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PHOTOCHEMISTRY OF α DIALKYLAMINOENONES
II. PHOTOCYCLISATION OF DIALKYLAMINOCYCLOHEXENONES AND TOSYLALKYLAMINO CYCLOHEXENONES.

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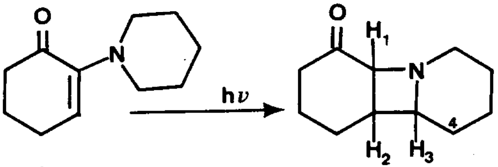
In previous papers we reported that α-methylene oxetanols and α-ketooxetanes are the main products of the photolysis of α-alkoxyenones (1). However, when linear α-enaminoketones are irradiated, deconjugation, elimination and oxidative cyclisation are the only observable reactions (2).

Since, all these reactions involve a γ hydrogen abstraction by the excited carbonyl group it was of interest to see if α-ketoazetidines and α-methyleneazetidinols might be produced in the photolysis of α-enaminoketones. We report here that such a photocyclisation process is possible.



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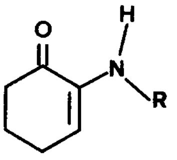

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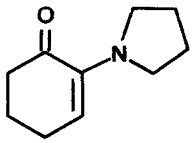

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Irradiation of a solution of 2-piperidino-2-cyclohexenone in ether or ethanol at 366 mn gives 2 as the volatile and isolable product (yield > 30% has not been optimized). We could not obtain the sensitization of this reaction. The structure of 2 is derived from spectroscopic date : IR (CCl_4) $\nu_{C=O}$ = 1715 cm^{-1} ; NMR (CCl_4) H_1 : 3,7 ppm d(J=7 Hz) ; H_3 : 3,25 ppm t (J=7 Hz) Mass $\frac{m}{e}$: 179 (22%), 84 (83%), 83 (100%). The cis junction of cyclohexanone and cyclobutane rings is deduced from the coupling constants in the NMR spectra (3) Further we note that H_3 is coupled with H_2 and only one of the H_4 protons ; this originates from diedral angle H_3-C-C-$H_{4\alpha}$ close to 90°.

The absence of cyclisation in 3 and 4 might originate from an efficient deactivation consecutive to electron transfer from nitrogen to the enone in the excited state (4).

It has been shown that γ hydrogen abstraction in α amino ketones is more favorable when nitrogen is substituted by an electron withdrawing group such as β toluene sulfonyl (5). The preparation of α-ketoazetidines and α-methylene azetidinols should be possible from tosylalkylaminocyclohexenones, so we prepared compounds 5, 7 and 10.

When compound 5a in solution in ether or ethanol is irradiated at 366 nm, several products are isolated. The structure 6a is attributed to the major component (Yield > 30%) of the reaction mixture. IR $\nu_{C=O}$ = 1720 cm^{-1} ;UV : λ_{max} 300 nm (40) ; 227 (11720), RMN ($CDCl_3$) : 4,1 ppm (1H,m) ; 3,9 (1H,d, J=8 Hz) ; 1,4 (3H,d; J =6,5) Mass : $\frac{m}{e}$ 293 (30%) ; 155 (90%), 91 (100%). Similarly, 5b is transformed in 6b (50%).

During our studies on the photochemistry of 2-alkoxy-2-cyclohexene ones, we found that α methylene oxetanols are the major products when the β extremity of the carbon carbon double bond is substituted ; the same effect is observed in the photolysis of these α enaminoketones. When 7 alcoholic in solution is irradiated at 366 nm, a mixture is obtained from which two compounds are isolated 8 (40%) and 9 (35%). These structures are proposed on the basis of specstoscopic data : 8 NMR : vinyl group 6,1 ; 5,5 ; 5,3 ppm (3H,m) ; 4,5 ppm (1H, t, J=7) 4 ppm (1H,d, J=8) mass $\frac{m}{e}$: 305 (4%), 150 (100%), 91 (90%) 9 IR $CDCl_3$: 3480, 1695, 1595 cm^{-1}; UV : λ^{EtOH}_{max} 246 nm (422) 222 (12200) NMR($CDCl_3$) : 5,6 ppm (4H,m) ; 4,2 ppm (1H, d, J=8) ; 2,5 ppm (1H). This signal disappears in the presence of D_2O. However, by photolysis of 10, the substituted analog of 7 in alcoholic solution, 11 is the only isolable material (25% yield).

All these results are rationalized in scheme 2 by a γ hydrogen abstraction followed by a cyclisation.

Several aspects of the reactivity of these α-enaminocyclohexenones have to be noted :

1. α-methylene azetidinols and α-ketoazetidines are isolated from cyclohexenones. 1, 5, 7, 10 even though no cyclisation is detectable from the corresponding 2-alkoxy-2-cyclohexenones (1c).

