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2,4-DI-PARA-METHOXYPHENYLCYCLOBUTADIENE-1,3-QUINONE

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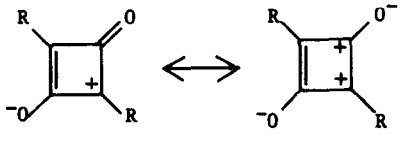
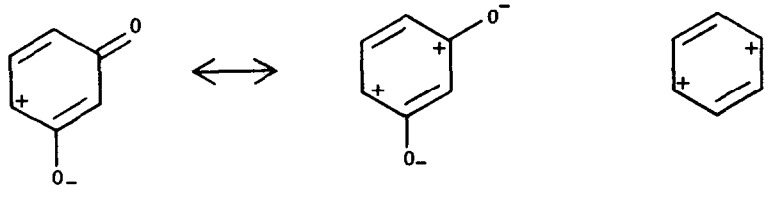
Among the structures of interest related to cyclobutadiene (I), the corresponding dication (II) has been the object of synthetic efforts because of its potential stability as a dication with a closed shell π electron configuration (1,2). We report here the synthesis of a substituted cyclobutadiene-1,3-quinone (III), a zwitterionic system formally related to closed shell dication (II) in the same way that the unknown benzene-1,3-quinone (IV) is formally related to the open shell benzene dication (V).

I II

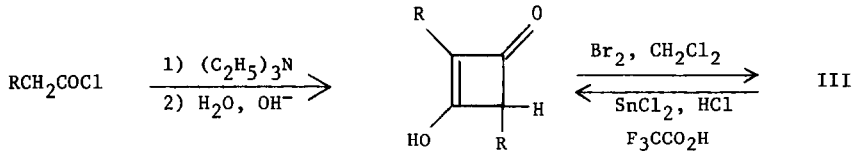


III



IV V

Two groups of workers have assigned structures of type III (R = substituted aromatic or heterocyclic groups) to products obtained by the condensation of squaric acid with highly electron-rich aromatic or heterocyclic compounds (3,4). We chose to attempt the synthesis of III (R = p-methoxyphenyl) by oxidation of the dihydro compound VI, readily available from the reaction of p-methoxyphenylacetylchloride with triethylamine (5). Indeed, treatment of the dihydro compound (VI) with bromine or mercuric oxide in methylene chloride solution gave a 20-50% yield of a highly insoluble, high melting, bromine free, purple, crystalline solid, characterized as (III) (R = p-methoxyphenyl) by the properties and transformations described below.



VI

The substance could be recrystallized from benzonitrile-acetonitrile to give long, deep purple, lustrous needles, m.p. 212-214° (dec.).* The ir spectrum was free from carbonyl absorption higher than 1650 cm^{-1} but had strong, broadened absorption at 1640 and 1590 cm^{-1} consistent with a highly conjugated carbonyl group. The nmr spectrum in trifluoroacetic acid-deuterochloroform gave only one sharp peak for the methoxy protons at τ 5.97 (area = 3.0) and a sharp AB type quartet at τ 2.6 ($\Delta\nu$ = 1.35 ppm, J = 9 cps, area = 4.1), thus establishing the magnetic equivalence of the p-methoxyphenyl groups. The integrity of the four membered ring was demonstrated by the reduction of quinone III (R = p-methoxyphenyl) to its precursor, dihydro-compound VI (R = p-methoxyphenyl), m.p. 166-169°,** in 15-20% yield with stannous chloride in trifluoroacetic acid-hydrochloric acid.

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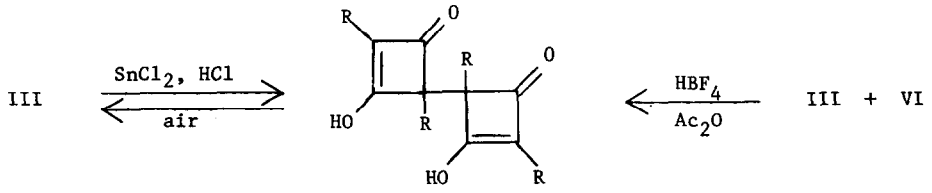
* All new compounds gave satisfactory combustion analyses.

** The melting point of 152-154° reported in our earlier work (5) seems to have been in error. Although the melting point is variable, all later pure samples of the substance have melted somewhere between 165 and 175°. The reduction product was identified by ir comparison.

Attempted reduction in hydrochloric acid solvent alone gave a dimer, VII, m.p. 167°,* which quantitatively reverted to the purple quinone upon exposure to the atmosphere in trifluoroacetic acid-deuterochloroform as judged by nmr analysis of the reacting solution. The dimer could also be obtained by reduction of the purple quinone III with tropilidene in acetic anhydride-fluoroboric acid. The symmetry of the dimer was established by the above reoxidation, by its nmr spectrum in deuterochloroform-trifluoroacetic acid, which gave only two sharp peaks at τ 6.17 and 6.20 for the methoxy protons and two overlapping AB type quartets centered at τ 2.80 and 2.99, and by its independent preparation from an equimolar mixture of quinone III and dihydrocompound VI in fluoroboric acid in acetic anhydride. Neither quinone III nor dihydrocompound VI alone gave dimer VII under these conditions.



VII R = p$CH_3OC_6H_4^-$

Sprenger assigned the structure III (R = p-dimethylaminophenyl) to the deep blue product obtained from N,N-dimethylaniline and squaric acid (4). We have prepared this compound by our method starting with p-dimethylaminophenylacetylchloride hydrochloride. A small yield of a blue crystalline solid, m.p. 290-305° (dec.)** with an ir and uv - vis spectrum identical to those of material obtained by Sprenger's procedure was isolated. The ir spectrum in the carbonyl region was very similar to that of the purple compound. We were unsuccessful in our attempts to prepare the purple quinone from squaric acid and anisole. Thus the two procedures

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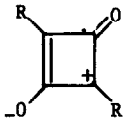
* The dimer crystallized from ethyl acetate with 0.5 equivalents of solvent of crystallization indicated by nmr and combustion analysis.

** Although the recorded melting point is 276° (4), we found that material prepared by either our procedure or Sprenger's had a variable decomposition point in the neighborhood of 300° on a hot stage.

complement one another for the preparation of derivatives of III. The electronic spectra of the two products are compared in Table I.

TABLE I

Electronic Spectra of Derivatives of Cyclobutadiene-1,3-quinone in Chloroform Solution



R = p-$CH_3OC_6H_4^-$	λ_{max}	536	500		348	
	ϵ_{max}	1.41×10^5	4.15×10^4		9730	
R = p-$(CH_3)_2NC_6H_4^-$	λ_{max}	623	416	392	368	314
	ϵ_{max}	3.53×10^5	556	2840	3210	2220

Attempts to prepare the unsubstituted phenyl derivative of III have thus far led to a transient red intermediate which agressively scavenges any nucleophiles present to give derivatives of the dihydro compound VI (R = phenyl).

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