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SYNTHESIS OF QUININDINE DERIVATIVES: ISOELECTRONIC ANALOGUES OF BENZAZULINES*

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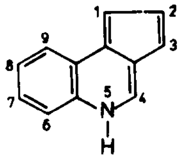
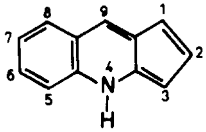
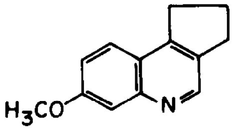
In view of a recent publication describing the synthesis of substituted 4-H-β-quinindines[1], we wish to report our work on the synthesis of some 5-methyl-5H-α-quinindine and 4-methyl-4H-β-quinindine derivatives. The parent ring systems (I) and (II) represent non-alternant 14πelectron systems which are isoelectronic with benzazuline.



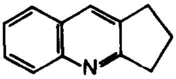
(I)



(II)



(III)



(IV)

In a recent communication[2] we have reported the synthesis of 7-methoxycyclopenteno[c]quinoline (III) and cyclopenteno[b]quinoline (IV) has also been reported earlier[3]. These may be regarded as dihydro derivatives of the respective quinindine ring systems (I) and (II). It was expected that prototropic

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shift in dehydro-quinindines, obtained by dehydrogenation of (III) and (IV), would lead to the ring systems (I) and (II). However, all attempts to introduce a double bond in the cyclopenteno residue in (III) and (IV) by treatment with NBS and subsequent dehydrobromination by various bases like triethylamine, DMF, collidine, $LiCO_3$, NaOMe failed. Catalytic dehydrogenation of (III) by treatment with Pd/C in boiling p-cymene was also unsuccessful whereas treatment with DDQ gave charge-transfer complexes.

Another approach to facilitate the removal of hydrogen atoms from the cyclopenteno ring in (III) and (IV) was to quaternize these quinolines. With this end in view, 7-methoxy-5-methyl-cyclopenteno[c]quinolinium iodide (V)[2] and 4-methyl-cyclopenteno[b]quinolinium iodide (VI)[3] were prepared by interaction of (III) and (IV) with methyl iodide. When (V) was treated with two molar equivalents of chloranil in methylene chloride and the resulting product chromatographed over neutral alumina, a deep green compound was obtained, which crystallised from methanol-benzene in emerald green rhombic crystals (slowly blackens above 300°). The structure (VII), $C_{26}H_{11}NO_5Cl_6$[†] [IR (Nujol) ν cm^{-1}: 695 (s); 1000 (s), 1160 (s), 1220 (s), 1350 (m), (bands characteristic to 1:3 disubstituted azulenes[4]); 1680 (s) (quinone). PMR, 60 Mc, CF_3COOH, TMS, δppm: OCH_3(4.31, singlet, 3p), N-CH_3(4.75, broad singlet, 3p), aromatic protons (6.9-8.6, multiplet, 4p), C_4H(9, singlet, 1p). Visible spectrum: λ_{max}^{DMSO} mμ (log ϵ): 710(3.58), 435(3.84).] was assigned to this compound.

Interaction of two molar equivalents of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) with (V) in boiling acetonitrile gave compound (VIII) containing two DDQ residues. Compound (VIII) on recrystallisation from acetonitrile-benzene afforded greenish rhombic crystals (dec. temp. 290-330°). The structure (VIII), $C_{30}H_{11}N_5O_5Cl_2$ [IR(Nujol) ν cm^{-1}: 1020 (m), 1210 (s), 1250 (s), 1370 (s); 1640 (s) (quinone); 2200 (w) (-CN). PMR, DMSO-d_6, δppm: OCH_3 (4.16, singlet, 3p), N-CH_3 (4.6, singlet, 3p), aromatic protons (7.5-9.3, multiplet, 5p). Visible spectrum λ_{max}^{DMSO} mμ (log ϵ): 660 (3.6).] was assigned

