The Cyclic Voltammetry of *p*-Tropoquinone Acetals

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Synopsis. The cyclic voltammetry of *p*-tropoquinone mono- and bisacetals was analyzed. Monoacetals showed an irreversible redox couple and an oxidation wave around +0.16 to −0.1 V vs. Ag/AgCl, the latter of which was due to a dianion species.

Recently, we have shown that, according to a cyclic voltammetry (CV) analysis, the redox process of tropoquinones generally occurs via two one-electron paths; however, the intensity of the second oxidation wave was sometimes diminished by subsequent chemical reactions of the anion radical species.[1,2] Here, we show the electrochemical behaviors of *p*-tropoquinone acetals, masked tropoquinone derivatives, which are suitable for CV studies when tropoquinones are unstable under the experimental conditions.

p-Tropoquinone acetals **1**—**3** were prepared as previously described,[3] except for 5-cyano-3-methyl-7,7-dimethoxy-2,5-cycloheptadiene-1,4-dione (**4**), which was prepared as shown in Scheme 1; 2,5-dimethoxy-4,6-bis(morpholinomethyl)tropone (**5**)[4] was treated with ethyl chloroformate[5] to give bis(chloromethyl) derivative (**6**) in 78% yield.

Next, an acetic acid solution of **6** with silver acetate at 80 °C quantitatively gave 4-acetoxymethyl-6-chloromethyl-2,5-dimethoxytropone (**7**), the saponification of which afforded air-sensitive 6-chloromethyl-4-hydroxymethyl-2,5-dimethoxytropone (**8**). The manganese(IV) oxide oxidation of **8** gave aldehydes **9** and **10**.

An oxime **11**, prepared from **9**, was a syn/anti-mixture (2:3) and dehydrated to a cyano derivative **12** in 28% yield. A subsequent cerium(IV) ammonium nitrate (CAN)-oxidation[6] of **12** gave a bisacetal **13** in 31% yield; upon an acid hydrolysis at 40 °C for 1.5 h, **13** gave a monoacetal **4** in 94% yield; however, the same treatment at 50 °C for 4.5 h gave 4-cyano-6-methyl-*p*-tropoquinone (**14**) in 1% yield.

The redox potentials of acetals, determined by CV, are summarized in Table 1. Among them, the second redox couple of **4** was hardly recognizable and the peak height of the second oxidation peak of **1** and **2** decreased.

The first and second reduction peak potentials ($E_{pr}1$ and $E_{pr}2$) of **1** were ca. 0.6 V more negative than those

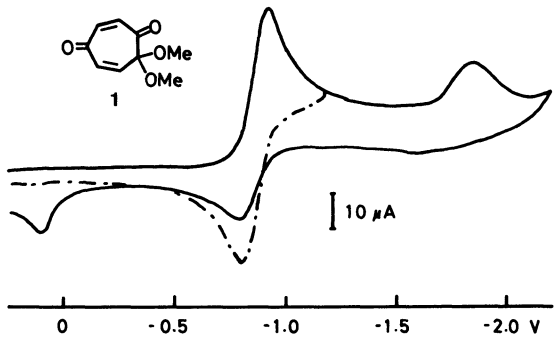


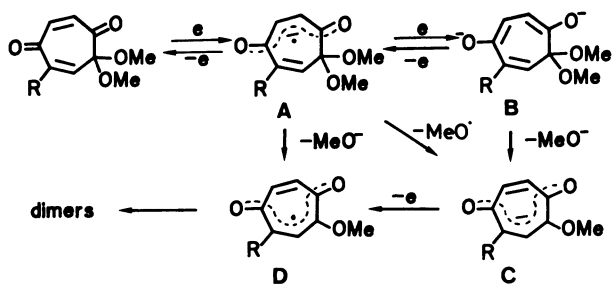
Fig. 1. The CV curves of **1**.

