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Synthesis and Properties of Tropones Fused with p-Benzoquinone and 1,4-Naphthoquinone

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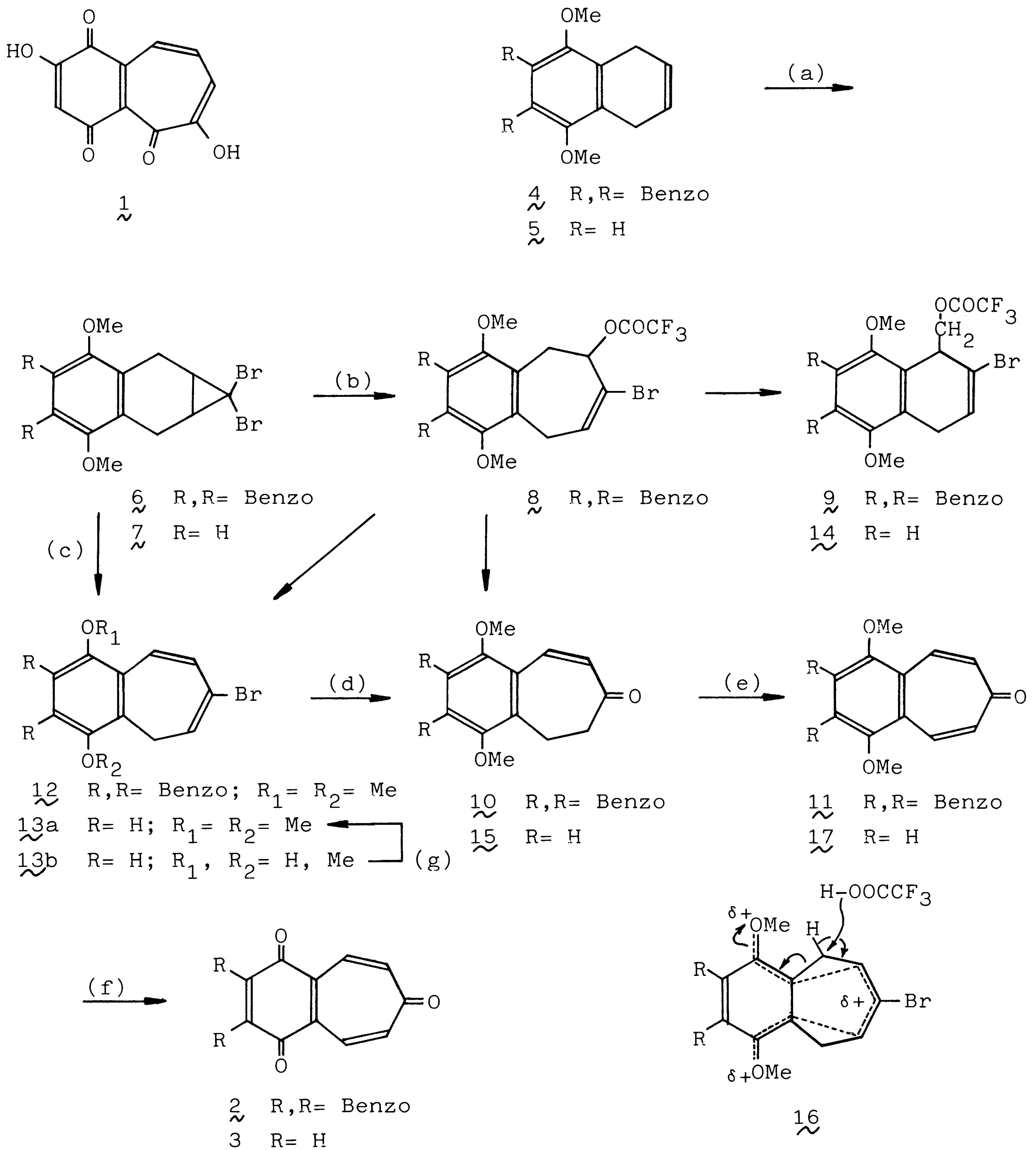
The first synthesis of 8H-cyclohepta[b]naphthalene-5,8,11-trione and 7H-benzocycloheptene-1,4,7-trione are described. The cyclic voltammograms of these compounds showed that the electron affinities of quinones are considerably increased by the annelation of a tropone ring.

For the recent several years, exploitation of new types of electron donors and acceptors is of growing importance in the field of organic chemistry.1) Therefore, it is interesting to investigate how the electron affinities of the parent quinones would be affected by the fusion of tropone ring(s) because the electron delocalization in the latter may cause an increase in the electron accepting abilities of the quinones. To the best of our knowledge, only a few of these types of compounds has been reported as polyhydroxylated forms (tropolone derivatives such as **1**).2)

Here we want to report the first syntheses of 8H-cyclohepta[b]naphthalene-5,8,11-trione (**2**) and 7H-benzocycloheptene-1,4,7-trione (**3**). These compounds showed expectedly enhanced electron affinities in the cyclic voltammograms.