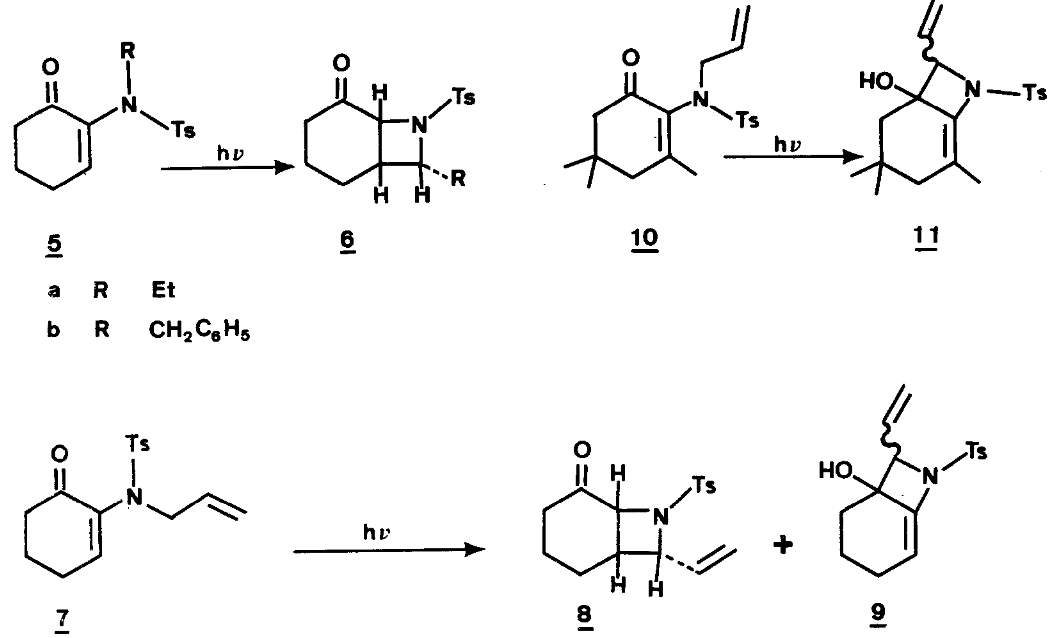
2. The cyclisation is made easier for the N.tosyl derivatives ; the orientation of the cyclisation depends on the substitution on the C=C bond of the enone.

3. No cyclisation occurs from the enones 3 and 4. It has been shown that in the ground state, the structure of enamines is more planar and the electron delocalisation better when pyrrolidine rather than piperidine is used to form the enamine (6). We think that in the singlet excited state a faster deactivation of 3 and 4 compared to 1 might occur and be competitive with γ hydrogen abstraction.

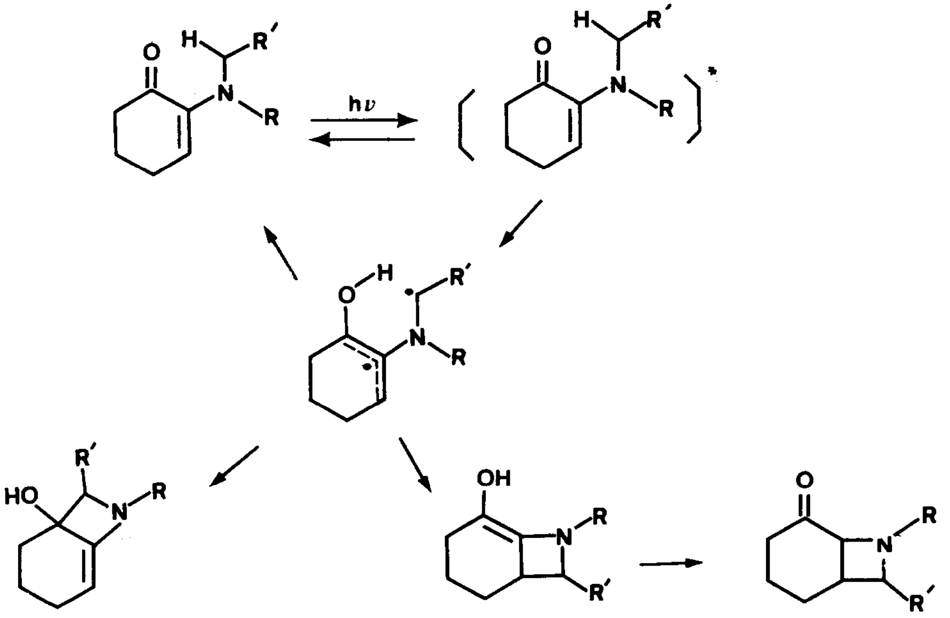
4. No inhibition has been detected in the presence of piperylene, and benzophenone does not sensitize the cyclisations of 5, 7 or 9. However, when sensitizers are used, new products are formed exclusively (7). Therefore we can conclude that the formation of ketoazetidines 6, 8 and α methyl azetidinols 9, 11, is a singlet state reaction (8).

5. Although cyclisations consecutive to γ hydrogen abstraction and involving the extre-

SCHEME I



SCHEME 2



mity of an allylic chain have been observed (9), no such cyclisation has been detected from 7 and 10.

In conclusion, we have shown that α-ketoazetidines and α-methylene azetidinols may be produced from irradiated α-enaminoketones. Work is in progress in order to develop synthetic applications and to study mechanistic aspects of these reactions.

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