2,4,6-Tri-t-butylresorcinol and its Diketo-tautomer from Thermolysis of a 3-Hydroxy-4-vinylcyclobut-2-enone

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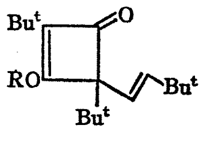
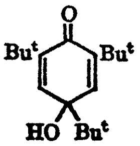
Summary The products of the thermal rearrangement of 3-hydroxy-4-(3,3-dimethyl-*trans*-but-1-enyl)-2,4-di-t-butylcyclobut-2-enone are 2,4,6-tri-t-butylresorcinol and its diketo-tautomer.

IT has been found[1] that a vinylcyclobutenone photoproduct (Ia) can be obtained from the u.v. irradiation of 4-hydroxy-2,4,6-tri-t-butyl-cyclohexa-2,5-dienone (II). While the proof of the structure of (Ia) was being carried out, the thermal instability of this compound was noted. For example, it was found that upon heating a mixture of (Ia) in tetrachlorothiophen to a temperature sufficient to give a homogeneous solution (*ca.* 160°), the n.m.r. spectrum no longer corresponded to that of (Ia). Instead, the solution showed absorptions at δ 6·92 (s, 1H, Ar-H), 5·05 (s, 2H, exchangeable with acid, OH), 1·52 (s, 9H, $\mathrm{Bu^t}$), and 1·30 p.p.m. (s, 18H, $\mathrm{Bu^t}$) plus absorptions corresponding to approximately 10% of the known diketone (III).[2] On the basis of the n.m.r. spectrum and an absorption in the i.r. characteristic of hindered phenols (2·76 μm, sharp), the major component was assigned the structure of 2,4,6-tri-t-butylresorcinol (IVa). To our knowledge, this is the first reported synthesis of this highly hindered resorcinol itself, although both the monomethyl ether derivative[3] (IVb) and the diketo-tautomer[2] (III) of (IVa) have been reported previously. Confirmation of the structure assigned to (IVa) was obtained by analogy when it was found that heating the methyl ether (Ib)[1] in tetrachlorothiophen at 160° gave a compound with an n.m.r. spectrum identical with that reported for the monomethyl ether (IVb).[3]

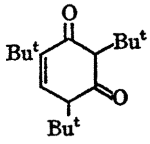


(I)a; R=H, b; R=Me

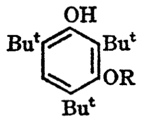


(II)

Although several studies of thermolyses of cyclobutenones have been made,[4] the thermal reorganization of the vinylcyclobutenone (I) to give an aromatic product (IV) represents a type of ring-expansion reaction which, to our knowledge, is without precedent.



(III)



(IV) a; R=H, b; R=Me

Varying ratios of (III) and (IVa) could be obtained when the thermolysis of (Ia) was carried out under other conditions [*e.g.*, heating (Ia) to its melting point or heating a solution of (Ia) in t-butyl alcohol in a sealed tube to 130—140°], thus suggesting that it might be possible for (III) and (IVa) to exist in equilibrium together.† We found that a solution of (III) in tetrachlorothiophen containing a drop of pyridine gave a 60 : 40 mixture of (III) and (IVa) upon heating for 20 min. at 133°. Moreover, under identical heating conditions, a 15 : 85 mixture of (III) and (IVa) in tetrachlorothiophen containing a drop of pyridine afforded a 40 : 60 mixture of (III) and (IVa). Further heating of either sample in an attempt to approach the equilibrium more closely caused considerable degradation.

Models indicate that the diketo compound (III) has considerably less steric hindrance between adjacent t-butyl and carbonyl groups than exists between adjacent t-butyl and hydroxy-groups in the resorcinol (IVa). The aromatic resonance stability of (IVa) is thus apparently offset by destabilization of (IVa) relative to (III) due to steric hindrance, thereby causing (III) and (IVa) to be of approximately equal stability. There have been reported a limited number of examples in which both a monocyclic phenol or resorcinol‡ and its keto-tautomer have been prepared.[3,5] However, in no other system that we are aware of involving a monocyclic phenol or resorcinol are there major amounts of both the keto- and enol tautomers at equilibrium.

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† Matsuura and Ogura[2] had commented on the stability of (III), noting that it does not tend to aromatize either in the crystalline state or in neutral or weakly acidic solvents.

‡ Keto-tautomers of hydroquinones[6] and certain fused-ring aromatic systems[7] have also been prepared.

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