

## REGIOSPECIFIC 2+2 PHOTOADDITION OF PHENYL SUBSTITUTED ACETYLENES TO PENTAFLUOROPYRIDINE

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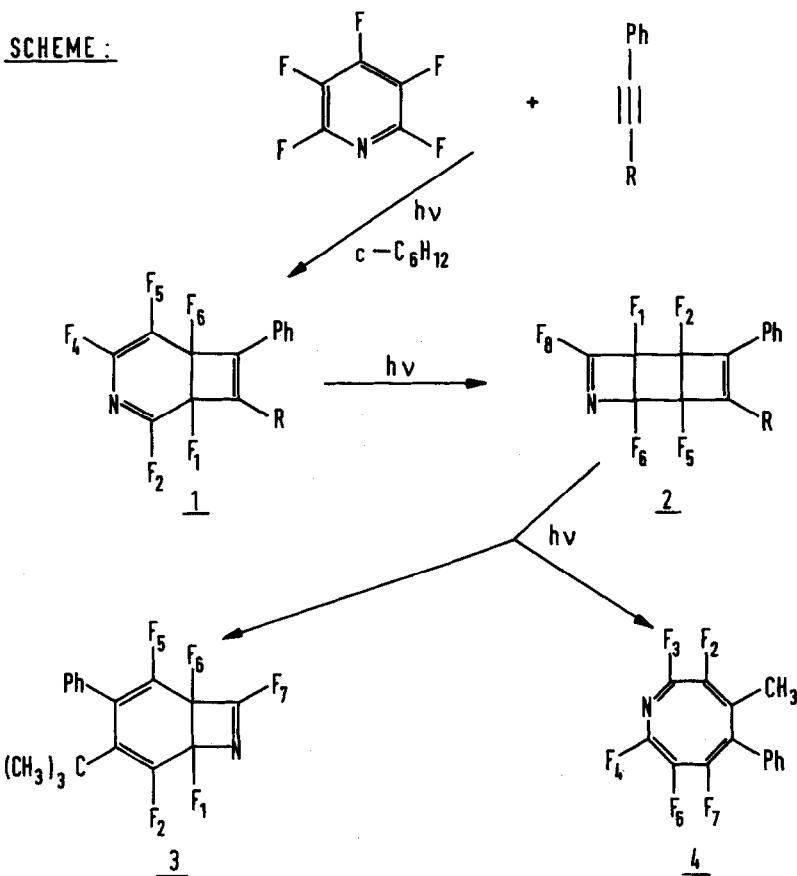
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**ABSTRACT:** Irradiation of a cyclohexane solution of pentafluoropyridine and 1-phenyl-2-alkyl-acetylenes produced regiospecific 2+2 photocycloaddition, thus forming 3-aza-bicyclo[4.2.0]octa-2,4,7-triene derivatives, which further phototransformed to 7-aza-tricyclo[4.2.0.0<sup>2,5</sup>]octa-3,7-diene derivatives. Further phototransformation of the tricyclic system depended on the alkyl substituent: in the case of tert-butyl, 1,2,5,6,7-pentafluoro-3-tert-butyl-4-phenyl-8-aza-bicyclo[4.2.0]octa-2,4,7-triene was formed, while in the case of a methyl substituent, 1-methyl-2,3,5,6,7-pentafluoro-8-phenyl-4-aza-cycloocta-1,3,5,7-tetraene resulted.

Benzene and substituted benzenes undergo several types of photoprocesses, such as valence isomerization to benzvalene<sup>1</sup> and to bicyclo[2.2.0]hexa-2,5-diene<sup>2</sup>, and addition of olefins and acetylenes<sup>3</sup>. On the other hand, pyridine forms only an unstable para-bonded isomer<sup>4</sup> and undergoes no cycloaddition reactions, a finding which is explained by the fact that the highest occupied molecular orbital for pyridine is a non-bonding rather than a  $\pi$ -orbital<sup>5</sup>. It is also known that the fluorine atom in pentafluoropyridine lowers the energy of the non-bonding orbital, the  $\pi$ -orbital being thus the highest occupied orbital<sup>6</sup>, resulting in the  $\pi - \pi^*$  character of the first excited state, favouring the formation of cycloadducts. Recently, some authors have found that UV irradiation of pentafluoropyridine and ethylene or some cyclic olefins<sup>5,7</sup> led to the formation of 1 : 1 and 2 : 1 adducts, resulting in 2+2 regiospecific photoaddition.

