Heterocyclic Studies. The Photoisomerization of 2,3-Dihydro-5-methyl-6-phenyl-4*H*-1,2-diazepin-4-one and Derivatives

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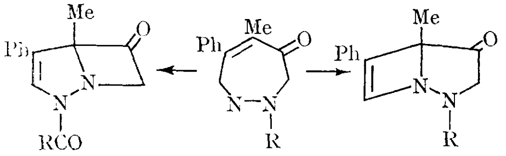
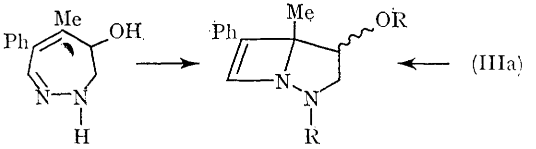
THE diazepinone (I) undergoes several types of ring contraction and transannular bonding in ionic reactions,[1] including formation of the 1,2-diazabicyclo[3,2,0]-hept-2-en-6-ones (II) on acylation. We now report another major transannular pathway of (I) in a very efficient photo-induced valence tautomerization to the 1,2-diazabicyclo-[3,2,0]hept-6-en-4-ones (III). Such photoisomerizations are characteristic for carbocyclic and heterocyclic hepta-2,4-dienones,[2,3] but this appears to be the first case in this ring system in which a hetero-atom is directly involved in the transannular bonding.



(II) (Ia) R=H (IIIa) R=H
(Ib) R=Me (IIIb) R=Me
(Ic) R=COMe (IIIc) R=COMe

Irradiation of (Ia, b, or c)[4] in 0·2—0·4 M-methanolic solution (Pyrex flask) at 25° with sunlight, or, in cloudy weather, a Xenon lamp (Hanovia Type 510C1), gives the bicyclic ketones (IIIa, b, and c) respectively. The acetyl compound (IIIc) is crystalline, m.p. 119—120°;[5] (IIIa) and (IIIb) are oils. Spectral data [for (IIIc): λ_{max}(MeOH) 273 mμ; $\nu_{C=O}$(CCl_4) 1767, 1678 cm.$^{-1}$; δ_{max} ($CDCl_3$) 1·71 (*s*, 3, CH_3), 2·30 (*s*, 3, $COCH_3$), *AB* 4·39, 4·71, J_{AB} 18·5 c./sec. (*dd*, 2, CH_2), 6·78 (*s*, 1, H.7), 7·35 p.p.m. (*s*, 5, C_6H_5)] are consistent with the structural assignments for all of the compounds. Reduction of the ketone (IIIa) with sodium borohydride gave a single alcohol, m.p. 215—220° (dec.), in 92% yield. Crystalline semicarbazones were obtained from (IIIa) and (IIIc), and the semicarbazone of (IIIa) was also obtained by irradiation of the semicarbazone of (Ia) under the same conditions used for the ketone.

Photoisomerization of the diazepine carbinol (IV) (λ_{max} 303 mμ), obtained by reduction of (I) with sodium borohydride,[6] was carried out with a high-pressure mercury lamp with Corex filter in quartz flasks, leading to a mixture of bicyclic alcohols, (Va and b), m.p. 168—170° and 217—220°. The latter, minor, product was identical with the reduction product of (IIIa). Both alcohols gave crystalline diacetyl derivatives, (VIa and b), m.p. 146° and 124°, respectively. Definite assignment of configuration of the hydroxyl groups cannot yet be made.



(IV) (Va and b) R=H
(VIa and b) R=COMe

The conversion of the diazepinone (Ia) into the photo-product (IIIa) was complete in 30 min. under the conditions specified, as indicated by absence of absorbance at 400 mμ. The acetyl ketone (IIIc) was isolated in 99% yield after the irradiated solution became colourless. Prolonged irradiation led to the appearance of additional products. The relative rates of isomerization of the three diazepinones were [Ib(NMe) > Ia(NH) > Ic(NAc)], indicating a dependence upon the

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[1] J. A. Moore, *Trans. N.Y. Acad. Sci.*, 1965, **27**, 591.
[2] O. L. Chapman, *Adv. Photochem.*, 1963, **1**, 323.
[3] (*a*) O. L. Chapman, and E. D. Hoganson, *J. Amer. Chem. Soc.*, 1964, **86**, 498. (*b*) L. A. Paquette, *ibid.*, 1964, **86**, 500.
[4] J. A. Moore and J. Blinkert, *J. Amer. Chem. Soc.*, 1959, **81**, 6029.
[5] Analytical values (C, H, N) with a maximum deviation of 0·35% from calculated were obtained for all crystalline compounds reported.
[6] J. A. Moore, R. W. Medeiros, and R. L. Williams, *J. Org. Chem.*, 1965, in press.

electron-donor properties of nitrogen; such effects have been observed in other photochemical reactions.[7,8]

The acetyl bicyclic ketone (IIIc) and the bicyclic carbinols (Va and b) and acetates (VIa and b) are stable indefinitely at room temperature and are unaffected by brief heating. The bicyclic ketones (IIIa) and (IIIb), however, revert to the diazepinones in the dark. The relative rates of the reverse reaction are the same as for the photo-isomerization, (IIIb $>$ IIIa $>$ IIIc). The facility of the interconversions (Ia $\rightleftharpoons$ IIIa) and (Ib $\rightleftharpoons$ IIIb) seems to qualify them as photochromic processes.[9] The unsubstituted photo-ketone (IIIa) gives the hydrochloride, m.p. 139—140°, which is stable on storage. Treatment of (IIIa) with base brings about rapid conversion into a yellow compound, m.p. 160—161°, isomeric with (Ia). The structure of this product and other aspects of these compounds will be reported subsequently.

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[8] F. B. Mallory, J. T. Gordon, and C. S. Wood, *J. Amer. Chem. Soc.*, 1963, **85**, 828.
[9] R. Dessauer and J. P. Paris, ref. 2, p. 275.