

95. Photochemical Synthesis of 2-Alkylidene-4-pyrrolin-3-ones¹⁾

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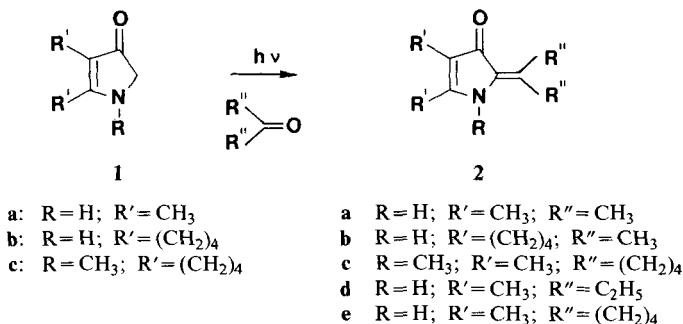
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Summary

Irradiation ($\lambda = 313$ nm) of the 4-pyrrolin-3-ones **1a–1c** in acetone-, 3-pentanone- and cyclopentanone solution affords the title compounds **2**, formally *via* H-abstraction by the excited ketone and recombination of the radical pair formed.

Light-induced [2+2]-cycloadditions of 2-cycloalkenones to olefins to form cyclobutanes have become one of the most important preparative useful photochemical reactions [1]. Oxa-enones, *e. g.* 2,3-dihydropyran-4-ones or 2,3-dihydrofuran-3-ones, have been successfully utilized in such cycloadditions [1] [2]. Although it has been shown, that uracil and derivatives [3] add to alkenes in acetone sensitized reactions, no results on the photochemical behaviour of simple aza-enones are found in the literature. We have investigated the photochemistry of the 4-pyrrolin-3-ones **1** [4] [5] in order to determine the effects due to substitution of oxygen in oxa-enones by nitrogen.

Scheme 1



In contrast to oxa-enones, intersystem crossing from S_1 to T_1 for the compounds **1** studied seems to be extremely inefficient. Irradiations of **1** ($\lambda = 313$ or 366 nm) in acetonitrile in the presence or absence of olefins, *e. g.* isobutene or 2,3-dimethyl-2-butene, leads to similar slow degradation of starting material only.

¹⁾ Diplomarbeit R.G.-T., University of Hamburg, 1981.

Acetone-sensitized reactions of **1a** gave unexpected results. Again the T_1 state of **1** seems not to be populated, as the results in the presence or absence of the above mentioned olefins are again similar, but in contrast to direct excitation a new product **2a** is now formed selectively. This formation of 2-alkylidene-4-pyrrolin-3-ones (**2**) by irradiating **1** in a ketonic solvent seems to be quite general (*Scheme 1*). Similar thermal aldol condensations of compounds **1** [6] or the corresponding indoleninones [7] occur with aromatic and unsaturated aliphatic aldehydes but not with aliphatic ketones.

We assume that the initial step in the formation of **2** consists in electron transfer from **1** to the excited ketone [8] [9] followed by proton transfer to afford a radical pair; recombination and subsequent elimination of water then gives **2** (*Scheme 2*). The same radical pair would be formed by H-abstraction, as proposed for the formation of 2'-hydroxy-2'-methyl-2-ethylcyclohexene from excited acetone and cyclohexene [10] [11].

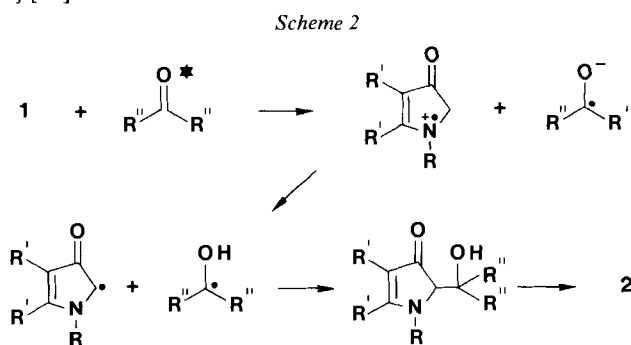


Table. Spectroscopic data of compounds **2a**)

