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REACTION OF DUROQUINONE WITH DIAZOMETHANE: FORMATION OF TRICYCLO[5,1,0,$0^{3,5}$]OCTANE DERIVATIVES

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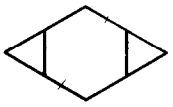
It has been reported previously (1) that duroquinone, in contrast to many other p-quinones (2,3), reacts with diazomethane by direct addition at the carbonyl groups. We have reinvestigated this system and find that, in fact, the reaction proceeds by addition to the olefinic centres of the duroquinone. New structural formulas are assigned to each of the compounds arising from the reaction and a convenient method is elaborated for the synthesis of potentially interesting derivatives of the little-known tricyclo[5,1,0,$0^{3,5}$]octane, I (4).

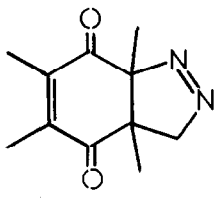


I

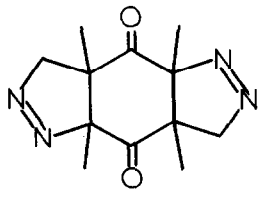
The interaction of duroquinone and diazomethane in cold ethereal solution in the manner described by Smith and Pings (1) leads to the formation of four principal products. Two of these have the composition, $C_{11}H_{14}O_2N_2$, corresponding to monoadducts and the other two are the corresponding diadducts, $C_{12}H_{16}O_2N_4$.

One of the monoadducts is isolated as an unstable yellow oil which has not been obtained crystalline. Its ultraviolet and infrared spectra:

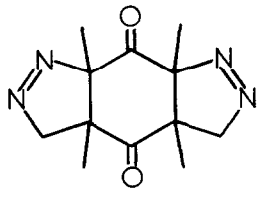
λ_{max}^{EtOH}252 mμ(ε13,500); $\nu_{max}^{CHCl_3}$1667 cm^{-1}(>C=O) and 1550 cm^{-1}(-N=N-), are consistent with its formulation as the Δ^1-pyrazoline,II, formed by addition of diazomethane to the quinonoid double bond in the usual manner (2,3). The second monoadduct, obtained readily as a bright yellow, crystalline solid, m.p. 103°, exhibits absorption bands in the ultraviolet at λ_{max}^{EtOH}226 mμ (ε12,500), 248 mμ(ε13,800) and in the infrared at $\nu_{max}^{CHCl_3}$ 3336 cm^{-1}(N-H), 1670 cm^{-1}(>C=O) and 1621 cm^{-1}(-C=N-) which are consistent with structure III, isomeric with II, and containing a Δ^2-pyrazoline ring. The proton NMR spectra[1] of the two compounds provide excellent confirmation of these structural assignments. In particular, II shows an AB quartet (δ_A 4.34 ppm, δ_B 5.04 ppm; J_{AB} 17.5 c/s) which may be attributed to the methylene group of the Δ^1-pyrazoline ring whereas III lacks the AB pattern but has two single proton signals at 6.59 ppm(N-H) and 6.73 ppm(-N=C-H).



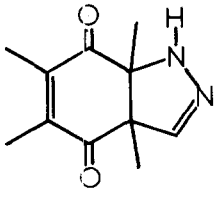
II



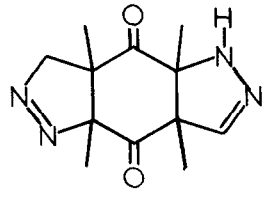
IVa



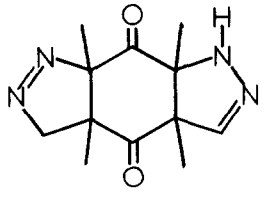
IVb



III



Va



Vb

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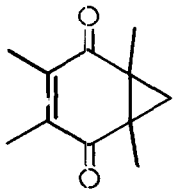
[1] Spectra measured at 60 Mc/sec in $CDCl_3$. Chemical shifts (δ) are reported in ppm from internal tetramethylsilane.

Spectral analysis of the two diadducts supports their formulation also as isomeric dipyrazolines arising from addition of diazomethane to each of the quinonoid double bonds. One, colorless crystals, m.p. 128°(dec.), lacks intense absorption in the ultraviolet, λ_{max}^{EtOH} 333 mμ(ε42.7), but in the infrared absorbs strongly at 1707 cm^{-1}(saturated 6-ring>C=O) and weakly at 1555 cm^{-1}(-N=N-). The NMR spectrum has two sharp singlets for the methyl protons as well as the characteristic AB quartet (δ_A 4.32 ppm, δ_B 5.31 ppm; J_{AB} 18.7 c/s) for the pyrazolino methylene. The other, colorless crystals, m.p. 145°(dec.), also absorbs weakly in the ultraviolet, λ_{max}^{EtOH} 327 mμ(ε450), but now has infrared bands at 3344 cm^{-1}(N-H) and 1708 cm^{-1}(>C=O). The NMR spectrum shows in addition to four non-equivalent methyl singlets, an AB pattern (δ_A 4.29 ppm, δ_B 5.25 ppm; J_{AB} 17.8 c/s) and single proton signals at 6.53 ppm(N-H) and at 6.61 ppm (N=C-H). On this basis, the former compound (m.p. 128°) is assigned structure IV, and the latter (m.p. 145°), structure V.

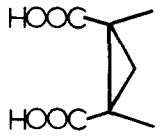
These inter-relationships are confirmed by the fact that quantitative isomerisation of II to III and of IV to V is effected by filtration of their chloroform solutions through a column of alumina (Woelm, neutral, activity III).

