CHEMISTRY LETTERS, pp. 1647-1650, 1988.

Synthesis and Properties of 8H-3-Oxaheptalen-8-one

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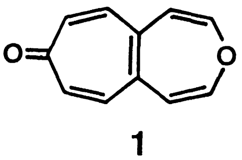
An ethanol solution of 12-oxatricyclo[7.2.1.$0^{2,8}$]dodeca-2(8),3,6,10-tetraen-5-one was irradiated with a 100-W Hg lamp through pyrex filter to give 8H-3-oxaheptalen-8-one, an oxepine condensed with tropone, in good yield together with a slight amount of 6-hydroxyazulene.

Oxepine is a well-documented seven-membered heterocycle and its properties have extensively been studied.1) Although annelated oxepines with aromatic rings are also known, no oxepines condensed with nonbenzenoid aromatic species have so far been reported. We are interested in a novel ring system, 8H-3-oxaheptalen-8-one (**1**), in which oxepine is fused with tropone.

During the course of our study on 4,5-dehydrotropone as a building block for the synthesis of tropylium systems incorporated into three-dimensional frameworks,2) we have prepared 12-oxatricyclo[7.2.1.$0^{2,8}$]dodeca-2(8),3,6,10-tetraen-5-one (**2**) and its bridgehead alkyl derivatives (**3**).3) The efficient photochemical conversion of 7-oxanorbornadienes into the corresponding 6-hydroxyfulvenes, 7-oxaquadricyclanes, and oxepines4) prompted us to study the photochemical behaviors of **2** and **3**. We have already reported that the irradiation of **3** in methanol gave 1-alkyl and 3-acyl-1-alkyl-6-hydroxyazulenes in good combined yields.5) Contrary to these observations, the unsubstituted compound **2** behaved quite differently on irradiation leading to the expected oxepine.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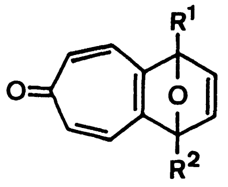
2, $R^1 = R^2 = H$
3, $R^1 = H$, $R^2 =$ alkyl
$R^1 = R^2 =$ alkyl

Monitoring of the photolysis of **2** (1.2×10^{-4} mol/L in ethanol, 500-W Hg lamp, $310 < \lambda < 390$ nm irradiation6)) reveals that the clean conversion of **2** into photoproducts was completed within 1 min. However, the spectrum of the product mixture

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is quite different from that of azulene type obtained on irradiation of **3** in a methanol.[5] In a typical preparative experiment, an ethanol solution of **2** (1-2 x 10^{-3} mol/L) was irradiated with a 100-W Hg lamp through pyrex for 0.5-1 h. Careful workup of the reaction mixture under nitrogen gave 8H-3-oxaheptalen-8-one (**1**)[7,8] in 87 - 93% yield together with a tiny amount (1 – 2%) of 6-hydroxyazulene (**4**).[9] The ^{13}C NMR [($CDCl_3$) δ 119.7 (C-1,5), 139.2, 139.9 (C-6,10,7,9), 142.0 (C-5a, 10a), 149.3 (C-2,4), 186.4 (C-8)] as well as the ^{1}H NMR spectrum[8] of **1** confirms its symmetrical structure. The vicinal proton coupling constants, $J_{1,2} = J_{4,5} = 6.0$ Hz (in $CDCl_3$) and $J_{6,7} = J_{9,10} = 12.0$ Hz (in CD_3CN) are comparable to the corresponding coupling constants of 1-benzoxepine (5.5 Hz)[10] and tropone (12 Hz),[2b,11] respectively, revealing that the oxepine ring maintained its boat conformation[12] whereas the tropone moiety remains almost planar geometry[13] in **1**.

