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NOVEL DIPHENOQUINONE-TYPE REDOX SYSTEMS CONTAINING SEVEN-MEMBERED QUINONOID STRUCTURE

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Summary: 5-(3,5-Di-t-buty)-4-hydroxypheny)tropolone (5) and 5,5'-bitropolone (7) were synthesized using transition-metal-catalyzed coupling reactions. Oxidation of 5 afforded the diphenoquinone-type trione (6); however, 7 could not be converted into 8. The quinonoid character of 6 is discussed on the basis of the electrochemical redox behavior.

Cyclohepta-3,6-diene-1,2,5-trione $\binom{2}{2}$,¹⁾ designated as *p*-tropoquinone,²⁾ has a unique seven-membered quinonoid system and occupies an important position in organic structural chemistry due to its analogy with *p*-benzoquinone.³⁾ Although a reversible redox process between 5-hydroxytropolone (1) and *p*-tropoquinone (2) has been reported in detail,⁴⁾ few was investigated to synthesize a new type of redox systems containing *p*-tropoquinonoid unit in the molecule (*e.g.*, $3 \neq 4$ and $7 \neq 8$).

In this paper, we report the synthesis of 5-(3,5-di-t-buty]-4-hydroxyphenyl)tropolone (5) and 5,5'-bitropolone (7), and the properties of the trione (6) derived from 5 together with the attempted synthesis of the tetraone (8).



We first synthesized the redox system which is made up of the combination of 5 and 6, because *t*-butyl group is known to increase both stability and solubility. Although little is known about the transition-metal-catalyzed reactions of halotropolones, except for the Heck reaction of iodo- and bromotropolones reported by Horino and Asao,⁵⁾ the palladium-

catalyzed cross-coupling of the arylzinc compound (11) and 5-bromo-2-diethylaminotropone (12)⁶⁾ was successfully carried out under the reaction conditions reported by Negishi.⁷⁾ Thus, the reaction of 12 with the arylzinc derivative (11), which was prepared by successive treatments of 9^{8} with *t*-butyllithium and zinc chloride at -90 °C, proceeded smoothly in the presence of Pd(0)-catalyst [PdCl₂(PPh₃)₂ and *i*-Bu₂AlH] at room temperature for 1 h to afford the cross-coupling product (13) in 77% yield. Hydrolysis of 13 with KOH in refluxing aq. EtOH for 6 h gave 5 in 51% yield. Oxidation of 5 with DDQ in MeOH at room temperature for 1 h gave the desired trione (6) in an almost quantitative yield.



For the synthesis of 5,5'-bitropolone (7), we employed the nickel-catalyzed homo-coupling reaction. Recently, we have reported the reductive coupling of vinyl, aryl, benzyl, and phenacyl halides using an active nickel complex.⁹⁾ Application of this active nickel complex enable us to prepare a moderate amount of 5,5'-bitropolone (7). Treatment of 5-bromo-2-di-ethylaminotropone (12) (1 equiv.) in benzene at 50 °C for 3 h with the active nickel complex $[NiBr_2(PPh_3)_2$ (0.2 equiv.), Et₄NI (2 equiv.), and Zn (2 equiv.)] afforded 2,2'-bis(diethyl-amino)-5,5'-bitropone (14) in 17% yield [based on the recovered starting material (58%)]. Hydrolysis of 14 with KOH in refluxing aq. EtOH for 1.5 h gave 5,5'-bitropolone (7) in 60% yield, as hardly soluble pale yellow crystalline powder. Methylation of 7 with excess of



diazomethane gave 2,2'-dimethoxy-5,5'-bitropone (15) and treatment of 7 with CF_3SO_3H in CD_3CN gave the tetrahydroxybitropyrium ion (16). All attempts to convert 7 into the tetraone (8) with various oxidants or oxidizing agents were unsuccessful, presumably owing to the remarkably poor solubility of 7 in organic solvents.

