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PHOTOCYCLIZATION MECHANISM OF ENAMINOKETONE

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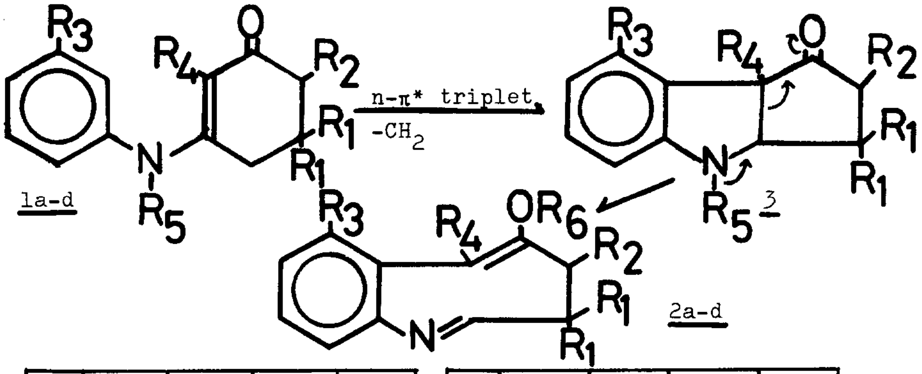
Previously, we reported[1,2] the formation of eight-member ring products by the photolysis of 3-anilinocyclohex-2-en-1-one derivatives. We wish now to report the results of the photolysis of enaminoketone derivatives and deuterium-labeled enaminoketone,[3] and the sensitizing and quenching effect for the enaminoketone's eight-member ring formation, which shed light on the mechanism of this photoreaction. A series of substituted 3-anilinocyclohex-2-en-1-ones has been studied in order to determine the mechanism of this enaminoketone eight-member ring formation.

When the irradiation of enaminoketones is carried out with a low-pressure mercury lamp, no eight-member ring products are obtained, but a high-pressure mercury lamp, eight-member ring products are obtained. These results indicate that the excited state in this photoreaction should be the n-π* triplet. In order to confirm this, the quantum yields of the eight-member ring formation of enaminoketone are studied. The quantum yields of this photoreaction are determined by using uranyl oxalate actinometry.[4] A benzene solution of 5,5-dimethyl-3-(3-methoxyanilino)-cyclohex-2-en-1-one (1a) and a benzene solution of 1a containing anthracene are irradiated. The light from an Ushio Type UM-452 100-W high-pressure mercury lamp is filtered through a solid filter (transmission 330-350 nm.). The results are given in the figure. From the good linearity of the figure,[5] we may conclude that this photoreaction is probably car-

