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PHOTOCHEMISTRY OF 2H-AZEPIN-2-ONES

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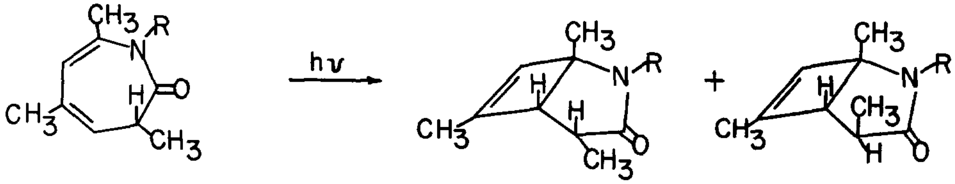
The photochemistry of 3,5-cycloheptadienones is unusually varied.[1] By contrast, however, the photochemistry of 2H-azepin-2-ones, the nitrogen-hetero analogues of 3,5-cycloheptadienones, has been suggested to be much more simple. Thus irradiation of 1,3-dihydro-3,5,7-trimethyl-2H-azepin-2-one **1a** in diethyl ether, tetrahydrofuran, or methanol solvent or of 1,3-dihydro-1,3,5,7-tetramethyl-2H-azepin-2-one **1b** in diethyl ether solvent has each been reported to yield a single valence isomer **2a** or **2b**.[2,3] Recent work in our laboratory, however, reveals that the photochemistry of these azepinones is more complex than previously considered.



1a,b 2a,b 3a,b

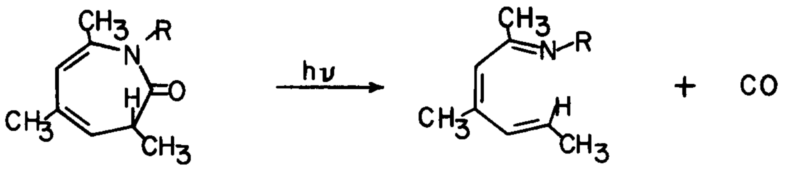
(a: R=H ; b: $R=CH_3$)

Direct irradiation of **1a** in diethyl ether was accompanied by loss of the uv-absorption band at 256 nm due to **1a** without formation of any new absorption maxima above 220 nm. Gas chromatographic examination of the irradiated solution showed the presence of two volatile products in a ratio of ∿50 to 1. The major product was assigned structure **2a** on the basis of its spectroscopic properties [ir(CCl_4)3.13,3.33(N-H),3.35,3.43(C-H),5.90(amide C=O), and 6.10μ(C=C):NMR($CDCl_3$)δ1.20,d,J=7Hz,3H;1.40,s,3H;1.76,s,3H;2.70,m,1H;3.06,d, J=9Hz,1H;6.10,s,1H;6.68br,s,1H] which were very similar to those previously reported.[2,3] In particular, the proton at C-5 was observed at δ3.06 ppm as a doublet (J=9Hz) due to its coupling with the proton at C-4. The magnitude of this coupling constant is thus consistent with the assigned stereochemistry in which these two hydrogens are cis to each other. The minor product was assigned structure 3a. As expected for a stereoisomer, 3a had spectroscopic properties [ir(CCl_4)3.13,3.23(N-H),3.35,3.43(C-H),5.90(amide C=O), and 6.09μ (C=C):NMR($CDCl_3$)δ1.25,d,J=7Hz,3H;1.42,s,3H;1.70,s,3H;2.39,m,1H;2.60,s,1H;6.00, s,1H;6.85br.s,1H] very similar to those of 2a. As predicted by the Karplus generalization, in this instance, where the C-4 and C-5 protons are trans, the C-5 proton was observed as a broadened singlet (J=<3Hz) at δ2.60 ppm.

In the case of 1b, direct irradiation in diethyl ether was also accompanied by loss of uv absorption above 220 nm to yield 2b [ir(CCl_4)3.25,3.38,3.43(C-H), 5.94(amide C=O), and 6.10μ(C=C):NMR($CDCl_3$)δ1.15,d,J=7Hz,3H;1.29,s,3H;1.77,s,3H; 2.64,m,1H;2.75,s,3H;3.08,d,J=10Hz,6.15,s,1H] and a trace amount (∿300 to 1 ratio) of a second product. Although this latter product was not isolated in sufficient quantity for complete characterization, it was assigned structure 3b on the basis of its infrared spectrum [ir(CCl_4)3.38,3.43(C-H),5.94(amide C=O), and 6.10μ(C=C)] and chromatographic properties.

Irradiation of 1b in methanol solvent was accompanied by pronounced changes in both the relative and absolute yields of both valence isomers. Thus in this solvent a seven-fold decrease in the yield of 2b was accompanied by a five-fold increase in the yield of 3b resulting in a valence isomer ratio of 7 to 1. No other gc-volatile products were detected.

Concomitant with these changes, Figure 1a shows that irradiation of 1b in methanol ($2x10^{-4}$M) is also accompanied by the formation of a uv-absorbing species (λmax 368 and 267 nm) which was not observed in diethyl ether solvent. Furthermore, experimental evidence reveals that this product is not photochemically or thermally derived by reaction of either valence isomer with methanol. Figure 2b shows that this uv-absorbing primary photoproduct is not stable in methanol but is converted photochemically or, more slowly, thermally($t_{1/2}$∿5 hrs. at ambient temperature) to a secondary uv-absorbing product (λmax 323 nm). Although thermally stable, this secondary product is also photolabile.



