Preparation and Solvolysis of Dispirotetraenediones

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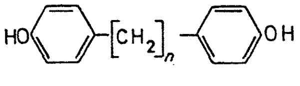
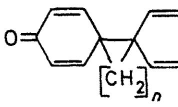
Summary Dispiro[5,0,5,4]hexadeca-1,4,8,11-tetraene-3,10-dione and a lower homologue, prepared by oxidation of the appropriate diphenols, decompose in neutral alcoholic solutions to give benzylic ethers arising, apparently, from quinone methide intermediates.

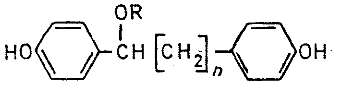
OXIDATION of the diphenol[1] (I; $n = 4$) with potassium ferricyanide (two-phase system, sodium hydroxide–benzene) gave the bisdienone (II; $n = 4$), m.p. 85° (decomp.), in 15% yield. Oxidation of the corresponding monobenzyl ether gave products lacking significant carbonyl absorption, supporting the suggestion[2] that cyclisation involves coupling of a diradical rather than radical or oxonium ion substitution. The product (II; $n = 4$), λ_{max} (EtOH) 240 nm. (ϵ 22,000), ν_{max} ($CHCl_3$) 1665, 1625 cm.$^{-1}$, τ ($CDCl_3$) 2·91 and 3·71 (J 10 Hz.), decomposed[3] at room temperature in the solid state to give an insoluble, polymeric product lacking carbonyl absorption. A dilute solution in neutral ethanol remained unchanged (u.v. control) for several days at 20° but at 74° (sealed tube, under N_2) the absorption at 240 nm. diminished, $t_{\frac{1}{2}} = 55$ min., and was replaced by phenolic absorption at 281 nm. The decomposition rate was not significantly different in acid-washed or alkali-washed tubes. The major (50% yield) crystalline product was the benzylic ether (III; R = Et, $n = 3$), m.p. 135—140° (decomp.). The structure followed from the appearance of a methine proton triplet, τ [$(CD_3)_2SO$] 5·86, in the n.m.r. spectrum and a fragment ion m/e 151·0759 ($C_9H_{11}O_2$ requires 151·0759) in the mass spectrum. In confirmation, catalytic (Pd/C, $HClO_4$) hydrogenation in ethyl acetate gave the parent diphenol (I; $n = 4$). An analogous ether (III; R = Me, $n = 3$), m.p. 162—165°, was obtained (82%) from the decomposition of the bisdienone (II; $n = 4$) in methanol. The structure of the products (III) suggests their formation from a quinone methide intermediate (IV). This could arise by intramolecular hydrogen transfer in a diradical (V) or dipolar species formed thermally by cleavage of the bond linking the dienone rings.



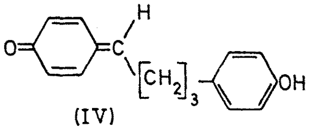
(I)



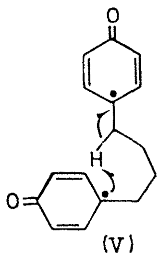
(II)



(III)



(IV)



(V)

Similar observations were made with the bisdienone (II; $n = 3$), λ_{max} (EtOH) 234 nm. (ϵ 19,200) and 258 nm. (ϵ 15,700), ν_{max} ($CHCl_3$) 1665, 1625 cm.$^{-1}$, τ ($CDCl_3$) 3·05 and 3·71 (J 10 Hz), prepared by oxidation (20% yield) of the diphenol[1,4] (I; $n = 3$). Catalytic hydrogenation of the dienone regenerated the diphenol. Decomposition in neutral ethanol at 74° was much slower, $t_{\frac{1}{2}} = 40$ hr., than for the higher homologue although, again, polymerisation occurred in the solid state at room temperature. The expected benzylic ether, m.p. 219—220° (III; R = Et, $n = 2$) was obtained from the reaction mixture but only in low yield (8%) suggesting that hydrogen transfer *via* a five-membered rather than a six-membered transition state competes less successfully with polymerisation of a diradical or dipolar intermediate.

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