

atmosphere to a stirred solution of  $8^8$  (540 mg) in 10 mL of DME to which 2.47 g of  $\text{Et}_4\text{NBr}$  had been added. After 40 h the usual workup and chromatography afforded 230 mg of pure **9**, which was crystallized from  $\text{Et}_2\text{O}$ : mp 106–107 °C;  $[\alpha]_D^{20} +20.8$  (c 0.5,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ , 200 MHz)  $\delta$  1.88, 1.98, 2.00 (9 H, s, OAc), 3.42 (1 H, m,  $J_{4,5} = 12$  Hz,  $J_{5,6} = 5$  Hz,  $J_{6,6'} = 2.5$  Hz, H-5), 4.22 (1 H, dd,  $J_{6,6'} = 13.5$  Hz,  $J_{5,6} = 2.5$  Hz, H-6'), 4.25 (1 H, d,  $J_{1,1'} = 6$  Hz, H-1'), 4.26 (1 H, dd,  $J_{1,2} = 10$  Hz,  $J_{2,3} = 10$  Hz, H-2), 4.39 (1 H, dd,  $J_{1,1'} = 6$  Hz,  $J_{1,2} = 10$  Hz, H-1), 4.52 (1 H, dd,  $J_{6,6'} = 13.5$  Hz,  $J_{5,6} = 5$  Hz, H-6), 4.90 (2 H, d,  $J = 1$  Hz,  $\text{OCH}_2\text{Ph}$ ), 5.20 (2 H, s,  $\text{PhCH}_2\text{COO}$ ), 5.22 (2 H, s,  $\text{PhCH}_2\text{COO}$ ), 5.5 0 (1 H, dd,  $J_{3,4} = 10$  Hz,  $J_{4,5} = 12$  Hz, H-4), 5.62 (1 H, dd,  $J_{3,4} = 10$  Hz,  $J_{2,3} = 10$  Hz, H-3), 7.46 (5 H, PhH);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ) 53.40 ppm (C-1').

(1-Deoxy- $\alpha$ -D-glucopyranosyl)methanephosphonic Acid (**17**). To a stirred solution of 5.8 g of the mercurio derivative **14**<sup>13</sup> in 40 mL of  $\text{CH}_2\text{Cl}_2$  was added 1.34 g of  $\text{Br}_2$  in 40 mL of  $\text{CH}_2\text{Cl}_2$  dropwise under an argon atmosphere. After 16 h at room temperature the solvent was removed under reduced pressure, and the residue was chromatographed, affording **15**: 2.3 g (50%); oily product;  $^{13}\text{C NMR}$  ( $\text{C}_6\text{D}_6$ ) 29.03 ppm ( $\text{CH}_2\text{Br}$ ). The bromide **15** (2.3 g) was refluxed under an argon atmosphere with 35 mL of  $\text{P}(\text{OEt})_3$  for 7 h. The excess of reagent was then removed under reduced pressure (0.5 mmHg), and the residue afforded, after chromatography, 1.5 g (60%) of **16** as an oily product:  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  1.02 (3 H, t,  $J = 7$  Hz,  $\text{OCH}_2\text{CH}_3$ ), 2.62 (2 H, m, H-1'), 4.50, 4.53, 4.66 (8 H,  $\text{OCH}_2\text{Ph}$ ), 3.5–4.5 (7 H), 7.25 (20 H, PhH);  $^{13}\text{C NMR}$  ( $\text{C}_6\text{D}_6$ ) 16.31, 16.55 ( $\text{OCH}_2\text{CH}_3$ ), 26.90 ppm (d,  $J_{\text{C,P}} = 139$  Hz, C-1');  $^{31}\text{P NMR}$  ( $\text{CDCl}_3$ ) -27.02 ppm.