We found that UV irradiation of a cyclohexane solution of hexafluorobenzene and phenyl substituted acetylenes resulted in the formation of bicyclo[4.2.0]octatriene derivatives<sup>8</sup>, which stimulated us to study the reaction of pentafluoropyridine with acetylenes. A 20-hour irradiation of a cyclohexane solution of pentafluoropyridine and 1-phenyl-2-tert-butylacetylene at  $\lambda = 253.7$  nm at room temperature resulted in the formation of three products (Scheme), in the relative ratio of 1:1:2. Separation by tlc (SiO<sub>2</sub>) gave 14% of product 3 and 30% of product 1, while product 2 decomposed and was isolated in 12% yield on Al<sub>2</sub>O<sub>3</sub> plates. The mass spectrum of the product 1, with the following fragments: m/e 327 (M<sup>+</sup>, 40%), 271(50), 143(85), 57(100), showed that the 1 : 1 adduct of pentafluoropyridine and acetylene was formed. The adduct showed ir absorption which indicated the presence of an azadiene chromophore with  $\nu_{\max}$  1720 cm<sup>-1</sup> (CF=N str.), and 1710 cm<sup>-1</sup> (CF=CF) and absorption at  $\nu_{\max}$  1650 cm<sup>-1</sup>, corresponding to the double bond stretching vibration in the cyclobutene ring<sup>9</sup>. Its <sup>19</sup>F nmr spectrum (CCl<sub>3</sub>F as internal reference) showed absorptions at -60.75 (td 30, 6 Hz; FC=N), 129.0 (td 15, 6 Hz, F<sub>4</sub>), 132.75 (tdd 33, 15, 6 Hz, F<sub>1</sub>), 159.0 (ddd 33, 15, 6 Hz, F<sub>6</sub>) and 166.5 ppm (dt 30, 6 Hz, F<sub>5</sub>). On the basis of above mentioned spectroscopic data, and by comparison to those already published<sup>5</sup>, we established that 7-phenyl-8-tert-butyl-1,2,4,5,6-pentafluoro-3-aza-bicyclo[4.2.0]octa-2,4,7-triene was formed. In contrast to adduct 1, the ir spectrum of product 2 showed only absorption at  $\nu_{\max}$  1710 cm<sup>-1</sup> and indicated the absence of an azadiene chromophore, while its <sup>19</sup>F nmr spectrum showed absorptions at -47.25 (tt 42, 10 Hz, F<sub>6</sub>), 117 (d 10 Hz, F<sub>6</sub>), 160.5 (ddd 42, 18, 10 Hz, F<sub>1</sub>), 162.5 (dtd 30, 10, 3 Hz, F<sub>5</sub>) and 167 ppm (dd 30, 18 Hz, F<sub>2</sub>). Its mass spectrum showed prominent ions at m/e 327 (M<sup>+</sup>, 17%), 271(38), 243(91) and 57(100). We established the structure of the product 2 as 1,2,5,6,8-pentafluoro-3-phenyl-4-tert-butyl-7-aza-tricyclo[4.2.0.0<sup>2,5</sup>]octa-



3,7-diene. The spectroscopic data of product 3 were as follows:  $^{19}F$  nmr spectrum  $\delta = -32.25$  (dm 39 Hz,  $F_7$ ), 101.25 (m,  $F_5$ ), 117 (broad singlet,  $F_2$ ), 157 (dm 33 Hz,  $F_1$ ), 165.75 ppm (dd 39, 33 Hz,  $F_6$ ), the frequencies in the ir spectrum indicating the presence of a CF=N bond ( $\nu_{max} = 1700\text{ cm}^{-1}$ ) and two different CF=C vibrations at  $\nu = 1680$  and  $1665\text{ cm}^{-1}$ , and the following mass spectrum  $m/e$ : 327 ( $M^+$ , 31%), 271(42), 143(54), 57(100). The structure of the product 3, based on its spectroscopic data, is 1,2,5,6,7-pentafluoro-3-tert-butyl-4-phenyl-8-aza-bicyclo[4.2.0]octa-2,4,7-triene.

