Photolysis of 2,6-Di-t-butyl-1,4-benzoquinone: a New Rearrangement

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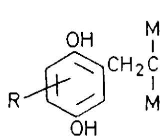
Summary U.v. irradiation of 2,6-di-t-butyl-1,4-benzoquinone in benzene gives a fused dioxocyclopentanocyclopentene.

Photolysis of t-butyl-1,4-benzoquinones produces a number of products, the most interesting containing a rearranged side chain as in (**1**)[1] (formed in alcoholic solvents) and (**2**)[1] (in carboxylic acid solutions). The first step is regarded[1,2] as an intramolecular hydrogen abstraction to give (**3**) leading to the spiro-intermediate (**4**) from which (**1**) and (**2**), and other solvent-derived products[3] arise.



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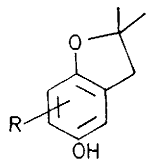

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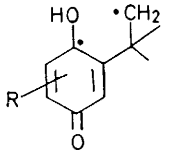

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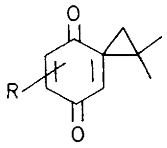

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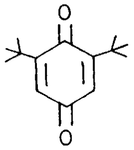

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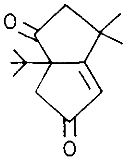

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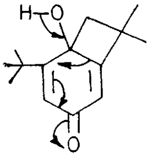

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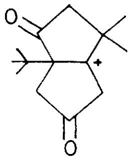

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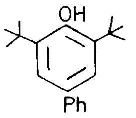

(9)

The photoreaction of 2,6-di-t-butylbenzoquinone (**5**) in benzene[4] in visible light is extremely slow but we now find that irradiation with u.v. light† gives a mixture of products including an isomeric diketone (1%), m.p. 90—91°, λ_{max} 266 nm, ν_{CO} 1735 and 1710 cm^{-1}, δ 1·03 (Bu^t), 1·31 (Me), 1·61 (Me), 6·19 (=CHCO), and 1H doublets (*J ca.* 18 Hz) at 2·32, 2·37, 2·77, and 2·97. Initially the mass spectrum suggested a dimeric compound and as these data were irreconcilable the problem was solved by X-ray crystallography which established the bicyclic structure (**6**).

The crystals are monoclinic, space group $C2/c$ with $a = 24{\cdot}003(1)$, $b = 7{\cdot}464(1)$, $c = 15{\cdot}507(1)$ Å, $\alpha = 90$, $\beta = 110{\cdot}59(1)$, $\gamma = 90°$, and $Z = 4$. The intensities of 1943 observed reflections were measured on a Hilger-Watt four-circle diffractometer using Cu-K_α radiation out to a θ angle of 76°. The structure was solved by direct methods using MULTAN. Refinement was by block-diagonal least-squares with anisotropic temperature factors, and the hydrogen atoms were located from a difference map. The final R-value with the hydrogens included in the computation was 6·4%. All bond lengths and angles are close to the expected values for (**6**).

In the mass spectrum of (**6**) the molecular ion peak is minute and the main fragmentation derives from the $M + 1$ ion at m/e 221 (4%) (**8**) to give m/e 164 (100%) ($M + 1$ — Bu^t), followed by loss of Me• and CO.

Formation of (**6**) can be attributed to intramolecular coupling of (**3**) to give the strained cyclobutane (**7**) which rearranges as indicated, *i.e.* (**5**) → (**3**) → (**7**) → (**6**).

Another minor product (0·5%) identified in the reaction mixture is the phenol (**9**) which may be formed by the addition of benzene to an excited carbonyl group followed by deoxygenation.

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† Hanovia 500 S mercury vapour lamp, 6 h at 20° under N_2.

[1] C. M. Orlando, H. Mark, A. K. Bose, and M. S. Manhas, *J. Amer. Chem. Soc.*, 1967, **89**, 6527.
[2] S. Farid, *Chem. Comm.*, 1971, 73.
[3] S. Farid, *Chem. Comm.*, 1970, 303.
[4] J. M. Bruce and A. Chaudhry, *J.C.S. Perkin I*, 1972, 372.
[5] P. Main, M. M. Wolfson, and G. Germain, 'Multan, A Computer Program for the Automatic Solution of Crystal Structures,' University of York, 1971.

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