

SYNTHESIS OF 2-PHENYL-1,3-OXAZEPINE BY THE IRRADIATION
OF 4-PHENYL-2,3-OXAZABICYCLO[3.2.0]HEPTA-3,6-DIENE¹

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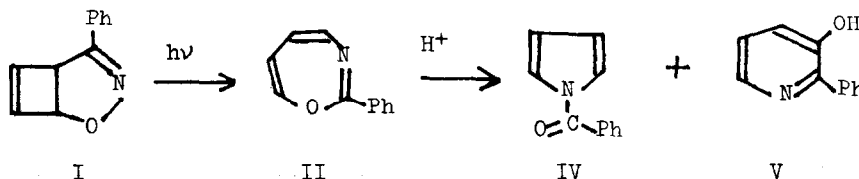
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It is well known that 1,3-oxazepine derivatives are formed by the irradiation of aromatic amine N-oxides (2), but in the case of monocyclic system the isolation of the 1,3-oxazepines is rather exceptional (3,4), and they usually exist as transient intermediates (5). However, we found that the irradiation of 4-phenyl-2,3-oxazabicyclo[3.2.0]hepta-3,6-diene (I) (6) afforded easily 2-phenyl-1,3-oxazepine (II) in high yields. Therefore this procedure is a valuable method for the synthesis of the monocyclic 1,3-oxazepines. In addition, this is probably the first example of the formation of heteropines by the irradiation of bicyclo[3.2.0]heptadienes with two heteroatoms. We wish to describe here preliminary results obtained and our interpretation of the the reaction mechanism for the formation of II.

When a n-hexane solution of I (1.17×10^{-3} M) was irradiated in a quartz vessel using a Rayonet photoreactor (2537 Å), a clean reaction occurred and a yellow oil (II), $C_{11}H_9ON$, (7) was obtained in a high yield (80 %). Neither sensitizing nor quenching effects were observed when the irradiation was carried out in the presence of acetophenone, fluorenone and isoprene, indicating that the photo-reaction proceeded via an excited singlet state. The structural assignment of II, especially being not expected 3-phenyl-1,2-oxazepine (III), was based on the following spectral and chemical evidence : Uv max (EtOH), 238 nm ($\log \epsilon$, 4.16), 323 (3.66) and ca 400 (tailing); ir max (neat), 1630 and 1610 cm^{-1} (8); nmr (100 MHz, $CDCl_3$, δ), phenyl protons, 8.00 (m, 2H), and 7.40 (m, 3H), vinyl protons, 7.00 (pair of triplet, C_4 -H) and 5.90 (m, 3H), J in Hz, $J_{4,5} = 7.5$, $J_{5,6} = J_{6,7} = 5.0$, $J_{4,6} = J_{4,7} = J_{5,7} = ca 1.0$; mass (m/e), 171 (, 12 %), 103 (C_6H_5CN , 4 %), 77 (24 %), 68 ($M-C_6H_5CN$, 100 %) and 40 (31 %) and 39 (66 %). The nmr and mass spectra of II are essentially similar to those of 2-phenylbenzo[f]1,3-oxazepine (9). Treatment of I

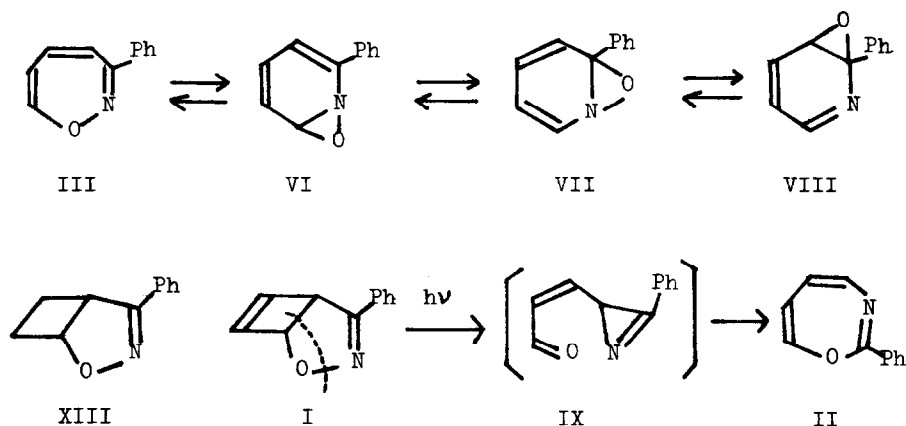
with 1 N hydrochloric acid at room temperature afforded N-benzoyl pyrrole (IV), an oil, and 3-hydroxy-2-phenylpyridine (V), mp 205° (10), in 48 and 11 % yields respectively. The constitution of IV and V was deduced by comparison of their spectral properties with those of authentic samples. The same type of the rearrangement was observed when benzene fused 1,3-oxazepines obtained from quino-line N-oxides were treated with protic solvents, and the reaction mechanism was already established (11, 12, 13, 14). Thus these facts should support the correctness of the structure of II.



