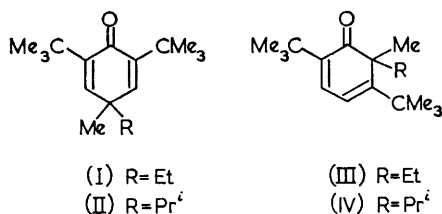


Photo-rearrangements of 2,6-Di-*t*-butylcyclohexadienones¹

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IRRADIATION of hexane solutions of 4-ethyl-4-methyl-2,6-di-*t*-butyl-cyclohexadien-1-one (I)² for 4 hr. by a 450 W Hanovia ultraviolet lamp through a Vycor filter gave 60—70% yields of a single product, which was isolated as an oil by chromatography on alumina or by vapour-phase chromatography (v.p.c.). This product was assigned structure (III) on the basis of the following evidence:



The product is an isomer of (I). Its i.r. spectrum has λ_{\max} 6.07 μ , 6.10 μ (shoulder) and 6.33 μ . Its u.v. spectrum in cyclohexane has λ_{\max} 315 m μ (ϵ , 4300); in methanol, λ_{\max} 322 m μ (ϵ , 3900). These values are typical of homoannular linearly-conjugated cyclohexadienones.³ The n.m.r. spectrum of (III) shows the presence of two *t*-butyl

groups (τ 8.69 and 8.77), an isolated methyl group (τ 8.61), and an isolated ethyl group (τ 8.05 and 9.39). The positions of the peaks for the methyl group and of the methylene quartet show that they are located on the quaternary carbon of the cyclohexadienone. This is, in any case, required by the chemical properties of (III) since linearly-conjugated cyclohexadienones very rapidly lose *t*-butyl groups from quaternary carbons under conditions (*e.g.*, chromatography on silica gel or activated alumina) in which (III) is stable.^{1,2}

The most distinctive feature of the n.m.r. spectrum of (III) is the presence of a pair of doublets at τ 3.15 and 3.65 ($J = 7.1$) in the vinyl hydrogen region. The two vinyl hydrogens, therefore, must be on adjacent carbon atoms.

The location of one of the two *t*-butyl groups α to the carbonyl group of (III) is shown by the complete inertness of (III) to sodium borohydride, even upon heating under reflux in ethanol.

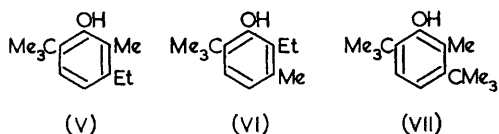
These facts leave just two possible structures to be considered for the photo-rearrangement product: (III), and its isomer with two adjacent *t*-butyl groups. The latter possibility was eliminated by rearranging (III) in a 10% solution of sulphuric acid in acetic acid to give a single product. This

¹ Reactions of Cyclohexadienones, X. Part IX, B. Miller, *J. Org. Chem.*, 1965, **30**, 1964.

² Cyclohexadienones (I) and (II) were prepared by alkylation of potassium 2,6-di-*t*-butyl-4-methylphenoxide in *t*-butanol. B. Miller and H. Margulies, to be reported.

³ *e.g.*, H. Hart and C. H. Buehler, *J. Org. Chem.*, 1964, **29**, 2397.

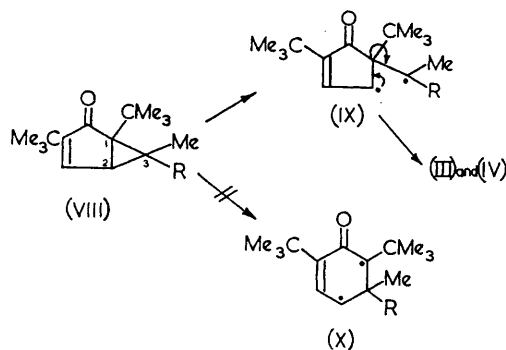
product, a phenol, $C_{13}H_{20}O$, had lost a *t*-butyl group, as shown by its n.m.r. spectrum and empirical formula. Surprisingly, the n.m.r. spectrum of the phenol (in $CDCl_3$) showed a single peak (2 H) at $\tau 3.09$, with no evidence of any spin-spin coupling. However, a solution of the phenol in dimethyl sulphoxide containing potassium *t*-butoxide (from which it was recovered unchanged) had a typical pair of doublets at $\tau 3.30$ and $\tau 3.62$ ($J = 7.5$ c./sec.) in the n.m.r. spectrum, showing that the two aromatic hydrogens remain on adjacent carbons. The position of the aromatic hydrogen peak,⁴ as well as the physical properties of the phenol (hydroxyl peak at 2.76μ , insolubility in base, low retention times on alumina and v.p.c. columns) showed that it had retained a *t*-butyl group in the *ortho*-position, and it was therefore assigned structure (V) or (VI).



Formation of (V) or (VI) is the expected result of acid-catalyzed rearrangement of (III),^{1,4} but would be quite difficult to rationalize as the result of rearrangement of isomers of (III).

Irradiation of the 4-isopropylcyclohexadienone (II) gave a product whose i.r., u.v., and n.m.r. spectra were very similar to those of (III). Although this evidence allowed structure (IV) to be assigned to the photo-rearrangement product of (II), (IV) could not be obtained completely pure, since attempts at isolation by v.p.c. or chromatography on silica gel or deactivated alumina gave a phenol, $C_{15}H_{24}O$, m.p. $76-78^\circ$, resulting from loss of an

isopropyl group. The n.m.r. and i.r. spectra of this phenol show the presence of the hindered hydroxyl group, two adjacent aromatic hydrogens, and two distinct *t*-butyl groups expected of structure (VII).



Loss of an isopropyl group from a carbon atom under such mild conditions appears to be unique.

Formation of (III) and (IV) from (I) and (II) presumably proceeds through the intermediate lumi-product (VIII).⁵ Irradiation of such lumi-products normally opens the cyclopropane ring between C-1 and C-2, to give resonance-stabilized intermediates (whether radical or ionic) similar to (X), which rearrange further to phenols⁶ or dienones.^{7,8} Formation of (X), however, would force a *t*-butyl group into close proximity to the quaternary C-3 and the oxygen atom. The less resonance-stabilized but less strained intermediate (IX), therefore, is formed by opening the cyclopropane ring⁹ between C-2 and C-3. Rearrangement of (IX) can give (III) and (IV), either directly or by formation and cyclization of a keten.

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⁴ A hydrogen atom in the *ortho*-position would appear at $\tau 3.7-3.8$. B. Miller and H. Margulies, *Tetrahedron Letters*, 1965, 1727.

⁵ Although the intermediacy of (VIII) could not be demonstrated, Matsuura (*Bull. Chem. Soc. Japan*, 1964, **37**, 564) has isolated low yields of similar bicyclic ketones from the photo-rearrangements of 2,4,6-tri-*t*-butyl-4-methoxycyclohexadien-1-one and 2,4-di-*t*-butyl-4-methoxy-4-methylcyclohexadien-1-one.

⁶ L. Chapman, *Adv. Photochem.*, 1963, **1**, 323.

⁷ O. L. Chapman and L. F. Engert, *J. Amer. Chem. Soc.*, 1963, **85**, 3029.

⁸ P. J. Kropp, *J. Amer. Chem. Soc.*, 1964, **86**, 4053.

⁹ A 1% yield of a dienone resulting from a similar process in a steroid has been reported by H. Dutler, C. Ganter, H. Ryf, E. C. Utzinger, K. Weinberg, K. Schaffner, D. Arigoni, and O. Jeger, *Helv. Chim. Acta*, 1962, **45**, 2346.