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1,2,3-BENZOTROPOQUINONE

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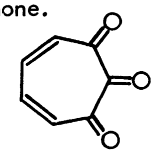
The title compound, a benzolog of o-tropoquinone, was synthesized by the DDQ oxidation of the corresponding hydroxytropolone. Effect of benzene annelation on the physical properties (UV, PMR, CMR, electron affinity) of o-tropoquinone was evaluated. The annelation causes more modification to o-tropoquinone than to o-benzoquinone. This may be due to the reduced planarity of 7-membered quinone ring in the title compound. Easy reduction by HCl and facile BF_3-induced aromatization to 1,2-dihydroxynaphthalene were observed.

Our recent studies on physical and chemical properties of o- and p-tropoquinones, the seven-membered quinones of the structures 1 and 2[1,2,3], revealed that both compounds possess the quinone characters as in benzoquinone series[4]. Since benzene annelation was shown by the properties of 1,2,5-benzotropoquinone 3[3], to modify the original quinone character of p-tropoquinone, the corresponding benzolog of ortho series, 1,2,3-benzotropoquinone 4, was synthesized and its properties were examined in comparison with those of 1 and 1,2-naphthoquinone.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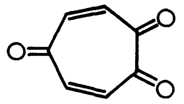
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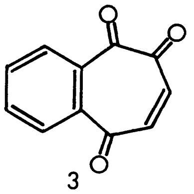
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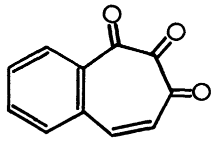
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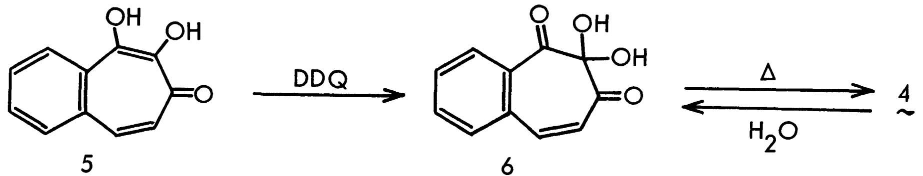
Synthesis Admixture of dichlorodicyanobenzoquinone (DDQ) with 3-hydroxybenzo(d)tropolone 5[5] in acetone at room temperature caused immediate change in color (pale yellow→dark green→ reddish orange), and, on addition of water, 1,2,3-benzotropoquinone hydrate 6, yellow needles, m.p. 115°C (dec.), was obtained in 81% yield[6].



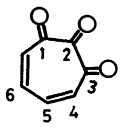
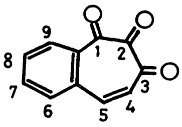
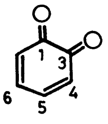
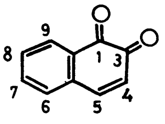
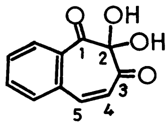
5 6

Careful sublimation of 6 at 50-55°C (at 0.005-0.01 Torr) gave the desired 1,2,3-benzotropoquinone 4, red granules, m.p. 95°C (dec.), in 18% yield. 4 is unstable (gradual decomposition in dry air) and highly hygroscopic giving 6 (tendency of hydration: 4 > 1 > 3 > 2).

Physical properties Mass spectrum of 4 shows a prominent M+2 peak (m/e 188) characteristic of potent quinones in addition to the molecular ion (m/e 186). Fragmentation pattern [158 (M^+-CO), 130 (base, M^+-2CO) and 102 (M^+-3CO)] is almost identical with that of 1,2-naphthoquinone 7[7]. Its IR frequencies [1713, 1658, 1620, 1590 cm^{-1} (nujol)] in $\nu_{C=O}$ and $\nu_{C=C}$ region, and UV maxima [λmax (CH_2Cl_2) 250 (log ϵ 4.44), 358 (3.83), 522 nm (1.45)] are very similar to those of 1[1]. However, the latter shows some general effect of annelation (hypsochromic shift in the last maximum and bathochromic shift in the second) similar to o-benzoquinone series[8]. The electron affinity (E^A=1.08 eV) obtained by polarography[9] (E_1=-0.33V vs SCE in MeCN at 25°C, supporting electrolyte: 0.05M Et_4NClO_4) is weaker than that of 1 (E^A=1.27 eV)[10].

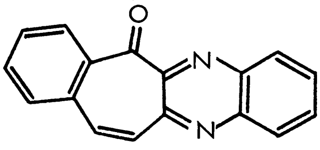
NMR parameters of 4 are listed[11] in Table together with those of 1, 6, 7 and o-benzoquinone 8[1b]. Comparison of these data reveals the difference in the effect of benzene annelation on o-tropoquinone and o-benzoquinone. Thus, the annelation causes the following changes. (1) Both δH_5 and δC_5 show down-field shifts but the shift is larger in tropoquinone than in benzoquinone; (2) δH_4 moves up-field in the former and down-field in the latter. δC_4 exhibits up-field shift in both cases, but the shift is larger in the former than in the latter; (3) δC_3 shows up-field shift in both cases, while δC_1 moves down-field especially in the former; (4) The resulted chemical shift differences $\Delta\delta C_{5-4}$ show the increase in both series, the value for the former

