Synthetical Approaches to Simple Derivatives of *as*-Indacene

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as-INDACENE (I) has been the subject of much theoretical study[1], but as yet, both the parent compound and its simple derivatives have eluded synthesis. 11,12-Diphenylindeno[2,1,-*a*]fluorene has been reported[2] but the *as*-indacene group involved in this molecule is so heavily perturbed,[3] that correlation between its properties and those predicted for *as*-indacene itself is unlikely to be profitable. (I) is expected to be highly reactive, particularly at C-1 and C-4,[1c] so we set out to prepare a derivative in which the *as*-indacene system is perturbed only by one benzenoid ring fused across C-4–C-5. We now report the synthesis of two isomeric dihydrobenz[*e*]-*as*-indacene-7,10-diones, (II) and (III), which are potentially tautomeric with the *as*-indacene (IV).

Treatment of the known[4] 1 : 1 Diels–Alder adduct of 1,1′-bicyclopentenyl and *p*-benzoquinone with alcoholic sodium hydroxide followed by oxidation of the quinol (V) so obtained with silver oxide in ether affords a quantitative yield of the unstable quinone (VI), m.p. 129—131°; ν_{max} (Nujol) 1650, 1595, 1295, 845 cm.$^{-1}$; λ_{max} (cyclohexane) 250 mμ (log ϵ 4·14), 366 (3·10), sh 430 (1·78). The latter readily undergoes disproportionation reaction in benzene solution at room temperature to give a black crystalline quinhydrone complex which dissociates in acetone yielding the quinol (V), 34%, m.p. 155—157° and the naphthaquinone (VII), 45%, m.p. 196°; ν_{max} (Nujol) 1648, 1609, 1560, 1283, 861 cm.$^{-1}$; λ_{max} (cyclohexane) 216 mμ (log ϵ 4·58), 253 (4·33), 262 (4·21), 3·67), 455 sh (2·07). The n.m.r. spectrum of (VII) (CDCl$_3$) was consistent with the assigned structure [τ 3·01 (s, 2H); 6·58, (t, J 8 c./sec., 4H); 7·10, (t, J 8 c./sec., 4H); 7·80 (m, 4H)]. The hydroquinone (V) gives the known[4] diacetate (VIII) with warm acetic anhydride. Treatment of the naphthoquinone (VII) with two molar equivalents of *N*-bromosuccinimide in carbon tetrachloride yields (reflux, ten days) a mixture of two double bond isomers of dihydrobenz-[*e*]-*as*-indacene-7,10-dione, separable by chromatography on silica gel. The major product (orange), 30%, m.p. 150—190° (decomp.), showed ν_{max} (Nujol) 1648, 1605, 1573, 1540, 865 cm^{-1}, λ_{max} (cyclohexane) 248 mμ (log ϵ 4·34), 288—312, (broad band with fine structure, log ϵ 4·0—3·8), 396 (3·69), 426 sh (3·59) and n.m.r. absorption (CDCl$_3$) at τ 3·2 (m, 6H) and 6·2 (m, 4H). The i.r. spectrum of the minor product (red), 20%, m.p. 150—170° (decomp.), was identical with that of the major product except for additional bands at 1420 and 900 cm.$^{-1}$. It showed λ_{max} (cyclohexane) 249 mμ (log ϵ 4·34) 279—315 (broad band with fine structure, log ϵ 4·08—3·85), 420 (3·66), 450 sh (3·49) and n.m.r. absorption (CDCl$_3$) at τ 3·2, (m, 6H); 4·3 (m, 2H), and 6·6 (m, 2H). This data is consistent with the assignment of structures (II) and (III) for the major and minor products respectively.

We were unable to detect, under a wide variety of conditions, including ultraviolet irradiation, any evidence that either isomer was in equilibrium with the tautomer (IV). Furthermore, all attempts to obtain derivatives of the diones (II) and (III) in the *as*-indacene form have been unsuccessful.

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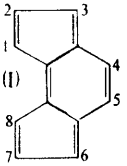
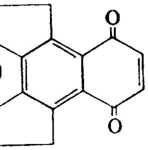
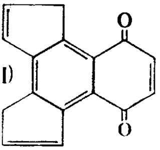
(I)



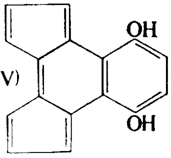
(II)

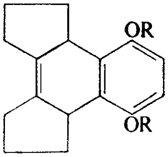


(III)



(IV)

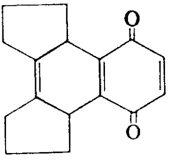




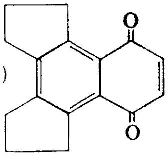
(V) R=H

(VIII) R=OAc

(VI)



(VII)



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