BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (8), 2420—2423 (1979)

Electron-organic Chemistry. IV.1) Structure—Anodic Potential Relationship and Electron-transfer-induced Reactions of [2.2]Para- and -Metaparacyclophanes

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(Received February 16, 1979)

The anodic peak potentials of [2.2]para- and -metaparacyclophanes were found to be highly dependent on the solvent. A cleavage reaction occured when [2.2]paracyclophane was electrolyzed anodically, using acids or alcohols as nucleophilic solvents, whereas lead tetraacetate oxidation in trifluoroacetic acid–dichloromethane gave nuclear substitution products. The cathodic reduction in hexamethylphosphoric triamide–lithium chloride–acetic acid gave 1,2-di-*p*-tolylethane and its Birch reduction products. On anodic oxidation, [2.2]metaparacyclophane gave a rearrangement reaction product, 4-hydroxy[2.2]metacyclophane. Possible reaction pathways for these reactions were formulated.

The dependence of the half-wave potentials on a molecular geometry and the reaction of the resulting radical ions have aroused considerable current interests.1–5) Recent findings that cyclophane-radical ions undergo intramolecular reactions,3–5) such as a transannular reaction, as well as rearrangement and fragmentation reactions led us to investigate the electron-transfer-induced reactions of basic cyclophanes [2.2]paracyclophane (**1**) and [2.2]metaparacyclophane (**13**).

The anodic half-wave potential of **1**, $+1.52$ V *vs.* SCE in acetonitrile–tetrabutylammonium perchlorate4) ($+1.47$ V in acetonitrile–lithium perchlorate6)), is anomalously low and is more cathodic by *ca.* 0.5 V4) than those of [*m*]paracyclophane or 1,2-bis(4-alkylphenyl)ethane. This fact indicates that one of the benzene rings serves as an internal π donor for stabilizing the aryl-cation radical formed. The enhanced π basicity of **1** towards tetracyanoethylene is explainable along the same lines.7) The anodic peak potential, E_{pa}, for [2.2]metaparacyclophane (**13**) was determined by the cyclic voltammetry at 250 mV/s and was found to be $+1.79$ V in acetonitrile–tetrabutylammonium perchlorate.4) It is more cathodic than those of the above model compounds by *ca.* 0.3 V.

The peak potential for these compounds, as determined by the cyclic voltammetry, showed a marked solvent dependence. The results are summarized in Table 1. At the scan rate of 250 mV/s, E_{pa} for **1** varied from $+1.57$ V in acetonitrile to $+1.12$ V in trifluoroacetic acid–dichloromethane (1: 1). A slight cathodic shift was also observed in solutions containing acetic acid, but no peak was recorded in acetic acid–sodium acetate or in acetic acid–ammonium salts.

The controlled potential electrolysis of **1** was carried out in trifluoroacetic acid or trifluoroacetic acid–dichloromethane, using tetrabutylammonium fluoroborate (TBAF) at $+1.5$—1.7 V, but no product was obtained. When **1** was electrolyzed in acetic acid–TBAF8) at $+1.7$—1.9 V, 1,2-bis[4-(acetoxymethyl)-phenyl]ethane (**2**) was obtained in a 24% yield. The structure was confirmed by the ^{1}H NMR and MS spectra and by elemental analyses.

Compound **2** was also formed in a 15% yield when **1** was electrolyzed anodically in acetic acid–sodium acetate.9) When a similar reaction was carried out in propionic acid–TBAF bispropionate, **3** was obtained.

In order to compare the electrochemical results with these of a chemical method, **1** was treated with lead tetraacetate in acetic acid–dichloromethane.10) This resulted in the formation of **2** and [2.2]paracyclophan-4-yl acetate (**7**)11) in 21 and 13% yields respectively. When the oxidation was carried out in trifluoroacetic

Table 1. Anodic peak potentials of [2.2]para- (**1**) and -metaparacyclophanes (**13**) in various solvents, +V *vs.* SCEa)

Scan rate mV/s	MeCN	TFA–CH_2Cl_2 (1: 1)	AcOH–CH_2Cl_2 (1: 4)	AcOH–MeCN (1: 1)	$PhNO_2$
	[2.2]paracyclophane (**1**)				
50	1.52, 1.75	1.06	1.40 sh	1.28	
100	1.54, 1.77	1.10	1.47 sh	1.32	1.69
250	1.57, 1.80	1.12	1.54 sh	1.36	1.74 sh
500	1.59, 1.82	1.15	1.62 sh	1.43	1.83 sh
	[2.2]metaparacyclophane (**13**)				
50	1.73	1.30, 1.60 sh	—b)	1.57 sh, 1.73	
100	1.76	1.32, 1.61 sh		1.60 sh, 1.75	
250	1.79	1.34, 1.64 sh		1.65 sh, 1.81 sh	
500	1.82	1.40, 1.71 sh		1.74	

a) Determined in the specified solvent using tetrabutylammonium perchlorate (0.1 M) as the supporting electrolyte. Scan range, 0—+2.2 V. Shoulders are denoted sh. b) No anodic peak was observed up to +2.2 V.

