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THE EFFECT OF CYCLOBUTENE RING ANNELATION ON *p*-BENZOQUINONE: SYNTHESIS AND PROPERTIES OF 1,2,3,4,5,6-HEXAHYDROBENZO[1,2:4,5]-DICYCLOBUTENE-3,6-DIONE ([2,3:5,6]DICYCLOBUTA-*p*-BENZOQUINONE)

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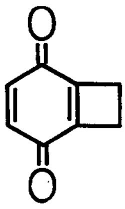
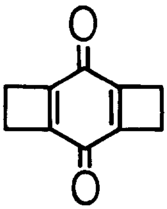
Summary: The title compound has been synthesized, and the effects of strain imposed by mono- and bis-annelation of cyclobutene ring on *p*-benzoquinone are clearly observed in the IR carbonyl absorptions, ^{13}C NMR chemical shifts, and electrochemical reduction potentials.

Benzenoid hydrocarbons annelated with strained small rings have recently received considerable attention.1) It would be also interesting to examine the effects of strain on the properties of quinones in view of their close relation to benzenoid compounds and their potential versatility as synthetic intermediates We have recently reported the synthesis and enhanced Diels-Alder reactivity (at the strained internal double bond) of 1,2,3,6-tetrahydrobenzocyclobutene-3,6-dione (2,3-cyclobuta-*p*-benzoquinone) (1).2,3) To examine in detail the effects of annelation of strained cyclobutene ring on *p*-benzoquinone, it was hoped to synthesize bis-annelated quinone, the title compound 2, which is presently the most strained annelated *p*-benzoquinone. We wish here to report the synthesis of 2 and the effects of strain on the properties of *p*-benzoquinone.

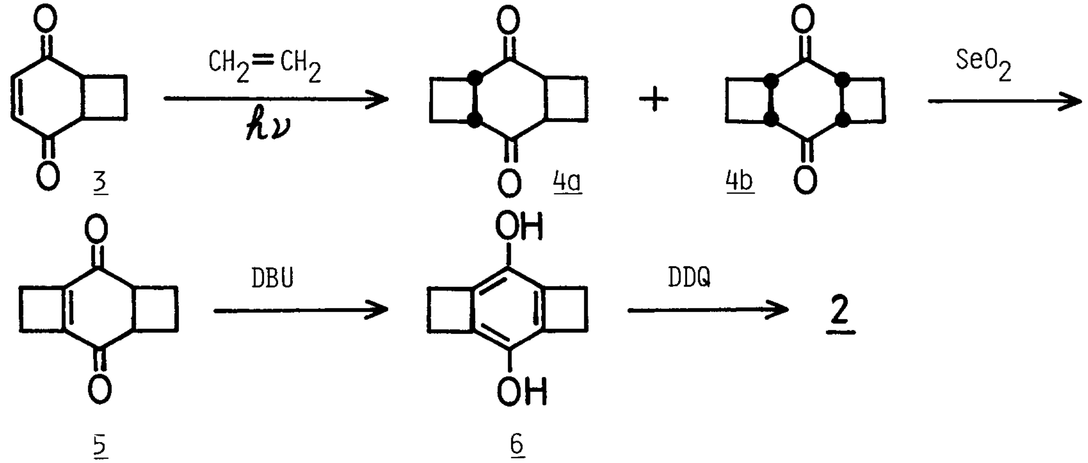


1



2

Photochemical [2+2] cycloaddition of bicyclo[4.2.0]oct-3-ene-2,5-dione (3)2) and ethylene (high pressure Hg lamp, Pyrex filter, CH_2Cl_2, 0°C) gave a mixture of the *anti*- and *syn*-adduct, 4a and 4b (37 and 29% isolated yield, respectively).4) Oxidation of the mixture with selenium dioxide (0.75 molar equiv., ethyl acetate, reflux, 3 h) gave the enedione 5 5) as the major product (40%), which was in turn enolized to the hydroquinone 6 6) by treatment with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (THF, room temp., 83%). Oxidation of 6 with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) in acetonitrile at room temperature provided 2 (yellow needles from CH_2Cl_2-hexane, mp 120-130°C dec.) in 74% yield.



Some of the spectral properties of 2 are as follows: Mass (25 eV), m/e 160 (M^+, 100%), 132 (15%), 108 (44%), 104 (40%), 103 (70%), 80 (43%), 52 (75%); IR (CCl_4) ν_{max} 2980(w), 2930(w), 1670(s), 1583(m), 1332(m), 1162(m), 932(m), 668(m) cm^{-1}; UV (cyclohexane), λ_{max} 261 (log ε 4.22), 270 (4.24), 346 (2.21), 464 nm (1.45); ^{1}H NMR ($CDCl_3$) δ 2.90 s ($J_{^{13}C-H}$=141 Hz).

