

169. Photochemistry of 8,8,9,9-Tetramethyl-1,3,4,6,7,8-hexahydro-1,4-ethanonaphthalene-2,5-dione, a δ -Oxo- β,γ -unsaturated Ketone

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(13.VII.84)

Summary

The oxa-di- π -methane rearrangement product 4,4,9,9-tetramethyltetracyclo[6.4.0.0^{1,5}.0^{2,8}]dodecane-7,12-dione (**2**) is formed selectively in a variety of solvents on either direct ($\lambda = 254, 300, 350$ nm) or sensitized (xanthone, acetone, benzene) irradiation of the title compound **1**. The efficiency for this rearrangement is higher on S_0-S_1 excitation ($\phi_{-1} = 0.67$) than on either S_0-S_2 or S_0-S_3 excitation ($\phi_{-1} = 0.58$).

The photochemical behaviour of β,γ -unsaturated ketones has been investigated in detail [1–4], but only very few results on light-induced reactions of δ -keto-unsaturated ketones ($O=C-C=C-C-C=O$) have been reported [5] [6]. From these reports it would seem [2] that such compounds undergo the oxa-di- π -methane rearrangement – a reaction which is typical for β,γ -enones – selectively, on either direct or sensitized irradiation. The UV-absorption spectra of simple β,γ -enones are characterized by two absorption bands, one at $\lambda = 210$ – 250 nm, related to a $\pi-\pi^*$ transition, and the second at $\lambda = 280$ – 300 nm, related to a $n-\pi^*$ transition [2]. The UV spectrum of 4,4-dimethyl-17 β -acetoxy- Δ^5 -androstene-3,7-dione, one of the δ -keto- β,γ -unsaturated ketones investigated [6] exhibits an additional $n-\pi^*$ absorption band at $\lambda = 348$ nm (in cyclohexane) attributable to the supplementary α,β -enone carbonyl group.

We have recently [7] reported the synthesis of the tricyclic δ -keto- β,γ -unsaturated ketone **1** and found that its UV spectrum ($\lambda_{\max} = 254, 298$ and 340 nm in cyclohexane) contained the same features as that of the steroidal diketone mentioned above. We now report results on the photochemical behaviour of **1** and on the efficiency of its photoconversion as function of the wavelength of light used in the excitation process.

Irradiation of **1** at different wavelengths, $\lambda = 254, 300$ and 350 nm (corresponding to S_0-S_3, S_0-S_2 and S_0-S_1 excitation) in either cyclohexane or acetonitrile affords one new product **2** selectively (*Scheme*) as monitored by GC and TLC. The same compound **2** is again exclusively formed on sensitized irradiation of **1** using either xanthone, acetone or benzene as sensitizer. From the spectroscopic data summarized in the *Table*, it can be safely concluded that **2** is the oxa-di- π -methane rearrangement product 4,4,9,9,-tetramethyltetracyclo[6.4.0.0^{1,5}.0^{2,8}]dodecane-2,7-dione (**2**).

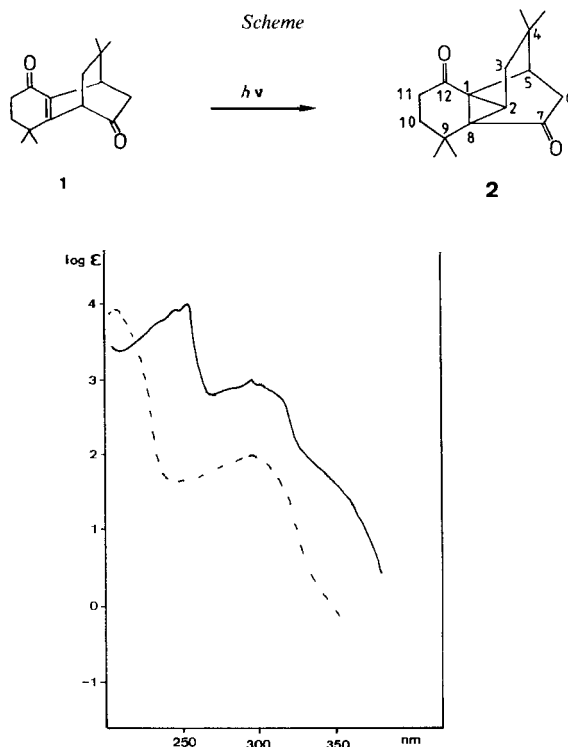


Figure. UV Spectra of **1** (—) and **2** (---) in Cyclohexane

We have measured the quantum yields for the reaction **1**→**2** in cyclohexane at three different wavelengths, $\lambda = 254, 313$ and 366 nm. As seen in the *Figure* the extinction coefficients of **1** at these wavelengths are more than tenfold higher than those of **2** and therefore the disappearance of **1** can easily be monitored by UV spectroscopy. The values for ϕ_{-1} obtained are 0.67 ± 0.01 at 366 nm and 0.58 ± 0.01 at 313 and 254 nm. From these values it becomes evident that the reactive triplet (presumably T_1) state is populated more efficiently *via* S_1 than *via* either S_2 or S_3 . This finding can be explained by the fact that the rate of intersystem crossing for α,β -enones is much higher than that for β,γ -enones [2], and thus requires an additional deactivation path from S_2 to the ground state of **1**, as no additional product is formed on either S_0 - S_2 or S_0 - S_3 excitation.