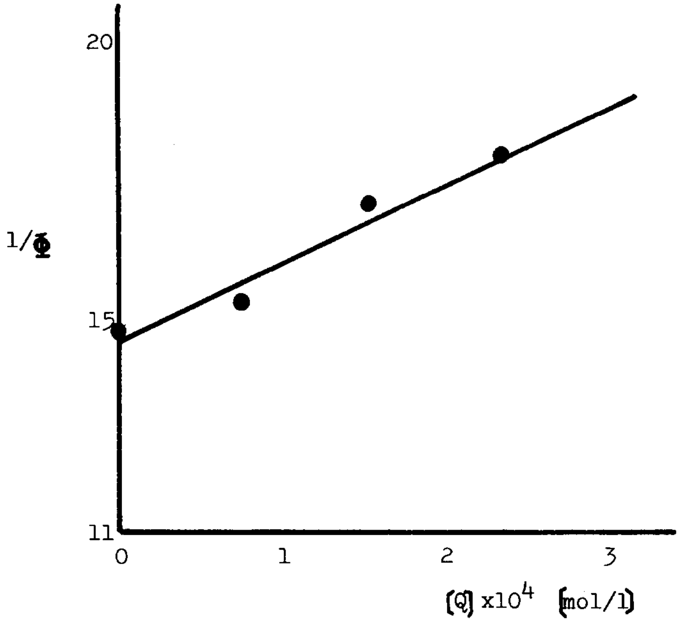


1	R_1	R_2	R_3	R_4&R_5
a	$-CH_3$	-H	$-OCH_3$	-H
b	-H	$-CH_3$	-H	-H
c	$-CH_3$	-H	$-OCH_3$	-D
d	-H	$-CH_3$	-H	-D

2	R_1	R_2	R_3	R_4&R_6
a	$-CH_3$	-H	$-OCH_3$	-H
b	-H	$-CH_3$	-H	-H
c	$-CH_3$	-H	$-OCH_3$	-D
d	-H	$-CH_3$	-H	-D

ried out by only one excited species ($\tau=1.1\times10^{-7}$sec.) and the n-π* triplet. The reaction of 1a was found to be completely quenched in the presence of anthracene (E_T ca.42 kcal./mol) and could be sensitized by anthraquinone and naphthalene (E_T ca.62 and 61 kcal./mol respectively). These observations therefore also suggested that the photocyclization occurred from a enaminoketone triplet state. (From the measurment of fluorescence of 1a solution, the excited singlet energy is ca.61 kcal./mol.)

In this eight-member ring formation, the methylene was eliminated. In order to determine the position of eliminated methylene, derivative of 3-anilinocyclohex-2-en-1-one is irradiated. The irradiation of 1a has previously been reported[1,2] to yield 3,3-dimethyl-5-hydroxy-7-methoxy-3,4-dihydro-1-benzazocine (2a). The synthesis of 3-anilino-6-methylcyclohex-2-en-1-one (1b) (mp 161°C; mass spectrum $M^{+\cdot}$ m/e 201; uv, λ_{max}^{EtOH} 225.4 (ε 7340) and 309.6 nm (ε 21400), $\lambda_{max}^{EtOH\cdot H^+}$ 299 nm (ε 20900); ir, 3250 (ν_{N-H}), 1580 ($\nu_{C=O}$) and 768 and 700 cm^{-1} (δ_{Ar-H}); nmr (δ in $CDCl_3$), 1.10



Figure

Quencher concentration [Q] effect on quantum yield (Φ) of eight-member ring formation

(3H, doublet, -CH_3), 1.95 (2H, H^5), 2.20 (1H, H^6), 2.54 (2H, H^4), 5.49 (1H, singlet, H^2) and 6.9-7.5 (6H, multiplet, N-H and Ar-H)) is readily accomplished by the reaction of 4-methylcyclohexane-1,3-dione[6] and aniline. The irradiation of 1b gives 3,4-dihydro-5-hydroxy-4-methylbenzazocine (2b) (mass spectrum $M^{+\cdot}$ m/e 187; uv, λ_{max}^{EtOH} 228.5, 253, 303 and 312 nm; nmr (δ in $CDCl_3$), 1.23 (3H, doublet, -CH_3), 2.31 (2H, H^3), 2.90 (1H, H^4), 6.63 (1H, triplet, H^2), 6.97 (1H, broad singlet, H^6), 6.98 (2H, multiplet, H^8 and H^9) and 7.27 (2H, multiplet, H^7 and H^{10})). These results show that the 5- and 6-positions of methylene are not eliminated. Moreover we prepared and irradiated deuterium-labeled enaminoketone 1c.[7] Mass spectroscopy shows that the R_4 of 1c is deuterated in the ratio of 25%.[8] The irradiation of 1c gives 2c. From mass spectroscopic data, the ratio of deuterium to hydrogen in R_4 of 2c is calculated to be 24%.[9] This shows that the elimination of methylene at 2 does not occur. Clearly, though, the elimination of the methylene of the 4-position does occur.

In this photoreaction, two alternative reactions - pathway intra- and inter-molecular retro transannular ring opening - are considered. Finally we prepared[7] and irradiated the N-D compound 1d in order to determine the reaction pathway for the photocleavage of the intermediate 3. The irradiation of 1d gives the deuterio hydroxy compound 2d. From those results, this photoreaction can be said to be carried out by intramolecular retro transannular ring opening.

From the above results, we may conclude that this photo eight-member ring formation is carried out by intramolecular retro transannular ring opening, that the 4-position of methylene is eliminated, and that the excited species is the n-π* triplet.

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8) The percentage of deuterium is measured by mass spectrometry at m/e 245, 246, 247 and 248 ($M^{+\cdot}$).
9) The percentage of deuterium is measured by mass spectrometry at m/e 231, 232, 233 and 234 ($M^{+\cdot}$) and at 148 and 149 ($M^{+\cdot}-\cdot CH_3-CO-C_3D_2H_2$).