

## ANNULENEDIONES HAVING QUINONOID PROPERTIES

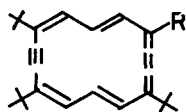
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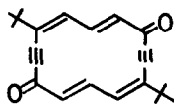
**Summary:** Chemical and Electrochemical reductions of bisdehydro[14]- and [18]annulenediones clearly revealed their quinonoid nature.

In the previous papers, we reported the syntheses of hydroxy[14]annulene (1)<sup>1</sup> and amino-[14]annulene (2)<sup>2</sup>, which can be regarded as nonbenzenoid analogues of phenol and aniline. Our continuing interest in this area prompted us to investigate the synthesis of annulenediones being formal counterparts of *p*-benzoquinone. As reported in the preceding communication<sup>3</sup>, the synthesis of the bisdehydro[14]- and [18]annulenediones has been achieved by the cyclic dimerization of  $\omega$ -ethynyl acid chloride using  $(\text{PPh}_3)_2\text{PdCl}_2\text{-CuI}$  catalyst.

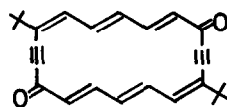
Facile and reversible chemical and electrochemical reductions are regarded as one of the most characteristic behavior of quinones. In this paper, we wish to report chemical and electrochemical reductions of bisdehydro[14]- and [18]annulenediones (3 and 4) performed with the purpose to confirm the quinonoid nature of the annulenediones (3 and 4).



1: R = OH, 2: R = NH<sub>2</sub>



3



4

### Chemical reduction.

Reduction of di-*t*-butylbisdehydro[14]annulenedione (3) with zinc powder-acetic anhydride in the presence of pyridine yielded diacetoxylbisdehydro[14]annulene (5, red plates, mp 232.0-233.4<sup>4</sup>), 81%, Mass(m/e): 406(M<sup>+</sup>); IR(KBr-disk): 2015w, 1763vs cm<sup>-1</sup>; ES:  $\lambda_{\text{max}}^{\text{THF}}$  ( $\epsilon$ ) 226(6430), 299(26900), 326(239000), 423sh(11400), 445(25500), 498(120), 523(100), 535(160), 549(220), 566sh(245), 587(465) nm). The electronic spectrum of 5 exhibits characteristic feature of aromatic annulene system consisting of sharp three main peaks and differs drastically from that of 3. Dimethoxybisdehydro[14]annulene (6) was also obtained by a reductive methylation of 3. To a solution of 3 in THF were added dimethyl sulfate, conc. sulfuric acid, and zinc powder at 0°C under argon atmosphere. Potassium hydroxide was added to the reaction mixture at the same temperature. The reaction mixture was worked up to afford dimethoxybisdehydro[14]annulene (6, reddish violet

crystals, mp 227.5–228.0°C<sup>4)</sup>, 30%, Mass(m/e): 350(M<sup>+</sup>) base peak, 335; IR(KBr-disk): 2020s cm<sup>-1</sup>; ES:  $\lambda_{\text{max}}^{\text{THF}}$  ( $\epsilon$ ) 227.5(6910), 303(23800), 333.5(228000), 429(10400), 452(24400), 497(590), 539.5(600), 563(990), 607(9910) nm).

Reduction of di-*t*-butylbisdehydro[18]annulenedione (**3**) with zinc-acetic anhydride in the presence of pyridine gave diacetoxybisdehydro[18]annulene (**5**) as dark red solution. The diacetoxy[18]annulene was found to be unstable and gradual decomposition was observed even at -10°C. Therefore, a solution of **5** obtained using zinc powder, acetic anhydride-d<sub>6</sub>, and pyridine-d<sub>5</sub> was directly subjected to measurement of <sup>1</sup>H NMR spectrum. Electronic spectrum could be measured using a dilute solution prepared by a similar procedure ( $\lambda_{\text{max}}^{\text{THF}}$  356, 370, 462sh, 491, 525, 543sh, 665, 684, 715, 747 nm<sup>5)</sup>). The absorption curve was closely related with that of tetra-*t*-butylbisdehydro[18]annulene<sup>6)</sup>. Successive treatment of **5** with zinc-conc. sulfuric acid and with dimethyl sulfate-potassium hydroxide gave dimethoxybisdehydro[18]annulene (**6**, dark reddish violet crystals, mp ca. 215°C (dec.), 42%, Mass(m/e): 402(M<sup>+</sup>) base peak, 387; IR(KBr-disk): 2020m cm<sup>-1</sup>; ES:  $\lambda_{\text{max}}^{\text{THF}}$  360sh, 377, 464sh, 496, 526, 5, 601, 618, 680, 770 nm<sup>5)</sup>). The dimethoxybisdehydro[18]annulene in solution decomposed slowly at room temperature.

