98-99°C, was obtained. Nmr spectrum: δ_{F_1} -155.25 (dd), δ_{F_2} -151.9 (ddd), δ_{F_4} -156.4 (m), δ_{F_5} -153.75 (dddd) δ_{F_6} -157.5 (dd), $\delta_{C(CH_3)_3}$ 1.2 (broad s,9H), δ_{CH_3} 1.3 (m,3H), δ_{CH_2} 4.05 (m,2H), $\delta_{C_6H_5}$ 7.2 (m,5H), ${}^3J_{F_1F_2}$ = 33 Hz, ${}^3J_{F_5F_6}$ = 30 Hz, ${}^4J_{F_1F_5}$ = ${}^4J_{2F_6}$ = 15 Hz, ${}^5J_{F_2F_5}$ = 21 Hz, ${}^3J_{F_4F_5}$ = 7.5 Hz. Mass spectrum calcd. for $C_{20}H_{19}F_5O$ m/e 370.1356, found m/e 370.1347, m/e: 371 (M^++1,8%), 370 (M^+,24), 158 (32), 144 (14), 143 (100), 128 (21), 127 (10), 115 (14), 77 (11), 58 (36).

3-iso-Propoxy-7-Phenyl-8-tert-Butyl-1,2,4,5,6-Pentafluorobicyclo|4.2.0|octatriene

The product was isolated by preparative tlc /Al_2O_3, petrol ether: chloroform 95:5/, crystallized from methanol and 1g /32.5%/ of crystalline product, mp 86-88°C, was obtained. Nmr spectrum: δ_{F_1} -155.3 (dd), δ_{F_2} -148.1 (ddd), δ_{F_4} -155.6 (m), δ_{F_5} -153.4 (dddd), δ_{F_6} -157.2 (dd), $\delta_{C(CH_3)_3}$ 1.26 (broad s,9H), $\delta_{(CH_3)_2}$ 1.3 (m,6H), δ_{CH} 4.35(m,1H), $\delta_{C_6H_5}$ 7.3 (m,5H), ${}^3J_{F_1F_2}$ = 33 Hz, ${}^3J_{F_5F_6}$ = 30 Hz, ${}^4J_{F_1F_5}$ = ${}^4J_{F_2F_6}$ = 15 Hz, ${}^5J_{F_2F_5}$ =21 Hz, ${}^3J_{F_4F_5}$ = 7.5 Hz. Mass spectrum: calcd. for $C_{12}H_{21}F_5O$ m/e 384.1512, found m/e 384.1520, m/e: 385 (M^++1,1%), 384 (M^+,5), 342 (19), 327 (14), 322 (15), 307 (41), 281 (28), 264 (30), 229 (15), 158 (97), 144 (23), 143 (100), 128 (40), 127 (18), 115 (21), 77 (21), 61 (19), 57 (89).

C. Reactions of Alkoxypentafluorobenzenes with 1-Phenylpropyne-1

8 mmols of alkoxypentafluorobenzene and 8 mmols of 1-phenylpropyne-1 were dissolved in 144 ml of cyclohexane and irradiated for 71 hours /R_3=CH_3/, 17 hours /R_3=C_2H_5/ or 15 hours /R_3=C_3H_7/ at λ = 253.7 nm. The solvent was evaporated in vacuo, the crude reaction mixture was analyzed by ^{19}F nmr and the crude products were purified.

3-Phenyl-4-Methyl-7-Methoxy-1,2,5,6,8-Pentafluoro|4.2.0|octatriene

The product was isolated by preparative tlc /Al_2O_3, petrol ether: chloroform 95:5/ crystallized from methanol, and 65 mg /2.6%/ of crystalline product, mp = 79-80°C, was obtained. Nmr spctrum: δ_{F_1} -163.5 (ddd), δ_{F_2} -126.0 (dddd), δ_{F_5} -129.4 (dddq), δ_{F_6} -157.8 (dddq), δ_{F_8} -133.5 (ddd), δ_{CH_3} 1.65(t,3H), δ_{OCH_3} 3.96 (broad s, 3H), $\delta_{C_6H_5}$ 7.2 (m,5H), ${}^3J_{F_1F_2}$ = 36 Hz, ${}^3J_{F_5F_6}$ = 30 Hz, ${}^5J_{F_2F_5}$ = 30 Hz, ${}^3J_{F_1F_8}$ = 24 Hz, ${}^4J_{F_1F_5}$ = ${}^4J_{F_2F_6}$ = 12 Hz, ${}^4J_{F_6F_8}$ = 9 Hz, ${}^4J_{F_8F_2}$ = 3 Hz, ${}^4J_{F_5CH_3}$ = 3Hz. Mass spectrum: calcd. for $C_{16}H_{11}F_5O$ m/e 314.0730, found m/e 314.0730, m/e: 315 (M^++ 1,16%), 314 (M^+,100), 300 (27), 299 (77), 280 (46), 279 (46), 271 (24), 252 (45), 251 (47), 250 (45), 237 (46), 233 (28), 232 (50), 219 (50), 206 (21), 202 (37), 201 (58), 194 (33), 183 (23), 181 (24), 143 (19), 117 (19), 116 (58), 115 (47), 77 (35), 75 (24), 69 (44), 61 (27), 51 (47).

