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PHOTOCHEMISTRY OF α DIALKYLAMINO ENONES. I
A NEW OXIDATIVE CYCLISATION OF CHALCONE DERIVATIVES

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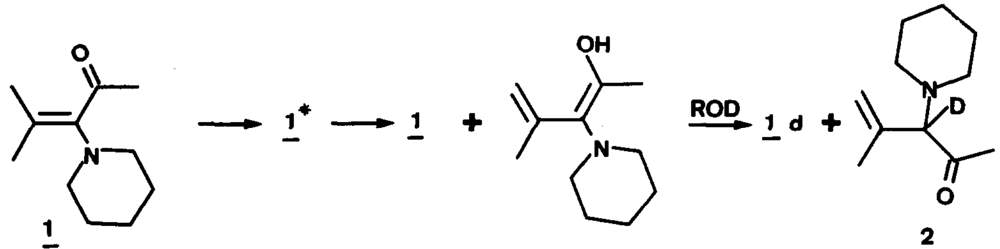
In a previous work, we described that α methylene oxetanols and α keto oxetanes were produced in the photolysis of 2-alkoxy-cyclohexenones (1). Independently, other workers by the photolysis of α-alkyl conjugated enones usually obtained cyclobutyl ketones as the major products (2). We report here that deconjugation, elimination and oxidative cyclisation may be major processes in the photolysis of α dialkylamino enones (3).

- Deconjugation.

Irradiation of 1 in ether or methanol gives 2 as the only new volatile and isolable product ; 2 (50%) has been identified by comparison with an authentic sample (4). When the same irradiation is carried out in CH_3-OD,1(0,36 d_1;0,15 d_2), 2 (0,4 d_1) have incorporated deuterium.



The fact that the deconjugation competes here with desactivation of the excited state 1^* by a free rotor process (5) is not very surprising. Mesityl oxide (6) and pentene-3-one-2 (7) are indeed deconjugated by irradiation.

- Elimination and oxidative cyclisation.

To check whether other reactions might be observable when deconjugation is no more possible we decided to study the photolysis of 2- dialkylamino-1,3-diphenyl-2-propen-1 ones

3 and 4.

When 3a or 4a are irradiated in ether, a photostationnary equilibrium takes place very rapidly between these enones. For longer irradiation times however, a mixture of cis and trans chalcone 5 (30%) and 6a (40%) is obtained. The structure of 6a is established on spectroscopic evidence : IR (CCl_4) : 1650 cm^{-1}, NMR (CCl_4, ppm : between 6,7 and 8 (9H) ; 5,53 (1H,s) ; Mass $\frac{m}{e}$: 291 (30%) - 186 (80%) - 105 (75%).

Similarly, 6b (50%) and 6c (55%) are the main products of the photolysis of 3b, 4b and 3c, 4c respectively ; small amounts of chalcones are also isolated from these irradiations.

Several mechanisms might a priori explain the formation of chalcones ; so we verified that chalcones are primary products of the photolysis of 3a and 4a. When we plot the yield of chalcones against the irradiation time, we get a straight line until 50% conversion or more has taken place. We think that chalcones result from a Norrish type II elimination (Scheme II b) ; to our knowledge it is the first time that an allenol seems to be involved as an intermediate in a NII reaction.

The cyclisation[♠] products 6 are the result of an oxidative process. We think that the biradical formed from a γ hydrogen abstraction may rearrange and form a new σ bond between the alkylamino group and the benzene ring. This cyclisation destroys the aromaticity of the system. In the presence of traces of oxydant 7 is oxidized to 6 ; however, we get the same results when oxygen is carefully removed from the solution.

The irradiation of the chalcone derivatives 3 and 4 contrasts sharply with the photolysis of the corresponding saturated compound. When 1,3-diphenyl-2-diethylamino-1-propanone is irradiated in similar conditions 1,3-diphenyl-1-propanone, resulting from a NII elimination process, is isolated in high yield and no competing reaction has been detected (9). The cyclisation needs an enone skeleton to occur and is similar to the recently described photocyclisations of several alkoxy flavones (10).

In conclusion, we have described a photochemical cyclisation of α enaminoketones and we are currently investigating this method as a means of synthesising alkaloïds and to explain several aspects of the mechanism.

