J. Chem. Research (S), 1998, 142–143†

Site-selectivity in [2+2]-Photocycloadditions of 2*H*,8*H*-Benzo[1,2-*b*:3,4-*b*′]dipyran-2,8-dione to Alkenes†‡

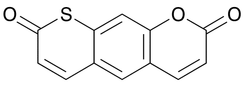
John Bethke,[a] Paul Margaretha,*[a] Anna M. Wynne[b] and Richard A. Caldwell[b]

[a] *Institut für Organische Chemie, Universität Hamburg, M.L. King Platz 6, D-20146 Hamburg, Germany*

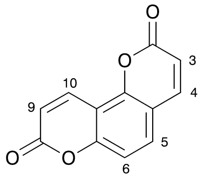
[b] *Department of Chemistry, The University of Texas at Dallas, Richardson, TX 75083, USA*

On irradiation ($\lambda = 350$ nm) in the presence of 2,3-dimethylbut-2-ene or 2-methylpropene the title compound **2** undergoes cycloaddition at the C(9)—C(10) double bond selectively (>15:1) to afford the 8a,9,10,10a-tetrahydro-2*H*,8*H*-cyclobuta[*c*]pyrano[2,3-*f*][1]benzopyran-2,8-diones **3**.

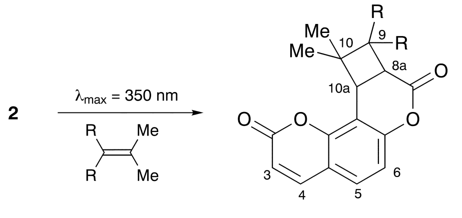
In studies on the photochemical reactivity towards alkenes of tricyclic 1,3-diethenylbenzenes containing two *a priori* different olefinic moieties, we recently found[1] that 2*H*,8*H*-thiopyrano[3,2-*g*]benzopyran-2,8-dione (**1**) undergoes [2 + 2]-photocycloaddition to 2,3-dimethylbut-2-ene unselectively, *i.e.* giving cycloadducts at both olefinic double bonds in equal amounts. Here we report that the angular benzodipyrandione **2** does indeed exhibit a remarkable site-selectivity in such light induced reactions.



1



2



3a R = Me
b R = H

Monitoring the irradiation of an Ar-degassed solution of **2** in MeCN containing 2,3-dimethylbut-2-ene by ^{1}H NMR indicates the almost exclusive (>92%) formation of one product **3a**. Similarly, on irradiation of **2** in MeCN saturated with isobutene only one product (>95%) **3b** is formed. The assignment of structures **3** stems from ^{1}H,^{1}H-COSY, ^{1}H,^{13}C-COSY and ^{1}H,^{13}C-HMBC (*heteronuclear multiple bond correlation*) spectra and is facilitated by the observation[2] that H(4) in 5-methoxycoumarin resonates at a distinctly lower field than in the 7-MeO-isomer (8.08 *vs.* 7.68 ppm in $CDCl_3$). The corresponding H-atoms in **2**, *i.e.* H(10) and H(4) resonate at 8.30 and 7.76 ppm, respectively, while that in compounds **3**, *i.e.* H(7), resonates at 7.65 ppm. Preliminary experiments point to a reactive triplet excited state of **2**, as the conversion $\mathbf{2} \rightarrow \mathbf{3}$ also occurs at $\lambda > 390$ nm using thioxanthone as sensitizer. Interestingly energy transfer from triplet thioxanthone to **3** is more efficient than to **2**, and therefore a mixture of two diastereomeric bicycloadducts is formed almost quantitatively under these conditions.

If one neglects steric aspects, the only difference between the reactive, *i.e.* C(9)—C(10), and the unreactive, *i.e.* C(3)—C(4), styrenic double bond, is that the former bears an acetoxy substituent [O(1)] in the *ortho* position and the latter the same substituent [O(7)] in the *para* position. It has been shown that *ortho–meta* transmission is characteristic of the first excited state chemistry of substituted benzenes,[3] *i.e.* electron donors will increase the π electron densities on both the *ortho* and the *meta*, but *not* on the *para* C-atom. A 'vinylogous' extension of this so-called '*meta*-effect' has recently been reported[4] in comparing the excited state behaviour of the corresponding substituted aminostilbenes.

Experimental

NMR spectra (Bruker WM 500 spectrometer: ^{1}H, 500 MHz, ^{13}C, 100.62 MH) were recorded in $CDCl_3$. Photolyses were run in a *Rayonet RPR-100* photoreactor equipped with 350 nm lamps. Flash column chromatography was performed with silica gel 60.