3-Phenyl-4-Methyl-7-Ethoxy-1,2,5,6,8-Pentafluoro|4.2.0|octatriene

The product was isolated by preparative tlc (Al_2O_3, petrol ether: chloroform 95:5/ and 142 mg /10.8%/ of oily product was isolated. Nmr spectrum: δ_{F_1} -163.5 (ddd), δ_{F_2} - 125.8 (ddddd), δ_{F_5} -129.0 (dddq), δ_{F_6} -158.0 (dddq), δ_{F_8} -132.8 (ddd), δ_{CH_3} 1.65 (t,3H), $\delta_{C\underline{H}_3CH_2}$ 1.35 (m,3H), δ_{CH_2} 4.3 (m,2H), $\delta_{C_6H_5}$ 7.2 (m,5H), ${}^3J_{F_1F_2}$ = 36 Hz, ${}^3J_{F_5F_6}$ = 30 Hz, ${}^5J_{F_2F_5}$ = 30 Hz, ${}^3J_{F_1F_8}$ = 24 Hz, ${}^4J_{F_1F_5}$ = ${}^4J_{F_2F_6}$ = 12 Hz, ${}^4J_{F_6F_8}$ = 9 Hz, ${}^4J_{F_8F_2}$ = 3 Hz, ${}^4J_{F_5CH_3}$ = ${}^5J_{F_6CH_3}$ = 3 Hz. Mass spectrum: calcd. for $C_{17}H_{13}F_5O$ m/e 328.1124, found m/e 328.1120, m/e: 329 (M^++ 1,14%), 328 (M^+,70), 300 (48), 299 (50), 280 (92), 279 (36), 251 (35), 237 (42), 232 (31), 219 (33), 201 (53), 121 (39), 120 (36), 119 (95), 117 (100), 116 (72), 115 (66), 82 (36), 57 (18), 55 (22).

3-Phenyl-4-Methyl-7-iso-Propoxy-1,2,5,6,8-Pentafluoro|4.2.0|octatriene

The product was isolated by preparative tlc /Al_2O_3, petrol ether: chloroform 95:5/, crystallized from methanol, and 540 mg /19.7%/ of crystalline product, mp 64-66°C, was obtained. Nmr spectrum: δ_{F_1} -163.8 (ddd), δ_{F_2} -126.0 (ddddd), δ_{F_5} -129.3 (dddq), δ_{F_6} -157.5 (dddq), δ_{F_8} -131.3 (ddd), δ_{CH_3} 1.6 (t,3H), $\delta_{(CH_3)_2}$ 1.35 (m,6H), δ_{CH} 4.62 (m,1H), ${}^3J_{F_1F_2}$ = 36 Hz, ${}^3J_{F_5F_6}$ = 30 Hz, ${}^5J_{F_2F_5}$ = 30 Hz, ${}^3J_{F_1F_8}$ = 24 Hz, ${}^4J_{F_1F_5}$ = ${}^4J_{F_2F_6}$ = 12 Hz, ${}^4J_{F_6F_8}$ = 9 Hz, ${}^4J_{F_8F_2}$ = 3 Hz, ${}^4J_{F_5CH_3}$ = ${}^5J_{F_6CH_3}$ = 3 Hz.Mass spectrum: calcd. for $C_{18}H_{15}F_5O$ m/e 342.1043, found m/e 342.1042, m/e 343 (M^++ 1,5%), 342 (M^+, 23), 301 (19), 300 (100), 299 (19), 281 (24), 280 (90), 279 (24), 253 (32), 252(48), 251 (37), 250 (18), 237 (55), 233 (35), 232 (37), 219 (29), 202 (23), 201 (53), 120 (34), 117 (11), 116 (77), 115 (35), 77 (18), 51 (21).

Determination of Quantum Yields

Quantum yields were measured by using a ferrioxalate actinometer and in each experiment the amount of transmitted light was meassured. Quartz cuvettes /12 ml/ were filled with 10 ml of a solution /cyclohexane, n-hexane, methanol, or acetone/, of nexafluorobenzene or alkoxysubstituted pentafluorobenzene and phenylsubstituted acetylene, and thermostatted by external cooling, and the temperature of the solution was measured. The light source was an RPR 253.7 nm without filters. In a separate experiment with filters we found only 2-3% difference. Products were analyzed using ^{19}F nmr spectroscopy with $CF_3C_6H_5$ or octafluoronaphthalene as an internal standard which was added after solvent evaporation. Irradiation times were chosen so that conversion of fluorosubstituted benzenes was no larger than 5-7% of their initial concentration. Each quantum yield determination was repeated at least three times and the average data are presented in the Tables. The concentrations of reagents, light intensity and temperatures are also listed in the Tables.

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