PHOTOCHEMICAL REACTIONS OF 3-N,N-DIETHYLAMINO-CYCLOBUT-2-EN-1-ONES

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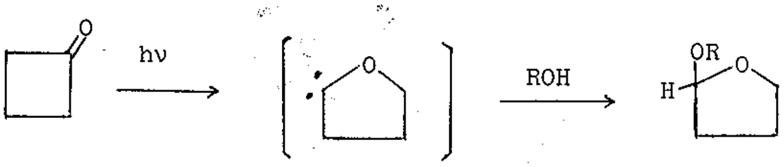
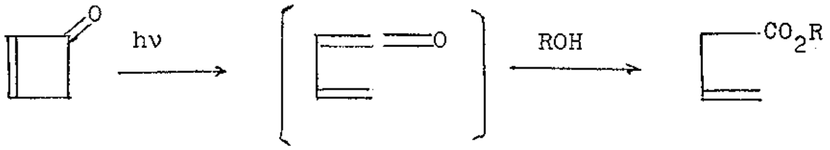
Irradiation of 3-N,N-diethylamino-4-phenyl-cyclobut-2-en-1-one (I) in methanol afforded two kinds of β-keto esters III and IV. While irradiation of 2,4-diphenyl-3-N,N-diethylamino-cyclobut-2-en-1-one (II) in benzene gave a furan derivative V.

Previously, we reported that acyclic β-aminovinyl ketones gave pyrrole derivatives via δ-hydrogen abstraction by an excited carbonyl on irradiation[1]. However, photoreactions of cyclic β-aminovinyl ketones have recieved little attention[2]. Also two types of the photoreaction of four-membered ketones to give the ring-expansion via oxacarbene intermediates (1)[3], and ring-cleavage product via ketene intermediate (2)[4] have been reported.

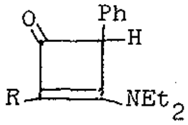


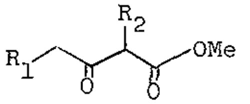
(1)

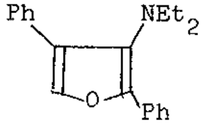


(2)

We have studied the photochemical reactions of four-membered β-aminovinyl ketones I[5] and II[5], in order to confirm which type of reaction is more favorable. The photochemical reaction between the enone and amino groups is also of interest.







(I) R=H
(II) R=Ph

(III) R_1=Ph R_2=H
(IV) R_1=H R_2=Ph

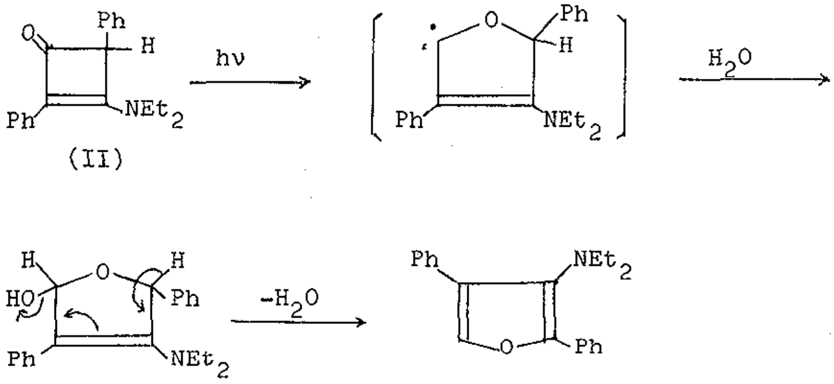
(V)

When 3-N,N-diethylamino-4-phenyl-cyclobut-2-en-1-one (I) in methanol was irradiated in a quartz vessel with low pressure mercury lamp under argon for 60 hr, two kinds of β-keto esters III (15 %), [b.p. 125°C/3 mmHg; ν_{max}^{film} 1735 and 1685 cm^{-1}; δ ($CDCl_3$) 3.45 (s, 2H), 3.70 (s, 3H), 3.80 (s, 2H), and 7.28 (s, 5H)] and IV (trace) were obtained. Irradiation of I in benzene resulted in recovery of the starting material. The photolysis of I to afford III and IV corresponds to the type of reaction (2).

Irradiation of 2,4-diphenyl-3-N,N-diethylamino-cyclobut-2-en-1-one (II) in benzene under the same conditions as described above.

for 20 hr gave 2,4-diphenyl-3-N,N-diethylamino-furan (V) (20 %); b.p. 202°C/4 mmHg; ν_{max}^{film} 1620, 1600, 1583, 1560, and 1495 cm^{-1}; δ ($CDCl_3$) 1.09 (t, 3H), 3.17 (q, 4H), 6.83 (s, 1H), and 7.0-7.9 (m, 10H); m/e 291 (M^+). The yield of V increased to 30 % when benzene saturated with water was used. When II was irradiated in methanol, II was recovered unchanged. This result indicates that the reaction in benzene is sensitized one.

A reasonable mechanism for the formation of furan (V) is proposed in Scheme I, in which an oxacarbene intermediate traps water dissolved in benzene (type (1) reaction), followed by elimination of water.



(II)

(V)

Scheme I

On the other hand, irradiation of I or II in both solvents with high pressure mercury lamp through a Pyrex vessel did not any changes and starting materials were recovered almost quantitatively.

References

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