As the strategy of the formation of 7-membered ring, ring opening of 7,7-dibromonorcarene derivatives was chosen. Because of the instabilities under the reaction conditions of dibromocarbene addition, 1,4,4a,9a-tetrahydroanthraquinone and 4a,5,8,8a-tetrahydronaphthoquinone3) were transformed to their corresponding dimethyl ethers, **4** and **5**, which were then subjected to dibromocarbene addition to give norcarenes, **6** and **7**,4) respectively. On treatment of 6 with silver trifluoroacetate (TFAg) in trifluoroacetic acid (TFA) for a short period of time at 80 °C,5) a trifluoroacetate (**8**) was obtained in good yield (80%) along with a small amount of **9** (8%). On prolonged heating, the amounts of **9** and a new enone (**10**), mp 137.5-138.5 °C, were gradually increased in compensation with a decrease in the amount of **8** and reached to 50% and 30% yields, respectively. In the same time, a small amount of a tropone (**11**), mp 216-217 °C, was also formed. Variation of the reaction conditions did not allow any increase in the total amount (37%) of **10** and **11**. However, a bromotriene (**12**) could be obtained in a moderate yield (70% from **6**) by heating **8** in DMF at 180 °C.

On the other hand, treatment of **6** with lithium bromide and lithium carbonate



Reaction conditions. (a) 4 /$CHBr_3$/CH_2Cl_2/aq.NaOH/Benzyltrietylammonium chloride (BTEAC), room temperature (r.t.), overnight (o.n.)→ 6 (44%); 5 / $CHBr_3$/aq.NaOH/BTEAC (EtOH), r.t., o.n.→ 7 (50%). (b) TFAg/TFA; 6 /80 °C, 3 d→ 9 (50%)+ 10 (30%); 7 /80 °C, 6 h→ 14 (80%)+ 15 (10%). (c) LiBr/Li_2CO_3 /DMF; 6 /180 °C, 6 h→ 12 (17%); 7 /180 °C, 20 h→ 13a (17%)+ 13b (71%). (d) $Hg(OAc)_2$/TFA; 12 /r.t., o.n.→ 10 (70%)+ 11 (3%); 13a /r.t., o.n.→ 15 (43%)+ 17 (12%). (e) DDQ/p-TsOH/dioxane; 10 /110 °C, 1 h→ 11 (46%); 15 / 110 °C, 3 h→ 17 (40%). (f) 11 /CAN/$CHCl_3$-CH_3CN, 1 h→ 2 (47%); 17 /CAN/ CH_3CN, r.t., 30 min→ 3 (47%). (g) 13b /aq.NaOH/Me_2SO_4→ 13a (93%).

in DMF$^{7)}$ at 180 °C gave only a small amount of the expected **12**. In the case of the tricyclic dibromide (**7**), it gave with this reagent a mixture of the cycloheptatriene (**13**a), mp 105 °C, and its monodemethylated products (**13**b) in 88% yield. The latter product was converted to the former by methylation with dimethyl sulfate. The ring opening of **7** with TFAg in TFA was also examined and found that **7** gave mainly a dihydronaphthalene derivative (**14**) along with a small amount of an enone (**15**), mp 91-92 °C.

The mechanism of ring opening of **6** and **7** under the conditions of TFAg in TFA is considered as follows: From the fact that the trifluoroacetate (**8**) was obtained in good yield from **6** at a short reaction time, the opening of the three-membered ring of **6** and **7** would furnish the trifluoroacetates of cycloheptadienols like **8**, which then might give intermediates (**16**) by loss of trifluoroacetate anion under the influence of oxygen lone pair of methoxyl group. The intermediates would next be either deprotonated to **12** and **13**a or attacked by trifluoroacetate ion to give six-membered compounds, **9** and **14**. The former two could be finally solvolyzed by TFA (TFAg) to enone, **10** and **15**, respectively.

The enone (**15**) was also obtained, along with the corresponding tropone (**17**), mp 132-133 °C, by the treatment of 1,4-dimethoxy-7-bromo-5H-benzocycloheptene (**13**a) with mercuric acetate in TFA.$^{8)}$ With excess of mercuric acetate, the yield of **17** was not improved. The enone, **10** and **15**, were dehydrogenated with DDQ to the corresponding tropones, **11** and **17**, which were then oxidized to quinones, **2**, mp 150 °C (dec.),$^{8)}$ and **3**, mp 123 °C (dec.),$^{8)}$ by means of ceric ammonium nitrate (CAN) in acetonitrile.$^{9)}$ Both quinones were obtained as yellowish brown solids and unstable under the chromatographic conditions (silica gel, alumina, and florisil).

