Benzynequinone

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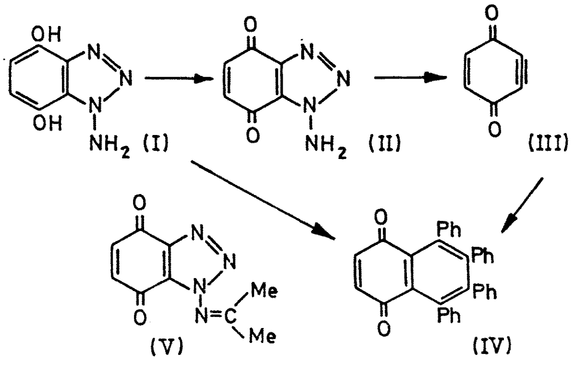
Summary Cyclohex-1-en-4-yn-3,6-dione (benzynequinone) (III) is generated by oxidation of 1-aminobenzotriazole-4,7-dione (II) with lead tetra-acetate, and isolated as 5,6,7,8-tetraphenyl-1,4-naphthaquinone (IV) (40%) from a reaction with tetracyclone.

ALTHOUGH a large number of dehydro-aromatic species have now been reported,[1] no analogous dehydro-quinones appear to have been described. It would be interesting to know how the adjacent quinone carbonyl groups modify the aryne orbitals, especially in view of the possibility of interaction with the filled lone-pair orbitals on oxygen; the geometry of this latter interaction is, for example, very similar to that in 1,8-dehydronaphthalene.[2] These intermediates could also be of value in synthesis, *e.g.* of naturally-occurring quinones. We report the generation and trapping of the simplest of these, cyclohex-1-en-4-yn-3,6-dione or "benzynequinone" (III).

2-Nitro-3,6-dimethoxyaniline, m.p. 77°, was converted by a modification of Trave and Bianchetti's method[3] (successive treatment with nitrous acid, ethyl cyanoacetate, hydrogen and palladium, nitrous acid, and hydrochloric acid) into 1-amino-4,7-dimethoxybenzotriazole, m.p. 117—118°, (40% overall), which was demethylated with boron tribromide in methylene chloride to give 1-amino-4,7-dihydroxybenzotriazole (I) (65%), m.p. >300°.

Silver oxide in tetrahydrofuran containing anhydrous sodium sulphate oxidised a suspension of quinol (I) cleanly at room temperature to give, after filtration and rapid evaporation under reduced pressure, 1-aminobenzotriazole-4,7-dione (II) as an unstable orange-brown oil. This decomposed too rapidly for full characterization but showed typical quinone absorption at 1680 and 1630 cm.$^{-1}$. Its crystalline isopropylidene derivative (V) (50%), m.p. 140—143°, formed by similar oxidation of (I) but in acetone, was more stable and also absorbed at 1680 and 1630 cm.$^{-1}$.



When the oily triazoloquinone (II) was rapidly dissolved in methylene chloride containing 1 equiv. of tetraphenylcyclopentadienone (tetracyclone), and oxidised with lead tetra-acetate, 5,6,7,8-tetraphenyl-1,4-naphthaquinone (IV), orange prisms, m.p. 302—303°, was obtained in 40% yield. The only simple explanation of this result is generation of benzynequinone (III) followed by cycloaddition to tetracyclone and decarbonylation; it thus extends the scope of this oxidative fragmentation route to dehydro-intermediates.[4]

Oxidation of the quinol (I) with lead tetra-acetate in the presence of tetracyclone also gave tetraphenylnaphthaquinone (IV) in higher yield (60%), but the intermediate here could well be 3,6-dihydroxybenzyne rather than benzynequinone (III).

When benzyne and benzynequinone, generated as above from 1-aminobenzotriazole[3] (1 mmole) and 1-aminobenzotriazole-4,7-dione [from the quinol (I) 1 mmole] competed for tetracyclone (1 mmole), much more 1,2,3,4-tetraphenyl naphthalene (80%) than 5,6,7,8-tetraphenyl-1,4-naphthaquinone (8%) was obtained, possibly because benzynequinone is indeed less reactive than benzyne in this [2 + 4]-cycloaddition.

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