A solution of 520 mg of **16** in 2 mL of  $\text{CCl}_4$  was treated at 0 °C with 1 mL of  $\text{Me}_3\text{SiI}$ . After 30 min, 1 mL of water was added to the reaction mixture, and the solvent was removed under reduced pressure. The residue (220 mg), which exhibited a single spot of  $R_f$  0.41 on cellulose TLC [developed with 1-propanol-ammonia-water (4:3:1) and visualized with molybdate reagent], was chromatographed on cellulose. The recovered pure **17** (204 mg) was crystallized by rubbing under ethanol. The material is hygroscopic and analyzed for the monohydrate monoammonium salt:  $^1\text{H NMR}$  ( $\text{D}_2\text{O}$ , 200 MHz)  $\delta$  1.95 (2 H, ABMX system,  $J_{\text{H,P}} = 18$  Hz,  $J_{1,1'} = 7$  Hz, H-1'), 3.5–4.5 (7 H), 4.38 (1 H, dd,  $J_{1,2} = 3$  Hz,  $J_{1,1'} = 7$  Hz, H-1);  $^{13}\text{C NMR}$  ( $\text{D}_2\text{O}$ , dioxane as reference) -38.12 ppm (d,  $J_{\text{C,P}} = 129$  Hz, C-1');  $^{31}\text{P NMR}$  ( $\text{D}_2\text{O}$ ) -20.41 ppm. Anal. Calcd for  $\text{C}_7\text{H}_{18}\text{O}_8\text{PN}$ ,  $\text{H}_2\text{O}$ : C, 28.68; H, 6.87; N, 4.77. Found: C, 28.48; H, 6.86; N, 5.33.

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**Registry No.** 1, 4196-35-4; 2, 4132-26-7; 4, 34010-30-5; 5, 82933-03-7; 6, 82933-04-8; 7, 82977-27-3; 7-NH<sub>3</sub>, 82977-28-4; 8, 29741-69-3; 9, 82933-05-9; 10, 38768-81-9; 11, 82933-07-1; 14, 79258-17-6; 15, 82701-47-1; 16, 82701-48-2; 17, 82933-06-0; 17-NH<sub>3</sub>, 82978-36-7; P-(OEt)<sub>3</sub>, 122-52-1; (carboethoxymethylene)triphenylphosphorane, 1099-45-2; methylenetriphenylphosphorane, 3487-44-3; sodium dibenzyl malonate, 65460-99-3.

## Regio- and Stereospecific [2 + 2] Photoaddition of Cycloalkenes to Pentafluoropyridine<sup>1</sup>

Boris Šket, Nataša Zupančič, and Marko Zupan\*

Department of Chemistry and "J. Stefan" Institute, "E. Kardelj" University of Ljubljana, Ljubljana, Yugoslavia

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Cyclohexane as a solvent plays an important role in the stereochemistry of photocycloaddition of cycloalkenes to pentafluoropyridine. [2 + 2] photoaddition of cyclopentene or cycloheptene to pentafluoropyridine in cyclohexane proceeds regiospecifically at positions C-3 and C-4 and is stereospecifically exo. The primary [2 + 2] adducts formed undergo further photochemical and thermal [2 + 4] cycloaddition with cycloalkenes. The quantum yield of [2 + 2] photocycloaddition depends on ring size and the concentration of cycloalkene.

The photochemical transformations and cycloaddition reactions of aromatic molecules and their derivatives have been widely investigated in the last 20 years.<sup>2</sup> On the other hand, reactions of heteroaromatic molecules have received much less attention.<sup>3</sup>

The use of fluorine as a convenient substituent for photochemical transformations of organic molecules has been variously reported and has been reviewed.<sup>4</sup> The photocycloaddition reaction of hexafluorobenzene with

cis-cyclooctene gave various 1:1 cycloadducts which are formed via 1,2- and 1,3-addition processes.<sup>5</sup> On the other hand, we have demonstrated that cyclohexane as a solvent plays an important role in [2 + 2] photocycloaddition reactions of hexafluorobenzene with cycloalkenes, the stereochemistry depending also on the structure of the cycloalkene.<sup>6</sup> Recently, Haszeldine and co-workers<sup>7</sup> have shown that irradiation of a mixture of cycloalkenes and pentafluoropyridine gave two pairs of 2:1 adducts, which are formed by [2 + 2] addition at C-3 and C-4, and [4 + 2] addition at C-2 and C-5, the ratio of the products de-

(1) Presented in part: Zupan, M.; Sket, B. Yugoslave Symposium on Organic Chemistry, Beograd, Yugoslavia, Jan 17–19, 1977. Sket, B.; Zupan, M.; Kovač, Z. 7th IUPAC Symposium on Photochemistry, Lueven, July, 24–28 1978.