In order to estimate the quinonoid character of the trione (6), electrochemical reduction potentials of 6 were compared by the cyclic voltammetry (CV) method with those of *p*-benzoquinone (1χ) , 3,3',5,5'-tetra-*t*-butyl-4,4'-diphenoquinone $(1\aleph)$ and *p*-tropoquinone (2) (Table 1). As shown in Fig. 1, the trione (6) reveals electrochemical reversibility at both the first and second waves which correspond to the two one-electron redox processes between 6 and 19. The first half-wave potential (E_1) of & is the most positive shown in Table 1, proving a strong electron affinity of &. The E_1 -value for 1χ is similar to that for $1\aleph$, because the electron-donating effect due to the *t*-butyl groups in $1\aleph$ counteracts some lowering in the LUMO energy level of this compound [diphenoquinone system possesses the essentially lower energy LUMO level than *p*-benzoquinones]. Interestingly, the E_1 -value for the *p*-tropoquinone (2) is more positive than that of *p*-benzoquinone, but the trione (&) is a much stronger oxidizing agent than 2. The difference in reduction potentials for the first and second waves (ΔE) is known to reflect the electrostatic repulsion of two negative charges in the same molecular orbital. The observed small ΔE -value for \S is the result of small electrostatic repulsion effect in $1\aleph$.

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Compound		ΕŢ	E2	∆E (E1 - E2)
p-Benzoquinone	(17)	-0.62	-1.28	0.66
Tetra- <i>t</i> -butyl- diphenoquinone	(18)	-0.63	-1.03	0.40
p-Tropoquinone	(<u>2</u>)	-0.39	-1.05	0.66
Trione (၇)		-0.28	-0.66	0.38

a) Potentials were determined by CV method in a standard three-electrode cell (working electrode: glassy-carbon; counter electrode: platinum; reference electrode: SCE) at 20 °C in acetonitrile with 0.1 M Bu_aNClO_a under Ar.







Cyclic voltammograms of hydroquinones (QH_2) are known to show one irreversible two-electron oxidation wave, followed by one irreversible two-electron reduction wave.¹⁰⁾ Since this oxidation step can be assumed to indicate the conversion of hydroquinone (QH_2) into protonated quinone (QH^+) , electrochemical oxidation of 5 and 7 may give further information about their quinonoid forms (e.g., 6 and 8). Potentials of hydroquinone, 5 and 7 were determined by CV method in a standard three-electron cell (glassy-carbon, platinum and SCE) at 20 °C in CH_2Cl_2 with 0.1 M Bu₄NClO₄ under Ar: hydroquinone, +0.93V; 5, +1.03 V; 7, +1.06 V. Oxidation potential of χ is comparable to that of 5 and somewhat larger than that of hydroquinone. It therefore seems likely that the difficulty of oxidation of 7 to the tetraone (8) is based on the poor solubility of χ in organic solvents [oxidation of 5-hydroxytropolone (1) is possible under limited conditions to give p-tropoquinone (2)].¹

Spectral data and physical properties of new compounds in this work are listed in Table 2.

Table 2. Spectral Data and Physical Properties of New Compounds.

