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-5one (2) and its bridgehead alkyl derivatives (3).³⁾ The efficient photochemical conversion of 7-oxanorbornadienes into the corresponding 6-hydroxyfulvenes, 7oxaquadricyclanes, 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 1alkyl 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.



Monitoring of the photolysis of 2 (1.2 x 10^{-4} mol/L in ethanol, 500-W Hg lamp, 310 < λ < 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 guite 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- 2×10^{-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-8one $(1)^{7,8}$ in 87 - 93% yield together with a tiny amount (1-2%) of 6-hydroxyazulene (4).⁹⁾ The ¹³C NMR [(CDCl₃) 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 ¹H NMR spec $trum^{8}$ 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 CD₃CN) are comparable to the corresponding coupling constants of 1-benzoxepine $(5.5 \text{ Hz})^{10}$ and tropone (12 Hz),^{2b,11)} respectively, revealing that the oxepine ring maintained its boat conformation¹²⁾ whereas the tropone moiety remains almost planar geometry¹³⁾ in 1.



Wavelength/nm

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 $[\lambda_{max} nm (\log \varepsilon) of the longest wavelength absorption which has been shown to be the transition polarized along the long axis of 1¹⁴: in hexane, 324 (3.72); in benzene, 335 (3.76); in methanol, 347 (3.85); in 15% aqueous methanol, 355 (3.90)]. As would be expected, 1 was protonated in CF₃COOH to give 8-hydroxy-3H-3-oxa-heptalenium ion (5) [¹H NMR (CF₃COOH) & 5.27 (d, J = 8 Hz, H-2,4), 5.88 (d, J = 8 Hz, H-1,5), 7.56 (d, J = 12 Hz, H-6,10 or H-7,9), 7.66 (d, J = 12 Hz), H-7,9 or H-6,10]. Downfield chemical shift (<math>\Delta$ = 0.67 - 0.80 ppm) of the troponoid protons in the ¹H 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 CF₃COOH, **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 °C. 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, $2 \div 1$, 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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- 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 (CH₃OH) 274 (4.31), 347 (3.85); ¹H NMR (CDCl₃) & 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 (C₆D₆) & 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 (CD₃CN) & 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 (CH₃OD) & 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 % (dec.); ¹H NMR (DMSO-d₆) 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); ¹³C NMR (DMSO-d₆) δ 118.9, 118.9, 127.9, 130.6, 134.7, 136.5, 137.5, 140.8, 141.4, 159.5, 187.1; UV (CH₃OH) 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.).

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