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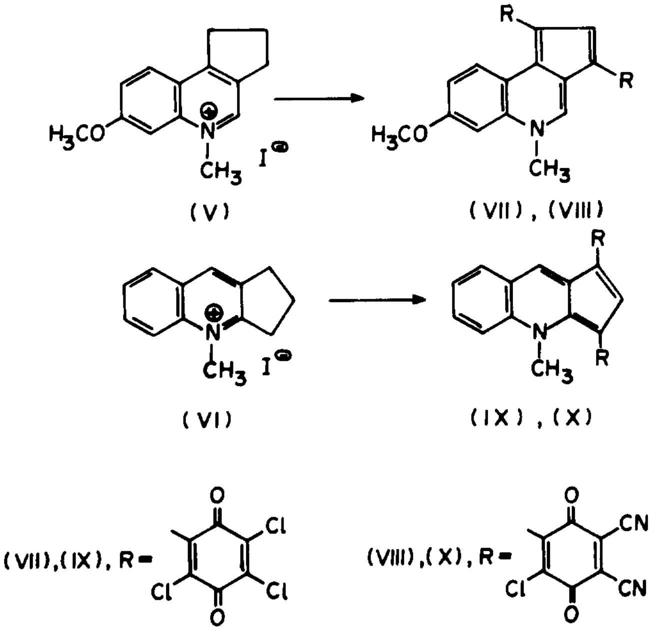
[†] All new compounds gave satisfactory elemental analysis.

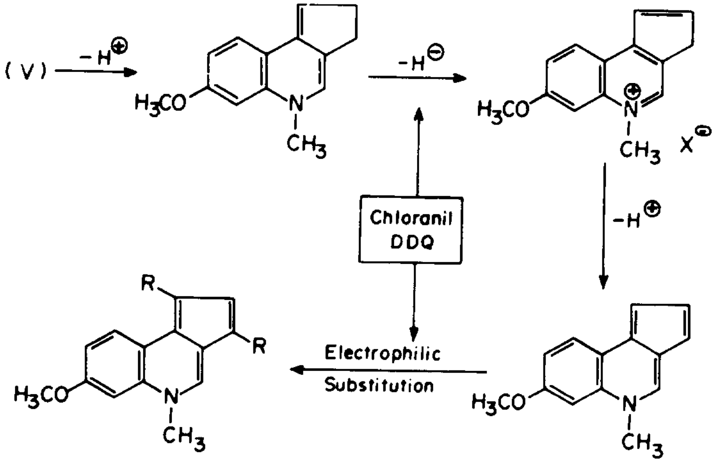


to this compound.

The methiodide (VI) on treatment with chloranil as above also gave the corresponding substituted linear quinindine derivative (IX). Compound (IX) on recrystallisation from benzene-petroleum ether gave dark green rhombic crystals m.p. >340° (dec.). The structure (IX), $C_{25}H_9NO_4Cl_6$ [IR (Nujol) ν cm^{-1}: 695 (m); 1050 (s), 1175 (s), 1240 (s), 1370 (s); 1680 (s) (quinone). PMR, $AsCl_3$, δppm: N-CH_3 (4.16, singlet, 3p), aromatic protons (7.66-8.75, multiplet, 6p). Visible spectrum λ_{max}^{DMSO} mμ (log ε): 710 (3.77)] was assigned to this compound.

Similarly methiodide (VI) on treatment with DDQ in acetonitrile gave (X). The structure (X) is confirmed by IR, PMR and visible spectra.

The formation of (VII) and (VIII) by the reaction of (V) with chloranil and DDQ may be explained as follows:



The synthesis of (IX) and (X) by interaction of (VI) with chloranil and DDQ may also follow a reaction path analogous to the above scheme.

To our knowledge, the above is the first example of dehydrogenation of a hydroaromatic heterocyclic quaternary salt by chloranil or DDQ. It is interesting to note that the stable cationoid heterocyclic ring systems (V, VI) have been converted by the above procedure to the non-alternant 14 π electron systems (VII-X), wherein the highly reactive aromatic substrate formed by dehydrogenation undergoes electrophilic substitution. The positions of electrophilic substitution C_1 and C_3 conform to the reactivity predicted by HMO calculations of $14\pi^5$ and $10\pi^6$ electron systems.

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