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Note

## Regio and Stereospecific 2 + 2 Photoaddition of Cyclopentene to Pentafluoro-alkoxybenzene

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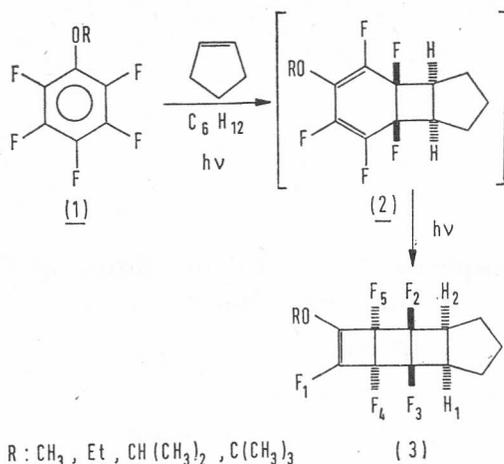
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2 + 2 photoaddition of cyclopentene to pentafluoro-alkoxybenzene in cyclohexane solution proceeds stereoselectively anti and regiospecifically to the 3,4 position.

Benzene and substituted benzenes undergo several types of cycloaddition reactions with olefins. Reaction pathways leading to the 1, 2 or 1, 3 or 1, 4 cycloaddition product depend on the substituent on the phenyl ring and on the structure of the olefin.<sup>1</sup> Recently we have found that 2 + 2 cycloaddition of indene or 1, 2 dihydronaphthalene to hexafluorobenzene occurred stereospecifically *syn*.<sup>2</sup> On the other hand, 2 + 2 photoaddition of cyclopentene proceeded predominantly via an *anti* attack.<sup>3</sup>

We now report an investigation of the regio and stereoselectivity of photoaddition of cyclopentene to pentafluoroanisole. Anisole undergoes photochemical 1, 3 addition with a variety of olefins.<sup>4</sup> A cyclohexane solution of cyclopentene (5 mmol) and pentafluoroanisole (5 mmol) was irradiated for forty hours.\* <sup>19</sup>F NMR spectra of the crude reaction mixture showed only five signals:  $\delta F_1 = -134$  (d),  $\delta F_2 = -183$  (m),  $\delta F_3 = -184$  (m),  $\delta F_4 = -189.75$  (td),  $\delta F_5 = 193.88$  (dd), and in its <sup>1</sup>H spectrum:  $\delta OCH_3 = 4$  (s),  $\delta CH_{1,2} = 3, 1$  (m),  $\delta CH_2 = 2$  (m, 6H), with the following coupling constants:  $^3J_{F_1, F_4} = ^3J_{F_3, F_4} = 16$  Hz,  $^3J_{F_4, F_5} = 7.5$  Hz,  $^3J_{F_2, F_5} = 19$  Hz,  $^3J_{F_2, H_2} = ^3J_{F_3, H_1} = 6$  Hz. The product was purified by preparative glc and 65% of the liquid product was isolated. The product shows the following fragments in its mass spectrum: *m/e* 266 (M<sup>+</sup>, 20%, calcd. for C<sub>12</sub>H<sub>11</sub>OF<sub>5</sub>, *m/e* = 266.0730 found *m/e* = 266.0730), 198 (94, pentafluoroanisole species), 184(33), 155(16), 119(20), 117(20), 99(20), 67(100), 68(63). On the basis of a comparison of the NMR, mass and IR data of the product (3) with the literature ones<sup>2,3,5</sup>, we have assigned the structure as 1,2,3,5,6-pentafluoro-4-methoxy-tetracyclo(5,4,0,0<sup>2,5</sup>,0<sup>7,11</sup>)undecene-3 with the stereochemistry outlined in the Scheme. By reduction of the irradiation time from 40 hours to 3 hours, only 30% of pentafluoroanisole was converted to two products. In this reaction 10% of product 3 and 20% of a new product 2 were formed with the following signals in the <sup>19</sup>F NMR spectrum:  $\delta F = -159.75, -165.0, -166.5, -187.5, -188.25$ . We were unable to isolate

\* Irradiation was carried out in a Rayonet photochemical chamber reactor, model RPR-100, with RPR-253.7 nm lamps.



this product; however, comparison of the NMR data to a similar product formed by reaction with hexafluorobenzene<sup>2,3,5</sup> and on the basis of its further photo-transformation to product 3, we assigned the structure of product 3 as 1,2,4,5,6-pentafluoro-3-methoxy-tricyclo (5,4,0,0<sup>7,11</sup>) undecadiene-2,4, which was formed by *regio* and *stereoselective anti* 2 + 2 photoaddition of cyclopentene to the 3,4 position in pentafluoroanisole.

In order to study the effect of the size of the alkoxy group on both regio and stereoselectivity of 2 + 2 photoaddition of cyclopentene to alkoxy substituted pentafluorobenzene, we chose the following alkoxy substituents: ethoxy, *iso*-propoxy, and *t*-butoxy. In all the cases 2 + 2 addition occurred regio-selectively to the positions 3, 4 and stereoselectively *anti*.

TABLE  
NMR data for 3<sup>a</sup>

R	OCH <sub>3</sub>	OEt	OCH(CH <sub>3</sub> ) <sub>2</sub>	O(CH <sub>3</sub> ) <sub>3</sub>
δ F <sub>1</sub>	-134	-131.2	-131.2	-125.4
δ F <sub>2</sub>	-183	-179.6	-182.25	-182.6
δ F <sub>3</sub>	-184	-180.5	-183	-183.4
δ F <sub>4</sub>	-189.75	-185.8	-187.5	-188.4
δ F <sub>5</sub>	-193.9	-190	-192.7	-193
δ H <sub>1</sub> H <sub>2</sub>	3.1	3.04	3.2	3.08

<sup>a</sup> CCl<sub>4</sub> solution/CCl<sub>3</sub>F internal standard, JNM-PS-100

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## IZVLEČEK

**Regio in stereospecifična 2+2 fotoadicija ciklopentena na pentafluoro-alkoksi substituirane benzenove derivate***B. Šket in M. Zupan*

2 + 2 fotoadicija ciklopentena na pentafluoro-alkoksi substituirane derivate benzena v cikloheksanski raztopini poteka stereospecifično anti ter regiospecifično na položaj 3, 4.

ODDELEK ZA KEMIJO UNIVERZE

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INSTITUT J. STEFAN

LJUBLJANA

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