The <sup>1</sup>H NMR parameters of **5**, **6**, **7**, and **8** are summarized in Table 1. The dramatic difference of <sup>1</sup>H NMR spectra between **3** and **5**, **6**, and **4** and **7**, **8** clearly indicates the aromatic nature of these reduction products. The diatropicity of the dihydroxybisdehydro[14]- and [18]annulene derivatives (**5** ~ **8**) were found to be comparable to those of the parent bisdehydro[14]- and [18]annulenes<sup>6)</sup>.

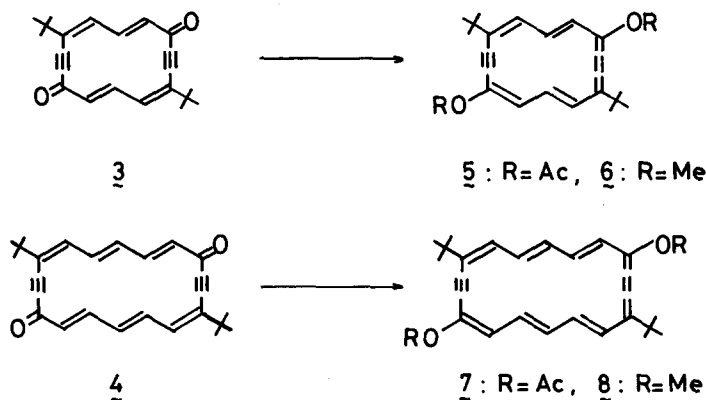


Table 1. <sup>1</sup>H NMR Parameters of **5**, **6**, **7**, and **8** ( $\tau$ -values).

Solv.	Temp.	H <sup>1</sup>	H <sup>3</sup>	H <sup>5</sup>	H <sup>2</sup>	H <sup>4</sup>	<i>t</i> -Bu	
<b>5</b>	CDCl <sub>3</sub>	35°C	0.63, d <sup>a)</sup>	0.85, d <sup>b)</sup>	14.91, dd <sup>c)</sup>		8.15, s	
<b>6</b>	CDCl <sub>3</sub>	35°C	0.97, d <sup>a)</sup>	0.84, d <sup>b)</sup>	14.75, dd <sup>c)</sup>		8.14, s	
<b>7</b>	CD <sub>2</sub> Cl <sub>2</sub>	-10°C	0.63, d <sup>d)</sup>	-0.12, t <sup>e)</sup>	0.39, d <sup>e)</sup>	14.40, dd <sup>f)</sup>	14.26, t <sup>e)</sup>	8.08, s
<b>8</b>	CDCl <sub>3</sub>	-20°C	0.61, d <sup>g)</sup>	0.09, t <sup>e)</sup>	0.81, d <sup>e)</sup>	14.08, dd <sup>h)</sup>	14.21, t <sup>e)</sup>	8.04, s

a) 13.7Hz. b) 13.2Hz. c) 13.2, 13.7Hz. d) 13.8Hz. e) 13.0Hz. f) 13.0, 13.8Hz. g) 13.8Hz. h) 13.0, 13.9Hz.

### Electrochemical properties.

Electrochemical reduction of some tetrakisdehydro[18]annulenediones was reported by Breslow *et al.* and Sondheimer<sup>7)</sup> by cyclic voltammetry. Our investigation of 'acetylene-cumlene' dehydroannulenes shows that bisdehydro[4n+2]annulenes are more stable than tetrakisdehydro[4n+2]annulenes<sup>6)</sup>. Therefore, bisdehydro[4n+2]annulenediones seem to be more suitable to examine quinonoid properties.

All electrochemical measurements were carried out in *N,N*-dimethylformamide (DMF) containing 0.1 M tetrabutylammonium perchlorate at  $20 \pm 0.2^\circ\text{C}$  using a three electrode cell. The concentrations of substrates were 0.65-1.48 mM, and the reduction potentials were determined under argon atmosphere. A glassy-carbon electrode was used as the working electrode and the counter electrode was platinum. The reference electrode was a silver-silver chloride wire in a glass tube provided with an asbestos plug at the bottom and filled with the solvent-electrolyte medium. The silver-silver chloride reference electrode showed  $-0.15\text{ V vs. a saturated calomel electrode (SCE)}$  and the potentials referred to SCE were measured.

The reduction potentials of annulenediones ( $\mathfrak{3}$  and  $\mathfrak{4}$ ) are summarized in Table 2 together with reference compounds. The cyclic voltammograms of annulenediones and reference acyclic diketone ( $\mathfrak{9}$ ) are shown in Figures 1 ~ 3.

The annulenediones ( $\mathfrak{3}$  and  $\mathfrak{4}$ ) show electrochemical reversibility at both the first and second waves even at low scan rates ( $16\text{ mV/sec} \sim$ )<sup>8)</sup>. The well defined two wave pattern corresponds to two discrete one-electron transfer processes forming radical anions initially and then dianions. This behavior is consistent with that observed for *p*-quinones. On the other hand, the cyclic voltammogram of  $\mathfrak{9}$  (see Figure 3) shows that the first step is quasi-reversible with potential separation of 80 mV, while the second step seems to be nearly irreversible. Thus, a marked difference between the annulenediones and acyclic diketone was observed.

