55. Photochemistry of 2,2-Dimethyl-2*H*-furo[3,4-*b*]pyran-4,7(3*H*,5*H*)-dione

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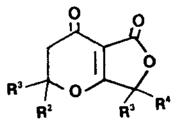
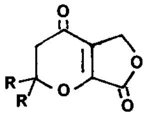
Irradiation ($\lambda > 340$ nm) of the title compound **2a** in *t*-BuOH affords 3,3,10,10-tetramethyl-2,8-dioxatricyclo-[4.3.2.$0^{1,6}$]undecane-5,9-dione (**3**) *via* photoextrusion of 2-methylpropene and subsequent photocycloaddition of **2a** to the alkene. The same regioisomer **3** is formed selectively and in much higher yields on irradiating **2a** in the presence of excess 2-methylpropene. Irradiation of **3** ($\lambda = 300$ nm) in *t*-BuOH in the presence of the same alkene gives a 6:1 mixture of spirooxetanes **7a** and **7b** but not α-cleavage products. In 2-propanol, **2a** is photoreduced to a 2:1 mixture of diastereoisomeric hydrodimers **9**.

For some time, we have been interested in 2,3-dihydro-4-pyranones [1–4] and in 2(5*H*)-furanones [5] as model compounds in [2 + 2] photocycloaddition reactions. Two type of molecules, both isomers of the antibiotic patulin [6], contain these two ring systems fused *via* the common C–C bond, the 2*H*-furo[3,4-*b*]pyran-4,5(3*H*,7*H*)-diones **1** [7] and the corresponding furopyran-4,7(3*H*,5*H*)-diones **2** [8] [9]. We now report on the photochemistry of the title compound **2a**.



1



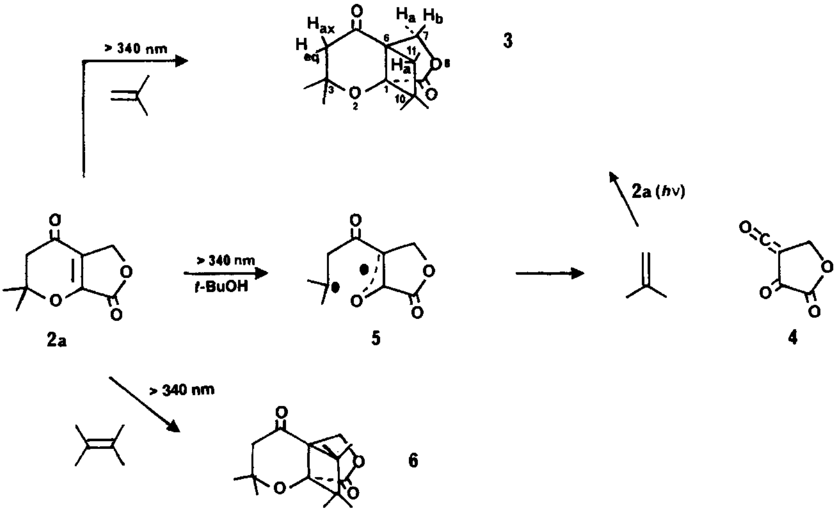
2

2a R=CH_3

Irradiation ($\lambda > 340$ nm) of **2a** in *t*-BuOH leads to decomposition of the starting material with formation of one new product **3**, albeit in low yield (15%). The CI-MS of **3** shows [$M + H^+$] at m/z 239 and the ^{1}H-NMR indicates the presence of 1 additional CH_2 group and 2 additional CH_3 groups. Both results combined suggest that **3** is formed from **2a** and 2-methylpropene. Indeed, irradiation of **2a** in *t*-BuOH saturated with this alkene affords **3** much faster and in very good yield. Competitive experiments in a 'merry-go-round' setup show that for total conversion of **2a** to **3** in the presence of alkene, only 10% of **2a** are decomposed in its absence with very little formation of **3**. It, thus, becomes evident that **2a** undergoes photoextrusion of 2-methylpropene and that remaining **2a** undergoes [2 + 2] photocycloaddition to this alkene. The primary reaction product **4** apparently decomposes quantitatively to CO, CO_2 and $CH_2{=}C{=}C{=}O$ (*Scheme 1*).