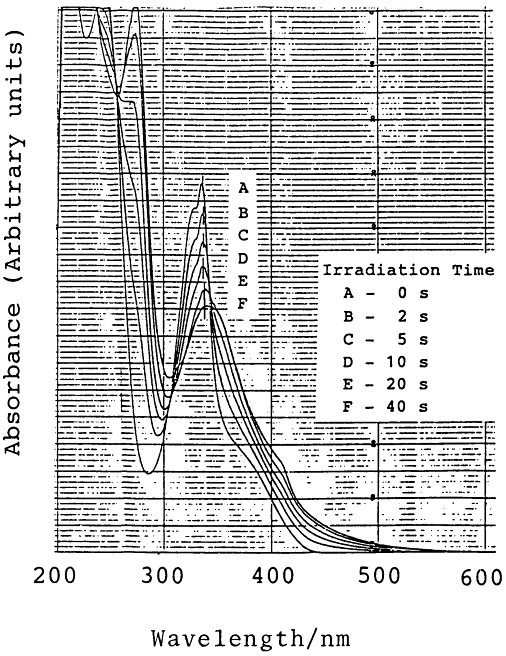
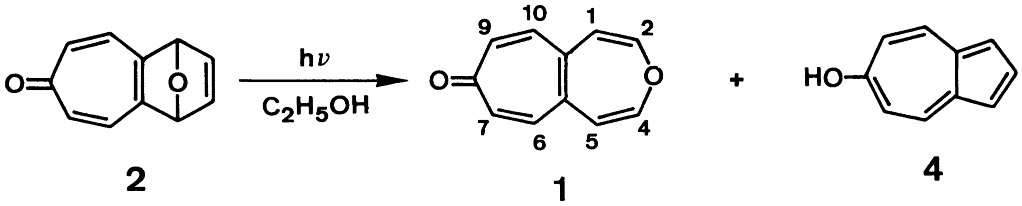
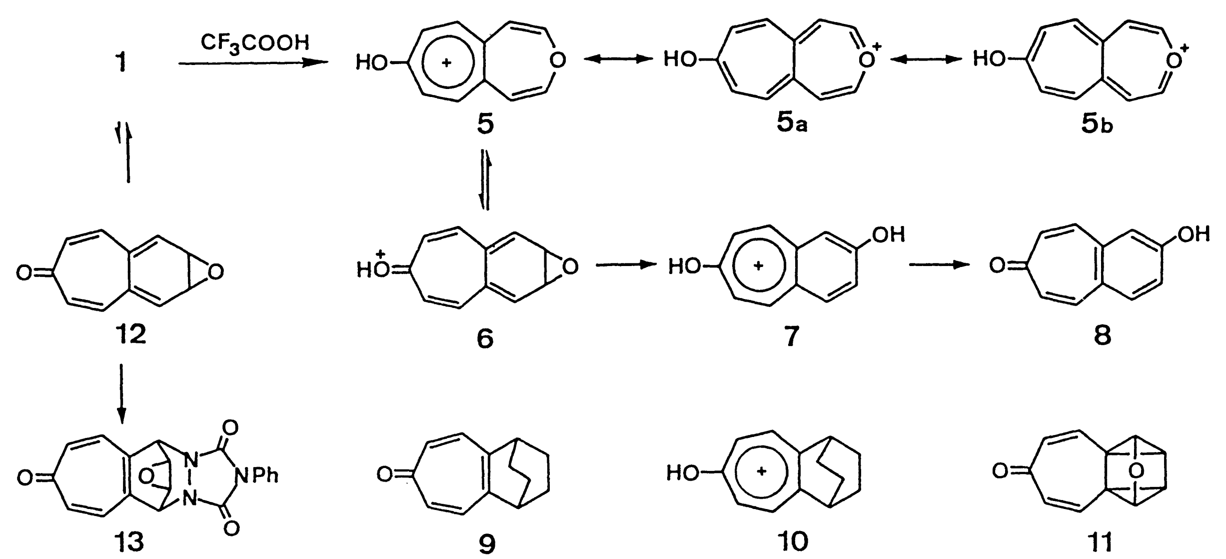


Fig. 1. UV/VIS spectral change of **2** upon irradiation with a 500-W Hg lamp.