1a,b 4a,b

(a: R=H ; b: R=CH_3)

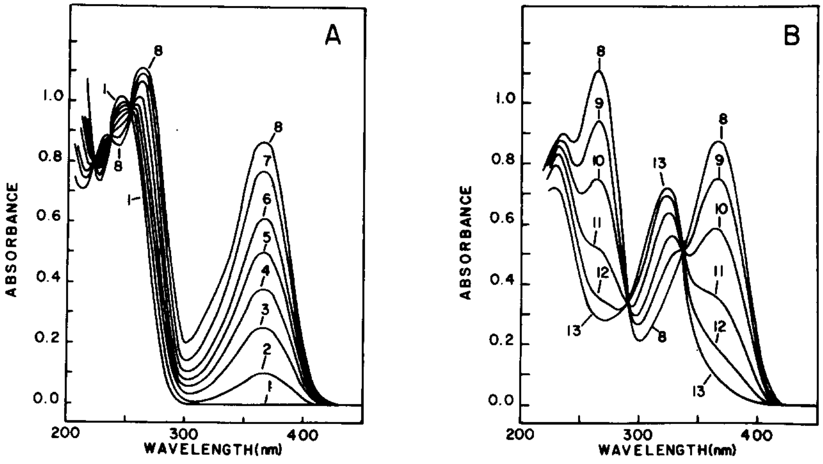


Figure 1. a) UV-absorption spectrum of **1b** in methanol: 1, before irradiation; 2-8 after consecutive irradiations (26 seconds total) and b) 9-13 after additional consecutive irradiations (260 seconds total) at 254 nm.

Whereas the photochemical and thermal instability of these new products have thus far precluded their isolation, uv-spectral properties show that their formation has been accompanied by a significant extension of conjugation. This is consistent with formation of imine **4b**, formed from **1b** by decarbonylation--a known primary photoprocess of 3,5-cycloheptadienones.[1a] The observed instability of this primary photoproduct is also consistent with structure **4b** since such an imine would be expected to add methanol either photochemically or thermally. Furthermore, in the case of **1a**, photodecarbonylation would yield unsubstituted imine **4a** which would be less stable in methanol than **4b**. Consistent with this, irradiation of **1a** in methanol was accompanied by a weak transient absorption at ∿350 nm, presumably due to **4a**, and a more intense absorption at 310 nm, presumably due to the subsequent methanol addition product of **4a**. This latter absorbance subsequently decreased with further photolysis or upon standing in the dark at room temperature.

Photovalence isomerization of **1a** or **1b** to **2a** and **3a** or **2b** and **3b** could be sensitized by irradiation of the azepinones in neat acetone ($E_T \sim 82$Kcal) or in diethyl ether or methanol solvent by acetophenone ($E_T=73.6$Kcal) but not by benzophenone ($E_T=68.5$Kcal). In turn, azepinone **1a** was found to efficiently quench the photoreduction of acetophenone with 1-phenylethanol in diethyl ether solvent despite absorption of 98 percent of the incident irradiation by acetophenone. This confirms that acetophenone is acting as a triplet sensitizer.

When the above sensitized photolyses were carried out to low percent conversions of **1a** or **1b**, the quantities of the minor valence isomers **3a** or **3b** were insufficient to permit quantitative determination of the relative yields of **2a** and **3a** or **2b** and **3b**. Furthermore, upon more prolonged sensitized photolysis these relative yields were dependent on irradiation time indicating that the valence isomers are photolabile under these conditions.

Both the disappearance of the azepinones **1a** or **1b** and the formation of valence isomers **2a** or **2b** could be quenched with biacetyl (E_T=54.9Kcal) in methanol or diethyl ether solvent. Least square plots of Φ_o/Φ vs. [biacetyl] were linear with $k_q\tau_o$ for **2a** formation in methanol being equal to 0.69 l. mole^{-1} and $k_q\tau_o$ for **2b** formation in diethyl ether being equal to 1.35 l. mole^{-1}. Assuming that biacetyl quenching occurs at the maximum diffusion controlled rate, these data correspond to a triplet lifetime for **1a** and **1b** of approximately 1 nsec. This is comparable to lifetimes reported for other cyclohexadienones and cycloheptadienones.[4]

Whereas photovalence isomerization appears to occur from a triplet excited state, the origin of **4b** is less certain. Although its formation could not be spectroscopically monitored upon sensitized photolysis of **1b** in methanol due to the uv absorption properties of the acetophenone, sensitized photolysis of **1b** in acetone was not accompanied by an increase in absorption at 368 nm due to **4b**. Furthermore, saturation of the solution with oxygen did not quench the formation of **4b** upon direct photolysis of **1b** in methanol. Accordingly, it appears that this uv-absorbing product is formed from an excited singlet state of **1b**.

In these respects the photochemistry of azepinones **1a** and **1b** appears to be analogous to 3,5-cycloheptadienone[1a] which undergoes decarbonylation and valence isomerization from S_1 and T_1 respectively rather than to 2,2,7,7-tetramethyl-3,5-cycloheptadienone[1b] which undergoes these primary processes from S_1 and S_2 respectively.

References

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