The reduction potentials of the quinotropones (**2** and **3**), together with troponohydroquinone dimethyl ethers (**11** and **17**), were meassured by the cyclic voltammetry.$^{10)}$ The first reduction potentials of **2** (-0.39, -0.92, and -1.02 V) and **3** (-0.26 and -1.05 V)$^{11)}$ were found ca. 0.3 V more positive than those of 1,4-naphthoquinone and p-benzoquinone,$^{12)}$ respectively, by the annelation of a tropone ring. Further, the third reduction potentials of **2** and **3**, which are corresponding to the reduction of the tropone ring, also shifted more positive side by 0.58 and 0.73 V than those of **11** (-1.60 V) and **17** (-1.78 V), respectively. It is worth noting that, when these values of reduction potential were plotted versus the energy levels of LUMOs (LUMO1 vs. 1st and LUMO2 vs. 3rd reduction potentials) calculated by MNDO for the planar models of **2** and **3**,$^{13)}$ a linear correlation line was obtained.$^{12)}$

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116, 2408 (1983); L. T. Scott, M. D. Rozeboom, K. N. Houk, T. Fukunaga, H. Lindner, and K. Hafner, J. Am. Chem. Soc., 102, 5169 (1980).

2) L. Horner, W. Drückheimer, K.-H. Weber, and K. Dölling, Chem. Ber., 97, 312 (1964).

3) K. Alder and G. Stein, Ann. Chem., 501, 247 (1933).

4) **6** mp 145-146 °C; **7** mp 102-103 °C.

5) Previously, we found that quinone (**i**) was successfully opened the three-membered ring to give a bromocycloheptatriene (**ii**) with silver acetate in TFA in good yield (80%), whereas the reaction was unsuccessful with LiBr-Li_2CO_3 in DMF.[6] Y. Morizono and M. Kato et al., unpublished work.

6) M. Kato, T. Yoshihara, S. Nomura, Y. Morizono, and T. Miwa, unpublished work.

7) S. F. Martin and T.-S. Chou, Tetrahedron Lett., 1978, 1943.

8) Spectral data. ^{1}H-NMR. (400 MHz; $CDCl_3$) δ: **2** 7.28 (2H, dm, J=12.6 Hz), 7.84-7.88 (2H, m), 8.22-8.26 (2H, m), 8.25 (2H, dm, J=12.6 Hz); **3** 7.04 (2H, s), 7.25 (2H, dm, J=12.5 Hz), 7.99 (2H, dm, J=12.5 Hz). ^{13}C-NMR (100 MHz; $CDCl_3$) δ: **2** 185.6 (s), 182.3 (s), 143.9 (d), 138.0 (s), 134.6 (d), 131.8 (d), 131.5 (s), 127.0 (d); **3** 186.1 (s), 184.8 (s), 144.5 (d), 137.3 (d), 136.3 (s), 131.3 (d).

IR ν_{max} ($CHCl_3$): **2** 1668, 1628, 1610, 1590, 1580, 1282, 1202; **3** 1668, 1638, 1612, 1586, 1286, 1220, 1110, 840, 720 cm^{-1}.

UV $\lambda_{max}^{CH_3CN}$ (log ε): **2** 218 (3.77), 256 (4.00), 305 nm (3.68); **3** 255 (4.50), 396 nm (3.28).

Mass m/z (%): **2** 236 (25, M^+), 208 (100).

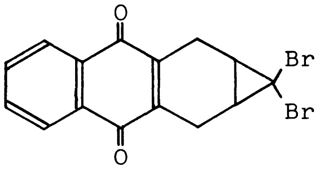
9) K. Tatsuya, K. Akimoto, and K. Annaka, Bull. Chem. Soc. Jpn., 58, 1699 (1985).

10) Cyclic voltammograms were run on a potentiometer, Model HA-305 (Hakuto-Denko Co. Ltd.) using platinum wire electrodes (SCE) at room temperature. The 10^{-3} mol dm^{-3} solution of each substrate was made in acetonitrile containing tetrabutylammonium perchlorate (10^{-1} mol dm^{-3}).

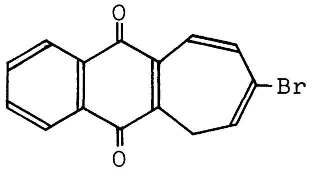
11) From the shape of the cyclic voltammogram of compound **3** compared with that of **2**, it is reasonable to assume that the 2nd and the 3rd reduction potentials of 3 appear unresolved.

12) J. Q. Chambers, "Electrochemistry of Quinones," in "The Chemistry of the Quinonoid Compounds," ed by S. Patai, John Wiley and Sons, New York (1974), part 2, pp. 737-791.

13) The obtained values for LUMO1 and LUMO2 of compound **2** were -1.891 and -0.930 eV and those of **3** were -2.065 and -0.866 eV, respectively.



(**i**)



(**ii**)

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