Table 1. Reduction and Oxidation Peak Potentials of Acetals and the Related Compounds[a]

	$E_{pr}1/E_{po}1$	$E_{pr}2/E_{po}2$
1[b]	−0.87/−0.74 (−0.81)[c]	−1.68/−1.46 (−1.65)
2[b]	−0.93/−0.77 (−0.85)	−1.88/— (−1.70)
3	−1.54/−1.38 (−1.48)	
4[b]	−0.56/−0.48 (−0.49)	−1.43/—
p-Tropoquinone	(−0.21)	(−1.10)
4-Methyl-*p*-tropoquinone	(−0.28)	(−1.15)

a) The CV were measured in anhydrous DMF with 0.1 M TBAF using Pyrex-glass sealed Pt wire as working and counter electrodes and standard Ag/AgCl as a reference electrode at 22—23 °C under N_2 atmosphere with a scan rate of 100 mV/s. b) Additional oxidation peaks were observed at +0.16, +0.09, and −0.11 V for **1**, **2**, and **4**, respectively. c) The values in parentheses showed the half-wave potentials.

of *p*-tropoquinone. The substituent effect (0.04 V) of a methyl group in *p*-tropoquinone acetal series was nearly the same as that (0.07 V) of the *p*-tropoquinone series.[1] In the case of **4**, the first reduction peak potential became more positive (by 0.36 V) due to a cyano group, a strong electron-attractive group. In the CV of monoacetals **1** and **2**, an oxidation wave was observed around +0.16 to −0.1 V vs. Ag/AgCl. These waves in **1** and **2** disappeared and their CV showed a reversible redox couple when the scanning was returned around −1.2 V. While the CV of 5-hydroxy-2-methoxytropone (**15**) showed an oxidation peak at +0.16 V, together with E_{pr}=−1.34 and E_{po}=−0.57 V, it is conceivable that the anion **C** was formed by the eliminations of a methoxide anion from dianion **B** and/or the methoxide radical from **A**, and that **C** was oxidized to the radical **D** at +0.16 V. Furthermore, since it has been established[6] that the one-electron oxidation of **15** gave dimers together with **1**, the irreversible redox couples of monoacetals must be due to a formation of dimeric products under CV conditions. The low intensity of the second peak could, thus, be explained by the involvement of alternative routes to **D** via eliminations of a methoxide ion and/or radical. In the case of **4**, routes **A** to **D** might become easier since the cyano group at C-5 should stabilize the radical intermediate **D**. Therefore, the process from **A** to **B** might be diminished.



Furthermore, the CV of **3** showed a quasi-reversible couple at E_{pr}=−1.54 and E_{po}=−1.38 V, and the substituents varied with the electrochemical behaviors of tropoquinone acetals.

Since an introduction of each cyano group was estimated to enhance the redox potentials by 0.36 V, the enhanced redox potentials of the fully substituted *p*-tropoquinones, such as dicyanodihalogeno-*p*-tropoquinones, could be estimated as +0.65 V vs. Ag/AgCl,[1] which may overcome the potential of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), the strongest oxidizing aromatic quinone presently available.

Experimental

Preparation of 6. To an anhydrous benzene solution (10 cm³) of ethyl chloroformate (1 g) was added an anhydrous benzene solution (20 cm³) of **5**[4] (814 mg) at 0—5 °C. After stirring at 40 °C for 10 h, the precipitates were filtered off and the filtrate was chromatographed on a silica-gel column to give **6** [yellow needles, mp 71—73 °C, 460 mg; 78%. Found: C, 50.35; H, 4.65%; *m/z*, 262.0180, 264.0147, 266.0137 (M⁺).[7] Calcd for $C_{11}H_{12}O_3Cl_2$: C, 50.21; H, 4.60%; *m/z*, 262.0164, 264.0135, 266.0104. ^{1}H NMR δ[8]=3.87 (3H, s), 3.94 (3H, s), 4.50 (2H, s), 4.63 (2H, s), 6.68 (1H, s), and 7.40 (1H, s). ^{13}C NMR δ=44.4, 45.0, 56.4, 63.5, 114.0, 132.5, 138.4, 143.2, 154.9, 161.7, and 178.5. IR *ν*: 1620, 1595, and 1570 cm⁻¹].

