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N-PHENYLBENZOAZETINONE

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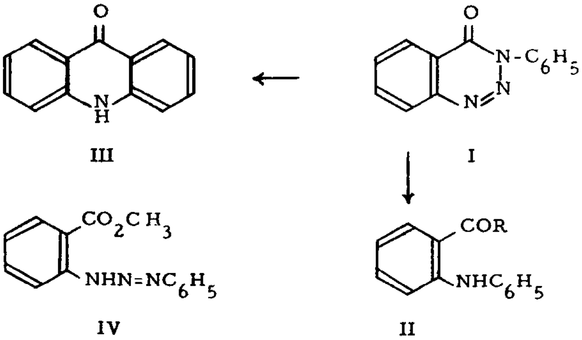
The recent communication by Ege(2) describing the photochemical conversion of 3-phenyl-3, 4-dihydro-4-oxobenzo-1, 2, 3-triazine, I, in the presence of various nucleophiles to the corresponding N-phenyl anthranilic acid derivatives, II, prompts us to report our observations in this area.

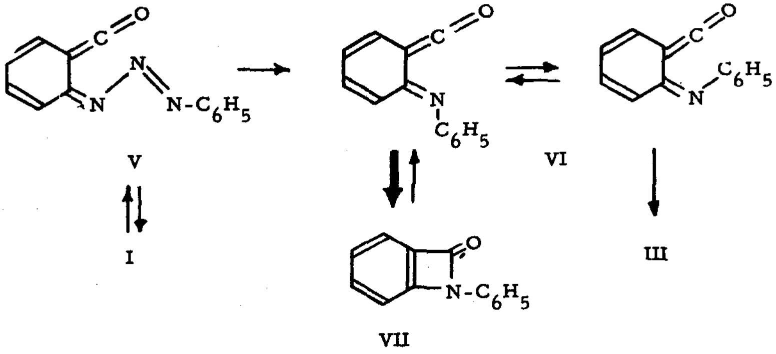
We have likewise observed that irradiation of I with ultraviolet light above 3000 Å (Hanovia A 450 watt lamp, PYREX filter) in water-tetrahydrofuran, methanol and cyclohexylamine-benzene leads to the



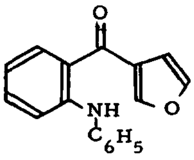
corresponding derivative(3) of II (R= -OH, -OCH$_3$ and NHC$_6$H$_{11}$ respectively in 80-90% yield. Photochemical decomposition in moist benzene affords N-phenyl anthranilic anhydride(3) while photolysis in anhydrous benzene slowly yields acridone, III(3). Quenching of this reaction by rapid addition of methanol after interrupting illumination provides in addition to II (R= -OCH$_3$) and unreacted I a low yield of methyl N-phenyl anthranilate(3) and the corresponding methyl diazoaminobenzene-2-carboxylate, IV(3).

Brief irradiation of I in benzene solution (10%) followed by scanning of the infrared spectrum produced strong absorption maxima at 1830, 1590 and 1500 cm.$^{-1}$ which slowly (one hour) disappear with the concomitant formation of the characteristic absorption of III. Addition of methanol instantaneously results in conversion to the spectrum of II (R= -OCH$_3$).

Among many alternatives(2) the following precidented(4) mechanism is consistent with the observed spectroscopic and chemical information for the photolysis in benzene.



The long wavelength transition (365 mμ.) of I has not been rigorously assigned but may be presumed to arise from the promotion of an anti-bonding, 1, 2-aza electron in the higher lone pair molecular orbital to the π* configuration(5). If the observed photochemical transformation occurs in the excited singlet state then overlap of the coplanar, odd electron, lone pair orbital with the 3, 4-σ bond leads to electron redistribution resulting in the trans-ketene, V. The intervention of V is substantiated by the isolation of IV by quenching the reaction with methanol. Thermal or photochemical rearrangement with the loss of nitrogen provides the anti-configuration of VI which is valence tautomeric with N-phenylbenzoazetinone, VII. The isomerization of anti- to syn-configurated VI or its subsequent rearrangement to acridone must be relatively slow compared to the rate or production of VII which spectroscopically appears to be the predominant tautomer present in the steady state at room temperature. However, the strongly electrophilic species responsible for some of the observed reactions may be the tautomer, VI (compare the lower reactivity of 1, 2-diphenyl-2-azetinone(6)). This reactivity is exemplified by the observation that I when photolyzed in furan affords in 90% yield an adduct, m. p. 178°, of composition $C_{17}H_{13}NO_2$ whose spectral properties suggest the structure VIII.



VIII

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(1) NSF Undergraduate Fellow, summer 1962, Yale University.

(2) G. Ege, *Angew. Chem.*, *Internat. Ed.*, **4**, 699 (1965).

(3) Identified by mixed melting point and infrared spectrum comparison.

(4) For analogous photochemical rearrangements of heterocyclic systems to ketenes see P. de Mayo and S. T. Reid, *Quart. Revs.*, **15**, 402 (1961).

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