(2) Bryce-Smith, D. "Photochemistry"; The Chemical Society, Burlington House: London, 1970–1980; Vol. 1–10, Bryce-Smith, D.; Gilbert, A. *Tetrahedron* 1976, 32, 1309; 1977, 33, 2459. Kaupp, G. *Angew. Chem.* 1980, 92, 245. Wagner-Jauregg, T. *Synthesis* 1980, 165, 769. Cornélise, J.; Havinga, E. *Chem. Rev.* 1975, 75, 353.

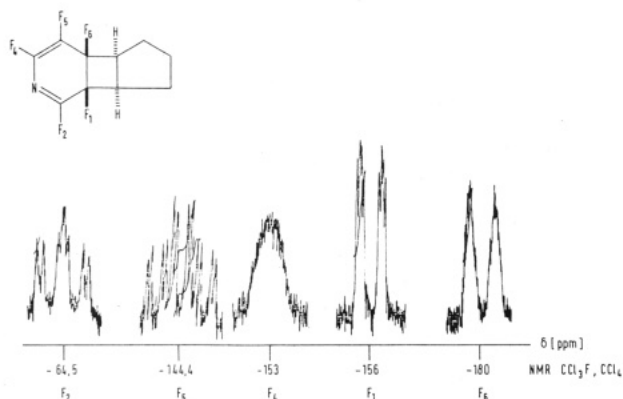
(3) Buchard, O. "Photochemistry of Heterocyclic Compounds"; Wiley: New York, 1976.

(4) Zupan, M.; Sket, B. *Isr. J. Chem.* 1978, 17, 92.

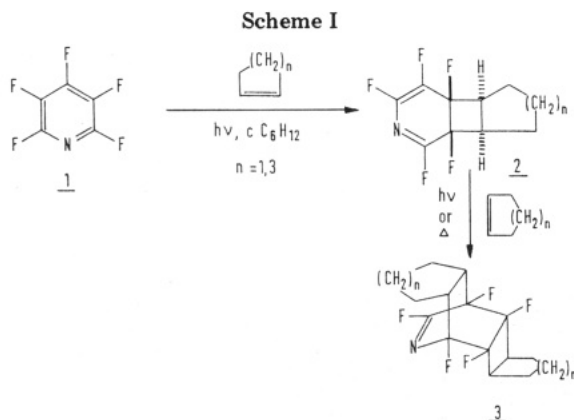
(5) Bryce-Smith, D.; Gilbert, A.; Orger, B. H. *J. Chem. Soc., Chem. Commun.* 1969, 800. Bryce-Smith, D.; Gilbert, A.; Orger, B. H.; Twichett, P. *J. J. Chem. Soc., Perkin Trans. 1* 1978, 232.

(6) Sket, B.; Zupan, M. *J. Chem. Soc., Chem. Commun.* 1976, 1053; 1977, 365. Sket, B.; Zupan, M. *Tetrahedron Lett.* 1977, 2811.

(7) Barlow, M. G.; Brown, D. E.; Haszeldine, R. N. *J. Chem. Soc., Chem. Commun.* 1977, 669. Barlow, M. G.; Brown, D. E.; Haszeldine, R. N. *J. Chem. Soc., Perkin Trans. 1* 1978, 363. Barlow, M. G.; Brown, D. E.; Haszeldine, R. N.; Langridge, J. R. *Ibid.* 1980, 129.



**Figure 1.**  $^{19}\text{F}$  NMR of the compound formed from irradiation of a cyclohexane solution of 2 mmol of pentafluoropyridine and 1 mmol of cyclopentene at 253.7 nm.



pending on the ring size. In the course of our continued interest in the photoreactions of fluoro-substituted organic molecules<sup>1,6</sup> we found it worthwhile to study the regio- and stereospecificity of [2 + 2] photocycloaddition reactions of cycloalkenes to pentafluoropyridine in cyclohexane.

### Results and Discussion

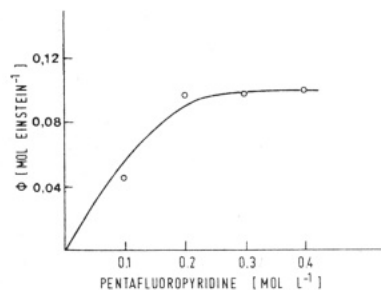
A 20-h irradiation of a cyclohexane solution of 1 mmol of pentafluoropyridine and 2 mmol of cyclopentene at  $\lambda = 253.7$  nm resulted in the formation of only one product, which shows five multiplet signals in its  $^{19}\text{F}$  NMR spectrum:  $\delta$  -51, -165, -202.5, -210, and -211.1. The mass spectrum shows that two cyclopentene rings are added to the pyridine nucleus.

