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PHOTOCHEMICAL 1,3-ACYL MIGRATION IN CYCLIC DIENAMIDES (AZEPINONES)

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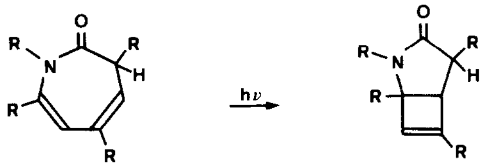
Abstract: Irradiation of 1,3-dihydro-2H-azepin-2-ones in aprotic solvents gives azabicycloheptenones by intramolecular cycloaddition, but photochemical isomerization in methanol results in 1,3-acyl migration involving cleavage of the amide bond.

Seven-membered heterocycles containing a conjugated diene system readily undergo photochemical valence isomerization to give annelated cyclobutenes.[1] Likewise, irradiation of 1,3-dihydro-2H-azepin-2-ones 1 in ether or benzene affords azabicycloheptenones 2 in generally excellent yields.[2] Recently, however, it was reported that irradiation of an azepinone (1, R=CH_3) in methanol gives rise to an elusive, thermally unstable product characterized by strong ultraviolet absorption (λ_{max} 267 and 368 nm).[3] These UV-spectroscopic properties are believed to be consistent with the structure of dienimine 3, proposed to be formed by photochemical decarbonylation of the azepinone.



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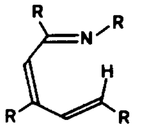

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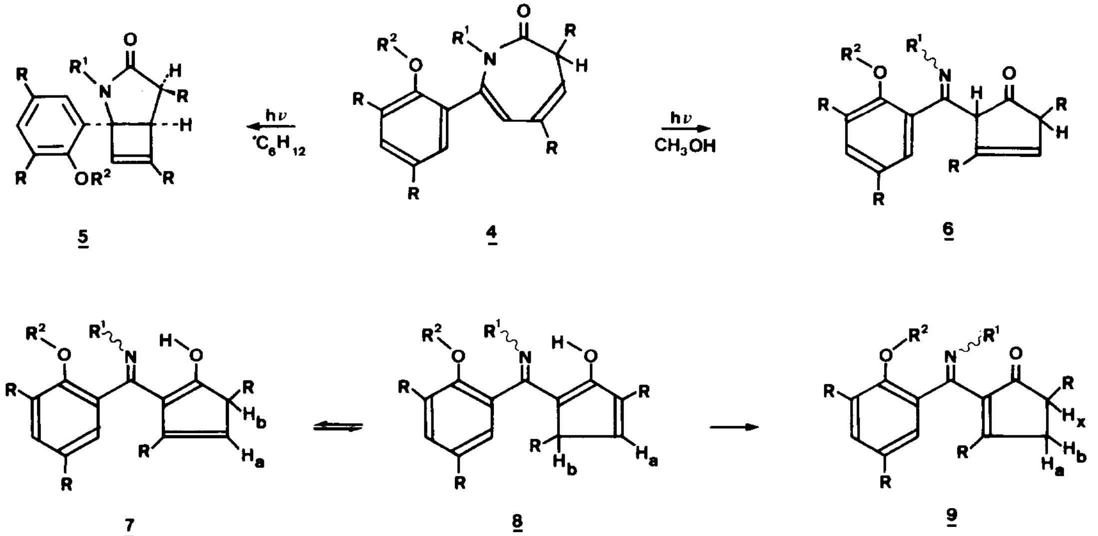
Investigating the photochemical properties of 7-aryl-substituted azepinones 4, we find that their valence isomerization in aprotic solvents leading to acetamido-annelated cyclobutenes 5 is drastically suppressed in methanol. For example, irradiation of 4a (0.23 g, high-pressure mercury lamp HPK 125 W, Pyrex, N_2, 12°) in ether or cyclohexane (75 ml) for 2 h gave the expected valence isomer 5a (colorless crystals, m.p. 194°) which was isolated in 80% yield.[4,5] In methanol, by contrast, irradiation of azepinone 4a under the same conditions yields only minute amounts of 5a. The major product, isolated in 60% yield, was found to be a yellow, crystalline substance (λ_{max} 268 and 371 nm, ε 10,800 and 10,200) whose elemental composition is that of the starting material rather than that of its decarbonylation product of dienimine structure 3. The infrared and 270 MHz ^{1}H-NMR spectral data listed in Table 1 are in agreement with a 1:1 mixture of two isomeric enols of the imino-substituted cyclopentenone 6, i.e. cyclopentadienols 7 and 8 ($R^1=R^2=CH_3$). We rationalize the formation of 6 by regioselective 1,3-acyl migration of photoexcited 4. Thus, in this isomerization the cyclic dienamide displays the excited state reactivity of a β,γ-unsaturated ketone.[6]



4-9, a: $R^1=R^2=CH_3$, R=t-C_4H_9; b: $R^1=CH_3$, $R^2=H$, R=t-C_4H_9

Table 1. 270 ^{1}H-NMR spectral data of cyclopentadienols 7a/8a in $CDCl_3$

H_a	H_b	OH	R^1	R^2	R	aromatic H
5.44	2.51 (J_{ab}=3 Hz)	11.4	2.64	3.35	0.76, 1.03 1.06, 1.29	7.26, 7.37 (J=2.5 Hz)
5.49	2.63$^{x)}$ (J_{ab}=2.2 Hz)	11.7	2.62	3.63	1.34	

