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SYNTHESIS OF BICYCLO[4.2.0]OCTA-3,7-DIENE-2,5-DIONE

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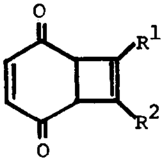
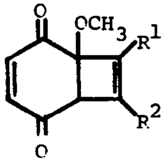
The bicyclo[4.2.0]octa-3,7-diene-2,5-dione 1 is of interest, since 1 is the valence-bond isomer of 1,4-cyclooctatriene dione (1,4-cyclooctatetraenoquinone) and hence could be a potential precursor for it. Recently Yates and Nair have reported the synthesis of dimethyl and phenyl derivative of 1, 2a and 2b, via *p*-benzoquinone-anthracene adducts[1]. Other derivatives, 3a-d, have been also prepared by photoaddition of alkynes to methoxy-*p*-benzoquinone[2]. However, photoaddition of diphenylacetylene to *p*-benzoquinone has been reported to give the adduct 4, presumably by an intermediacy of oxtene[3,4]. We here report the synthesis of the parent compound 1 starting from cyclooctatetraene.



1 $R^1=R^2=H$
2a $R^1=R^2=CH_3$
2b $R^1=H$, $R^2=Ph$



3a $R^1=R^2=Ph$
3b $R^1=R^2=CH_3$
3c $R^1=H$, $R^2=Ph$
3d $R^1=Ph$, $R^2=H$

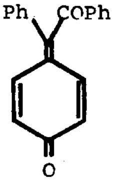


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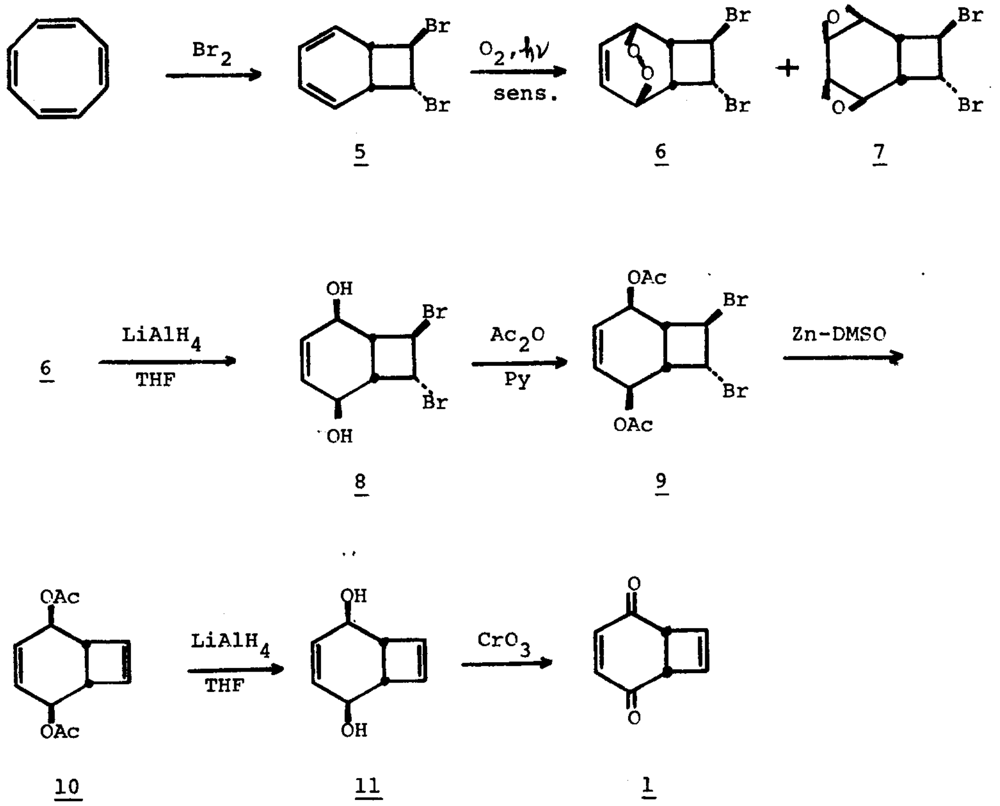
Photo-oxygenation of cyclooctatetraene dibromide 5, *trans*-7,8-dibromobicyclo[4.2.0]octa-2,4-diene[5], in acetone using hematoporphyrin as a sensitizer for 47 hrs gave the epidioxide 6 (colorless prisms, mp 106-107°) and the diepoxide 7 (colorless needles, mp 133.5-134.5°) in 78% and 3.5% yield (from COT), respectively. Reduction of 6 with lithium aluminum hydride in tetrahydrofuran gave the diol 8 (colorless needles, mp 135-136°) in 90% yield. 8 was then converted into the diacetate 9 (colorless prisms, mp 89-90°) by treatment with acetic anhydride in pyridine in 90% yield. Attempts to debrominate from 8 with naphthalene-sodium[6] gave complicate mixtures, however, we could obtain the debrominated product 10 (colorless prisms, mp 69-70°) in quantitative yield by heating of 9 with zinc dust, added with a small amount of iodine, at 90°C in dimethylsulfoxide for 2.5 hrs. Reduction of 10 with lithium aluminum hydride in tetrahydrofuran gave the diol 11 (liquid) in quantitative yield. The desired compound 1 was obtained by oxydation with Jones' reagent (2.2 equivalent) as pale yellow prisms (mp 51-52°) in 66% yield. Thus 1 now can be obtained in 41% overall yield from cyclooctatetraene.