To determine which of the three products formed primarily, we studied the influence of the irradiation times on the ratio of the products. Reduction of the irradiation time to 1.5 hour gave a relative ratio of the products of  $1:2:3 = 10:7:3$  respectively, while prolongation of the reaction time led to increased formation of product 3 and diminished amounts of products 1 and 2, until on 60-hour irradiation only 15% of products 1 and 2 were present in the reaction mixture (Figure). Irradiation of the pure product 1 gave a mixture of products 2 and 3.

The experimental observations led us to the conclusion that the product 1 is formed primarily, its formation being explained by the regiospecific 2+2 addition of 1-phenyl-2-tert-butylacetylene to pentafluoropyridine, while product 2 resulted from a very efficient secondary light-induced rearrangement of 1. On the other hand, the formation of product 3 can be explained by the subsequent UV induced transformation of 2 (Scheme).

Being interested in the effect of the magnitude of group R of alkyl substituted acetylenes on the photocycloaddition reaction, we found it instructive to study the reaction with 1-phenylpropyne, and the formation of three products was observed. The primarily formed product 1 (Scheme) had  $^{19}F$  and ir spectrum very similar to those of the product 1 formed by the reaction with 1-phenyl-2-tert-butylacetylene /see experimental details/. The structure of the product 2 was also established on the basis of similarities of its

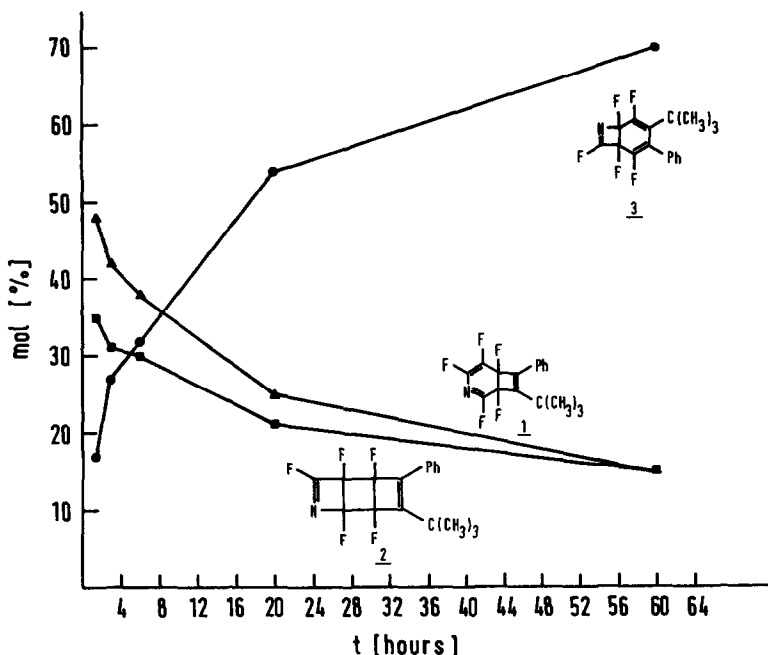


Figure: The effect of irradiation time on products distribution /determined by  $^{19}\text{F}$  nmr spectr./

spectroscopic data with those of product 2 previously studied, while no formation of product 3 was observed. Instead, product 4 was formed, with the following  $^{19}\text{F}$  nmr spectrum:  $\delta = -39$  (broad singlet,  $\text{F}_3$ ), 126.75 (m,  $\text{F}_2$ ,  $\text{F}_5$ ), 127.5 (m 21, 9 Hz,  $\text{F}_7$ ) and 160.12 ppm (m 21, 9 Hz,  $\text{F}_6$ ). It showed absorptions at  $\nu_{\text{max}} = 1760 \text{ cm}^{-1}$  (CF=N str.), 1720 (CF=CF str.) and in the region from 1650 to 1680  $\text{cm}^{-1}$ . On the basis of the spectroscopic data we established that 1-methyl-2,3,5,6,7-pentafluoro-8-phenyl-4-aza-cycloocta-1,3,5,7-tetraene was formed.

