Vinylic Quinones from the Base Induced Decomposition of a Quinone–Diazoalkane Adduct

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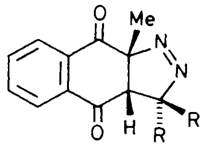
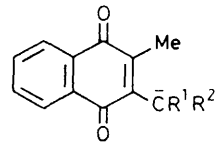
2-Methyl-3-(1-methylvinyl)-1,4-naphthoquinone (**4**) and related compounds have been prepared by the action of base upon the adduct (**1a**), 3,3,9a-trimethyl-3a,9a-dihydro-3*H*-benz[*f*]indazole-4,9-dione, from 2-diazopropane and 2-methylnaphthoquinone.

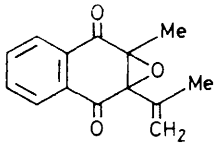
The adduct (**1a**),[1] from 2-diazopropane and 2-methylnaphthoquinone, did not react with sodium acetate to produce the anion (**2a**) in a manner analogous to the production of the anion (**2b**) from the adduct (**1b**).[2] However, it gave the expected instantaneous red coloration and evolution of nitrogen with the stronger base, methanolic potassium hydroxide. The nature of the products of such reactions was strongly influenced by concentration and also by the presence of oxy-



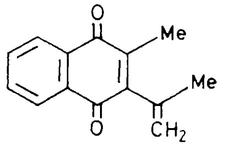
(1) a; R = Me
b; R = H



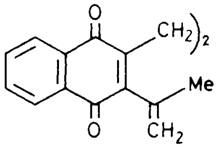
(2) a; $R^1 = R^2 = Me$
b; $R^1 = R^2 = H$
c; $R^1 = H$, $R^2 = Me$



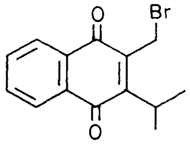
(3)



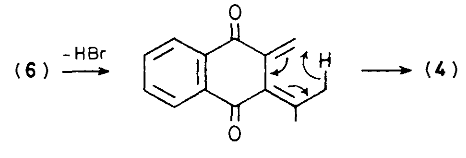
(4)



(5)



(6)

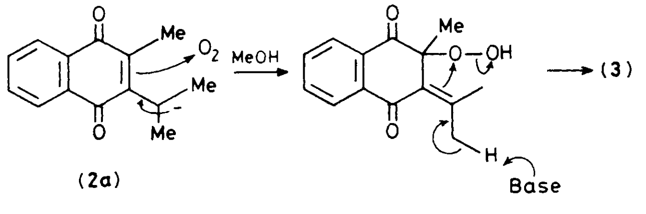


(7)

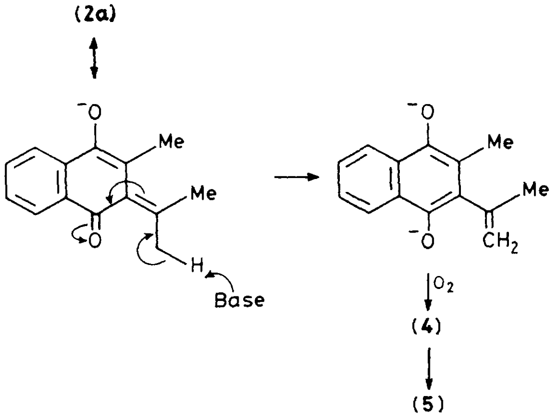
Scheme 1

gen. Dilute solutions yielded mainly the epoxide (3) (white rods, m.p. 84—85 °C)† with only traces of the dimer (5), whereas concentrated solutions yielded the dimer (5) (long yellow needles, m.p. 222—227 °C) in good yield (69%). Since the dimeric quinone (5) was being produced under conditions known to convert methylnaphthoquinones into ethylenebisquinones,[3] it was thought that the monomeric quinone (4) would be an intermediate and it was then isolated as yellow needles (m.p. 75—79 °C) by an acetic anhydride quench of the reaction of adduct (1a) one minute after the addition of base at 0 °C although the yield was never better than 34%.

In contrast to allylic quinones, vinylic quinones are uncommon and (1-methylvinyl)naphthoquinones unknown hitherto. For this reason, we explored alternative syntheses. The 1-methylvinyl substituent could not be introduced into the 2-methylnaphthoquinone moiety by any of the standard methods (12 tried) because they usually failed for steric reasons or because the quinones oxidised the reagents. Flash vacuum pyrolysis of the bromoquinone (6) avoided these problems: the quinone (6) [unstable orange needles, m.p. 88—110 °C (decomp.)(rapid heating)] was obtained quantitatively from 2-methyl-3-isopropylnaphthoquinone and *N*-bromosuccinimide and upon flow pyrolysis (nitrogen as carrier) at 650 °C and 4 × 10^{-2} mm Hg, followed by chromatography, gave the monomeric quinone (4) but only in very low yield (5—10%). This reaction requires both elimination to form a xylylene (7) and sigmatropic rearrangement to give (4) (Scheme 1).



Scheme 2



Scheme 3

The formation of a vinylic quinone and an epoxide from the anion (2a) contrasts with the products[2] obtained from the anions (2c) which included no similar species. Quinone epoxides are generally synthesized from the quinone and alkaline hydrogen peroxide,[4] but it is probable that an unusually easy nucleophilic oxygen capture is responsible in the present case (compare Baxter *et al.*[5]) since the red colour of (1a) in alkali under argon is rapidly discharged by oxygen and only then can the epoxide (3) be detected (Scheme 2; radical equivalents are also possible). A similar loss of a proton to form a vinyl quinonoid intermediate (Scheme 3) has been assumed elsewhere,[6] so the isolation of quinones (4) and (5), in which the 1-methylvinyl groups are intact, now confirms this suggestion.[6] The stability of these quinones is partly a result of the inability of the 1-methylvinyl group to attain coplanarity with the quinone ring. Thus, the u.v. spectra of the quinones (4) and (5) show no additional conjugation and the vinyl groups resist hydrogenation since both sides of the double bond are flanked by substituents.

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† Satisfactory u.v., i.r., n.m.r., mass spectral, and elemental analyses were obtained for the new compounds (3), (4), and (5).