The first step in the photoextrusion of 2-methylpropene from **2a** is the cleavage of the $(CH_3)_2C{-}O$ bond to give the alkyl-vinyloxy biradical **5**. This is in analogy to the behaviour of benzyl enol ethers which undergo 1,3-migration of the benzyl group on irradiation

Scheme 1



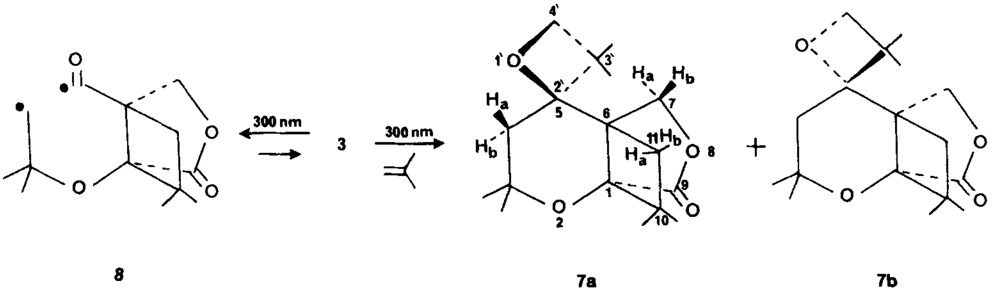
[10]. For biradical **5**, β-cleavage to 2-methylpropene and **4** seems to be the preferred path over (a possible) spirocyclobutanone formation.

Cycloaddition of **2a** to 2-methylpropene is regiospecific, the orientation of addition being the one expected for the excited pyranone – but not for the furanone moiety [4]. The structure of **3** is proven by its ^{1}H-NMR spectrum wherein a *W*-coupling between $H_aC(7)$ and $H_aC(11)$ with $J(1,5) = 1.0$ is observed. No such coupling is observed for cycloadduct **6** formed from **2a** and 2,3-dimethyl-2-butene.

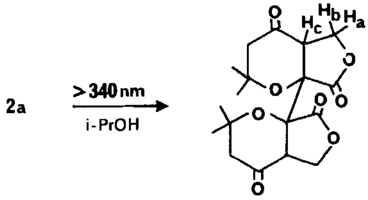
When the irradiation of **2a** and 2-methylpropene is performed with light of $\lambda = 300$ nm, **3** is again formed selectively but then undergoes a consecutive photocycloaddition to the alkene to afford a 6:1 mixture of the diastereoisomeric spirooxetanes **7a** and **7b** (*Scheme 2*). The relative configuration of the major product **7a** again results from ^{1}H-NMR, wherein $H_aC(11)$ and $H_aC(4)$ are deshielded due to the oxetane O-atom by 1.2 and 1.0 ppm as compared to $H_bC(11)$ and $H_bC(4)$, respectively. The MS of **7a** and **7b** are alike.

It is interesting to note that no α-cleavage products are formed from **3**. This reaction occurs efficiently with strained bicyclo[4.2.0]octan-2-ones in the 'abnormal' mode

Scheme 2



Scheme 3



9a,b

Table. *Spectroscopic Data of Compounds* **2a**, **3**, **6**, **7**, *and* **9**

Compound[a])	UV (CH_2Cl_2)	IR (KBr)	MS	^{1}H-NMR ($CDCl_3$)	^{13}C-NMR ($CDCl_3$)
2a	325 (34), 290 (sh, 4900), 280 (6600), 274 (sh, 6000)	1760, 1691, 1649	182 (40, $M^{+\cdot}$), *56*	4.99 (*s*, 2 H); 2.67 (*s*, 2 H); 1.57 (*s*, 6 H)	190, 168, 155, 124, 88, 67 (*t*), 49 (*t*), 26 (*q*)
3		1775, 1700	238 (1, $M^{+\cdot}$), *183*	4.78 (*dd*, *J* = 10.6, 1.0); 4.46 (*d*, *J* = 10.6); 2.76 (*dq*, *J* = 15.6, 0.9); 2.37 (*d*, *J* = 15.6); 2.32 (*dd*, *J* = 12.5, 1.0); 2.02 (*d*, *J* = 12.5); 1.49, 1.28, 1.22 (3*s*, CH_3); 1.08 (*d*, *J* = 0.9, CH_3)	206, 175, 81, 79, 73 (*t*), 49 (*t*), 43, 42 (*t*), 38, 30 (*q*), 26 (*q*), 25 (*q*), 24 (*q*)
6		1765, 1700	266 (1, $M^{+\cdot}$), *183*	4.70, 4.32 (*AB*, *J* = 11.0); 2.50 (*dq*, *J* = 16.8, 0.8); 2.42 (*d*, *J* = 16.8); 1.46, 1.18, 1.13, 1.12, 1.09 (5*s*, CH_3); 1.12 (*d*, *J* = 0.8, CH_3)	
7a		1762[b])	no M^+ at 294, 239 (20), 183 (95), *56*	4.30 (*d*, *J* = 10.4); 4.05 (*dd*, *J* = 10.5, 1.0); 4.30, 4.02 (*AB*, *J* = 5.6); 2.96 (*dd*, *J* = 12.0, 1.0); 2.37, 1.38 (*AB*, *J* = 14.8); 1.72 (*d*, *J* = 12.0); 1.48, 1.22, 1.15, 1.11, 1.10, 1.04 (6*s*, CH_3)	
9a		1765, 1718[c])	367 (100, $[M + 1]^+$)[d])	5.02 (*dd*, *J* = 8.7, 1.7); 4.44 (*dd*, *J* = 8.7, 8.2); 4.23 (*dd*, *J* = 8.2, 1.7); 2.49, 2.40 (*AB*, *J* = 14.0); 1.40, 1.07 (2*s*, CH_3)	
9b				4.83 (*dd*, *J* = 9.5, 2.5); 4.47 (*dd*, *J* = 9.5, 9.1); 4.00 (*dd*, *J* = 9.1, 2.5); 2.64, 2.47 (*AB*, *J* = 13.9); 1.46, 1.07 (2*s*, CH_3)	