	M.p.	Yield	UV. (CH ₃ CN)	IR. (KBr)	MS.	¹ H-NMR. (CDCl ₃)		
2a	260°	74%	260 (4.05)	3200	151 (<i>M</i> ⁺)	1.70 (<i>s</i> , 3H)	1.89 (<i>s</i> , 3H)	
			387 (3.50)	1660		2.13 (<i>s</i> , 3H)	2.41 (<i>s</i> , 3H)	
2b	220°	47%	261 (3.96)	3200	177 (<i>M</i> ⁺)	1.71 (<i>m</i> , 4H)	1.89 (<i>s</i> , 3H)	
			382 (3.61)	1660		2.23 (<i>m</i> , 2H)	2.35 (<i>s</i> , 3H)	
			262	1540		149	2.41 (<i>m</i> , 2H)	5.76 (NH)
2c	Oil ^{b)}	55%	410	1680 ^{c)}	191 (<i>M</i> ⁺)	1.70 (<i>m</i> , 4H)	2.07 (<i>s</i> , 3H)	
			262	1540		2.18 (<i>m</i> , 2H)	2.36 (<i>s</i> , 3H)	
			252 (4.07)	1640		179 (<i>M</i> ⁺)	2.40 (<i>m</i> , 2H)	3.40 (<i>s</i> , 3H)
2d	201°	56%	388 (3.29)	1560	150	1.05 (<i>t</i> , 3H)	1.09 (<i>t</i> , 3H)	
			410	1640		1.67 (<i>s</i> , 3H)	2.10 (<i>s</i> , 3H)	
			264 (4.12)	3130		177 (<i>M</i> ⁺)	2.19 (<i>qa</i> , 2H)	2.85 (<i>qa</i> , 2H)
2e	215°	63%	388 (3.29)	1560	150	5.73 (NH)		
			264 (4.12)	3130		177 (<i>M</i> ⁺)	1.55 (<i>m</i> , 4H)	1.70 (<i>s</i> , 3H)
			386 (3.55)	1540		176	2.13 (<i>s</i> , 3H)	2.42 (<i>m</i> , 2H)
						2.89 (<i>m</i> , 2H)	5.68 (NH)	

a) Satisfactory elemental analyses were obtained for **2a**, **2b**, **2d** and **2e**.

b) Data for crude reaction product; attempts to purify **2c** were unsuccessful.

c) In CCl₄.

Physical and spectroscopic data of compounds **2** is summarized in the *Table*.

Results on the irradiation of **1** in the presence of non-ketonic sensitizers as well as of pyrrolinones with alkyl groups on C(5), reflecting a more typical enone behaviour will be published in a forthcoming paper.

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Experimental Part

General. Absorptions in the IR. spectra are given in cm^{-1} and in the UV. spectra in nm ($\log \epsilon$). Chemical shifts in the NMR. spectra are given in ppm relative to TMS (= 0 ppm) as internal standard.

Starting materials. Compounds **1** were synthesized according to [4] and [5]. Cyclopentanone and 3-pentanone were purified by distillation. Acetone and acetonitrile were analytical grade reagents.

Photolyses. Irradiations were carried out in Ar-degassed solutions by filtering the light of a 125W mercury lamp through pyrex glass.

Preparation of 2. A solution of **1** (10^{-3} mol) in either 10 ml acetone or in 10 ml 3-pentanone/ cyclopentanone/acetonitrile 1:1, acetonitrile being added for solubility reasons, was irradiated for 20 h. After evaporation of the solvent the residue was chromatographed (SiO_2 , ethyl acetate) and sublimed (100° , 0.01 Torr). Compound **2a** partially precipitates under these reaction conditions and can be obtained by filtration. Yields and m.p. are given in the *Table*.

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