The Photochemistry of Hydroxycyclohexadienones

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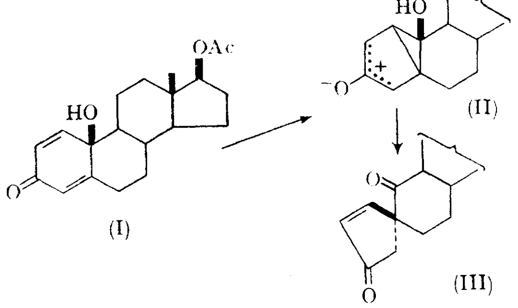
THE photochemistry of cyclohexadienones has attracted wide attention in recent years.[1] We now report the course taken by the photolysis of a number of 4-hydroxycyclohexa-2,5-dienones and their transformation products. In 1963, a Swiss group reported[2] that the steroidal hydroxy-dienone (I) was transformed on irradiation with ultraviolet light into the spiro-diketone (III) whose formation was rationalised as proceeding through the dipolar intermediate (II). The intermediacy of such species in the photochemistry of 4-alkylcyclohexa-2,5-dienones is now widely accepted.[1]

We now present evidence indicating that such a dipolar intermediate is an important one in the photolysis of a number of 4-hydroxycyclohexa-2,5-dienones. The bicyclic dienones (IVa, b, c) were prepared by the lead tetra-acetate oxidation of the corresponding phenols followed by hydrolysis.† Photolysis of (IVa and b) in benzene using a Pyrex-jacketed 125w medium-pressure mercury lamp gave perhydroazulene ketones as major products. Dienone (IVa) gave the ketone (Va) in 38% yield, as an oil, ν_{max} (CCl_4) 1725 (cycloheptanone), 1717 (cyclopentenone), and 1630 cm.$^{-1}$ (conjugated C=C); λ_{max} 234 mμ (ϵ 10,700) 283 mμ (ϵ 1100) ($\beta\gamma$-unsaturated cycloheptanone); δ 6·26 (1 vinyl H) while dienone (IVb) gave the ketone (Vb), $C_{11}H_{14}O_2$ (mass spectrum) as an oil, ν_{max} 1723, 1714, and 1646 cm.$^{-1}$, λ_{max} 240 mμ (ϵ 11,800), δ 1·67 (doublet, J 1·0 c./sec., vinyl methyl). Hydrogenation over platinum oxide in ethanol resulted in the uptake of 1 mole of hydrogen to give a product showing ν_{max} 1743 (cyclopentanone) and 1711 cm.$^{-1}$.



(I)
(II)
(III)

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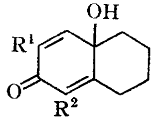
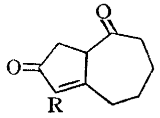
† The acid-catalysed rearrangement of these dienones will be described in a subsequent communication.

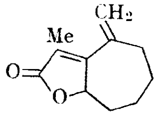
In contrast, the dienone (IVc) gave the unsaturated butenolide (VI) in 50% yield, $C_{11}H_{14}O_2$ (mass spectrum); ν_{max} (CCl_4) 3111 and 912 (=CH_2), 1760 (1740 in $CHCl_3$) ($\alpha\beta$-unsaturated-γ-lactone), 1668 (C=C), 1641 and 1606 cm.$^{-1}$ (conjugated diene); λ_{max} 262 mμ (ϵ 11,000); δ 1·97 (3H, doublet, J 1·6 c./sec., vinyl Me, collapsed to a singlet with irradiation at 4·89 δ), 4·89 (1H, 2 quartets, J 9·6 and 1·6 c./sec.), 5·53 (2H, $w_{\frac{1}{2}}$ 3·2 c./sec., =CH_2).



