

## Photodimerization of 6-Styryl-2-Pyrones

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Received: September 12, 1989; November 13, 1989

Os fotoprodutos de 6-*trans*-estiril-2-pirona e de 6-*trans*-estiril-4-metoxi-2-pirona, previamente caracterizados como os isômeros *cis*, foram reconhecidos serem *r*-1, *c*-2, *t*-3, *t*-4-1, 3-difenil-2, 4-di-[6-(2-pironil)]-ciclobutano e *r*-1, *c*-2, *t*-3, *t*-4, 1, 3-difenil-2, 4-di-[6-(4-metoxi-2-pironil)]-ciclobutano respectivamente.

The structures of the photoproducts of 6-*trans* styryl-2-pyrone and of 6-*trans*-styryl-4-methoxy-2-pyrone, previously characterized as the *cis*-isomers, were revised to *r*-1, *c*-2, *t*-3, *t*-4-1, 3-diphenyl-2, 4-di-[6-(2-pyronyl)]-cyclobutane and to *r*-1, *c*-2, *t*-3, *t*-4-1, 3-diphenyl-2, 4-di-[6-(4-methoxy-2-pyronyl)]-cyclobutane respectively.

**Key Words:** 6-*trans*-styryl-2-pyrone; 6-*trans*-styryl-4-methoxy-2-pyrone; photodimerization.

## Introduction

Exposure of crystals of 6-*trans*-styryl-2-pyrone (**1a**) and of 6-*trans*-styryl-4-methoxy-2-pyrone (**1b**) to sunlight or to a tungsten lamp has been reported to lead to the *cis*-isomers **2a**<sup>1</sup> and **2b**<sup>1,2</sup> respectively. Secondary photoproducts of **1b** were the cyclobutane derivative **3**<sup>1</sup> in two stereoisomeric forms<sup>2</sup> and **4**.<sup>2</sup> We wish to report that the reinvestigation by modern techniques of the compounds to which the structures **2a** and **2b** had previously been assigned indicated that they are also cyclobutane derivatives, respectively **5a** and **5b**.

## Experimental

Photoproducts were again obtained, as in the original work<sup>1,2</sup>, by exposure of crystals of the relevant compound either to sunlight or to a tungsten lamp. Thus **1a** gave a mixture which was purified by fractional recrystallization from Me<sub>2</sub>CO to **5a**.

*r*-1,*c*-2,*t*-3,*t*-4-1,3-Diphenyl-2,4-di-[6-(2-pyronyl)]-cyclobutane (**5a**), m.p. 198-200°C (Me<sub>2</sub>CO). IR  $\nu_{\max}^{\text{KBr}}$  cm<sup>-1</sup>: 1718, 1626, 1541, 1095, 810, 758, 702. <sup>1</sup>H NMR (80 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.22 (s, Ph), 7.11 (dd, *J* = 7.5, 8.5 Hz, H-4''), 5.91 (d, *J* = 7.5 Hz, H-3''), 5.92 (d, *J* = 8.5 Hz, H-5''), 4.41 (d, *J* = 2.5 Hz, H-2), 4.36 (d, *J* = 2.5 Hz, H-1). <sup>13</sup>C NMR (20 MHz, CDCl<sub>3</sub>)  $\delta$ : 137.2 (s, C-1'), 127.0 (d, C-2', C-6'), 127.1 (d, C-4'), 128.3 (d, C-3', C-5'), 161.5 (s, C-2''), 113.2 (d, C-3''), 142.7 (d, C-4''), 104.1 (d, C-5''), 163.4 (s, C-6''), 43.7 (d, C-1, C-3), 44.9 (d, C-2, C-4). MS *m/z* (rel. int.): 198 (M<sup>+</sup>/2, 100), 170 (36), 141, (21), 103 (10), 95 (14).

