The Isolation of a Spiran in the Acid-catalysed Rearrangement of a Bicyclic Cyclohexadienone

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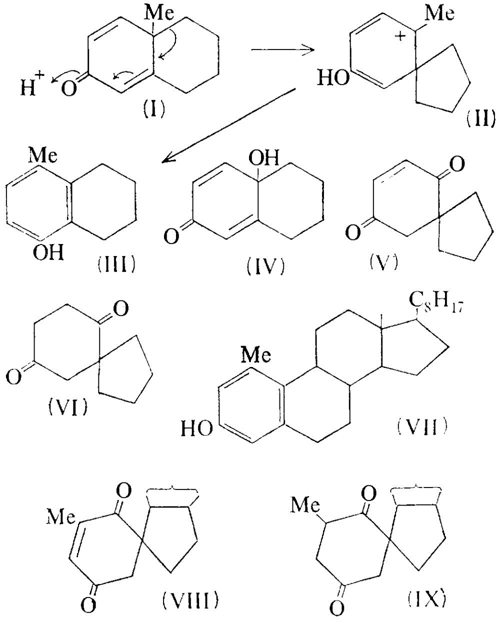
IN 1950, Woodward and Singh[1] postulated that the acid-catalysed rearrangement of the dienone (I) to give the phenol (III), proceeded by way of the cationic spiran intermediate (II), the rearrangement involving two 1,2-alkyl shifts. Later work[2,3] has served to confirm the correctness of this postulate in a number of related systems, but no spiran has been isolated. Introduction of an hydroxyl group into the angular position might allow a spiran to stabilise itself by loss of a proton rather than further alkyl migration. We now report the isolation of a spiran from the acid-catalysed rearrangement of the bicyclic dienone (IV).



Treatment of the dienone (IV) with a dilute solution of boron trifluoride in ether gave the spiran (V) as an unstable oil. The u.v. absorption, $\lambda_{\max}$ 235 mμ (ϵ = 9000), and i.r. maximum at 1685 cm.$^{-1}$ were consistent with the presence of an ene-dione grouping, while the n.m.r. spectrum showed two vinyl protons with very similar chemical shifts (6·70 δ) and two methylene protons adjacent to a carbonyl group (2·78 δ).

Zinc–acetic acid reduction of the total product gave a crystalline diketone, $C_{10}H_{14}O_2$, whose lack of intense absorption in the u.v., and whose i.r. ($\nu_{\max}$ 1710 cm.$^{-1}$) and n.m.r. spectra (no vinyl hydrogens) were entirely consistent with the structure (VI). The high-resolution mass spectrum could be interpreted in terms of this formulation, and in particular indicated that the two carbonyl groups were separated by two methylene groups.

A similar reaction was subsequently observed during the preparation of a steroidal hydroxydienone. Oxidation of the phenol (VII) with hydrogen peroxide and sulphuric acid in acetic anhydride gave a crystalline ketone assigned the structure (VIII). Reduction of this cyclohexenedione (VIII) with zinc in acetic acid gave a dihydroproduct (IX); the i.r., u.v., n.m.r., and mass spectra were consistent with the structures suggested, (VIII) and (IX). Decoupling experiments on the n.m.r. spectrum of the diketone (IX) showed the presence of a methyl group attached to a carbon atom bearing one hydrogen atom.

These experiments represent the first examples of the isolation of a spiran from the acid-catalysed rearrangement of a bicyclic dienone, and support the intermediacy of such systems in similar rearrangements.

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[1] R. B. Woodward and T. Singh, *J. Amer. Chem. Soc.*, **1950**, **72**, 494.

[2] R. B. Woodward in A. Todd, "Perspectives in Organic Chemistry", Interscience, New York, 1956, p. 178; S. M. Bloom, *J. Amer. Chem. Soc.*, **1958**, **80**, 6280.

[3] A. J. Waring, *Adv. Alicyclic Chem.*, **1966**, **1**, **131**, reviews the chemistry of cyclohexadienones.