Reaction of 6 with AgOAc. An AcOH solution (10 cm³) of **6** (55 mg) and AgOAc (370 mg) was heated at 80 °C for 2 h. The resultant precipitates were filtered off, and the filtrate was chromatographed on a silica-gel column to give **7** [yellow needles, mp 96—98 °C (decomp), 60 mg; 100%. Found: *m/z*, 286.0580, 288.0564 (M⁺). Calcd for $C_{13}H_{15}O_5Cl$: 286.0605, 288.0576. ^{1}H NMR δ=2.14 (3H, s), 3.83 (3H, s), 3.90 (3H, s), 4.52 (2H, s), 5.16 (2H, s), 6.77 (1H, s), and 7.42 (1H, s). ^{13}C NMR δ=20.6, 44.8, 55.9, 63.2, 63.5, 113.2, 131.4, 138.3, 143.3, 155.4, 161.7, 170.5, and 178.4. IR *ν*: 1750, 1625, and 1600 cm⁻¹].

Saponification of 7 to 8 and Subsequent MnO_2-Oxidation to 9 and 10. To an MeOH solution (10 cm³) of **7** (555 mg) was added aqueous NaOH (1 M, 2 cm³ (1 M=1 mol dm⁻³)). After stirring for 5 min, the resultant brown solution was heated in vacuo in order to remove the solvent; the residue was diluted with water, acidified with dil HCl, and extracted with $CHCl_3$. The organic layer was dried over $MgSO_4$ and evaporated in vacuo to give **8** [a brown oil, 468 mg; 99%. ^{1}H NMR δ=3.78 (3H, s), 3.90 (3H, s), 4.50 (2H, s), 4.76 (2H, s), 7.21 (1H, s), and 7.35 (1H, s). ^{13}C NMR δ=45.1, 58.4, 61.9, 62.9, 113.5, 137.5, 138.3, 144.1, 154.4, 162.5, and 178.7]. Subsequently, to an anhydrous benzene solution (10 cm³) of **8** (474 mg) was added MnO_2 (113 mg). After refluxing for 4 h, the mixture was passed through a Celite column. The combined eluent was evaporated in vacuo and the residue was chromatographed on a silica-gel column to give **9** [pale yellow needles, mp 121—122 °C, 396 mg; 98%. Found: *m/z*, 208.0732 (M⁺). Calcd for $C_{11}H_{12}O_4$: 208.0733. ^{1}H NMR δ=2.38 (3H, d, *J*=1 Hz), 3.84 (3H, s), 3.94 (3H, s) 7.16 (1H, s), 7.38 (1H, q, *J*=1 Hz), and 10.36 (1H, s). ^{13}C NMR δ=21.6, 56.4, 64.5, 106.6, 128.2, 141.5, 145.5, 161.2, 165.4, 179.1, and 190.7. IR *ν*: 1680, 1620, 1600, and 1575 cm⁻¹] and **10** [yellow needles, mp 158—159 °C, 1.6 mg; 0.3%. Found: *m/z*, 242.0308, 244.0297 (M⁺). Calcd for $C_{11}H_{11}O_4Cl$: 242.0343, 244.0304. ^{1}H NMR δ=3.97 (3H, s), 4.00 (3H, s), 4.55 (2H, s), 7.21 (1H, s), 7.54 (1H, s), and 10.34 (1H, s)].

Preparation of 11. An MeOH solution (10 cm³) of **9** (396 mg) and NH_2OH (100 mg) was refluxed for 1.5 h. After evaporating the solvent, the residue was diluted with water, and extracted with $CHCl_3$. The organic layer was dried over $MgSO_4$ and evaporated in vacuo, leaving **11** [pale yellow crystals, mp 171—172 °C, 386 mg; 91%. Found: *m/z*, 223.0841 (M⁺). Calcd for $C_{11}H_{13}O_4N$: 223.0842. ^{1}H NMR δ=2.33 (3H, d, *J*=1 Hz), 3.67 (3H, s), 3.90 (3H, s), 7.18 (1H, q, *J*=1 Hz), 7.36 (1H, s), and 8.44 (1H, s) for a major anti-isomer; 2.58 (3H, s), 3.47 (3H, s), 3.92 (3H, s), 6.78 (1H, s), 7.2 (1H, overlapped with solvent signal) and 8.55 (1H, s) for a minor syn-isomer. ^{13}C NMR δ=22.8, 56.7, 62.8, 111.1, 129.9, 137.8, 147.7, 148.9, 159.1, 162.0, and 180.7 for anti-isomer; 20.2, 57.0, 62.8, 106.1, 129.9, 137.0, 147.7, 148.9, 161.2, 163.1, and 180.7 for syn-isomer. IR *ν*: 3140, 3010, 2860, 1740, 1615, 1590, and 1545 cm⁻¹].