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x) Signal hidden under those of R^1. Position verified by decoupling

In chloroform solution at room temperature,[8] cyclopentadienols 7/8 are elusive inasmuch as they are spontaneously converted into the thermodynamically stable isomeric imino-substituted cyclopentenone 9a (m.p. 123-125°) whose structure, in turn, is supported by the exhibition of a characteristic ABX pattern in its 270 MHz ^1H-NMR spectrum (see Table 2). The NMR spectral properties of the imino-substituted cyclopentenone 9b (m.p. 156-157°), obtained[9] by irradiation of azepinone 4b, are in agreement with this structural assignment. Thus, the ^{13}C chemical shift of the carbonyl carbon in 9b is found at δ 206 ppm downfield from TMS. As for the electronic absorption spectra of imino-substituted cyclopentenones 9, intramolecular hydrogen bonding decreases the energy of their longest-wavelength transition. Compound 9a ($R^2=CH_3$) is colorless (λ_{max} 295 nm, ε 2,300, in EtOH), while β-hydroxy-substituted imine 9b (R^2=H) is yellow (λ_{max} 262 and 337 nm, ε 9,600 and 4,400, shoulder at 420 nm, ε 500).

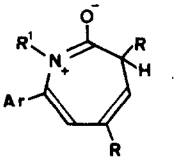
Table 2. 270 MHz ^1H-NMR spectral data of imino-substituted cyclopentenones 9

	H_a	H_b	H_x	R^1	R^2	aromatic H		R	R	R	R
9a :	2.79	2.57	2.11	3.30	3.81	6.94	7.36	0.96	1.23	1.28	1.39
9b :	2.93	2.69	2.35	3.15	15.92	6.88	7.32	1.09	1.19	1.19	1.44
9b' x):	2.93	2.64	2.38	3.17	15.66	6.83	7.31	1.06	1.16	1.21	1.43

In all cases: J_{ab}=19 Hz, J_{ax}=7 Hz, J_{bx}=3 Hz. $J_{arom.H}$=2.5 Hz

x) See Footnote 9

The effect of solvent on the electronic absorption spectra of azepinones 4 probably provides the rationale for the solvent-dependent course of their excited state reactions. In cyclohexane, solvent-solute interactions being negligible, azepinone 4a, for example, has its longest-wavelength absorption maximum at 285 nm (ε 10,700). It seems reasonable to assume that the azepinone resonance structure 10, whose contribution to the electronic ground state has been verified by an X-ray structure analysis of 4b,[7] is involved in this transition. Consequently, the photochemical valence isomerization in aprotic solvents leading to 5 may be explicable in terms of the excited state reactivity of a heterocyclic conjugated triene. In methanol, significantly, the longest-



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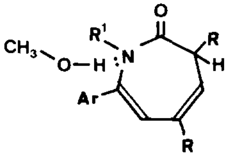

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wavelength maximum of 4a is hypsochromically shifted to 279 nm (ε 11,900). Most likely, hydrogen bonding of 4a with the solvent localizes the lone-pair electrons on nitrogen, thus favoring contributions of resonance structure 11 in which the amide bond assumes single bond character, and facilitating the photochemical reaction typical of a β,γ-unsaturated carbonyl compound.

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References and Notes

1. L.A. Paquette in "Nonbenzenoid Aromatics", Vol. I, J.P. Snyder, Edit., Academic Press, 1969.
2. H.-D. Becker and K. Gustafsson, J. Org. Chem., 42, 2966 (1977), and references therein.
3. J.W. Pavlik and C.A. Seymour, Tetrahedron Lett., 1977, 2555.
4. a) Satisfactory elemental analyses were obtained for all compounds isolated.
   b) UV-spectroscopic analysis of the crude reaction mixture reveals the presence of 7/8 (16%)
5. The stereochemistry of azabicycloheptenones 5 has been verified by X-ray structure analysis in the case of 5b (see ref. 7).
6. For a comprehensive review of the photochemistry of β,γ-unsaturated carbonyl compounds, see K.N. Houk, Chem. Rev., 76, 1 (1976).
7. H.-D. Becker, K. Gustafsson, C.L. Raston, and A.H. White, Aust. J. Chem., in press.
8. The rate of conversion appears to depend on the quality of the chloroform, probably because the isomerization is subject to acid catalysis. The conversion of 7/8 into 9 also is catalyzed by silica gel/CH_2Cl_2.
9. Isolated in 50% yield by chromatography (SiO_2/CH_2Cl_2) of the reaction mixture. No attempt was made to characterize any cyclopentadienol precursors. Two other photo-isomers of 4b were obtained in low yield. One of them (yellow crystals, m.p. 160-162°), whose ^{1}H-NMR data are listed in Table 2 under 9b' appears to be either a geometrical isomer of 9b, or a conceivable atropisomer. The other photoproduct (colorless crystals, m.p. 190°), is derived from 4b by intramolecular addition of the phenolic OH to an olefinic double bond.

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