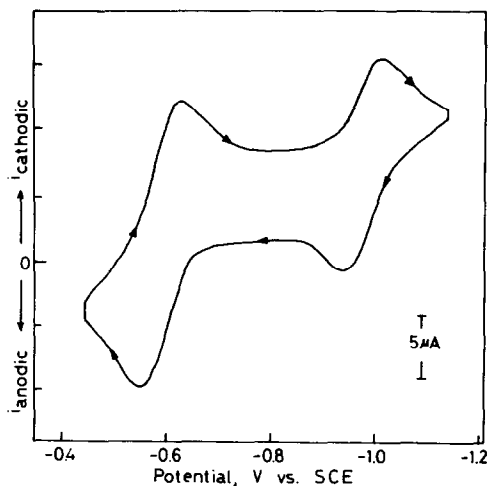


Figure 1. Cyclic voltammogram of  $\mathfrak{3}$ , 0.88 mM in DMF, scan rate 28 mV/sec.

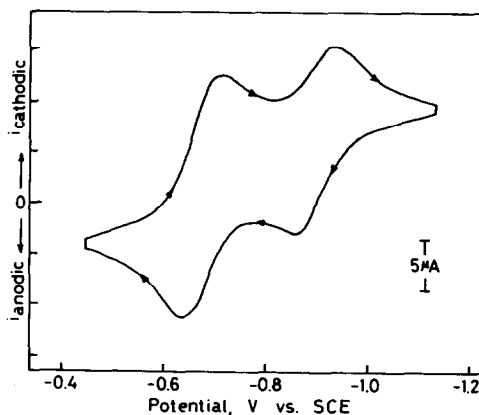


Figure 2. Cyclic voltammogram of  $\mathfrak{4}$ , 0.82 mM in DMF, scan rate 28 mV/sec.

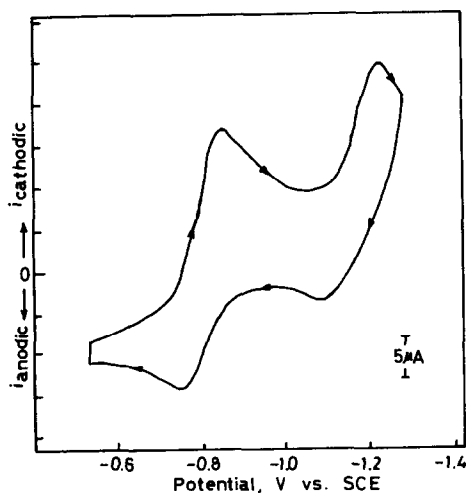
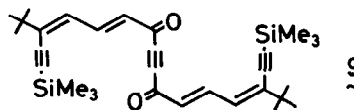


Table 2. Electrochemical Reduction Potentials.

Compound	Ep1(V vs. SCE)	Ep2(V vs. SCE)
<i>p</i> -Benzoquinone	-0.42	-1.18
1,4-Naphthoquinone	-0.59	-1.30
9,10-Anthraquinone	-0.82	-1.40
[14]Annulenedione ( <u>3</u> )	-0.63	-1.02
[18]Annulenedione ( <u>4</u> )	-0.72	-0.92
Acyclic Diketone ( <u>9</u> )	-0.81	-1.19

Figure 3. Cyclic voltammogram of 9, 1.48 mM in DMF, scan rate 73 mV/sec.

As shown in Table 2, the first reduction potentials of the annulenediones were found to be comparable with those of naphtho- and anthraquinones being smaller than that of benzoquinone. The second reduction potentials are smaller than those of *p*-quinones and similar to the tendency of tetrakisdehydro[18]annulenediones<sup>7),9)</sup>.

In conclusion, the chemical and electrochemical reductions of 3 and 4 clearly indicate that these annulenediones are indeed quinones derived from the aromatic bisdehydro[14]- and [18]-annulenes.

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#### References and Notes

- 1) Y. Onishi, T. Satake, M. Iyoda, and M. Nakagawa, *Tetrahedron Lett.*, 3169 (1979).
- 2) T. Satake, Y. Onishi, M. Iyoda, and M. Nakagawa, *Tetrahedron Lett.*, 3171 (1979).
- 3) Y. Onishi, M. Iyoda, and M. Nakagawa, see preceding paper.
- 4) A satisfactory elemental analysis was obtained.
- 5) The underlines denote the characteristic main absorption maxima of 'acetylene-cumulene' dehydroannulenes.
- 6) M. Nakagawa, *Pure Appl. Chem.*, **44**, 885 (1975).
- 7) R. Breslow, D. Murayama, R. Drury, and F. Sondheimer, *J. Am. Chem. Soc.*, **96**, 249 (1974).
- 8) Each electron-transfer step was found to be reversible by detail analysis of the  $E_p$  and  $i_p$  data.
- 9) The potentials listed in Table 2 could not be related directly to those obtained by Breslow's group<sup>7)</sup> and only the similar tendency was observed.

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