

## Formation of a Dihydrobenzofuran by Photochemical and Thermal Rearrangements of a Cross-conjugated Cyclohexadienone<sup>1</sup>

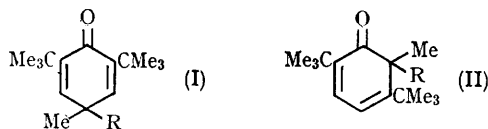
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PHOTOCHEMICAL rearrangements of 2,6-di-*t*-butylcyclohexa-2,5-dienones (I) have previously been shown to give linearly conjugated cyclohexadienones (II).<sup>2,3</sup> Irradiation of 4-(2,3-dibromopropyl)-4-methyl-2,6-di-*t*-butylcyclohexa-2,5-dienone (III) under the same conditions (450 w Hanovia u.v. lamp at 40–45° in hexane solution) has now been found to give 2-bromomethyl-2,3-dihydro-4,7-di-*t*-butylbenzofuran (IV) as the major product. It is the purpose of this communication to report the proof for the structure of (IV), and to provide evidence about the mechanism of this unusual transformation.

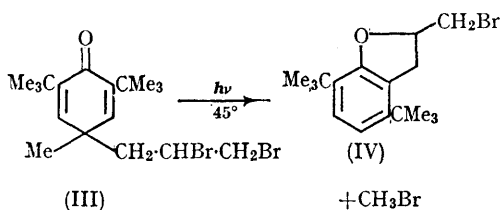
Compound (III) (m.p. 85–86°) was obtained in quantitative yield by addition of bromine to 4-allyl-4-methyl-2,6-di-*t*-butylcyclohexa-2,5-dienone (V).<sup>4</sup> Its u.v., i.r., and n.m.r. spectra are consistent

only with structure (III), and demonstrate that no rearrangement occurs during bromination of (V).

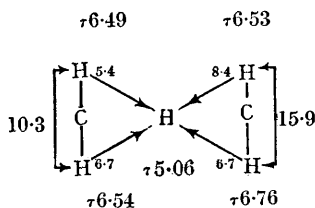


The photorearrangement product, (IV) was isolated by chromatography on alumina in 55% yield as a white solid, m.p. 66–67°. Its empirical formula, C<sub>14</sub>H<sub>25</sub>OBr, showed that one carbon atom had been lost during the rearrangement. Its molecular weight by mass spectroscopy was 324 (based on Br = 79). The i.r. spectrum of (IV) suggested that it was an ether, since no peaks

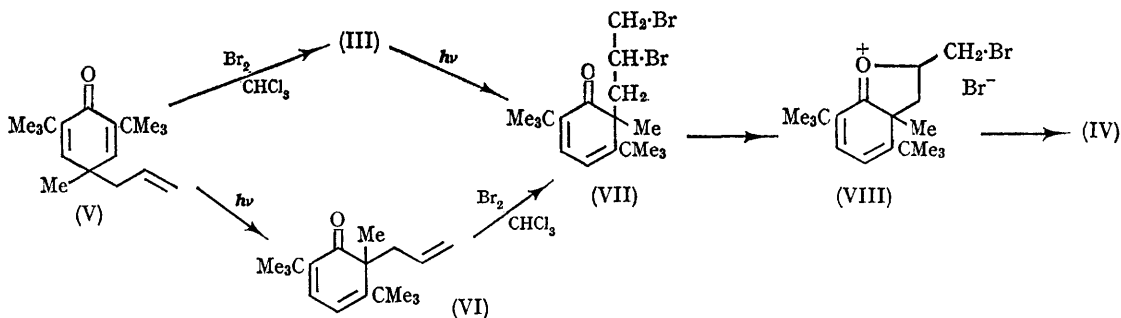
attributable to carbonyl or hydroxyl groups were present, while its u.v. spectrum in methanol ( $\lambda_{\max}$  286 and 277  $m\mu$ ,  $\log \epsilon = 2.9$ ) showed only aromatic absorption. Its n.m.r. spectrum in  $CDCl_3$  showed the presence of two *t*-butyl groups as a singlet ( $\tau$  8.67) and two adjacent aromatic protons ( $\tau$  2.98 and 3.22,  $J = 8.5$  c./sec.). A multiplet centred at