2H,8H-*Benzo*[1,2-b:3,4-b′]*dipyran*-2,8-*dione* (**2**).—The title compound was synthesized from 7-hydroxycoumarin and malic acid.[5] Additional purification by flash chromatography (ethyl acetate as eluent) afforded **2** in 14% yield, mp 267–269 °C; δ_H 6.46 and 7.76 [AB, *J* 10.2 Hz, H(3) and H(4)], 6.56 and 8.31 [AB, *J* 10.2 Hz, H(9) and H(10)], 7.25 and 7.62 [AB, *J* 8.4 Hz, H(6) and H(5)]; δ_C 107 [C(10a)], 113 [C(6)], 113.6 [C(4a)], 115 [C(3), 116 [C(9)], 129 [C(5)], 136 [C(10)], 142 [C(4), 149 [C(10b)], 155 [C(6a)], 158.2 [C(2)], 158.3 [C(8)] (Found: C, 67.35; H 2.85%. $C_{12}H_6O_4$ requires C, 67.30; H, 2.82%).

cis-9,9,10,10-*Tetramethyl*-8a,9,10,10a-*tetrahydro*-2H,8H-*cyclobuta*-[c]*pyrano*[2,3-f][1]*benzopyran*-2,8-*dione* (**3a**).—An argon degassed solution of **2** (85.6 mg, 0.4 mmol) and 2,3-dimethylbut-2-ene (670 mg, 8 mmol) in MeCN (200 ml) was irradiated in a pyrex vessel for 6 h. After evaporation of the solvent the residue was purified by flash chromatography (diethyl ether as eluent) to give **3** (89 mg, 75%), mp 166–167 °C; δ_H 0.70, 0.99, 1.27 and 1.31 (CH_3), 3.16 and 3.78 [AB, *J* 10.2 Hz, H(8a) and H(10a)], 6.28 and 7.60 [AB, *J* 9.6 Hz, H(3) and H(4)], 6.90 and 7.29 [AB, *J* 8.4 Hz, H(6) and H(5)]; δ_C 19.7, 20.2, 24.4 and 25.6 (CH_3), 36 [C(10a), 41 [C(8a)], 44.3 and 44.4 [C(10), C(9)], 109 [C(10b)], 113 [C(6)], 114 [C(3)], 114.1 [C(4a)], 126 [C(5)], 142 [C(4)], 151 [C(6a)], 153 [C(10c)], 159 [C(2)], 165 [C(8)] (Found: C, 72.44; H, 6.10%. $C_{18}H_{18}O_4$ requires C, 72.47; H, 6.08%).

cis-10,10-*Dimethyl*-8a,9,10,10a-*tetrahydro*-2H,8H-*cyclobuta*[c]-*pyrano*[2,3-f][1]*benzopyran*-2,8-*dione* (**3b**).—A solution of **2** (85.6 mg, 0.4 mmol) in MeCN (200 ml) was saturated with isobutene and irradiated for 12 h. Work-up as above afforded **3b** (68 mg, 70%), mp 156 °C; δ_H 0.86 and 1.47 (CH_3), 2.26 (dd, *J* 5, 11 Hz) and 2.59 (dd, *J* 11 Hz, 11) [2 × H(9)], 3.55 [ddd, *J* 5, 10, 11 Hz, H(8a)], 3.92 [d, *J* 10 Hz, H(10a)], 6.37 and 7.67 [AB, *J* 10.0 Hz, H(3) and H(4)], 6.98 and 7.39 [AB, *J* 8.5 Hz, H(6) and H(5)]; δ_C 23.5 and 29.0 (CH_3), 28.4 [C(9)], 38.9 [C(10a)], 39.2 [C(8a)], 39.9 [C(10)], 108 [C(10b)], 112 [C(6)], 114 [C(3)], 114.2 [C(4a)], 126 [C(5)], 142 [C(4)], 151 [C(6a)], 153 [C(10c)], 159 [C(2)],

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*To receive any correspondence (*e-mail:* margpaul@chemie.uni-hamburg.de).

†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1998, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

‡Dedicated to Prof. William C. Agosta, the Rockefeller University, New York on the occasion of his 65th birthday.

168 [C(8)] (Found: C, 71.05; H, 5.21%. $C_{16}H_{14}O_4$ requires C, 71.10; H, 5.22%).

Received, 30th October 1997; Accepted, 2nd December 1997
Paper E/7/07819F

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