Preparation of 12. An Ac_2O solution (5 cm³) of **11** (29.3 mg) was heated at 120 °C for 4 h. After removing the solvent, the residue was chromatographed on a silica-gel column to give **12** [pale yellow crystals, mp 157—158 °C, 4.8 mg; 28%. Found: *m/z*, 205.0721 (M⁺). Calcd for $C_{11}H_{11}O_3N$: 205.0737. ^{1}H NMR δ=2.33 (3H, d, *J*=1 Hz), 3.90 (3H, s), 3.95 (3H, s), 6.48 (1H, s), and 7.30 (1H, q, *J*=1 Hz). ^{13}C NMR δ=22.1, 56.7, 62.3, 107.5, 109.8, 117.7, 140.7, 143.9, 161.6, 164.2, and 178.5. IR *ν*: 2220, 1620, 1595, and 1575 cm⁻¹] and **11** (10.9 mg).

The CAN-Oxidation of 12. A mixture of **12** (72.7 mg) and CAN (798 mg) was stirred at room temperature for 4 h.

The resultant mixture was extracted with $CHCl_3$ and the organic layer was washed with aq $NaHCO_3$ and dried over $MgSO_4$. The solvent was evaporated in vacuo and the residue was chromatographed on a silica-gel column to give **13** [a pale yellow oil, 29.3 mg; 31%. Found: *m/z*, 267.1104 (M^+). Calcd for $C_{13}H_{17}O_5N$: 267.1104. ^1H NMR δ=1.93 (3H, d, J=1.3 Hz), 3.24 (6H, s), 3.29 (6H, s), 5.80 (1H, q, J=1.3 Hz), and 6.61 (1H, s). ^{13}C NMR δ=18.8, 50.7 (4C), 97.3, 100.7, 115.9, 124.2, 125.3, 147.6, 152.8, and 190.7. IR ν: 2230, 1745, 1710, and 1605 cm^{-1}].

Hydrolysis of 13 to 4. A mixture of acetone (5 cm^3), $HClO_4$ (2 M, 5 cm^3), and **13** (27 mg) was stirred at 40 °C for 1.5 h. The mixture was then diluted with water and extracted with $CHCl_3$. The extract was dried on $MgSO_4$ and evaporated in vacuo, leaving **4** [a yellow oil, 21 mg; 94%. Found: *m/z*, 221.0700 (M^+). Calcd for $C_{11}H_{11}O_4N$: 221.0689. ^1H NMR δ=2.10 (3H, d, J=1.3 Hz), 3.31 (6H, s), 6.06 (1H, q, J=1.3 Hz), and 6.78 (1H, s)].

Preparation of 14. To an acetone solution (1 cm^3) of **4** (12.9 mg) was added aq $HClO_4$ (1 M, 1 cm^3) and heated at 50 °C for 4.5 h. The mixture was diluted with water and extracted with $CHCl_3$. The extract was dried on $MgSO_4$ and evaporated in vacuo. The residue was chromatographed on a silica-gel column to give **14** [1 mg; 1%. Found: *m/z*, 175.0289 (M^+). Calcd for $C_9H_5O_3N$: 175.0269. ^1H NMR δ=2.44 (3H, d, J=1 Hz), 7.17 (1H, s), and 7.47 (1H, q, J=1 Hz)].

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7) Three separated peaks, due to $^{35}Cl_2$-, $^{35}Cl^{37}Cl$-, and $^{37}Cl_2$-isotope compositions, revealed a reasonable relative ratio of intensities, 9:3:1. Mass-spectral behaviors of other chloro derivatives were similar.

8) All the NMR spectra were measured in $CDCl_3$ solutions.