$\tau$  5.1 (1H) was attributed to a proton adjacent to the oxygen atom, while a 4H multiplet around  $\tau$  6.5 was considered to be the combined signals of a benzylic methylene group and a bromomethyl group.<sup>5</sup> These assignments are consistent only with a three-carbon chain with the structure shown in (IV). A complete analysis of the n.m.r. spectrum of (IV) is shown in the diagram below, in which all unlabelled numbers are *J*-values in c./sec.<sup>8</sup>

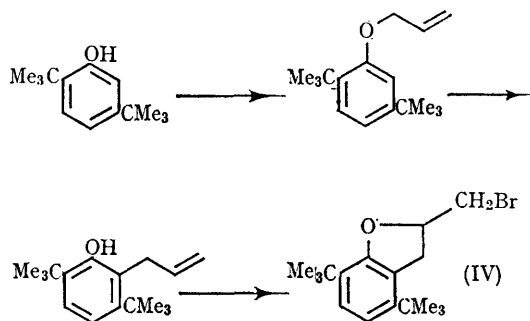


The positions of the *t*-butyl groups of (IV) were initially assigned only by the postulated derivation



of (IV) from a structure such as (II). The final proof for the structure of (IV) was its synthesis from 2,5-di-*t*-butylphenol, as is shown below.

Although (IV) was the first product which could be isolated from photolysis of (III), it seemed probable that the linear dienone (VII) was an intermediate in its formation.



In fact, when the reaction temperature was maintained below 35° and the solvent evaporated at low temperatures, the crude photolysis product showed a strong band at 309  $m\mu$  in its u.v. spectrum and peaks at 6.15 and 6.4  $\mu$  in its i.r. spectrum. These peaks are characteristic of linearly conjugated cyclohexadienones. When the crude photolysis product was heated on a steam bath for two minutes, methyl bromide (which was identified by its n.m.r. spectrum) was generated, and the u.v. and i.r. spectra of the products exhibited no peaks attributable to conjugated carbonyl groups. Compound (IV) was again isolated in good yield by chromatography on alumina.

That (VII) was indeed the intermediate involved in formation of (IV) was further confirmed by addition of bromine to the dienone (VI) resulting from photorearrangement of (V).<sup>3</sup> The immediate product of bromine addition retained the characteristic u.v. and i.r. bands of a linearly conjugated

cyclohexadienone, but these were again lost on gentle heating. Methyl bromide was evolved, and (IV) again obtained.

Formation of (IV) from (III), therefore, appears to involve the photochemical rearrangement of (III) to (VII), followed by a thermal conversion of (VII) into (IV), undoubtedly *via* the intermediate ketonium salt (VIII). The unusually easy cyclization to (VIII) is presumably facilitated by steric interference between the dibromopropyl group of (VII) and the adjacent *t*-butyl group.

Finally, attack of a bromide ion at the angular

methyl group of (VIII) gives methyl bromide and (IV). Nucleophilic displacement at the methyl group is aided both by the positive charge on the carbonyl group and the formation of an aromatic product. Nucleophilic attack at a methyl group attached to a saturated carbon under such mild conditions, nonetheless, seems to be without precedent.

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<sup>1</sup> "Reactions of Cyclohexadienones," Part XVI. Part XV, B. Miller, *J. Amer. Chem. Soc.*, 1966, **88**, 1841.

<sup>2</sup> B. Miller and H. Margulies, *Chem. Comm.*, 1965, 314.

<sup>3</sup> B. Miller, *J. Amer. Chem. Soc.*, 1965, **87**, 5515.

<sup>4</sup> B. Miller, *J. Org. Chem.*, 1965, **30**, 1964.

<sup>5</sup> L. M. Jackman, "Applications of Nuclear Magnetic Resonance in Organic Chemistry," Pergamon Press, New York, 1959.

<sup>6</sup> We thank Dr. John Lancaster for the analysis of the nmr spectrum of (IV).