However, on the basis of the spectroscopic data we were unable to establish the structure of the product. A change in the ratio of cyclopentene to pentafluoropyridine to 1:2 and diminishing the irradiation time to 3 h resulted in the formation of a new product with the  $^{19}\text{F}$  NMR spectrum presented in Figure 1. On the basis of the NMR data, the mass spectrum, and the IR spectrum, we concluded that a [2 + 2] adduct was formed regio- and stereospecifically (Scheme I; 2,  $n = 1$ ). Thermal or photochemical reaction (much quicker than thermal reaction) of 2 with cyclopentene in cyclohexane solution resulted in the formation of product 3 ( $n = 1$ ), which is identical with the one observed by photoreaction of 1 mmol of pentafluoropyridine and 2 mmol of cyclopentene. X-ray analysis of product 3<sup>8</sup> confirmed that photoaddition of cyclopentene to pentafluoropyridine proceeds in the first step as [2 + 2] addition at C-3 and C-4 of pentafluoropyridine via exo attack, while further addition of cyclopentene results in a [2 + 4]

**Table I.** Quantum Yields for [2 + 2] Photocycloaddition Reactions<sup>a</sup>

compd	cycloalkene	$\Phi$
pentafluoropyridine	cyclopentene	$0.096 \pm 0.008$
pentafluoropyridine	cycloheptene	$0.037 \pm 0.004$
hexafluorobenzene	cyclopentene	$0.063 \pm 0.004$

<sup>a</sup> The concentration of the cyclohexane solution of pentafluoropyridine or hexafluorobenzene was 0.2 mol/L, and that of cycloalkenes was 0.1 mol/L. The solution was irradiated at  $\lambda = 253.7$  nm and a temperature of 32 °C.

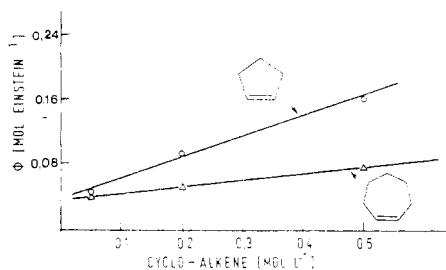


**Figure 2.** Dependence of quantum yield of pentafluoropyridine-cyclopentene addition on  $\text{C}_5\text{NF}_5$  concentration at a constant  $\text{C}_5\text{NF}_5/\text{C}_5\text{H}_8$  ratio of 2:1 in cyclohexane.

photo or thermal adduct (3).

It is interesting that irradiation in cyclohexane gave only one product, while there is the possibility of the formation of six [2 + 2] isomers, and further [2 + 4] reaction could result in 24 possible isomers, some of them being less probable from steric reasons. The important role of the solvent in the course of photocycloaddition reaction, as already demonstrated in the case of hexafluorobenzene,<sup>6</sup> has been again confirmed in the photocycloaddition reaction of cyclopentene to pentafluoropyridine. Haszeldine and co-workers<sup>7</sup> did not observe the formation of a 1:1 product after a 200-h irradiation of a mixture of pentafluoropyridine and cyclopentene, and the formation of only two 1:2 adducts was observed. On the basis of spectroscopic data they suggested that, in the case of cyclopentene, in the first step [2 + 2] endo attack is predominant over exo attack. The NMR data for the minor product (30%) are very similar to ours, as well as the mass spectrum, with the exception of the relative intensities. Irradiation of a cyclohexane solution of pentafluoropyridine and cyclohexane resulted in a mixture of at least three products, while the reaction with cycloheptene gave very similar results to those observed with cyclopentene (Scheme I,  $n = 3$ ).

Further, we studied the effect of the ring size of the cycloalkene on the quantum yield for the [2 + 2] cycloaddition reaction with pentafluoropyridine (Table I). The concentration of pentafluoropyridine was 0.2 mol/L and that of cycloalkene 0.1 mol/L. All measurements were made at 32 °C and at  $\lambda = 253.7$  nm. Irradiation times were chosen so that the conversion of pentafluoropyridine was not larger than 5% of the initial concentration. The amount of [2 + 2] adduct formed was determined by  $^{19}\text{F}$  NMR spectroscopy with trifluoromethylbenzene as an internal reference, which was added after the reaction. At the stated concentrations, the quantum yield for [2 + 2] addition is largest for reaction with cyclopentene. In the case of cyclopentene, the primary [2 + 2] adduct formed is much more easily converted to the 1:2 adduct than in the case of cycloheptene. The quantum yield of the [2 + 2] cycloaddition reaction of cyclopentene to hexafluorobenzene under similar conditions is lower than that in the photoaddition to pentafluoropyridine.



