A Photochemical Rearrangement involving Aminated Quinones

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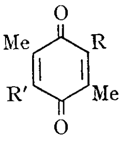
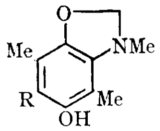
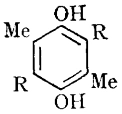
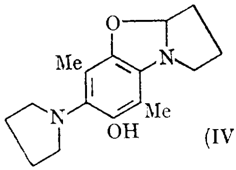
WE report a novel rearrangement involving diaminated 1,4-benzoquinones (I; $R,R'=NX_2$), compounds which can be prepared by direct amination of *p*-xyloquinone.[1] The bisdimethylamino-derivative (I; $R,R'=NMe_2$), for example, undergoes rapid isomerisation when its solutions in organic solvents are exposed to sunlight; it is converted in 65% yield into a colourless crystalline photo-product, formulated as (II; $R=NMe_2$). This new compound absorbs infrared radiation at 3240 cm.$^{-1}$ (OH), while its ultraviolet absorption (λ_{max} 308 mμ) is virtually identical with those of quinols (III; $R=NR_2$). Its n.m.r. spectrum ($CDCl_3$) contains singlets of correct intensity at τ 4·91 (·OCH_2N·), 7·18 (NMe_2), 7·23 (NMe), and 7·77 (ArMe). Chemical confirmation of this structure is provided by the production of formaldehyde (0·86 mole) on warming the compound with dilute sulphuric acid. The other product of this reaction, a quinol, undergoes aerial oxidation to a new unsymmetrically substituted quinone (I; R=NH·Me; $R'=NMe_2$). Irradiation of this compound similarly yields a new photo-product, too unstable to be obtained crystalline and formulated as (II; R=NH·Me), since it is readily converted by aerial oxidation into the bismonomethylamino quinone (I;R,R'=NH·Me), identified by comparison with authentic material.

Irradiation of the analogous bispyrrolidinoquinone (I; R,R'=pyrrolidino) similarly yields the benzoxazoline (IV). Its n.m.r. spectrum includes an unsymmetrical triplet at τ 4·16 (·O$\dot{C}$HN·). In contrast to compound (II; $R=NMe_2$), this product is recovered unchanged after treatment with acid, no volatile aldehyde being removed from the reaction mixture. Similar photo-products have also been obtained from the corresponding bis-piperidino-, -hexamethyleneimino- and -morpholino-quinones but not from their -azetidino- or -aziridino-analogues.


(I)


(II)


(III)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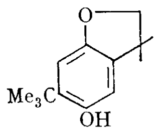
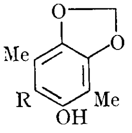

(V)


(VI)

Our observations on related systems will be reported in full in due course. Three schools[2-4] have recently described the ultraviolet irradiation of 2,5-di-t-butyl-1,4-benzoquinone and one of the minor products of this reaction has been formulated[3] as compound (V) (though the possibility of further rearrangement cannot be excluded[4]). Its formation would represent a carbon-substituted analogue of the reaction described here which

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[1] D. W. Cameron and P. M. Scott, *J. Chem. Soc.*, 1964, 5569.

[2] J. Petranek and O. Ryba, *Chem. and Ind.*, 1965, 225.

[3] A. T. Shulgin and H. O. Kerlinger, *Tetrahedron Letters*, 1965, 3355.

[4] C. M. Orlando and A. K. Bose, *J. Amer. Chem. Soc.*, 1965, **87**, 3782.

could occur by a mechanism analogous to that suggested.[3] Extension to oxygen-substituted quinones, *e.g.* the dimethoxy-compound (I; R,R′=OMe), would lead similarly to (VI; R=OMe) as irradiation product. Although we have been unable to effect this specific transformation experimentally, the possibility of generating methylenedioxy-groups by irradiation of suitable methoxy-quinones or -quinone methines is relevant to current knowledge of their biogenesis in natural products.[5,6]

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[5] D. H. R. Barton, G. W. Kirby, and J. B. Taylor, *Proc. Chem. Soc.*, 1962, 340.

[6] D. H. R. Barton, R. H. Hesse, and G. W. Kirby, *Proc. Chem. Soc.*, 1963, 267.