Photocycloaddition of Diphenylacetylene to a 2-Pyridone

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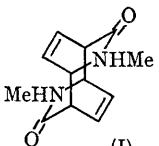
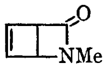
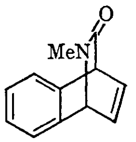
THE photochemical behaviour of 2-pyridones has been described with respect to dimeric (I)[1] and valence tautomeric (II)[2] products. Although cycloadditions of 2-pyridones (III) have recently been reported to occur thermally,[3,4] no photocycloaddition process is yet known.



(I)



(II)



(III)

We describe the results obtained upon irradiation of a methanolic solution of 5,6,7,8-tetrahydro-2-quinolone[5] (IV) and diphenylacetylene.† The major product (60%) isolated was the highly insoluble dimer [presumably (V)] which was deposited during the irradiation. Although (V) exhibited unconjugated lactam absorption at 6·0 μ (Nujol), the m.p. and mass-spectral data were identical to that of (IV), which attests to its highly labile nature. Reversal to (IV) was readily observed in acid or alkaline medium; this prevented firm characterization. When the solvent was removed from the irradiated mixture there was obtained, in 21% yield, a crystalline material (m.p. 203—205°; *m/e* 327) which showed only end u.v. absorption, i.r. ($CHCl_3$) 2·93, 5·92 μ, n.m.r. ($CDCl_3$), δ 7·61 (1H, N*H*); 6·9—7·5 (10H, aromatic *H*); 3·60 (doublet of doublets, J 1, 3 Hz, 1H, H_A); 2·55 (d, J 3 Hz, 1H, H_B); 1·5—2·0 (m, 8H, methylene *H*). On the basis of these data, the structure (VI) was assigned to the minor product. The chemical shift for H_A (3·60 p.p.m.) was assigned on the basis of the collapse of the doublet of doublets to a sharp doublet (J 3 Hz) when the NH proton was exchanged with deuterium oxide. This clearly indicates that the NH proton is coupling to H_A through the carbonyl group.‡ Presumably (VI) is derived from the *in situ* photocyclization of the Diels–Alder adduct (VII). Analogous isomerizations of homoconjugated dienes to quadricyclic systems is now a well-known process.[6] Similar irradiation of the *N*-methylquinolone (VIII) produced, after seven days, an 8% yield of (IX) as the only product. No trace of any dimeric product could be found. The *N*-methyl quadricyclic system (m.p. 166—169°; *m/e* 341) exhibited only end u.v. absorption, i.r. ($CHCl_3$) 5·97 μ. The n.m.r. spectrum ($CDCl_3$) was related to (VI) in that the NH signal was replaced by a sharp *N*-methyl singlet at 3·03 p.p.m. The H_A and H_B protons appeared as true doublets (J 3 Hz) at 3·61 and 2·61 p.p.m. respectively. Treatment of (VI) with methyl iodide and sodium hydride produced (IX) quantitatively thus confirming the relationship of the two photoadducts.

When (VI) was heated under reflux with acid or alkali, it was found (t.l.c.) to undergo reversal to diphenylacetylene and the quinolone (IV). On the other hand, it was surprising to find that (IX) was completely resistant to cleavage with hot

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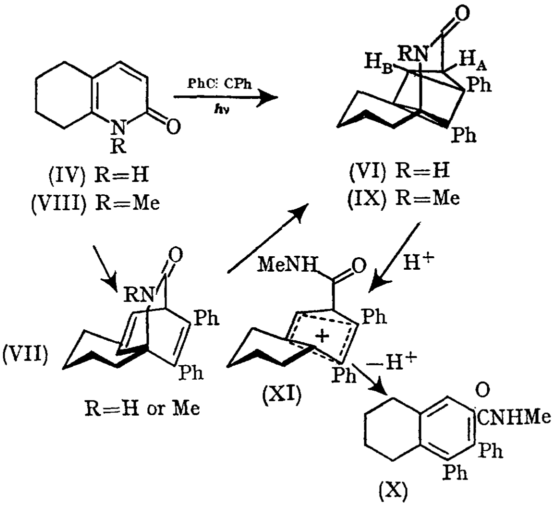
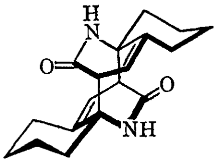
† Irradiations were performed for 3—12 days on 0·8 M solutions of (IV) containing 2—4 equivalents of diphenylacetylene, using a Rayonet Griffin–Srinivasan reactor equipped with Sylvania F8T5/BLB lamps. The solutions (in Pyrex) were kept under nitrogen after being degassed by the freeze-thaw technique. The products were isolated by preparative t.l.c. (Brinkman PF_{254}, 1·5 mm thickness).

‡ There appears to be no precedent for this phenomenon in the literature. Confirmation of this effect was gathered when the NH proton (7·61 p.p.m.) was irradiated causing the collapse of the doublet of doublets to a sharp doublet.





alkali even after prolonged treatment. Furthermore, when (IX) was heated overnight in methanolic hydrochloric acid, (X) was produced in 60% yield [m.p. 199—202°, m/e 341·17756; (Calc. 341·17796)].§ U.v. (EtOH) 230 $m\mu$, typical of o-terphenyl system (Sadtler Catalog); i.r. ($CHCl_3$) 2·91, 6·06 μ; n.m.r. ($CDCl_3$), δ 7·1—7·6 (11H, aromatic H); 5·12 (1H, NH); 2·5 (d, J 5 Hz, 3H, N-CH_3);¶ 2·3—2·8 (4H, benzylic H); 1·5—1·9 (4H, methylene H). Attempted hydrolysis of the amide (X) was unsuccessful, even after prolonged heating in concentrated methanolic potassium hydroxide, the material being recovered unchanged. Resistance of hindered amides to hydrolysis has been reported.[7] The acid-catalyzed rearrangement of (IX) to (X) undoubtedly proceeds *via* the ion (XI) which results from C–N bond-rupture to give a highly delocalized cation.

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§ Precise mass determined on a Varian M-66 instrument indicated that the molecule possessed fourteen sites of unsaturation and/or rings.

¶ Spin-decoupling of the NH proton resulted in collapse of the doublet to a singlet. The doublet was also found to collapse upon exchange of the NH proton with D_2O.

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