From the experimental observations we concluded that photocycloaddition reaction of pentafluoropyridine with phenyl substituted acetylenes resulted in regiospecific 2+2 addition with product 1 as the primarily formed one, transforming further to the tricyclic system 2, while subsequent phototransformation depended on the magnitude of the alkyl substituent, forming either product 3 in the case of a tert-butyl group, or product 4 in the case of a methyl group.

## EXPERIMENTAL

Irradiations 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  $^1\text{H}$  and  $^{19}\text{F}$  nmr spectra by a Jeol JNM-PS-100 spectrometer from  $\text{CDCl}_3$  or  $\text{CCl}_4$  solutions with  $\text{Me}_4\text{Si}$  or  $\text{CCl}_3\text{F}$  as an internal reference. Mass spectra and high resolution measurements were taken on a CEC 21-110 spectrometer. Tlc was carried out on Merck PSC Fertigplatten. Pentafluoropyridine and 1-phenylpropyne were commercially available and distilled before use; 1-phenyl-2-tert-butylacetylene was synthesized by known procedure<sup>10</sup>.

### Reaction of Pentafluoropyridine with 1-Phenyl-2-tert-Butylacetylene

1 mmol (158 mg) of 1-phenyl-2-tert-butylacetylene and 1 mmol (169 mg) of pentafluoropyridine was dissolved in 18 ml of cyclohexane, the solution was irradiated at  $\lambda = 253.7 \text{ nm}$  for 20 hours, the solvent was evaporated in vacuo, and 310 mg of crude reaction mixture was isolated. Products were separated by preparative tlc / $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ , chloroform : petrol ether 5:95/, and 46 mg (14%) of 1, 40 mg (12%) of 2, and 110 mg (33.6%) of 3 were obtained.

### 7-Phenyl-8-tert-Butyl-1,2,4,5,6-Pentafluoro-3-Aza-Bicyclo[4.2.0]Octa-2,4,7-Triene (1)

Crystallization from methanol resulted in a crystalline product, mp 72-74°C. Nmr spectrum:  $\delta\text{F-1} = -132.75$  (tdd 33, 15, 6 Hz),  $\delta\text{F-2} = -60.75$  (td 30, 6 Hz),  $\delta\text{F-4} = -129.0$  (td 15, 6 Hz),  $\delta\text{F-5} = -166.5$  (dt 30, 6 Hz),  $\delta\text{F-6} = -159.0$  ppm (ddd 33, 15, 6 Hz). Ir 1650, 1710, 1720  $\text{cm}^{-1}$ . Mass spectrum calcd. for  $\text{C}_{14}\text{H}_{17}\text{F}_5\text{N}$

m/e 327.1046, found m/e 327.1042, m/e 327 ( $M^+$ , 40%), 271(50), 143(85), 54(100).

1,2,5,6,8-Pentafluoro-3-Phenyl-4-tert-Butyl-7-Aza-Tricyclo[4.2.0.0<sup>2,5</sup>]Octa-3,7-Diene (2)

Oily product, nmr spectrum:  $\delta F-1=$  -160.5 (ddd 42, 18, 10 Hz),  $\delta F-2=$  -167 (dd 30, 18 Hz),  $\delta F-5=$  -162.5 (dtd 30, 10, 3 Hz),  $\delta F-6=$  -117 (d 10 Hz),  $\delta F-8=$  -47.25 ppm (tt 42, 10 Hz); ir 1710  $cm^{-1}$ ; mass spectrum calcd. for  $C_{14}H_{17}F_5N$  m/e 327.1046, found m/e 327.1040, m/e: 327 ( $M^+$ , 17%), 271(38), 243(91), 57(100).