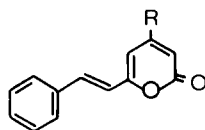
*r*-1,*c*-2,*t*-3,*t*-4-1,3-Diphenyl-2,4-[6-(4-methoxy-2-pyronyl)]-cyclobutane (**5b**), mp 231-233°C (Me<sub>2</sub>CO). UV  $\lambda_{\max}^{\text{EtOH}}$  nm: 288 ( $\epsilon$  7300). IR  $\nu_{\max}^{\text{KBr}}$  cm<sup>-1</sup>: 1720, 1653, 1578, 1568, 1261, 700. <sup>1</sup>H NMR (60 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.27 (s, Ph),

5.74 (d, *J* = 2.2 Hz, H-5''), 5.19 (d, *J* = 2.2 Hz, H-3''), 4.40 (d, *J* = 2.5 Hz, H-2), 4.33 (d, *J* = 2.5 Hz, H-1), 3.67 (s, OMe). MS *m/z* (rel. int.): 288 (M<sup>+</sup>/2, 100), 200 (23), 157 (14), 149 (5), 131 (8), 129 (10), 128 (7), 125 (15), 111 (7), 109, (6), 106 (5), 105 (5), 103 (10), 102 (5).

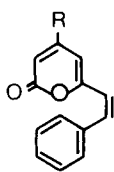
## Results and Conclusions

The erroneous structures **2a** and **2b** had been assigned on the following evidence: 1. Catalytic hydrogenation (whereby the presumptive **2a** and **2b** gave dihydro-**1a** and dihydro-**1b** respectively); 2. UV spectra (revealing loss of conjugation, attributed to steric hindrance of *cis*-forms); 3. EIMS (no peak above *m/z* 198 and 228 attributable to the two monomers **2a** and **2b** respectively); 4. <sup>1</sup>H NMR (high field absorptions at  $\delta$  4.33-4.41 for olefinic protons attributed to lack of coplanarity). However, cyclobutanes are known to be cleaved by catalytic hydrogenation<sup>3</sup> and loss of conjugation is better explained by the cyclobutane structures. Besides, indeed at 70eV the mass spectral peaks above *m/z* 198 ([**2a**]<sup>+</sup>, 100%) for **5a** and 228 ([**2b**]<sup>+</sup>, 100%) for **5b** are of very low intensity. Furthermore these MS do not show peaks at *m/z* 180 and thus **5a** and **5b** cannot possess vicinal phenyls and pyronyls as does **4** ([Ph CH=CH Ph]<sup>+</sup>, 80%)<sup>2</sup>.

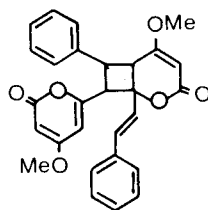
The mid points of the high field AA'BB' <sup>1</sup>H NMR signals of **5a** ( $\delta$  4.38) and **5b** ( $\delta$  4.36) are compatible with the analogous mid points given by 1,2-diphenyl-3, 4-dithienylcyclobutane and 1,3-diphenyl-2, 4-dithienylcyclobutane of the *r*-1,*c*-2,*t*-3,*t*-4-configuration ( $\delta$  4.43), but not of the *r*-1,*t*-2,*c*-3,*t*-4-configuration ( $\delta$  3.64)<sup>4</sup>. Only in one of the three possible *r*-1,*c*-2,*t*-3,*t*-4-diphenyldipyronyl isomers the substituents occupy alternative positions throughout, as required by the MS of **5a** and **5b**.



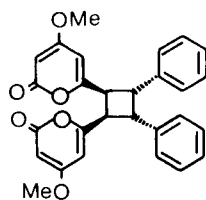
1a R: H  
1b R: OMe



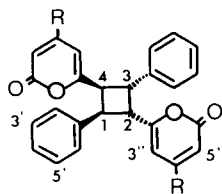
2a R: H  
2b R: OMe



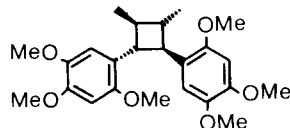
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4



5a R: H  
5b R: OMe



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Finally, and most importantly, the  $^{13}\text{C}$  NMR spectra demonstrate the presence of eleven  $\text{sp}^2$ -carbons per two  $\text{sp}^3$ -carbons in these molecules. The chemical shifts and coupling constants of the  $\text{sp}^3$ -carbons ( $\delta$  43.7, d,  $J = 144.2$  Hz; 44.9, d,  $J = 144.0$  Hz) are closely comparable with the corresponding data of acoradin (6,  $\delta$  43.5 and 44.5)<sup>5</sup> and cyclobutanes ( $J = 140.0$  Hz)<sup>6</sup>.

### Aknowledgements

This work is part of the MSc thesis submitted by DGM to the Universidade de São Paulo (1985).

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