Table NMR Parameters of 1, 4, 6, 7 and 8 (δ: ppm from TMS, J: Hz)

compounds		 1	 4	 8	 7	 6
PMR	solvent	$(CD_3)_2CO$	$CDCl_3$	$(CD_3)_2CO$	$CDCl_3$	acetone
	δ_4	6.44	6.39	6.35	6.45	6.15
	δ_5	7.01	7.40	7.19	7.48	7.39
	$J_{4,5}$	12.59	13.0	9.89	10.5	12.9
	$J_{5,6}$	8.26	0.5	5.88	—	
CMR	solvent	CD_3CN	$(CD_3)_2CO$	$CDCl_3$	$CDCl_3$	$(CD_3)_2CO$
	δ_1	188.7	193.4	180.4	180.5	200.1
	δ_2	185.5	194.9	—	—	99.0
	δ_3	188.7	187.5	180.4	178.5	194.6
	δ_4	131.4	125.7	130.8	127.5	124.1
	δ_5	137.1	145.1	139.7	145.3	144.6
	δ_5-δ_4	5.7	19.4	8.9	17.8	20.5

being very close to the corresponding values of 6 and cyclohexenone (20.5 ppm)12). All of these shifts suggest that (1) the benzene annelation modifies the π-electron density of o-quinones, (2) the annelated compounds show more αβ-unsaturated ketone characters and (3) this modification is larger in o-tropoquinone. One of the reasons for the amplified effect of annelation in o-tropoquinone would be the reduced planality of quinone ring in 4 13). This may be understood by the bond angle difference between 6- and 7-membered rings, which causes angular strain upon annelation.

Chemical reactions 6 reacts with o-phenylenediamine at room temperature to give the corresponding quinoxaline derivative 9, m.p. 178-179°C (15% yield), together with benzo(a)phenazine (13%)14). The site of quinoxaline ring in 9 was secured from the PMR spectrum of the corresponding alcohol, m.p. 156.5-157.5°C, the NaBH$_4$ reduction product: Carbinyl proton appears as a narrow doublet (δ 5.54, J=1.0), devoid of a large vicinal coupling. While NaN$_3$ caused conjugate addition (room temp. in aq. HOAc) to give triazinotropolone 10, m.p. 110°C (dec.), in 11% yield, conc. HCl reduced 6 at room temperature to 5 (80% yield)15). Acetylation of 6 in the presence of H$_2$SO$_4$ (room temp.) afforded only the corresponding diacetate 11, m.p. 187-188°C in 87% yield, but the reaction with BF$_3$ catalyst (Ac$_2$O, in ether, room temp., 21 h) afforded 1,2-diacetoxynaphthalene (25%) and 3,3',4,4'-tetraacetoxy-1,1'-binaphthyl16) (15%) along with 11 (15%). The aromatization should have taken place by BF$_3$, because 6 gave 1,2-dihydroxynaphthalene quantitatively on brief (1 h) treatment with BF$_3$ etherate, the latter giving 3,3',4,4'-tetrahydroxy-1,1'-binaphthyl16) on prolonged contact with the same reagent.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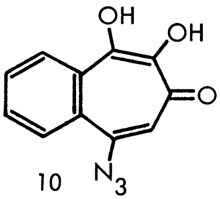
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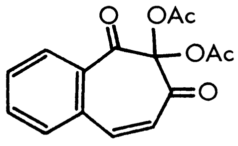
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Thus, the results discussed above demonstrate that, although 4 still retains genuine quinone characters, benzene annelation modifies the properties of o-tropoquinone more than those of o-benzoquinone.

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References and Notes

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5) H. Fernholz, E. Hartwig, and J.C. Salfeld, Justus Liebigs Ann. Chem., 576, 131 (1952).

6) MS (m/e) 188, 102 (base peak). UV [λmax(CH_2Cl_2)] 246 (log ϵ 4.44), 344.5 nm (3.85). IR (ν^{KBr}) 3420, 1705, 1668, 1312, 1135 cm^{-1} PMR (δ acetone) 6.19 (2H, br.-OH), 7.5-7.8 (4H, m, Bz) in addition to the values in Table.

7) R.W. Oliver and R.M. Rashman, J. Chem. Soc. (B), 1971, 341.

8) However, the second maximum is broad, unlike in **7** which has two maxima in the region. H.J. Jenber and N. Göts, Chem. Ber., 87, 1236 (1954). A. Kuboyama, Bull. Chem. Soc. Jpn., 32, 1226 (1959).

9) Only E_1 was observed showing instability of the anion radical under the conditions employed.

10) The similar decrease of E_1 by benzene annelation has been observed in benzoquinone series. M.E. Peover, J. Chem. Soc., 1962, 4540.

11) Only parameters on quinone rings are listed. Other PMR parameters of **4** are δ_6 7.49 (dddd), δ_7 7.76 (ddd), δ_8 7.60 (ddd), δ_9 7.94 (dddd), $J_{5,6}$=0.5, $J_{6,7}$=7.3, $J_{6,8}$=1.6, $J_{6,9}$=0.5, $J_{7,8}$=7.4, $J_{7,9}$=1.9, $J_{8,9}$=7.5, $J_{5,9}$=0.6 Hz.

12) M.J. Loots, L.R. Weingarten, and R.H. Levin, J. Am. Chem. Soc., 98, 4571 (1976).

13) The planarity of tropoquinone ring in **4** will be discussed elsewhere more in detail.

14) Since this compound is not formed from **9**, and **6** has no tendency to give 1,2-naphthoquinone, the ring contraction must have occurred at an intermediate stage.

15) **6** was completely recovered upon contact with 2N HCl.

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