**Figure 3.** Dependence of quantum yield of pentafluoropyridine-cycloalkene [2 + 2] photoaddition on cycloalkene concentration in cyclohexane. The concentration of  $C_5NF_5$  was  $0.1 \text{ mol L}^{-1}$ .

The effect of the concentration of pentafluoropyridine on the quantum yield at a constant ratio of pentafluoropyridine and cyclopentene (2:1) is shown in Figure 2: at lower concentrations, the quantum yield is lower, and an increasing concentration leads to an increasing quantum yield, until, at higher concentrations, it becomes constant.

Investigation of the effect of the concentration of *cis*-cyclooctene on the quantum yield of the photoaddition reaction to hexafluorobenzene showed that there is no dependence in the 1,3-photocycloaddition reaction, while in the 1,2-addition an increased concentration of hexafluorobenzene leads to higher quantum yields.<sup>5</sup> We studied the effect of the concentration of cyclopentene and cycloheptene on the quantum yield for [2 + 2] photoaddition at a constant concentration of pentafluoropyridine and found that an increasing concentration increased the quantum yield, the effect being more pronounced in the case of cyclopentene (Figure 3). As in the case of hexafluorobenzene photocycloaddition reactions,<sup>5</sup> we also found no effect of oxygen on the quantum yield of the reaction. The temperature has a very similar effect on quantum yield as that observed in photoaddition of *cis*-cyclooctene to hexafluorobenzene;<sup>5</sup> i.e., an increase in temperature results in higher quantum yields.

### Experimental Section

Preparative experiments were carried out with a Rayonet Model RPR 100 with RPR 253.7-nm lamps. IR spectra were recorded by using a Perkin-Elmer 272 B spectrometer and  $^1H$  and  $^{19}F$  NMR spectra by using a JEOL JNM PS 100 spectrometer from  $CDCl_3$  or  $CCl_4$  solutions, with  $Me_4Si$  or  $CCl_3F$  as an internal reference. Mass spectra and high-resolution measurements were taken on a CEC 21-110 spectrometer. TLC was carried on Merck silica gel Fertigplatten F-254 (activated for 3 h at  $120^\circ C$  before use).

**Materials.** Pentafluoropyridine, cyclopentene, and cycloheptene were commercially available and distilled before use. Cyclohexane was purified and distilled before use.

**Photochemical Addition of Pentafluoropyridine. (A) With Cyclopentene.** Pentafluoropyridine (2 mmol) and 1 mmol of cyclopentene were dissolved in 18 mL of cyclohexane, the solution was irradiated for 3 h at  $\lambda = 253.7 \text{ nm}$ , the solvent was evaporated in vacuo, and 180 mg of crude product was isolated; this was analyzed by  $^{19}F$  NMR spectroscopy. The product was purified by preparative TLC ( $SiO_2$ ; petroleum ether/chloroform, 95:5), and 95 mg (40%) of oily [2 + 2] adduct 2 ( $n = 1$ ) was isolated:

$^{19}F$  NMR  $\delta$  -64.5 ( $J = 30, 27, 7.5 \text{ Hz}$ ), -144.4 ( $J = 30, 30, 18, 4.5 \text{ Hz}$ ), -153 (m), -165 ( $J = 27, 4.5, 3 \text{ Hz}$ ), -180 ( $J = 30 \text{ Hz}$ ); Mass spectrum, calcd for  $C_{10}H_8NF_5$   $m/e$  237.0576, found  $m/e$  237.0570,  $m/e$  (relative intensity) 237 ( $M^+$ , 3), 68 (33), 67 (15), 66 (11), 56 (100), 55 (37).