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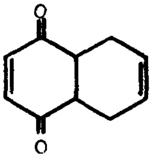

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Table

Spectral Data of 6 - 11

Compound	ir (cm^{-1})	^{1}H-nmr (ppm) (J Hz)[c]	
6	1615, 904, 813 [a]	7.10 ddd (8.0, 6.0, 2.0)	1H
	718	6.69 ddd (8.0, 6.0, 2.0)	1H
		4.80 m	3H
		4.24 m	1H
		3.60 m	2H
7	1265, 941, 854 [a]	4.68 m	1H
	790, 740	4.21 m	1H
		3.55 narrow m	2H
		3.18 m	4H
8	3280, 1260, 1065 [a]	d	
	933, 692		
9	1744, 1729 [a]	6.05 m	2H
	1640	5.54 m	1H
		5.15 m	1H
		4.63 dd (7.5, 1.2)	1H
		4.30 d (7.5)	1H
		3.00 m	2H
		2.09 s	6H
10	1730, 1650 [a]	6.13 s	2H
	1560, 738	5.96 dd (2.8, 1.0)	2H
		5.10 m	2H
		3.02 narrow m	2H
		2.00 s	6H
11	3300, 1640, 1560 [b]	6.10 narrow m	4H
	796, 738, 718	4.25 m	2H
		3.45 br. s (OH)	2H
		3.22 s	2H

a) in KBr disk
b) in liquid film
c) in $CDCl_3$ at 60 MHz
d) Good spectrum has not yet been obtained because of low solubility.

The spectral data for 6 - 11 are listed in the table. The stereochemistry (orientation of the four membered ring) of 6 may be *anti* in analogy with the Diels-Alder adducts of cyclooctatetraene[7]. The chemical shift of the bridgehead protons of 10 (δ 3.02) is 0.20 ppm higher than that of 11 (δ 3.22), indicating the *cis* relationship between the 0-functions and the bridgehead protons and consequently supporting the *anti* configuration of 6.

The mass spectrum of 1 shows the molecular ion at m/e 134 (21%) and fragments at m/e 106 (M-CO, 69%) and m/e 78 (benzene, 100%). The ^{1}H-nmr spectrum ($CDCl_3$) exhibits three singlets at δ 6.65 (H-3 and 4, $J_{^{13}C-H}$=167 Hz, J_{H-H}=10.3 Hz from the ^{13}C satelites), 6.37 (H-7 and 8, $J_{^{13}C-H}$=180 Hz, J_{H-H}=2.6, 1.3, 1.0 Hz), and 3.92 ppm (H-1 and 6, $J_{^{13}C-H}$=146 Hz, J_{H-H}=3.3, 1.3. 1.0 Hz) in the integrated area of 1:1:1. The ir spectrum (KBr) shows a carbonyl band at ν 1675 cm^{-1}, a conjugated double bond at 1603 cm^{-1}, a cyclobutene at 1560 cm^{-1}, and other significant absorptions at 962, 788, and 690 cm^{-1}. The uv spectrum (EtOH) exhibits λ_{max} 365 (ε 97) and 222 nm (11,800). The absorption at 365 nm is 13 nm longer than that of cyclohexene-1,4-dione 12[8] ($\lambda_{max}^{ethanol}$ 352 (64) and 233 (15,100)) and 5 nm longer than *p*-benzoquinone-butadiene adduct 13 ($\lambda_{max}^{ethanol}$ 360 (60) and 223 (11,900)[1]), which may suggest some spacial interaction of the cyclobutene double bond with the 2-en-1,4-dione chromophore.

The chemistry of 1 is now under active investigation.

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* To whom all correspondences should be addressed.

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