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Synthesis and Properties of Benzo[1,2:4,5]dicycloheptene-3,6,9,12-tetraone. A New Type of Electron Acceptor

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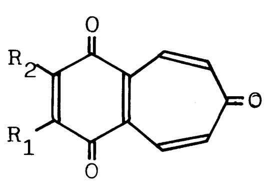
Benzo[1,2:4,5]dicycloheptene-3,6,9,12-tetraone was synthesized in two different routes. Its 1st and 2nd redox potentials (E_1 = -0.14 V, E_2 = -0.74 V) were found to be more positive than those of 7H-benzocycloheptene-1,4,7-trione (E_1 = -0.31 V, E_2 = -0.90 V) under the same conditions.

Recently, researches on the electron acceptors and donors which form organic metals have been undertaken extensively$^{1)}$ and the development of new type of acceptors is being awaited.

In a previous paper,$^{2)}$ we described the synthesis of tropone-annelated p-benzoquinone (**1**) and 1,4-naphthoquinone (**2**) and made clear that annelation of tropone at its 4,5-position to the 2,3-position of the quinones increases in the electron accepting ability compared with those of the original quinones. Therefore, it is fascinating to investigate how the degree of electron accepting ability of p-benzoquinone would be raised by annelation of two tropone rings.

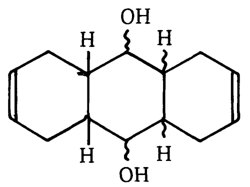
Now we wish to report the synthesis and properties of benzo[1,2:4,5]dicycloheptene-3,6,9,12-tetraone (**3**). Strategies to build 7-membered ring were examined in two different ways.

One of them (Scheme 1) includes an ordinary silver ion$^{2)}$ catalyzed ring opening of 7,7-dibromonorcarene (**9**). The first key step of this synthesis was the transformation of 1,4-cyclohexadione (**6**) to hydroquinone dimethyl ether (**9**). Because dehydrogenation of **6** to the corresponding hydroquinone was unsuccessful,



1 $R_1 = R_2 =$ H; 2 $R_1\text{-}R_2 = (CH{=}CH)_2$

3 $R_1\text{-}R_2 =$ CH=CH-CO-CH=CH



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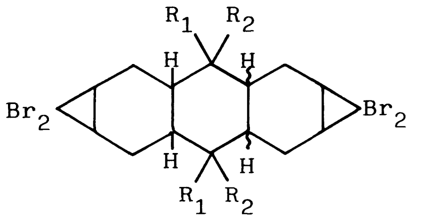
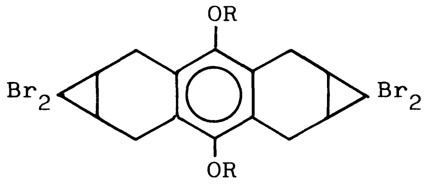


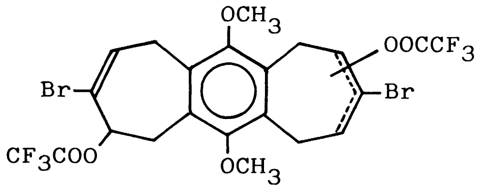
5 $R_1 =$ H, $R_2 =$ OH

6 $R_1\text{-}C\text{-}R_2$ = C=O



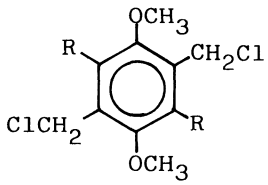
7 R= CH_3CO; 9 R= CH_3

8 corresponding quinone



10 syn-allylic ester

11 anti-allylic ester

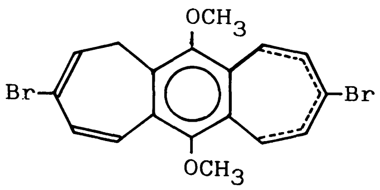


17 R= CH_3

18 R= CH_2Br

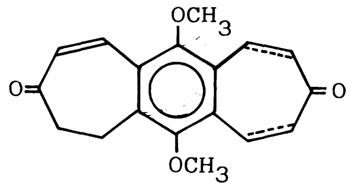
19 R= $(CH_2)_2CO\text{-}\bar{C}H\text{-}COOCH_3$