Pyrolysis of II yields 1,3,4,6-tetramethylbicyclo[4,1,0]hept-3-ene-2,5-dione, VI, m.p. 60-61°, ν 1663 cm^{-1}. The NMR spectrum of VI shows the expected AB quartet (δ_A 1.05 ppm, δ_B 1.73 ppm; J_{AB} 4.03 c/s) for the non-equivalent cyclopropyl methylene protons. Ozonolysis of VI gives cis-1,2-dimethylcyclopropane-1,2-dicarboxylic acid, VII, m.p. 116-117°(5). Consistent with its formulation as the isomeric Δ^2-pyrazoline, III is strikingly resistant to thermal decomposition (6) but may be converted to VI by refluxing in 20% hydrochloric acid.

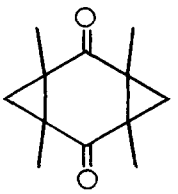
The diadduct IV decomposes on heating at the melting point to give 1,3,5,7-tetramethyltricyclo[5,1,0,$0^{3,5}$]octan-2,6-dione, VIII, m.p. 144-145°, ν1667 cm^{-1}. The NMR spectrum is particularly simple and revealing, consisting of a single methyl signal (1.30 ppm) and a single AB quartet (δ_A 0.81 ppm, δ_B 2.08 ppm; J_{AB} 5.3 c/s) for the cyclopropyl methylenes. Pyrolysis of V proceeds, as to be expected, to give IX, m.p. 129-130°(dec.) and with appropriate spectra.



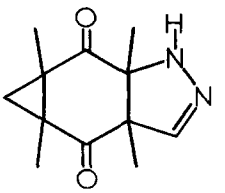
VI



VII



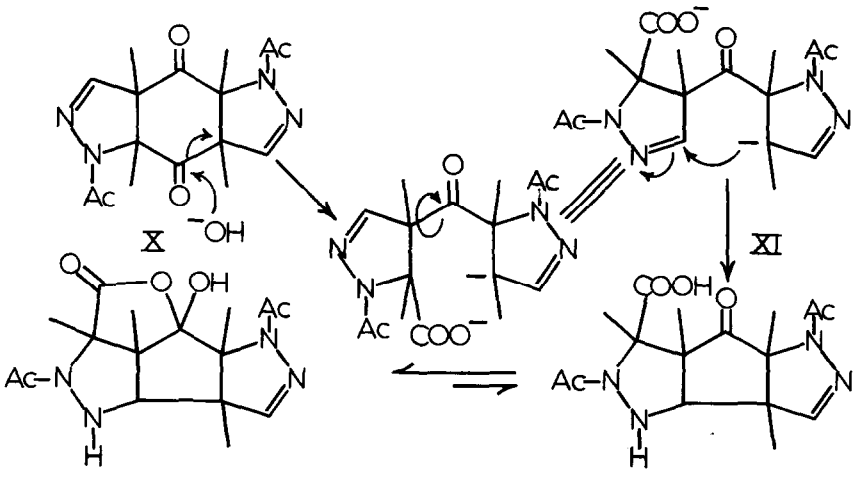
VIII



IX

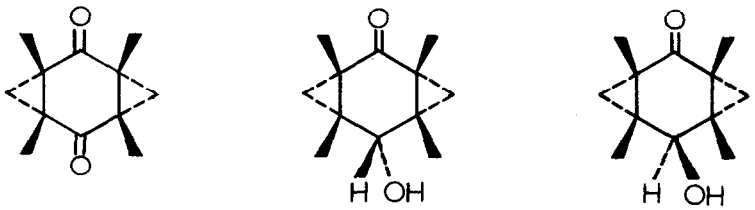
Each of these thermal decomposition products is more readily obtained by photolysis (7) of the corresponding adduct.

The structural ambiguity, IVa vs IVb(and Va vs Vb), which arises from the possibility of two orientations for the addition of the second diazomethane moiety was resolved by the observation that the diacetate X, obtained by acetylation of either IV or V, undergoes hydrolytic rearrangement on heating with dilute aqueous alkali to give the γ-lactol, XIII, $\nu_{max}^{CHCl_3}$ 1786 cm^{-1}. The presence of the central cyclopentanone ring is revealed by the infrared spectra of the sodium salt, ν_{max}^{nujol} 1748 cm^{-1}, and of the methyl ester, ν_{max}^{nujol} 1746 cm^{-1}, of the corresponding keto-carboxylic acid, XII. Rearrangement of the diacetate with formation of a cyclopentanone ring is consistent only with structures IVa and Va, respectively, for the diadducts.



X XI XIII XII

The stereochemical orientation of the rings in the diadducts, IVa and Va, and in their decomposition products, VIII and IX, follows from the formation of two diastereoisomeric mono-keto alcohols, XIV and XV, by partial reduction of VIII. This observation requires the syn-orientation, VIIIa, for the tricyclo-octane derivatives since reduction of the anti-isomer could yield only a single, racemic alcohol. Since it is well established that formation of pyrazolines in this manner proceeds by cis-addition (8), and since one bond remains intact in their decomposition to the corresponding cyclopropane, a syn-orientation of the rings is required of both IVa and Va and also the decomposition product IX.



VIIIa XIV XV

A detailed study of the transformations of the various tricyclo-[5,1,0,$0^{3,5}$]octane derivatives (eg. VIII, XIV, XV) is in progress.

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