A 20-h irradiation of a mixture of 1 mmol of pentafluoropyridine and 2 mmol of cyclopentene gave 198 mg of crude product, which was purified by TLC ( $SiO_2$ ; petroleum ether/chloroform, 95:5), the product was crystallized from methanol, and 110 mg (36.1%) of white crystalline product (3,  $n = 1$ ; mp  $115$ – $117^\circ C$ ) was isolated:  $^{19}F$  NMR  $\delta$  -151 (m), -165 (m), -202.5 (m), -210 (m), -211.1 (m); mass spectrum, calcd for  $C_{16}H_{16}NF_5$   $m/e$  305.1203, found  $m/e$  305.1203,  $m/e$  (relative intensity) 305 ( $M^+$ , 77), 238 (6), 175 (100), 170 (9), 68 (49), 67 (43). The structure of the product was also proven by X-ray analysis.<sup>8</sup>

**(B) With Cycloheptene.** A 3-h irradiation of a cyclohexane solution (18 mL) of 2 mmol of pentafluoropyridine and 1 mmol of cycloheptene gave, after TLC purification ( $Al_2O_3$ , petroleum ether/chloroform, 95:5), 75 mg (28.3%) of oily product 2 ( $n = 3$ ):  $^{19}F$  NMR  $\delta$  -64.5 ( $J = 33, 27, 7.5 \text{ Hz}$ ), -136.5 ( $J = 33, 33, 18, 6 \text{ Hz}$ ), -144 (m), -163.5 ( $J = 27, 4.5, 4.5 \text{ Hz}$ ), -174.1 ( $J = 33 \text{ Hz}$ ); mass spectrum, calcd for  $C_{12}H_{12}NF_5$   $m/e$  265.0890, found  $m/e$  265.0890,  $m/e$  (relative intensity) 265 ( $M^+$ , 2), 151 (6), 150 (6), 96 (30), 84 (58), 83 (17), 81 (53), 69 (24), 68 (30), 67 (50), 57 (12), 56 (96), 55 (80), 54 (44), 53 (15), 42 (30), 41 (100).

A 20-h irradiation of a cyclohexane solution (18 mL) of 1 mmol of pentafluoropyridine and 2 mmol of cycloheptene gave, after TLC purification, 162 mg (44.9%) of crystalline product 3 ( $n = 3$ ): mp  $148$ – $149^\circ C$ ;  $^{19}F$  NMR  $\delta$  -52.5 (m), -164 (m), -199.5 (m), -208 (m), -208.75 (m); mass spectrum, calcd for  $C_{19}H_{24}NF_5$   $m/e$  361.1829, found  $m/e$  361.1830,  $m/e$  (relative intensity) 361 ( $M^+$ , 56), 266 (12), 203 (9), 170 (5), 96 (100), 95 (22).

**Reaction of [2 + 2] Adduct 2 ( $n = 1$ ) with Cyclopentene.**

**(A) Photochemical Reaction.** Compound 2 ( $n = 1$ ; 40 mg) and 60 mg of cyclopentene were dissolved in 5 mL of cyclohexane, and the mixture was irradiated for 10 h at  $\lambda = 253.7 \text{ nm}$ . The solvent was evaporated in vacuo, and a  $^{19}F$  NMR spectrum was taken, which showed only signals corresponding to 3 ( $n = 1$ ).

**(B) Thermal Reaction.** A 40-mg sample of [2 + 2] adduct 2 ( $n = 1$ ) and 60 mg of cyclopentene were dissolved in 5 mL of cyclohexane and heated at  $40^\circ C$  for 10 h, and the solvent was evaporated. The  $^{19}F$  NMR spectrum shows the presence of compounds 2 ( $n = 1$ ) and 3 ( $n = 1$ ) in the ratio 4:1.

**Determination of Quantum Yields.** Quantum yields were measured by using a ferrioxalate 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 pentafluoropyridine and cycloalkene and thermostated by external cooling, and the temperature of the solution was measured. The light source was an RPR 253.7-nm lamp without filters. In a separate experiment with filters, we found only 2–3% differences. Products were analyzed by using  $^{19}F$  NMR spectroscopy, with  $CF_3C_6H_5$  as internal standard, which was added after solvent evaporation. Irradiation times were chosen so that conversions of pentafluoropyridine were not 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 Table I and the figures. It was demonstrated that the presence of oxygen has no effect on quantum yields, and for this reason no special attention was paid to its exclusion.

**Registry No.** 1, 700-16-3; 2 ( $n = 1$ ), 82838-69-5; 2 ( $n = 3$ ), 82838-70-8; 3 ( $n = 1$ ), 74184-34-2; 3 ( $n = 3$ ), 82838-71-9; cyclopentene, 142-29-0; cycloheptene, 628-92-2.