(IV) a; R^1=R^2=H
b; R^1=H, R^2=Me
c; R^1=Me, R^2=H

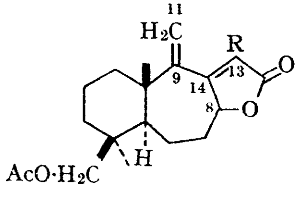


(V) a; R=H
b; R=Me

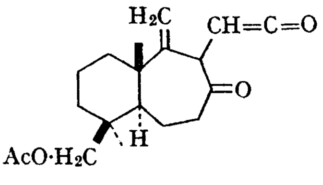


(VI)

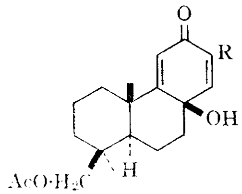
The genesis of this butenolide was indicated by a study of the photolysis of two hydroxy-dienones in the podocarpic acid series.[3] The dienone (VIIa) on irradiation under similar conditions as above gave the spiran (VIIIa), m.p. 175—177°, $C_{19}H_{26}O_4$ (mass spectrum), whose structure was evident from the similarity of its spectral properties with those of the steroidal spiran (III).[2] Further irradiation of this spiran gave the butenolide (IXa), $C_{19}H_{26}O_4$ (mass spectrum); ν_{max} (CCl_4) 1760 ($\alpha\beta$-unsaturated γ-lactone), 1740 (acetate), 3100 and 870 (=CH_2), 1650, and 1605 cm.$^{-1}$ (C=C stretching); λ_{max} 220 mμ (ϵ 6200); δ 5·0 (1H, multiplet, C-8), 4·85 and 5·15 (each 1H, singlets, =CH_2), 5·75 (1H, doublet, J 2 c./sec., C-13 vinyl H). Double irradiation established that coupling occurred between protons on C-13 and C-8, and C-8 and C-7. The n.m.r. spectrum showed striking similarities with the spectra of simple butenolides, prepared in this laboratory.[4] The lack of conjugation between the two double bonds ($\Delta^{9(11)}$ and $\Delta^{13(14)}$), as evidenced by the ultraviolet spectrum which is that of a normal butenolide, is attributed to the lack of planarity between these two double bonds. Such rigidity is not enforced in the bicyclic butenolide (VI).



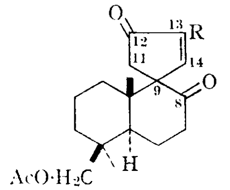
(IX) a; R=H
b; R=Me



(X)



(VII) a; R=H
b; R=Et



(VIII) a; R=H
b; R=Et

When the dienone (VIIb) was irradiated, both the spiran (VIIIb), m.p. 155—157°, identified by its i.r., u.v., and n.m.r. spectra, and the butenolide (IXb), $C_{21}H_{30}O_4$ (mass spectrum), m.p. 152—154°, identified by its i.r., u.v., and n.m.r. spectra, were obtained.

Both the spiro and the perhydroazulene diketones can arise from a mesoionic intermediate such as (II), where the location of the positive charge, and the direction of cleavage of the cyclopropanol ring determine the nature of the product.[1,5] The transformation of the spiro-diketones into the butenolides can be visualised as proceeding by homolysis of the bonds 11,12 and 8,9, both α to the carbonyl groups, followed by attack of a radical at C-8 on the double bond at C-14. Addition of the ketone to the keten, to give a β-lactone, and collapse of the cyclopropane ring, would give the observed product. Further studies of this process are under investigation. The mass spectrometry was carried out by Dr. R. Hodges, of Massey University, Palmerston North, using an A.E.I. MS9 mass-spectrometer.

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[1] K. Schaffner, *Adv. Photochem.*, 1966, **4**, 81, and references there cited.

[2] C. Ganter, R. Warszawski, H. Wehrli, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, 1963, **46**, 320.

[3] G. F. Burkinshaw and B. R. Davis, *Tetrahedron*, 1967, in the press.

[4] A. Singh, unpublished.

[5] *cf.* P. J. Kropp, *J. Amer. Chem. Soc.*, 1963, **85**, 2456; 1964, **86**, 4053.