- 5: Pale yellow needles, mp 172.5-174.0 °C, Mass (m/z) 326 (M⁺); ¹H-NMR (CDCl₃) δ 1.49 (s, 18H), 7.25 (s, 2H), 7.38 (d, J=11.5 Hz, 2H), 7.59 (d, J=11.5, 2H); IR (KBr) 3550, 3300, 1615, 1556 cm⁻¹; UV $\lambda_{max}^{CH_2CL_2}$ (log ϵ) 240 (4.42), 351.5 (4.29) nm.
- 6: Reddish purple needles, mp 149.5-150.5 °C, Mass (m/z) 326 (M+2), 324 (M⁺); ¹H-NMR (CDCl₃) δ 1.36 (s, 18H), 6.71 (d, J=13.0, 2H), 7.64 (s, 2H), 7.78 (d, J=13.0, 2H); ¹³C-NMR (CDCl₃) δ 29.7, 36.5, 126.1, 130.5, 134.2, 136.2, 143.2, 152.8, 185.1, 186.1; IR (CHCl₃) 1640, 1630, 1614, 1596, 1558 cm⁻¹; UV $\lambda_{max}^{CH_3CN}$ (log ε) 288 (3.69), 298 (3.70), 429 (4.72) nm. χ : Pale yellow powder, dp 260 °C, Mass (m/z) 242 (M⁺), 186 (base peak); ¹H-NMR (DMS0-d₆) δ
- χ : Pale yellow powder, dp 260 °C, Mass (m/z) 242 (M⁺), 186 (base peak); ¹H-NMR (DMSO-d₆) δ 7.26 (d, J=12.0, 4H), 7.58 (d, J=12.0, 4H); IR (KBr) 3170, 1618, 1558 cm⁻¹; UV $\lambda_{max}^{CH_2CL_2}$ (log ε) 231 (4.48), 244 (4.37), 360 (4.28), 435 (3.32) nm.
- 12: Dark yellow oil, Mass (m/z) 254, 256 (M⁺); ¹H-NMR (CDCl₃) δ 1.20 (t, J=7.0, 6H), 3.54 (q, J=7.0, 4H), 6.20 (d, J=11.0, 1H), 6.60 (d, J=12.0, 1H), 7.22 (dd, J=2.0, 12.0, 1H), 7.28 (dd, J=2.0, 11.0, 1H); IR (CCl_a) 1605, 1567 cm⁻¹.
-]3: Yellow leaflets, mp 130.0-131.0 °C, Mass (m/z) 453 (M⁺), 424; ¹H-NMR (CDC1₃) δ 0.39 (s, 9H), 1.22 (t, J=7.0, 6H), 1.41 (s, 18H), 3.57 (q, J=7.0, 4H), 6.61 (d, J=10.0, 1H), 6.96 (d, J=11.5, 1H), 7.1-7.5 (m, 4H); ¹³C-NMR (CDC1₃) δ 4.0, 12.7, 31.3, 35.3, 46.0, 114.0, 124.4, 131.7, 132.0, 134.6, 135.6, 136.5, 141.0, 152.7, 155.5, 180.2.
- 14: Yellow prisms, mp 129.5-130.5 °C, Mass (m/z) 352 (M⁺), 295 (base peak); ¹H-NMR (acetoned₆) δ 1.22 (t, J=7.0, 12H), 3.67 (q, J=7.0, 8H), 6.66 (d, J=11.0, 2H), 6.76 (d, J=12.5, 2H), 7.15 (dd, J=2.0, 11.0, 2H), 7.23 (dd, J=2.0, 12.5, 2H); ¹³C-NMR (CDC1₃) δ 12.5, 46.0, 112.8, 130.8, 132.2, 134.9, 136.6, 155.4, 179.6; IR (KBr) 1607, 1575, 1550, 1540, 1534 cm⁻¹; UV $\lambda_{max}^{CH_3CN}$ (log ε) 258 (4.37), 412 (4.37), 448 (4.45) nm.
- 15: Pale yellow needles, mp 232.5-234.0 °C, Mass (m/z) 270 (M⁺); ¹H-NMR (CDCl₃) δ 4.00 (s, 6H), 6.80 (d, J=10.0, 2H), 7.16 (br d, J=10.0, 2H), 7.33 (m, 4H); ¹³C-NMR (CDCl₃) δ 56.6, 112.2, 131.8, 137.1×2, 142.1, 164.9, 179.7; IR (KBr) 1625, 1562 cm⁻¹; UV $\lambda_{max}^{CH_3CN}$ (log ε) 229 (4.56), 245sh (4.44), 350 (4.44) nm.

 J_{0} : ¹H-NMR (CD₃CN-CF₃SO₃H) δ 8.36 (d, J=12.0, 4H), 8.54 (d, J=12.0, 4H); UV $\lambda_{max}^{CH_3CN-CF_3SO_3H}$ 359 nm.

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