While not appreciable in the UV spectra, the effects of strain in 1 and 2 are observed in the IR carbonyl frequencies, ^{13}C NMR chemical shifts, and electrochemical reduction potentials which are given in Table 1 compared with some related quinones. The following features are to be noted: (i) The carbonyl frequency of 1 and 2 is significantly higher than that of 2,3-dimethyl-*p*-benzoquinones (Me_2BQ) and duroquinone (Me_4BQ), respectively, and even slightly higher than the parent quinone (BQ). (ii) The carbonyl carbon chemical shifts move upfield with increasing number of cyclobutene ring from a value of 187.0 for BQ

Table 1. IR carbonyl absorptions, ^{13}C NMR chemical shifts, and reduction potentials of 1, 2, and some related quinones.

Compound	IR, ν cm^{-1} [a]	^{13}C NMR, δ [b]				V vs SCE [c]	
		$C_{1,4}$	$C_{2,3}$	$C_{5,6}$ [d]	CH_3 or CH_2	$^1E_{1/2}$	$^2E_{1/2}$
BQ	1671[e] 1659	187.0	136.4	136.4[f]		-0.63	-1.32
Me_2BQ	1659	187.3	141.0	136.2	12.1	-0.79	-1.45
Me_4BQ	1644	187.4	140.4	140.4[f]	12.4	-0.93	-1.48
1	1674	181.9	152.1	137.0[g]	28.6	-0.63	-1.31
2	1670	178.0	151.7	151.7	27.9	-0.66	-1.34

[a] In CCl_4. [b] From internal $(CH_3)_4Si$ in $CDCl_3$. [c] Measured by cyclic voltametry using a glassy carbon electrode; 0.1 M Et_4ClO_4-CH_3CN, sweep rate 40 mV s^{-1}, 25°C. [d] Numbering of 1 and 2 here is based on that of BQ for comparison. [e] Although BQ shows two carbonyl absorptions with nearly equal intensity, the other quinones do almost single strong absorption. [f] Ref. 7. [g] Ref. 2.

to 178.0 ppm for 2, while methyl groups cause little shift. (iii) The bridgehead carbons of 1 and 2 are 11 ∿ 12 ppm downfield compared with the corresponding carbons of Me_2BQ and Me_4BQ. (iv) The reduction potentials of 1 and 2 are less negative (more anodic) than those of Me_2BQ and Me_4BQ, respectively, and are both close to BQ itself. (v) Between 1 and 2, the effects of the second cyclobutene ring appear less significant than those of the first one.

Similar trends on ^{13}C NMR chemical shifts have been observed in series of benzocycloalkenes[8)] and benzo[1,2:4,5]dicycloalkenes[9)] with comparable magnitude of the shifts, and a rehybridization theory put forth by Streitwieser[10)] has been invoked to account for these trends. According to this theory, the σ bonds in the strained ring have increased p-character, whereas the σ bonds directed toward the alpha carbon ($C\alpha$) to the strained ring have increased s-character. This increase in orbital electronegativity causes polarization of σ electrons away from $C\alpha$ which consequently becomes more electronegative, also changing p-bond orders about $C\alpha$. This picture seems also compatible with the high frequency shifts of carbonyl absorptions and the upfield shifts of carbonyl carbons of 1 and 2, although other factors such as geometric distortions of the six-membered ring might be also responsible for. The factors on the chemical shifts of the bridgehead carbons may be more complex in view of less regular trends with size of ring as observed in cycloalkenes and benzocycloalkenes.[8,11)]

The anodic shifts of reduction potentials due to strain in contrast to the usual cathodic shifts by introduction of electron-donating alkyl groups have also been observed in 1,4-naphthoquinones and qualitatively interpreted by the rehybridization theory as well as a perturbation theory.[12)] The present results, thus, confirm the effect of strain on the reduction potentials of *p*-quinones in the parent system. It is interesting that cyclobutene ring annelation causes, as a net result of various influencing factors, only a slight shift in the reduction potentials of *p*-benzoquinone itself.

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References and Notes

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4) 4a: mp 46-48°C; ^{1}H NMR (CCl_4), δ 2.4 (8H, m), 3.6 (4H, m); 4b: mp 79-81°C; ^{1}H NMR (CCl_4) δ 2.3 (8H, m), 3.75 (4H, m). Compound 4a was identical in all respects with the hydrogenation product from bicyclo[4.2.0]octa-3,7-diene-2,5-dione-acetylene photoadduct[13)]
5) Mp 70-72°C; UV (cyclohexane), λ 245 (sh, log ε 4.05), 250 (4.10), 257 (sh, 3.96), 389 nm (1.88); ^{1}H NMR (CCl_4), δ 2.0-2.7 (4H, m), 2.92 (4H, s), 3.38 (2H, m).
6) Mp 246°C dec.; UV (EtOH), λ 221 (sh, 3.96), 276 (sh, 3.06), 282 nm (3.12); ^{1}H NMR ($CDCl_3$-CD_3OD) δ 2.98 (s).
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