We are grateful to *Deutsche Forschungsgemeinschaft* and *Fonds der Chemischen Industrie* for financial support, to Prof. Dr. K. Schaffner (*Max Planck Inst. für Strahlenchemie, Mülheim/Ruhr*) for providing the electronically integrating actinometer and to Dr. A. R. Holzwarth, Mr. H. V. Seeling and Mr. A. Pieper (*MPI für Strahlenchemie, Mülheim*) for their assistance in determining the quantum yields.

Experimental Part

General. Absorptions in the UV spectra are given in nm ($\log \epsilon$) and in the IR spectra in cm^{-1} . Chemical shifts in the 400-MHz ^1H - and 100.63-MHz ^{13}C -NMR spectra are given in ppm relative to TMS ($\delta = 0$ ppm) as internal standard. The mass spectra were measured at 70 eV. GC was performed on a 15% SE 30 column at 150°. TLC was performed on Al_2O_3 in CH_2Cl_2 .

Photolyses. These were run in a Rayonet RPR-100 photoreactor.

a) *Analytical.* N_2 -degassed solutions of 4.92 mg **1** in 1 ml solvent (cyclohexane or CH_3CN – direct irradiation with $\lambda = 350, 300$ or 254 nm –, or benzene/xanthone, acetone or benzene – sensitized irradiations at these wavelengths –) were irradiated for 1 h. GC and TLC indicated the selective conversion of **1** to **2**, no other product being detected.

b) *Preparative.* A N_2 -degassed solution of 1.23 g ($5 \cdot 10^{-3}$ mol) **1** in 300 ml cyclohexane was irradiated for 3 h ($\lambda = 300 \text{ nm}$). Evaporation of the solvent and recrystallization of the residue from pentane afforded 960 mg (78%) 4,4,9,9-tetramethyltetracyclo[6.4.0.0^{1,5}.0^{2,8}]dodecane-7,12-dione (**2**), m.p. 157–159°. UV (cyclohexane): 298 (2.00); 208 (3.90). IR (KBr): 3053, 1721. ^1H -NMR (CDCl_3)¹ 2.80 (*dd*, $J = 7.3, 2.4$, H–C(2)); 2.80 (*ddd*, $J = 9.0, 2.1, 1.2$, H–C(5)); 2.29 (*dd*, $J = 17.8, 9.0$, H_α –C(6)); 2.16 (*dd*, $J = 17.8, 1.2$, H_β –C(6)); 2.29–2.16 (*m*, H_α –C(11), H_β –C(11)); 1.75 (*ddd*, $J = 13.5, 7.3, 2.1$, H_α –C(3)); 1.57 (*ddd*, $J = 14.6, 9.6, 4.8$, H_α –C(10)); 1.37 (*dd*, $J = 13.5, 2.4$, H_β –C(3)); 1.32 (*ddd*, $J = 14.6, 5.2, 3.8$) H_β –C(10); 1.33, 1.10, 1.06, 0.92 (*s*, CH_3). ^{13}C -NMR (CDCl_3): 212.6 (*s*); 204.7 (*s*, C(7), C(12)); 60.5 (*s*, C(1)); 58.4 (*s*, C(8)); 49.9 (*s*, C(9)); 45.9 (*d*, $J = 140$, C(5)); 44.6 (*t*, $J = 130$, C(11)); 39.0 (*t*, $J = 126$, C(6)); 36.9 (*d*, $J = 169$, C(2)); 33.8 (*t*, $J = 130$, 33.3 (*t*, $J = 127$) C(10) & C(3)); 30.5 (*s*, C(4)); 28.8, 26.9, 23.6, 23.2 (*q*, $J = 125$, CH_3). MS: 246 (M^+), 189. Anal. calc. for $\text{C}_{16}\text{H}_{22}\text{O}_2$: C 78.01, H 9.00; found: C 78.24, H 9.02.

Actinometry. The quantum yields were measured at 20° using an electronically integrating actinometer [8]. The decrease of starting material **1** was monitored by UV spectroscopy. N_2 -degassed solutions of **1** ($97.5 \cdot 10^{-3} \text{ M}$ at $\lambda = 366 \text{ nm}$, $2.03 \cdot 10^{-3} \text{ M}$ at $\lambda = 313 \text{ nm}$ and $0.203 \cdot 10^{-3} \text{ M}$ at $\lambda = 254 \text{ nm}$) in 3 ml cyclohexane were irradiated to 30–40% conversion.

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¹) Coupling constants (Hz) from measurement in $\text{C}_5\text{D}_5\text{N}$.