A Cyclobutenone from Photolysis of a Cyclohexa-2,5-dienone

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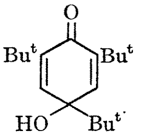
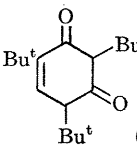
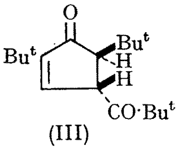
Summary A new type of photoproduct, a vinylcyclobutenone, has been isolated from the photolysis of a cyclohexa-2,5-dienone.

IRRADIATION of cyclohexa-2,5-dienones has been variously reported to yield phenols, bicyclohexenones, cyclopentenones, bicyclopentanones, hexadienoic acids, Δ^1-butenolides, and rearranged cyclohexadienones, depending upon the substituents and the reaction conditions.[1] We now report the isolation and identification of a new type of photoproduct, a cyclobutenone derivative, from photolysis of a cyclohexa-2,5-dienone.

The u.v. irradiation of 4-hydroxy-2,4,6-tri-t-butylcyclohexa-2,5-dienone (I) in benzene has been reported to yield diketone (II) (14%), cyclopentenone (III) (6%), and bicyclopentanone (IV) (4%).[1d] We repeated this reaction in an attempt to obtain a higher yield of (II). A solution of (I) (1·80 g.) in benzene (270 ml.) was irradiated for 1·5 hr. in Pyrex.† After removal of the solvent under reduced pressure, attempted dissolution of the residue in petroleum (b.p. 30—60°) gave 0·60 g. (33%) of an insoluble crystalline compound. Recrystallization of the product from ethanol–water gave white needles of 3-hydroxy-4-(3,3-dimethylbut-1-enyl)-2,4-di-t-butylcyclobut-2-enone (V):‡ m.p. 163—164·5°; λ_{max} (MeOH) 253·5 nm. (ϵ 7100); ν_{max} (KBr) 2959 (strong, Bu^t), 2880—2500 (broad, OH), 1730 (strong, C=O), and 1597 cm.$^{-1}$ (strong, C=C); n.m.r. [in $(CD_3)_2CO$] δ 5·47 (AB q, 2H, $\Delta\gamma$ 0·21 p.p.m., J_{AB} 13·9 Hz, *trans*-CH=CH), 1·18 (s, 9H, Bu^t), 1·11 (s, 9H, Bu^t), and 1·04 p.p.m. (s, 9H Bu^t); neutralization equiv., 282 [calc. for (V) 278].§ The structure assigned to (V) is suggested by the n.m.r. evidence for three nonequivalent t-butyl groups and a *trans*-disubstituted olefin moiety, and by a u.v. maximum typical of enolized cyclobutane-1,3-diones.[2] All the other data are consistent with this assignment. In particular, the i.r. spectrum of (V) closely resembles the spectrum reported[3] for 3-hydroxy-2,4-dimethylcyclobut-2-enone in the region between 1535 and 2900 cm.$^{-1}$. The enolic proton could not be detected in the n.m.r. spectrum of (V) in any of the several solvents tried, evidently due to line-broadening caused by ionization. However, potentiometric titration of (V) gave a pK_a of *ca.* 2·6, indicating an acidic proton. By comparison, the pK_a values reported for 2,4-dimethyl-[2] and 2,4-diethyl-3-hydroxycyclobut-2-enone[4] are *ca.* 2·8 and 3·5, respectively.


(I)


(II)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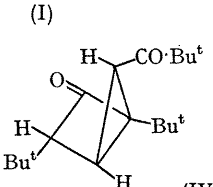
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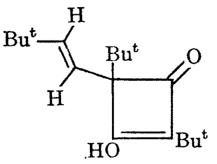
(V)

Hydrogenation of (V) over 10% palladium on charcoal at atmospheric pressure resulted in uptake of 1 equiv. of H_2 and gave an essentially quantitative yield of 3-hydroxy-4-(3,3-dimethylbutyl)-2,4-di-t-butylcyclobut-2-enone§ (sublimes 204°), n.m.r. (CD_3OD) δ 1·8—1·4 (m, 4H, $CH_2{\cdot}CH_2$), 1·16 (s, 9H, Bu^t), 0·99 (s, 9H, Bu^t), and 0·88 p.p.m. (s, 9H, Bu^t). Reaction of (V) with an ethereal solution of diazomethane yielded the corresponding methyl ether as a colourless oil: i.r. (KBr) 1751 cm.$^{-1}$ (strong, C=O), no OH (2880—2500 cm.$^{-1}$); n.m.r. ($CDCl_3$) δ 5·47 (AB q, 2H, $\Delta\gamma$ 0·31 p.p.m., J_{AB} 14·0 Hz., *trans*-CH=CH), 3·95 (s, 3H, OMe), 1·20 (s, 9H, Bu^t), 1·11 (s, 9H, Bu^t), and 1·06 p.p.m. (s, 9H, Bu^t).

The evidence outlined above completely confirms the structure of (V). To our knowledge, the formation of this unusual vinylcyclobutenone is completely without precedent

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† All irradiations were carried out with a Hanovia 450 w mercury-arc lamp in a Pyrex immersion-well apparatus under nitrogen.

‡ To our knowledge, this is the first reported synthesis of such a compound from a cyclohexadienone. However, Matsuura and Ogura[1d] reported obtaining a small yield of "colourless crystals of an unknown compound" using a similar work-up procedure. Small amounts of (II), (III), and (IV) were obtained from the fraction soluble in petroleum.

§ A satisfactory elemental analysis was obtained for this compound.

in cyclohexadienone photochemistry. Preliminary experiments designed to elucidate the mechanism of this rearrangement have indicated that (II) does not undergo photorearrangement to (V).

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[1] For reviews, see (a) H. E. Zimmerman, *Adv. Photochem.*, 1963, **1**, 183; (b) O. L. Chapman, *ibid.*, 1963, **1**, 323; (c) P. J. Kropp, "Organic Photochemistry," vol. 1, ed. O. L. Chapman, Marcel Dekker, New York, p. 1; (d) T. Matsuura and K. Ogura, *Tetrahedron*, 1968, **24**, 6167.

[2] *Cf.* the u.v. maximum of 3-hydroxy-2,4-dimethylcyclobut-2-enone, 252 nm. in EtOH (R. B. Woodward and G. Small, jun., *J. Amer. Chem. Soc.*, 1950, **72**, 1297).

[3] D. G. Farnum, M. A. T. Heybey, and B. Webster, *Tetrahedron Letters*, 1963, 307.

[4] E. B. Reid and S. J. Groszos, *J. Amer. Chem. Soc.*, 1953, **75**, 1655.