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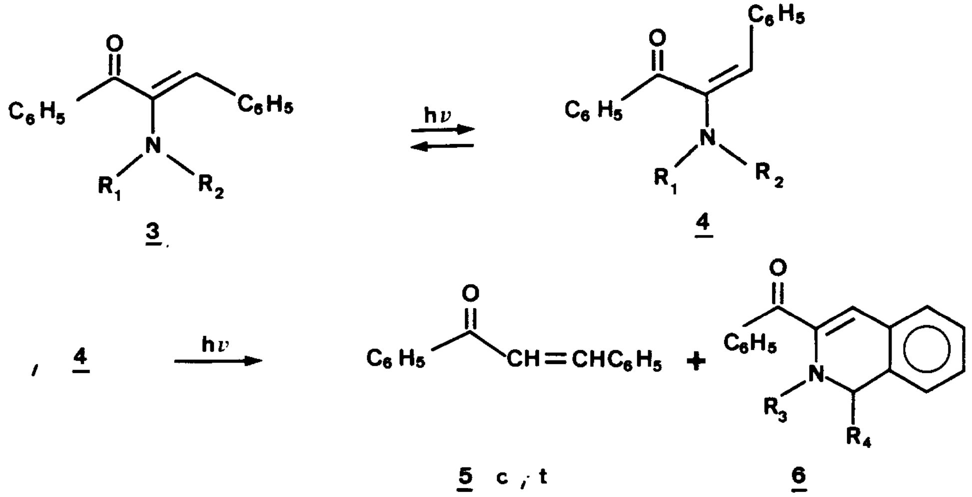
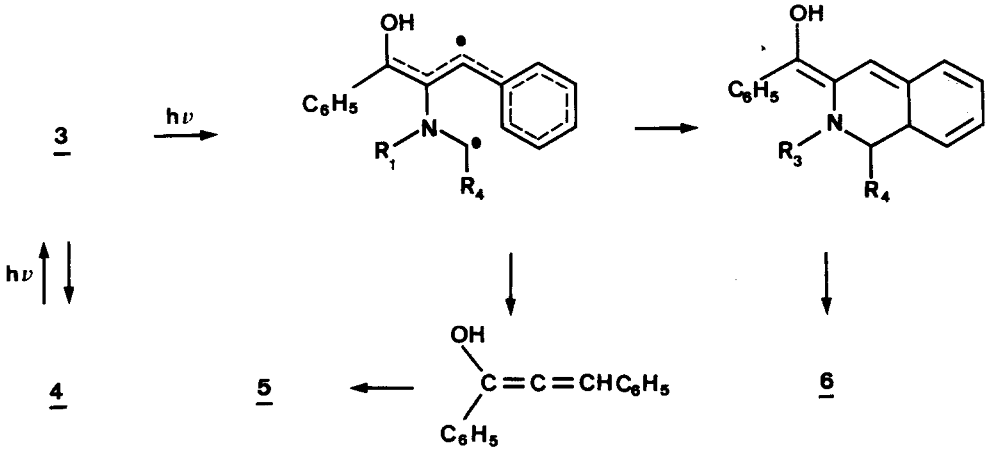
[♠] ; Examination of models shows that γ Hydrogen abstraction is only possible from the Z isomer (8).

SCHEME I



	R_1	R_2			R_3	R_4	
a:	C_2H_5	C_2H_5	30 %	a:	C_2H_5	CH_3	40 %
b:	$—(CH_2)_5—$		10	b:	$—(CH_2)_4—$		50
c:	$—(CH_2)\ O\ (CH_2)—$		10	c:	$—(CH_2)_2O\ (CH_2)–$		54

SCHEME II



References.

(1) a) A. Feigenbaum, J.P. Pete Tetrahedron Lett. 2767 (1972)
    b) J.P. Pete, J.L. Wolfhugel, Tetrahedron Lett. 4637 (1973)
    c) A. Enger, A. Feigenbaum, J.P. Pete, J.L. Wolfhugel Tetrahedron Lett 959 (1975)
    d) A. Enger, A. Feigenbaum, J.P. Pete, unpublished results.

(2) a) W.C. Agosta, A.B. Smith J.Amer.Chem.Soc. 93, 5513 (1971)
    b) W.L. Schreiber, W.C. Agosta, J.Amer.Chem.Soc., 93, 6292 (1971)
    c) R.A. Cormier, W.L. Schreiber, W.C. Agosta, J.Amer.Chem.Soc. 95, 4873 (1973)
    d) R.A. Cormier, W.C. Agosta, J.Amer.Chem.Soc., 96, 618 (1974)
    e) R.A. Cormier, W.C. Agosta, J.Amer.Chem.Soc., 96, 1867 (1974).

(3) a) M. Ogata, H. Kano Tetrahedron 24, 3725 (1968)
    b) R.G.F. Giles Tetrahedron Lett. 2253 (1972)
    c) K. Yamada, T. Konakahara, S. Ishihara, H. Kanamori, T. Itoh, K. Kimura, H. Iida, Tetrahedron Lett. 2513 (1972).
    d) R.G.F. Giles, P.R.K. Mitchell, G.H.P. Ross, I. Baxter, J.Chem.Soc.Perkin I 493 (1973)

(4) H. Moureu, P. Chovin, Bull.Soc.Chim.Fr. 586 (1953)

(5) For example see Photochemistry Specialist Periodical reports of the Chemical Society Vol 3 p.430 (1972).

(6) F. Bonnet, J. Lemaire, Bull.Soc.Chim.Fr. 1185 (1973)

(7) O.L. Chapman Advances in Photochem. New York Vol.1, 357 (1963)

(8) J.C. Arnould Thèse d'Etat REIMS 20 Janvier 1975

(9) A. Padwa, W. Eisenhardt, R. Gruber, D. Pashayan, J.Amer.Chem.Soc. 91, 1857 (1969)

(10) a) A.C. Waiss Jr., R.E. Lundin, A. Lee, J. Corse, J.Amer.Chem.Soc. 89, 6213 (1967)
    b) T. Matsuura, H. Matsushima, Tetrahedron 24, 6615 (1968)
    c) S. Gupta, S. Mukerjee, Indian J.Chem. II, 1263 (1973).