1,2,5,6,7-Pentafluoro-3-tert-Butyl-4-Phenyl-8-Aza-Bicyclo[4.2.0]Octa-2,4,7-triene (3)

Crystallization from methanol resulted in a crystalline compound, mp 67-69°C. Nmr spectrum:  $\delta F-1=$  -157 (dm 33 Hz),  $\delta F-2=$  -117 (broad singlet),  $\delta F-5=$  -101.25 (m),  $\delta F-6=$  -165.75 (dd 39, 33 Hz),  $\delta F-7=$  -32.25 ppm (dm 39 Hz); ir 1665, 1680, 1700  $cm^{-1}$ ; mass spectrum calcd. for  $C_{14}H_{17}F_5N$  m/e 327.1046, found m/e 327.1050, m/e: 327 ( $M^+$ , 31%), 271(42), 143(54), 57(100).

Reaction of Pentafluoropyridine with 1-Phenylpropyne

1 mmol (116 mg) of 1-phenylpropyne and 1 mmol (169 mg) of pentafluoropyridine were dissolved in 18 ml of cyclohexane, the solution was irradiated for 20 hours at  $\lambda = 253.7$  nm, the solvent was evaporated in vacuo and 270 mg of the crude reaction mixture was obtained. Products were separated by preparative tlc /SiO<sub>2</sub>, chloroform: petrol ether 5:95/ and 35 mg (13%) of 1, 62 mg (23%) of 2 and 53 mg (20%) of 4 were isolated.

8-Methyl-7-Phenyl-1,2,4,5,6-Pentafluoro-3-Aza-Bicyclo[4.2.0]Octa-2,4,7-Triene (1)

Oily product, nmr spectrum:  $\delta F-1=$  -132.75 (tdd 30, 12, 8 Hz),  $\delta F-2=$  -58 (td 30, 6 Hz),  $\delta F-4=$  -125.25 (m),  $\delta F-5=$  -162.0 (dd 30, 8 Hz),  $\delta F-6=$  -161.25 ppm (dt 30, 3 Hz); ir 1655, 1705, 1725  $cm^{-1}$ ; mass spectrum calcd. for  $C_{14}H_8F_5N$  m/e 285.0577, found m/e 285.0570.

4-Methyl-1,2,5,6,8-Pentafluoro-3-Phenyl-7-Aza-Tricyclo[4.2.0.0<sup>2,5</sup>]Octa-3,7-Diene (2)

Oily product, nmr spectrum:  $\delta F-1=$  -159.75 (m 42, 18 Hz),  $\delta F-2=$  -164.25 (m 42, 33, 18 Hz),  $\delta F-5=$  -160.5 (dm 33 Hz),  $\delta F-6=$  -114 (dd 9, 3 Hz),  $\delta F-8=$  -50.6 ppm (tt 42, 9 Hz); ir 1640, 1705  $cm^{-1}$ ; mass spectrum calcd. for  $C_{14}H_8F_5N$  m/e 285.0577, found m/e 285.0573.

1-Methyl-2,3,5,6,7-Pentafluoro-8-Phenyl-4-Aza-Cycloocta-1,3,5,7-Tetraene

Oily product, nmr spectrum:  $\delta F-2,F-5=$  -126.75 (m, 2F),  $\delta F-3=$  -39 (broad singlet),  $\delta F-6=$  -160.12 (m 21, 9 Hz),  $\delta F-7=$  -127.5 ppm (m 21, 9 Hz); ir 1650 to 1680, 1720, 1760  $cm^{-1}$ ; mass spectrum calcd. for  $C_{14}H_8F_5N$  m/e 285.0577, found m/e 285.0565, m/e: 285( $M^+$ , 64%), 116(78), 115(50), 86(37), 85(46), 84(57), 51(36), 49(100), 47(36).

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