Photo-valence Isomerization between 2-Phenyl-1,3-oxazepine and 3-Phenyl-2-oxa-4-azabicyclo[3,2,0]hepta-3,6-diene

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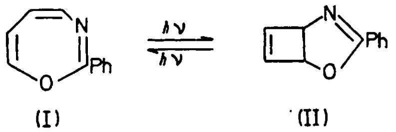
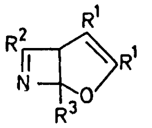
Summary Irradiation of 2-phenyl-1,3-oxazepine (I) with 300 or 350 nm light afforded 3-phenyl-2-oxa-4-azabicyclo-[3,2,0]hepta-3,6-diene (II), whereas irradiation of (II) with 250 nm light caused ring opening to give (I).

We have already reported that irradiation of the least substituted 1,3-oxazepine which is known, compound (I), gives no bicyclic valence isomer.[1] It has also been pointed out that tetra- and penta-aryl-1,3-oxazepines are quite photostable.[2] We have now found, contrary to our earlier report, that (I) can be transformed photochemically into the bicyclic isomer (II), and that (II), in turn, reverts to (I). To our knowledge, this is the first example of photochemical valence isomerization between monocyclic hetero-epines and the corresponding bicyclic isomers.

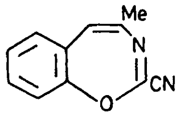
Irradiation of a solution of (I) in acetonitrile, tetrahydrofuran, or ether with 300 or 350 nm light gave the bicyclic isomer (II), m.p. 35 °C, in 50% yield, accompanied by two isomeric phenylpyrrole aldehydes, m.p. 176 and 137 °C (*ca.* 10%). The structures and mechanism of formation of these will be discussed elsewhere. Assignment of structure (II) was based on the following evidence: λ_{max} (cyclohexane), 228, 246, and 283 nm (ϵ 6640, 6640, and 1100); ν_{max} (KBr) 1632, 1329, 1295, 1101, and 1050 cm^{-1}; δ (100 MHz; CDCl$_3$), 7·50 (Ph), 6·73 (6-H), 6·26 (7-H), 5·30 (5-H), and 4·94 (1-H), $J_{1,5} = J_{5,6} = 3{\cdot}5$; $J_{1,7} = J_{6,7} = 3{\cdot}0$ Hz; *m/e* 171 (9%, M^+), 145 (18%, $M - C_2H_2$), 103 (3%, PhCN), and 68 (100%, C_4H_4O). The n.m.r. and mass spectra of (II) are in good agreement with those of 4-phenyl-2-oxa-3-azabicyclo[3,2,0]hepta-3,6-diene.[3] In addition, (II) on irradiation with 250 nm light reverted to (I) in 40% yield.



(I) (II)



(III)



(IV)

a; $R^1 = R^2 = H$, $R^3 = Ph$
b; R^1, R^1 = benzo, $R^2 = Me$, $R^3 = CN$

We note that: (i) an alternative bicyclic valence isomer (IIIa) was not detected; (ii) the presence of sensitizers such as benzophenone or acetone did not affect the rate of the formation of (II); (iii) the use of pentane, methanol, or dichloromethane as solvent sharply decreased the yield of (II).

Only one example of the photochemical formation of a bicyclic isomer in the 1,3-oxazepine system has been reported,[4] namely, the formation of (IIIb) from (IV), in which cyclization occurred at the diene fragment containing a nitrogen atom. However, the cyclization of (I) is in contrast to this, occurring at the non-nitrogen-containing diene fragment. This mode of the cyclization is similar to that in other monocyclic hetero-epines such as 1-alkoxycarbonyl-1,2-diazepine[5] and 3*H*-azepine derivatives.[6] Thus, it seems that the photocyclization of (IV) is a special case and is probably due to the effect of the condensed benzene ring.[7]

For comparison, the thermal reaction of (I) was examined. When a solution of (I) in anhydrous benzene was heated at 160 °C in a sealed tube, 2-phenyl-3-hydroxypyridine, m.p. 201 °C was obtained in a quantitative yield. A norcaradiene-type species may be an intermediate in this rearrangement.

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