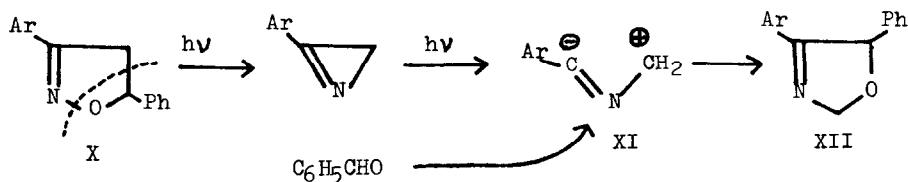
2-Phenyl-1,3-oxazepine (II), on standing in air at room temperatures, turns gradually into a resinous material, but can be distilled below 100° under low pressure (10^{-4} mm). A solution of II in aprotic solvents is not so labile. In the uv spectrum of II, no solvent effect was observed, being different from the case of oxepines (15), and in addition, upon direct irradiation of II, the existence of corresponding valence isomers was not detected.

Concerning the reaction mechanism, we considered firstly that the irradiation of 4-phenyl-2,3-oxazabicyclo[3.2.0]hepta-3,6-diene (I) results in disrotatory ring opening leading to 3-phenyl-1,2-oxazepine (III), followed by valence isomerization giving oxaziridine VI. Then, if the 1,5-oxygen shift occurred two times in the intermediary oxaziridine VI, oxirane VIII which is a valence isomer of II would be formed via another oxaziridine VII. The existence of such oxaziridines as transient intermediates as well as the thermal 1,5-oxygen shift from VII to VIII have been pointed out in the photochemical reaction of aromatic amine N-oxides, and the reaction mechanism was almost established (2). However, the N-O bond cleavage should occur preferentially to the C-O bond in the oxaziridine VI (16). Furthermore, it is somewhat strange that even a trace of 2-phenylpyridine, β -benzoyl pyrrole, phenylpyridone, and/or 3-hydroxy-2-phenylpyridine could not be isolated, because they are expected to be formed from the oxaziridines VI and VII and oxirane

VIII (5,11,17). In addition, it should be noted that, when I was irradiated in methanol (18), acetonitrile, acetone or benzene, the solvent effect expected to occur in the proposed intermediates III, VI, VII and VIII was not observed (14, 19). On the basis of these facts, the above mechanism should be withdrawn, and instead we wish to propose an alternative reaction path via azirine intermediate IX for the photochemical inversion of I into II.



This mechanism is reminiscent of the photochemical interconversion between isoxazoles and oxazoles (20). A recent finding by Schmid et al (21) that isoxazoline (X), upon irradiation, underwent a double cleavage followed by recombination of resulted azirine (as excited state XI) and benzaldehyde affording oxazoline derivative (XII) should support our interpretation. In addition, when I and 4-phenyl-2,3-oxazabicyclo[3.2.0]hept-3-ene (XIII), m. 34°, which was obtained by hydrogenation of I using Pd-C as catalyst, were irradiated under the same condition, both compounds I and XIII disappeared in the same rate. This would mean that the photochemical reaction of I starts not in ring opening of the cyclobutene but in cleavage of the isoxazoline ring.



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