Cycloaddition Reactions of a Crowned *p*-Benzoquinone

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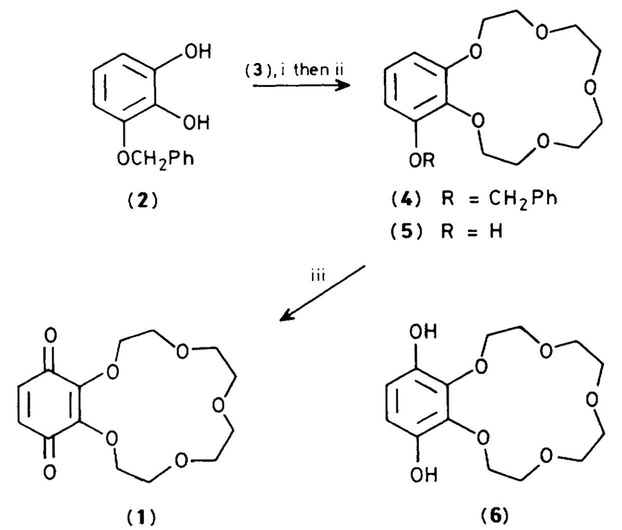
The crowned benzoquinone (**1**), prepared from pyrogallol in four steps, undergoes Diels–Alder reactions with cyclopentadiene and thebaine to give good yields of the respective adducts containing the crown ether moiety.

Design of dienophile reagents which possess an additional important function is of great interest, since that function might be easily introduced into various molecules by Diels–Alder reaction. As a continuation of our systematic studies on the design and preparation of multi-functional molecules,[1–3] we have investigated the synthesis and cycloaddition reactions of crowned benzoquinones such as (**1**) which can be regarded as dienophiles having the function of ionophores. A recent report[4] on the synthesis of (**1**) prompts us to report our results of independent studies using a similar strategy.

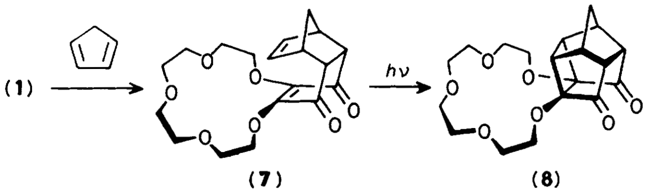
Treatment of 3-benzoxycatechol (**2**) (prepared by a one-pot method by the selective benzylation of pyrogallol, albeit in relatively low yield, using cyclic borate protection of the vicinal hydroxy groups[5]) with 1,11-dichloro-3,6,9-trioxaundecane (**3**)[6] and sodium hydroxide in aqueous Bu^nOH gave the 3′-benzoxybenzocrown (**4**) (64%). Hydrogenolyis of (**4**) over Pd black gave the phenol derivative (**5**) (100%) followed by oxidation with potassium nitrosodisulphonate (Fremy's salt)[7] afforded the 1,4-quinone of benzo[15]crown-5 (**1**)[†] as deep red crystals, m.p. 121—123 °C (CH_2Cl_2–ether) [lit.[4] m.p. 83—84 °C (2-methoxyethanol)] in 31—50% yield: $\nu_{max.}$ 1650 cm^{-1}; ^{1}H n.m.r., δ ($CDCl_3$) 3.67 (br. s, 8H), 3.84 (dd, *J* 6.0 and 4.2 Hz, 4H), 4.51 (dd, *J* 6.0 and 4.2 Hz, 4H), and 6.58 (s, 2H); $\lambda_{max.}$ (MeCN) 251 (ε 12 600) and 399 nm (ε 1390); *m/z* 298 (M^+, 44%) and 166 (100%)]. Hydrogenation of (**1**) over 5% Pd/C gave the hydroquinone (**6**)[†] (93%) as colourless crystals, m.p. 130—131 °C (lit.[4] m.p. 132 °C) (Scheme 1).

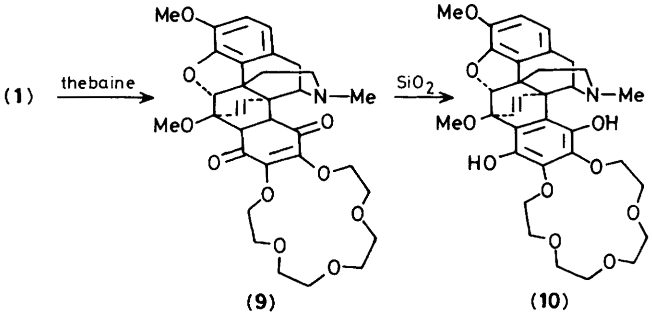
The utility of (**1**) as a potent dienophile was shown by the ready formation of Diels–Alder adducts with cyclopentadiene [CH_2Cl_2, 25 °C; (**7**),[†] 98%] and thebaine [benzene, 80 °C; (**9**),[†] >90%]. The *endo*-structure of (**7**) [m.p. 86—87.5 °C;

[†] All new compounds gave satisfactory analytical and spectral data.



Scheme 1. *Reagents:* i, $ClCH_2[CH_2OCH_2]_3CH_2Cl$ (**3**), NaOH, Bu^nOH, heat; ii, H_2, Pd black, EtOH; iii, Fremy's salt, acetone, buffer.





$\nu_{max.}$ 1650 cm^{-1}; ^{1}H n.m.r., δ 1.39 (dm, *J* 5.4 Hz, 1H), 1.56 (dm, *J* 5.4 Hz, 1H), 3.16—3.24 (m, 2H), 3.46—3.56 (m, 2H), and 6.08 (small m, 2H); $\lambda_{max.}$ 294 nm (ε 9370); *m/z* 364 (M^+, 8%) and 66 (100%)] was confirmed by its smooth conversion into the cage compound (**8**)† [$\nu_{max.}$ 1755 and 1737 cm^{-1}; *m/z* 364 (M^+, 47%) and 136 (100%)] in quantitative yield on irradiation with a 100 W high-pressure Hg lamp. On stirring with silica gel in chloroform or even on column chromatography on silica gel, the adduct (**9**) [$\nu_{max.}$ 1655 cm^{-1}; ^{1}H n.m.r., δ 2.44, 3.62, and 3.79 (each s, 3H)] readily isomerized to give the hydroquinone derivative (**10**)† [m.p. 193—195 °C; $\nu_{max.}$ 3320 cm^{-1}; ^{1}H n.m.r., δ 2.58, 3.88, and 3.92 (each s, 3H), 5.73 (d, *J* 4.8 Hz, 1H), 6.42 (dd, *J* 4.8 and 1.0 Hz, 1H), and 9.03 (s, 1H, D_2O-exchangeable); $\lambda_{max.}$ 308 nm (ε 6760); *m/z* 609 (M^+, 78%) and 391 (100%)]. The u.v. spectra of (**1**) and its adducts generally showed a small hypsochromic shift of their characteristic absorption bands at 250—400 nm in the presence of alkali-metal ions, indicating complex formation.

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