Generation and Trapping of 1,4-Diphenyl-2,3-naphthaquinone

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Summary Lead tetra-acetate oxidation of 1,4-diphenyl-2,3-dihydroxynaphthalene normally results in oxidative trimerisation but this process is suppressed and the intermediate 2,3-naphthaquinone trapped by corresponding oxidation in butadiene at −40°.

DESPITE some early attempts[1] no simple derivative of 2,3-naphthaquinone (I; R = H) has been prepared. In addition to their possible valence tautomerism with (II) and (III)[2] such high potential quinones would be of interest as dehydrogenating agents.[3] We have accordingly attempted to prepare the stabilised derivative (I; R = Ph).

The 2,3-dihydroxynaphthalene (IV; R = H) selected as starting material was prepared by dehydration (HCl–HOAc) of the 1,3-diphenylbenzo[*c*]furan–vinylene carbonate adduct.[4] Oxidation of (IV; R = H) with silver oxide[5] resulted in a novel oxidative trimerisation to the *cis–trans* isomers (V) and (VI). In accord with formulation as in (V) and (VI), the trimerides are cleaved by $Pb(OAc)_4$ to *different* bis-lactones (ν_{max} 1775 cm^{-1}) of gross structure (VII). The major oxidation product is allocated the less stable[6] *cis-anti-trans*-geometry (V) since its n.m.r. spectrum shows the presence of two different hydroxyl groups (τ 6·16 and 7·44). On heating in benzene, (V) affords a mixture of trimerides in which the more stable *trans-anti-trans*-isomer (VI) predominates. The n.m.r. spectrum of (V) shows resonance for two hydroxyl groups at τ 6·96. Interconversion of the trimerides presumably proceeds by the expected ready bond-cleavage indicated (V; arrows). The less stable isomer (V) is also the major product obtained on homogeneous oxidation of (IV; R = H) with $Pb(OAc)_4$–CH_2Cl_2. Phenol coupling reactions are known to be subject to kinetic control.[7]

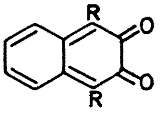
Whereas Ag_2O oxidation of (IV; R = H) may proceed *via* the radical (IV; R = ·) there were indications that the $Pb(OAc)_4$ oxidation involved initial formation of the quinone (I; R = Ph). Thus $Pb(OAc)_4$ oxidation of the mono-acetate (IV; R = Ac) gave the acetoxylation product (VIII; R = OAc) and no trace of the expected dimeride[8] which was however readily obtained by Ag_2O oxidation. Lead tetra-acetate oxidation of (IV; R = H) gave the trimerides (V) and (VI) and no isolable acetoxylation product. The presence of a second free hydroxyl group in (IV; R = H) clearly exerts a profound effect on the course of the $Pb(OAc)_4$ oxidation. This effect is most simply accommodated by assuming the quinone (I; R = Ph) is first formed.

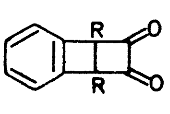
Support for this interpretation is provided by a trapping experiment. Slow addition of (IV; R = H) to $Pb(OAc)_4$ in butadiene at −40° produced a blue colour which faded to yellow on warming to −5°. Product isolation then gave the yellow (λ_{max} 452—453 nm.) adduct (IX) (67%) as well as the trimerides (V) and (VI). The structure of (IX) follows from its n.m.r. spectrum: τ 3·96—5·07 (3H, m, vinyl protons), 6·3 (1H, m, H_a), 6·9 (1H, t, J = 12·5 Hz, H_b or H_c), and 7·5 (1H, dd, J = 5 and 12·5 Hz, H_b or H_c). And is supported by the mass spectrum which shows a very strong peak corresponding to loss of C_2O_2.

The trimerides (V) and (VI) only were obtained in attempted trapping experiments carried out at room temperature. These results are attributed to ready hydrogen transfer reactions to the quinone from (IV; R = H) and/or the trap (*e.g.* norbornadiene) to give an intermediate radical (IV; R = ·) which proceeds to the trimerides (V) and (VI).

Indeed generation of the quinone under non-oxidative conditions shows it to be a potent dehydrogenation agent. Reaction of (IV; R = Ac) with *N*-bromosuccinimide gave the bromide (VIII; R = Br) which with NaOMe in diglyme (20°) gave the trimerides (V) and (VI) together with the dihydroxy-compound (IV; R = H).

These observations suggest that properly stabilised 2,3-naphthaquinones may be useful dehydrogenating agents and that low temperature $Pb(OAc)_4$ oxidation could provide a useful general route to *o*-quinones.


(I)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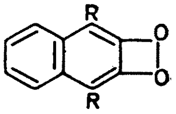
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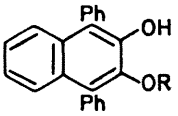

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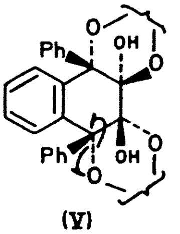
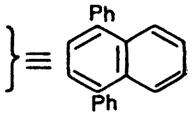
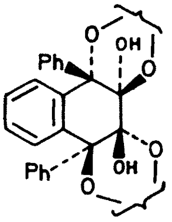
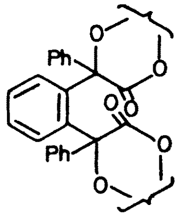


(V)

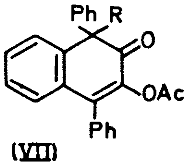




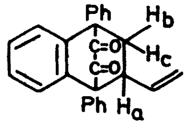
(VI)



(VII)



(VIII)



(IX)

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