The electronic spectrum of **1** was strongly dependent on the solvent polarity [λ_{max} nm (log ε) of the longest wavelength absorption which has been shown to be the transition polarized along the long axis of **1**[14]: in hexane, 324 (3.72); in benzene, 335 (3.76); in methanol, 347 (3.85); in 15% aqueous methanol, 355 (3.90)]. As would be expected, **1** was protonated in CF_3COOH to give 8-hydroxy-3H-3-oxaheptalenium ion (**5**) [^{1}H NMR (CF_3COOH) δ 5.27 (d, J = 8 Hz, H-2,4), 5.88 (d, J = 8 Hz, H-1,5), 7.56 (d, J = 12 Hz, H-6,10 or H-7,9), 7.66 (d, J = 12 Hz), H-7,9 or H-6,10)]. Downfield chemical shift (Δδ = 0.67 – 0.80 ppm) of the troponoid protons in the ^{1}H NMR spectrum of **5** compared with those of **1** are moderately smaller than the corresponding values (1.29 - 1.47 ppm) observed for **9** and its protonated species **10**.[15] These data could be interpreted in terms of the intramolecular electron transfer from the oxepine ring to the tropylium ring in **5**, that is, by a contribution of 3-oxoniaheptalen-8-ol forms **5a** and **5b** to some extent and/or by the



paratropic character associated with 12π electron framework of **5a** and **5b**. Consequently, the protonated species **5** should have a more planar conformation than **1**. On standing at room temperature for 4 h in CF_3COOH, **1** was quantitatively isomerized to 7H-2-hydroxybenzocyclohepten-7-one (**8**).[16] This rearrangement would proceed via a benzene oxide intermediate **6**.

The ^1H NMR spectrum of **1** ($CS_2/CDCl_3$) showed no sign of line broadening due to valence tautomerism even at -100 ℃. However, the reaction of **1** with 4-phenyl-1,2,4-triazoline-3,5-dione in dioxane at room temperature gave readily a product **13**[17] in 77% yield which corresponds to the cycloadduct of a valence tautomer **12** of the starting material.

As the precedented photochemical conversion of 7-oxanorbornadienes into oxepines,[4b] a possible intermediate for the present photolysis, **2** → **1**, should be **11**, isolation of which has not met with success. It should be noted that the course of the main photochemical reaction of **2** in ethanol is quite different from that of **3** in methanol. Studies aimed at clarifying the marked solvent and substituent effects are now in progress.

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6) Toshiba UV-D33S and UV-31 filters were used.

7) All the compounds isolated gave correct elemental analyses and/or correct high resolution mass spectral data.

8) **1**: Orange plates; mp 91-92 °C; UV (hexane) λ_{max} nm (log ε) 257sh (4.29), 264 (4.30), 324 (3.72), 335sh (3.69), 380sh (3.39); UV (CH_3OH) 274 (4.31), 347 (3.85); ^1H NMR ($CDCl_3$) δ 5.57 (d, J = 6 Hz, H-1,5), 6.08 (d, J = 6 Hz, H-2,4), 6.80 (bs, H-6,10,7,9); ^1H NMR (C_6D_6) δ 4.75 (d, J=6.1 Hz, H-1,5), 5.46 (d, J=6.1 Hz, H-2,4), 5.84, 6.60 (each d, J=12 Hz, H-6,7,9,10); ^1H NMR (CD_3CN) δ 5.74 (d, J=6.1 Hz, H-1,5), 6.13 (d, J=6.1 Hz, H-2,4), 6.75, 6.90 (each d, J=12 Hz, H-6,10,9,7); ^1H NMR (CH_3OD) δ 5.73 (d, J=6.2 Hz, H-1,5), 6.15 (d, J=6.2 Hz, H-2,4), 6.87, 7.05 (each d, J=12.5 Hz, H-6,10,7,9).

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16) **8**: Colorless needles; mp 238-240 °C (dec.); ^1H NMR (DMSO-d_6) δ 6.38-6.67 (m, H-6, 8), 7.08 (dd, J=8, 2 Hz, H-3), 7.18 (d, J=2 Hz, H-1), 7.48 (d, J=13 Hz, H-5 or 9), 7.51 (d, J=13 Hz, H-9 or 5), 7.69 (d, J=8 Hz, H-4), 10.46 (bs, OH); ^{13}C NMR (DMSO-d_6) δ 118.9, 118.9, 127.9, 130.6, 134.7, 136.5, 137.5, 140.8, 141.4, 159.5, 187.1; UV (CH_3OH) λ_{max} nm (log ε) 239 (4.49), 278 (4.56), 313 (3.89), 330 (3.94); UV (1M NaOH) 252 (4.38), 296 (4.44), 387 (4.06).

17) **13**: Colorless prisms; mp 242-245 °C (dec.).

(Received July 15, 1988)