Cyclohexadienones: Stereospecific Photochemical Rearrangements of o-Quinol Acetates

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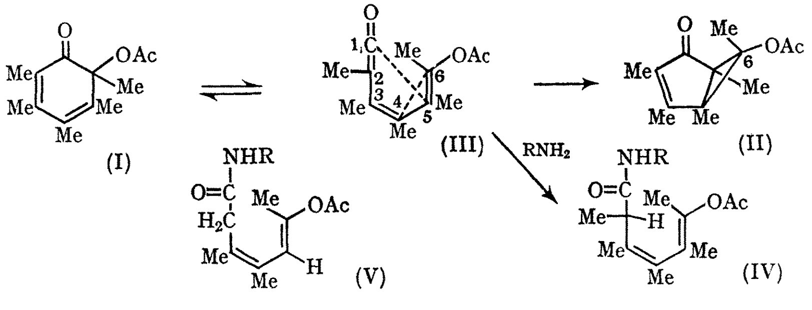
Summary The photochemically-induced rearrangement of some cyclohexa-2,4-dienones to bicyclo[3,1,0]hex-3-en-2-ones occurs by a general stereospecific ring opening to a keten, which is followed by a stereospecific thermal cyclisation.

ULTRAVIOLET IRRADIATION of 6-acetoxy-2,3,4,5,6-pentamethylcyclohexa-2,4-dienone (pentamethyl-*o*-quinol acetate) (I) leads stereospecifically to the single bicyclic *product (II).*[1] We report experiments which establish the nature of each step in this reaction (see Scheme), and extend our earlier[1] suggestions.

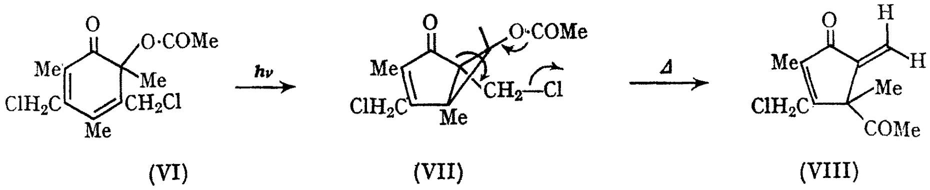


SCHEME

Irradiation of (I), and of a series of tetramethyl- and trimethyl-analogues in ether–cyclohexylamine, through Pyrex, led to a high yield of the single amide (IV; R = cyclohexyl) or its analogues.†‡ The spectra of all the amides differed only as expected for the change in substitution. The n.m.r. of the amide (V), derived from 3,4,6-trimethyl-*o*-quinol acetate, was recorded in CCl_4–C_6D_6 mixtures which allow all the methyl resonances to be separated. Decoupling showed that the C-5 proton and the protons of the 6-methyl group couple with *J* 0·7 to 0·8 c./sec., consistent[2] with the *trans*-arrangement shown in (III)—(V). We conclude that the ketens, and in particular (III) have their 6-methyl group *inside.* The formation of ketens from cyclohexa-2,4-dienones is well known;[3] their stereospecific formation from less substituted systems (which do not give bicyclic products) has since been noted, but the stereochemistry was not assigned.[4]

The skeletal rearrangement implied in (III) → (II) was proved by the use of quinol acetate (VI). Photolysis in ether converted this cleanly and stereospecifically to (VII), whose structure and stereochemistry were established by n.m.r. and an unusual elimination reaction. The 1-chloromethyl group of (VII) is in an asymmetric environment adjacent to the ring carbonyl group, and appears in the n.m.r. as an AB quartet, τ 5·70, 6·62 (*J* 12·0 c./sec.). On heating at 120° for a few minutes, (VII) decomposes to acetyl chloride and (VIII). The position of the methylene group in (VIII) is supported by its appearance in the n.m.r. as two peaks, τ 3·87, 4·68 (*J ca.* 0).

Each bicyclic product has the n.m.r. signal assigned to the 6-methyl group 0·13 to 0·21 p.p.m. upfield of the analogous group in simple 1-methylcyclopropyl acetates. Reduction of the olefinic bond of (II) moves this signal downfield by 0·1 p.p.m. Both the shielding of the 6-methyl by the cyclopentenone ring, and the easy elimination in (VII) establish the stereochemistry of (II) and (VII).



A solution of (I) in ether : isopentane : ethanol (5 : 5 : 2), cooled to a glass with liquid nitrogen, was irradiated with u.v. light, through Pyrex, until very little of its original spectrum remained. A new, intense peak appeared below 250 nm. On slowly warming the glass this peak disappeared, and the spectrum appeared of (I) and (II) in

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† Isomeric purities were determined by g.l.c. and n.m.r. All new compounds had microanalytical, mass spectral, i.r. u.v., and n.m.r. data consistent with the assigned structures.

‡ H. Perst and K. Dimroth (*Tetrahedron*, 1968, **4**, 5385) showed that a keten was produced thermally from a triphenyl substituted analogue of (II). We find that the amide (IV), and hence the keten (III), is not produced thermally from (I) or (II) even under vigorous conditions.

about a 2:3 ratio.§ Similar experiments with hydrocarbon glasses showed the intermediate to reach a stationary concentration; warming gave mainly (I), together with a little of (II), detected by g.l.c. These results are in accord with i.r. studies on hexamethylcyclohexa-2,4-dienone.[3d] We conclude that the frozen intermediate is the keten (III), whose conversion into bicyclic (II) is a thermal, and reversion to (I) is a thermal and most probably also a photochemical, process. The isomerisation of (III) to (II) represents a [π4a, π2a] pericyclic reaction: that is, a thermally allowed[5] *trans,trans*-Diels–Alder addition. The strong solvent effect on this step is presumed to reflect a highly asymmetric transition state in which bonding of C-1 to C-5 in the keten leads bonding of C-4 to C-6.

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§ G.l.c. studies confirmed the presence of (I) and (II), together with a third compound which may be the ester produced by trapping of the keten by ethanol.

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[3] (a) D. H. R. Barton and G. Quinkert, *J. Chem. Soc.*, 1960, 1; (b) G. Quinkert, *Angew. Chem. Internat. Edn.*, **1965**, **4**, 211; (c) O. L. Chapman and J. D. Lassila, *J. Amer. Chem. Soc.*, 1968, **90**, 2449; (d) J. Griffiths and H. Hart, *ibid.*, p. 3297.

[4] J. E. Baldwin and M. C. McDaniel, *J. Amer. Chem. Soc.*, 1968, **90**, 6118.

[5] R. B. Woodward and R. Hoffmann, Chemical Society Symposium on "Orbital Symmetry Correlations in Organic Chemistry," Cambridge, January 1969; *Accounts Chem. Res.*, 1968, **1**, 17.