[a]) All new compounds gave satisfactory elemental analyses.

[b]) In CH_2Cl_2.

[c]) Mixture **9a**/**9b**.

[d]) CI-MS spectrum.

[11–13]. Thus, biradical **8** should be formed, but this species cannot rearrange neither to a ketene nor to an unsaturated aldehyde and, therefore, will reclose to **3** *(Scheme 2)*.

Finally, irradiation ($\lambda > 340$ nm) of **2a** in 2-propanol gives a precipitate consisting of a 2:1 mixture **9a**/**9b**. Both compounds **9** have the molecular weight M^+ 366. The IR spectrum indicates both a ketonic and a lactone CO group and the ^{1}H-NMR, recorded immediately after dissolving **9** in $CDCl_3$ as decomposition occurs on standing at r.t. in $CDCl_3$ or CD_3COCD_3, indicates an *ABC* pattern for the CH_2 group next to the O-atom. These results suggest that **9a** and **9b** are *meso* and (*RS, RS*) hydrodimers *(Scheme 3)*.

The spectroscopic data of compounds **2a**, **3**, **6**, **7**, and **9** is summarized in the *Table*.

Experimental Part

General. See [5]. Anal. GC: 25-m *SE 30* capillary column.

Starting Materials. Furopyrandione **2a** was synthesized according to [9].

Photolyses. These were performed in a *Rayonet-RPR-100* photoreactor using either 350-nm lamps in combination with a liquid filter with cut-off at $\lambda = 340$ nm [14] (irradiation of **2a**) or $\lambda = 300$ nm lamps (irradiation of **3**).

Irradiation of **2a**. An Ar-degassed soln. of 182 mg (1 mmol) of **2a** in 5 ml of *t*-BuOH is irradiated ($\lambda > 340$ nm) for 80 h. Evaporation of the solvent and recrystallization of the residue from Et_2O/pentane affords 30 mg (13%) of *3,3,10,10-tetramethyl-2,8-dioxatricyclo[4.3.2.0^{1,6}]undecane-5,9-dione* (**3**). M.p. 128–130°.

Irradiation of **2a** *and 2-Methylpropene.* A soln. of 910 mg (5 mmol) of **2a** in 10 ml of *t*-BuOH saturated with 2-methylpropene is irradiated ($\lambda > 340$ nm) for 16 h. Work up as above affords 904 mg (76%) of **3**.

Irradiation of **2a** *and 2,3-Dimethyl-2-butene.* An Ar-degassed soln. of 910 mg (5 mmol) of **2a** and 2.1 g (25 mmol) of 2,3-dimethyl-2-butene in 10 ml of *t*-BuOH is irradiated ($\lambda > 340$ nm) for 32 h. Workup as above affords 905 mg (68%) of *3,3,10,10,11,11-hexamethyl-2,8-dioxatricyclo[4.3.2.0^{1,6}]undecane-5,9-dione* (**6**). M.p. 65–68°.

Irradiation of **2a** *in 2-Propanol.* An Ar-degassed soln. of 910 mg (5 mmol) **2a** in 10 ml of 2-propanol is irradiated for 14 h. Filtration and drying of the white crystalline precipitate affords 732 mg (80%) of a 2:1 mixture (GC) of diastereoisomeric hydrodimers **9a**/**9b**. M.p. 185° (dec.). Compounds **9** decompose at r.t. in $CHCl_3$ or acetone soln. to unknown products.

Irradiation of **3** *and 2-Methylpropene.* A soln. of 476 mg (2 mmol) of **3** in 5 ml of *t*-BuOH saturated with 2-methylpropene is irradiated ($\lambda = 300$ nm) for 40 h to afford a 6:1 mixture (GC) **7a**/**7b**. Chromatography (SiO_2, CH_2Cl_2) affords 282 mg (48%) 3,3,3',3',10,10-hexamethylspiro[2,8-dioxatricyclo[4.3.2.0^{1,6}]undecane-5,2'-oxetane]-9-one (**7a**). M.p. 81–84°. The minor component **7b** was not isolated.

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