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THE ISOMERISATION OF METHYLENEDIQUINONES BY BASES

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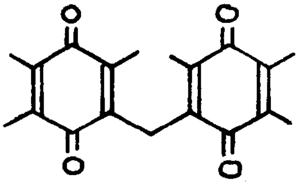
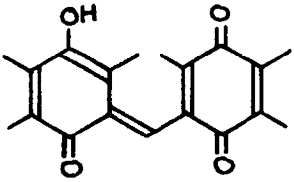
Smith, Davies, and Sogn (1) noted that bases isomerise the tetramethylmethylenedibenzoquinone (I) to a red substance which they studied in some detail because they believed it to have structure (II) and thus to be the first isolable 'pentad enol' (Fuson's nomenclature (2)). However, this structure does not adequately explain the stability of the substance to hydrogenation (which occurs only slowly even at high pressures at 170°) and to acids and bases, which should have been capable of regenerating to some extent the original compound (I). We suggest, therefore, that the reaction is related to the base-catalysed cyclisation of allylquinones to chromens (3), i.e. that the base removes a proton from the active methylene group giving an anion (III) which is capable of cyclising as shown thus affording the xanthen derivative (IV).



I



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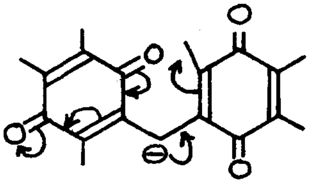

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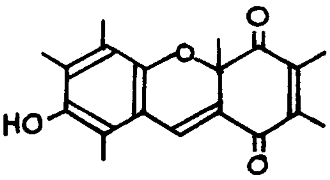
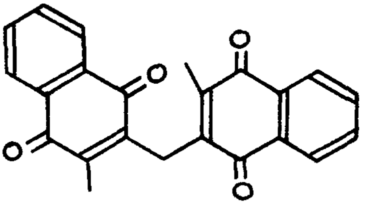
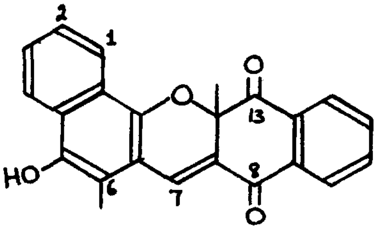


IV

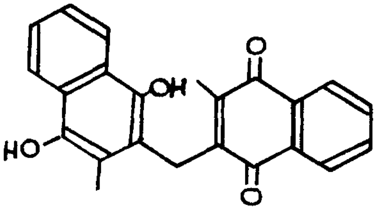
During another study (4) we had noticed that the methylenedinaphthaquinone (V) also rapidly reddens in alkali. For preparative purposes the dinaphthaquinone (0.25 g.) in pyridine (10 ml.) was kept at 60° for 40 min., whereafter evaporation of the solvent *in vacuo* and crystallisation of the residue from benzene gave 8,13-*dihydro*-5-*hydroxy*-6,13a-*dimethyl*-8,13-*dioxodibenz* [*b*, *h*] *xanthen* (VI) as scarlet prisms (0.21 g.), m.p. 196-197°, λ_{max} (ethanol) 237, 264, 313, 366 and 486 nm. (logε 4.60, 4.20, 4.14, 3.99, 3.88), ν_{max} (KBr) 3370 (OH), 1709 (C-13 carbonyl), and 1650 cm.$^{-1}$ (C-8 carbonyl) (Found: C, 77.7; H, 4.5. $C_{23}H_{16}O_4$ requires C, 77.5; H, 4.5%) Acetic anhydride and pyridine gave the *acetate*, which separated from ethanol as orange plates, m.p. 210-211°, ν_{max} (KBr) 1751 (acetate carbonyl), 1710 (C-13 carbonyl), and 1655 cm.$^{-1}$ (C-8 carbonyl) (Found: C, 75.4; H, 4.7. $C_{25}H_{18}O_5$ requires C, 75.4; H, 4.6%).



V



VI



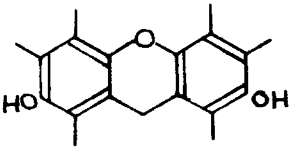
VII

The i.r. absorption bands near 1710 cm.$^{-1}$ eliminate structures similar to (II) for the new compound but are consistent with structure (VI) since this contains a simple benzoyl carbonyl group as part of an α-ketol system so orientated as to absorb at frequencies rather higher than usual (5). The n.m.r.

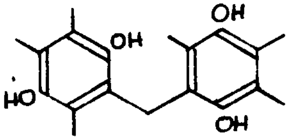
spectrum of the acetate in deuteriochloroform further supports structure (VI) by displaying bands of the appropriate intensities at τ 7.68 (acetate Me), 7.55 (C-6 Me), and 8.43 (C-13a Me). A singlet at 2.05 corresponds to the proton at position 7, while all other low field resonances are multiplets corresponding to aromatic protons.

Like the analogue (IV), the new compound is relatively stable towards heat and acids. It dissolves in aqueous alkali to give a deep red solution. It resists hydrogenation on platinum catalysts at 100 atm. and 40°, perhaps because the molecule is not planar but forms a shallow V-shaped arrangement the inside of which cannot readily lie flat on a catalytic surface and the outside of which is protected by the projecting angular methyl group. In agreement, the compound is readily reduced by borohydride though in a complex manner not yet understood. The existence of an α-ketol arrangement as in structure (VI) is convincingly supported by the rapid and quantitative reduction by zinc and acetic acid, which gives the quinhydrone (VII) described earlier (4).

The slow hydrogenation of the substance to which we now assign structure (IV) was found by the earlier workers to give the xanthen derivative (VIII), a change that is not a simple reduction. However, fission of the α-ketol system should produce the diquinol (IX) from which the xanthen (VIII) would be produced by a dehydration spontaneous at the temperature (170°) employed.



VIII



IX

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