20 R= $(CH_2)_2CO\text{-}CH_2COOCH_3$



12 syn-conjugated diene

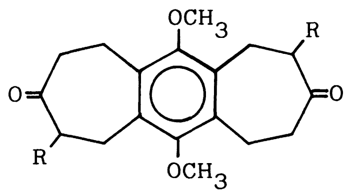
13 anti-conjugated diene



14 syn-enone

15 anti-enone

16 bistropone



21 R= $COOCH_3$; 22 R= H

$$4 \xrightarrow{(i)} 5 \xrightarrow{(ii)} 6 \longrightarrow 7 \longrightarrow 8 \longrightarrow 9 \xrightarrow{(iii)} (10 + 11) \longrightarrow$$

$$12 + 13\ (1:1) \longrightarrow 14 + 15\ (1:1) \xrightarrow{(iv)} 16 \longrightarrow 3$$

Scheme 1.

$$17 \xrightarrow{(v)} 18 \longrightarrow 20 \longrightarrow 19 \longrightarrow 21 \longrightarrow 22 \longrightarrow 16 \xrightarrow{(vi)} 3$$

Scheme 2.

Reaction conditions: (i) $CHBr_3$/aq. NaOH/$(C_6H_5CH_2(Et)_3NCl$-EtOH/benzene(58%); (ii) CrO_3/acetone (71%); (iii) (1) CF_3COOAg/CF_3COOH, 80 °C, 2 h, (2) DMF, 180 °C, 2 h (66%); (iv) DDQ/dioxane (50%); (v) NBS/CCl_4 (79%); (vi) 5% alc. KOH, reflux (74%).

6 was transformed to the hydroquinone diacetate (7) in 90% yield by refluxing with acetic acid and its anhydride in the presence of concd sulfuric acid (oxidizing agent).3) Because alkaline hydrolysis of 7 gave an intractable mixture, this was alcoholized in the presence of concd hydrochloric acid and oxygen to give quinone (8) in 90% yield. Reduction of 8 followed by methylation in one pot4) gave 9 in 87% yield. The second key step is the hydrolysis of a mixture of the vinyl bromides (12 and 13). This was carried out with mercuric trifluoroacetate prepared in situ in dichloromethane5) at room temperature in 79% yield. The third key step was the oxidation of 16, whose solubility in usual solvents for cerium (IV) oxidation6) was very low. After several attempts, this was overcome by oxidation with potassium bichromate in concd sulfuric acid. In this case, the tropone rings in 6 seem to be protected by protonation on carbonyl oxygen to form hydroxytropylium cation7) and only the middle ring was oxidized to quinone.

The other approach to form 7-membered ring was condensation of dianion of ethyl acetoacetate with α,α'-dihalo-o-xylene (Scheme 2). Thus, treatment of 1 equivalent of 2,5-bis(bromomethyl)-3,6-bis(chloromethyl)-p-hydroquinone dimethyl ether (18), obtained by bromination with NBS from the corresponding 2,5-dimethyl derivative (17),8) with 2 equivalents of dianion of ethyl acetoacetate in THF at -20 °C in ordinary fashion and warming the mixture gave very low yield of condensation product(s).9) However, the reverse addition of the anion to the halide solution led to a fair yield (45%) of bis(ketoester) (20), which was treated with sodium hydride in DMSO-benzene followed by hydrolysis with KOH in boiling ethanol10) to give 22 in 47% yield. Bromination and dehydrobromination10) of 22 gave a mixture of 16 and its monodemethylated product (1:1.6), which was oxidized as above to tetraone (3) in 47% yield.

The product 3 forms yellow crystals (CH_2Cl_2), mp 155-160 °C (dec.).11) As expected, the electron affinity of p-benzoquinone is enhanced by the annelation of two tropone rings; that is, the 1st and 2nd redox potentials (-0.14 V, -0.74 V) of 3 are more positive than those (-0.31 V, -0.90 V) of 112) and the former approaches the expected values (-0.02 V— +0.65 V) for acceptors making up the TCNQ-based organic metals.13) Fragmentation pattern in the mass spectrum of 3 is quite similar to that of 2 except the molecular ion peak and shows the sequential loss of four carbonyl groups before occurrence of other fragmentation.

References

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11) Physical data of **3**. IR (nujol mull) ν: 1660, 1635, 1605, 1585 cm^{-1}. 1H NMR (400 MHz, $CDCl_3$) δ: 8.10 (4H, d, J = 12.5 Hz), 7.29 (4H, d, J = 12.5 Hz). UV (CH_2Cl_2) λ_{max} (log ϵ): 276 (4.66), 320 (3.88), 362 (3.77), 425 (2.89). Mass m/z (%): 264 (53, M^+), 236 (7.9), 208 (87), 180 (97), 152 (100), 126 (16).

12) The redox potentials were measured in dichloromethane solution containing tetrabutyl ammonium perchlorate (0.1 mol dm^{-3}) as an electrolyte. Ferrocene was used as an internal standard (+0.40 V).[14]

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