Trapping of Dopaquinone with Cyclopentadiene

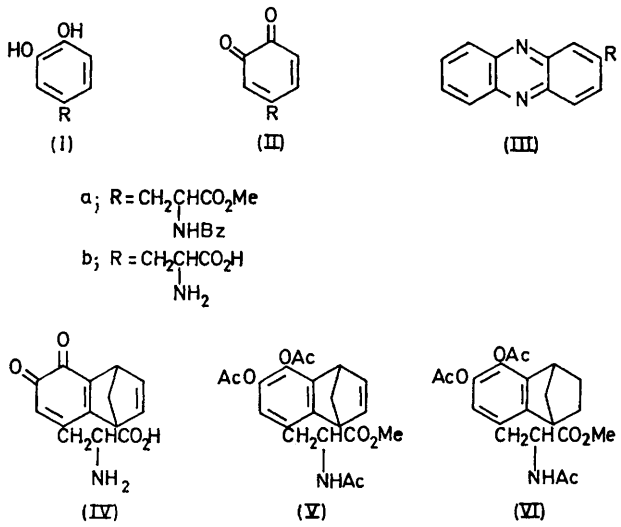
By YOSHIMORI OMOTE* and TOSHIHIKO KOMATSU

(*Department of Chemistry, University of Tsukuba, Sakura, Niihari, Ibaraki, 300–31 Japan*)

Summary Dopaquinone is chemically trapped in the form of adduct (IV) with cyclopentadiene; the structure is confirmed as being based on (VI).

RAPER[1] has suggested the intermediacy of dopaquinone (IIb) in the melanogenesis of dopa. Compound (IIb) is very labile and easily cyclized into the corresponding indoline and has never been synthesized or trapped in spite of many reports on *ortho*-benzoquinones.[2]

Dopa is protected by methylation and benzoylation and then oxidized by cerium(IV) sulphate to give a dark red oil having u.v. and n.m.r. spectra typical of a 4-substituted



orthoquinone, which is condensed with *o*-phenylenediamine into the crystalline phenazine derivative (IIIb) (m.p. 211—212). The corresponding derivative (IIIa) cannot be obtained by similar oxidation of dopa.

We have now modified the method of Evans *et al.*[3] and have trapped (IIb) produced by oxidation with *o*-chloranil in the presence of cyclopentadiene, to give the unstable product (IV), which after acetylation with acetic anhydride–pyridine–methanol (13 : 2 : 2 v/v) gives the stable compound (V). The structure of (V) is confirmed after quantitatively changing into (VI) (glassy solid) by catalytic hydrogenation over platinum oxide in acetic acid [(VI), $C_{21}H_{25}NO_7$(M^+ 403), λ (EtOH) 267(ϵ 610), 274(627) nm, ν (KBr) 1770, 1750, 1660 cm^{-1}, δ, 1·0—2·1(6H,m), 1·97(3H,s), 2·23(3H,s), 2·28(3H,s), 3·06(2H,d), 3·46(2H,m), 3·67(3H,s), 4·81(1H, br q), 6·30(1H, br d), 6·60(1H, s)].

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