A Convenient Synthesis of Homobenzoquinones[1]

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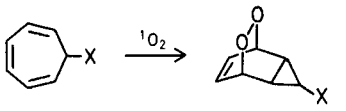
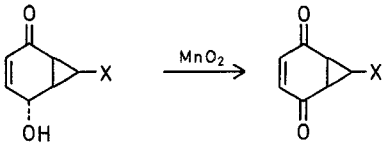
The classical methods for the preparation of *p*-homobenzoquinones **4** either via addition of diazoalkanes to *p*-benzoquinone and thermolysis of the resulting adducts[3] or addition of carbenes to *p*-benzoquinone[4] is limited to substituted derivatives. For this reason Chapleo and Dreiding[5] devised an involved indirect (3 stage) synthesis for the parent *p*-homobenzoquinone **4a** (X = H).



1a-e **2a-e**



3a-e **4a-e**

	a	b	c	d	e
X	H	$COOCH_3$	-CN	CHO	CH_3

Since singlet oxygenation[6] of cycloheptatrienes **1** affords norcaradiene derived (2+4)-*endo*-peroxides **2** and since *endo*-peroxides are readily isomerized[7] into 4-hydroxy-2-enones **3** on base treatment, it appeared to us that the latter should lead to the desired *p*-homobenzoquinones **4** on manganese dioxide oxidation[8]. Indeed, herein we demonstrate that the above synthetic strategy is a convenient method for the preparation of **4**. Moreover, this synthetic sequence permits stereospecific functionalization of the cyclopropane ring in the *p*-homobenzoquinone.

Table. *p*-Homobenzoquinones **4**

Product No.		Yield [%][a]	m.p. (solvent)	Molecular formula[b]	I.R. ($CHCl_3$) ν [cm^{-1}] C=O	C=C	X	^{1}H-N.M.R. ($CDCl_3$/TMS) δ [ppm]
4a	H	92	48°[e] (subl. 40°/1 torr)	$C_7H_6O_2$ (122.1)	1685; 1680	1610	—	1.6–1.9 (m, 2H, H-7); 2.4–2.7 (m, 2H, H-5, H-6); 6.4 (s, 2H, H-2, H-3)
exo-**4b**	$COOCH_3$	78	94° (chloroform/ethanol)	$C_9H_8O_4$ (180.2)	1695; 1685	1605	1730	1.5–1.9 (A_2B, 3H, H-5, H-6, H-7); 3.1 (s, 3H, CH_3); 6.25 (s, 2H, H-2, H-3)
exo-**4c**	CN	71	144–145° (chloroform)	$C_8H_5NO_2$ (147.1)	1685[c]	1600[c]	2240[c]	2.35 (t, 1H, $J_{H\text{-}6,H\text{-}7} = J_{H\text{-}5,H\text{-}7} = 4.33$ Hz, H-7); 2.85 (d, 2H, H-5, H-6); 6.22 (s, 2H, H-2, H-3)
endo-**4c**	CN	78	156–157° (dichloromethane)	$C_8H_5NO_2$ (147.1)	1685; 1675	1600	2240	2.4–3.0 (A_2B, 3H, H-5, H-6, H-7); 6.7 (s, 2H, H-2, H-3)
exo-**4d**[d]	CHO	23	137° (dichloromethane/ether)	$C_8H_6O_3$ (150.1)	1695	1605	1730	2.95 (s, 3H, H-5, H-6, H-7); 6.5 (s, 2H, H-2, H-3); 9.4 (b s, 1H, H-8)
exo-**4e**[9]	CH_3	81	48–49° (ether/pentane)	$C_8H_8O_2$ (136.1)	1680	1600	—	1.3 (d, 3H, CH_3); 1.7–2.4 (m, 3H, H-5, H-6, H-7); 6.4 (s, 2H, H-2, H-3)

[a] Overall yield after column chromatography.
[b] All products gave satisfactory microanalyses (C ±0.30%, H ±0.20%) and were performed by Atlantic Analytical Labs., Atlanta, Georgia.
[c] KBr pellet.
[d] Aldehyde is partly oxidized to carboxylic acid.
[e] Ref.[5] m.p. 47–49.5° (pale yellow needles).

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***p*-Homobenzoquinones 4; General Procedure:**
To a solution of the endoperoxide **2** (0.5 mmol), prepared by photosensitized oxygenation of the cycloheptatriene as described previously[6], in dichloromethane (10 ml) is added while stirring and cooling at 0° a solution of triethylamine (0.5 mmol) in dichloromethane (5 ml). The reaction mixture is allowed to stir for 3–4 h at room temperature, the solvent is roto-evaporated (~30°/25 torr) and the triethylamine removed by passing the residue through a small silica gel column (2 g), eluting with 95:5 chloroform/methanol. The crude 4-hydroxy-2-enone **3** is oxidized without purification by dissolving it in dichloromethane (5 ml) and stirring with freshly precipitated manganese dioxide (500 mg) at room temperature for 4–5 h. The manganese dioxide is removed by filtration, the solvent roto-evaporated (~30°/25 torr) and the residue chromatographed on silica gel (~2 g), eluting with chloroform. Final purification of the *p*-homobenzoquinone **4** is achieved by recrystallization. The results are summarized in the Table.

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