Table 2. The reaction of [2.2]paracyclophane (**1**) with lead tetraacetate[a)]

Compd **1**, mmol	$Pb(OAc)_4$, mmol	Yield/% **1**	**6**	**8**
3.0	1.5	50	15	trace
3.0	3.0	17	14	12
3.0	7.5	0	0	39

a) The reaction was carried out in trifluoroacetic acid–dichloromethane (1 : 2) at 0 °C for 12 h.

acid–dichloromethane at 0 °C, however, no cleavage products were obtained.[12)] Instead, 4-hydroxy[2.2]-paracyclophane (**6**)[11)] and *pseudo-para*-dihydroxy[2.2]-paracyclophanes (**8**)[13)] were formed. The results are shown in Table 2. The ready hydrolysis of trifluoroacetate during handling was noticed.

The formation of **7** is assumed to involve the nucleophilic reaction of acetic acid towards the [2.2]paracyclophane cation radical, **9**, to give **10**, which then undergoes further electron transfer and deprotonation. Oxidation with lead tetraacetate appears to favor this route, especially when trifluoroacetic acid is used as the solvent, for it is known to stabilize aryl-cation radicals.[14)]

On the other hand, the electron abstraction of **1** on a platinum anode gives the cation radical, **11**, which, *via* the acetate radical, **12**, gives diacetate, **2**. The expected side-chain acetoxylation[10)] did not occur, possibly because of an excessive internal strain[15)] present in **1** which was relieved by going into **11**. It is highly probable that electron-transfer and acetoxylation to give (**12**) occur in a concerted manner.

Solvolytic anodic-cleavage reactions occurred in alcoholic solvents, though in low yields. 1,2-Bis[4-(methoxymethyl)phenyl]ethane (**4**) was obtained when **1** was electrolyzed anodically in methanol–TBAF at +1.39 V using a platinum electrode. A similar reaction in ethanol gave a diethoxy compound, **5**.

The anodic electrolysis of **13** in acetic acid–sodium acetate at the controlled potential of +1.80 V gave 4-hydroxy[2.2]metacyclophane (**17**) in a 20% yield, together with the recovered material. The rearranged structure, **17**, was confirmed by comparing the sample with an authentic material prepared from [2.2]metacyclophane by treatment with benzoyl peroxide and copper(II) chloride, followed by hydrolysis.[16)] Although [2.2]metacyclophane and derivatives have been shown[4)] to undergo easy transannular dehydrogenation reaction by means of the anodic reaction in acetonitrile, no such reaction was found to occur in acetic acid–sodium acetate. Conversely, no skeletal change occurred when **13** was electrolyzed in a solvent containing acetonitrile.

The possible reaction scheme for the formation of **17** involves the oxygenation of the cation radical, **14**, to give **15**, which is then rearranged to **16**. The deprotonation of **16**, followed by hydrolysis, gives **17**. The addition of water increased the yield of **17**, and it might be possible that water instead of the presumed acetoxylation is responsible for the introduction of the hydroxyl group. That **17** was the initial product of the reaction was shown by gas chromatography of the reaction mixture, which was carefully handled to avoid hydrolysis.

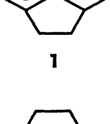
The cathodic reduction of **1** was then carried out under conditions which involved a solvated electron.[17)] To a solution of **1** in hexamethylphosphoric triamide containing lithium chloride, acetic acid was added as a proton source, after which the mixture was electrolyzed cathodically under constant current conditions using a current density of 12 mA/cm^2. As cathodes, titanium, lead, and platinum were used, while a platinum wire was used as the anode. We thus obtained three cleavage products, **18**—**20**, which were separated by column chromatography on alumina containing silver nitrate. Of the cathode materials, titanium gave the highest yield of cleavage products. When 7.4 F/mol of electricity was passed through, *ca.* 50% of the material was cleaved. The results are summarized in Table 3.

Table 3. The constant-current cathodic reduction of [2.2]paracyclophane (**1**)[a)]

Electrode	Yield/% **18**	**19**	**20**
Ti	17	21	7.5
Pb	5	trace	trace
Pt	trace	—	—

a) The reaction was carried out in hexamethylphosphoric triamide–lithium chloride–acetic acid at the current density of 12 mA/cm^2.

A usual Birch reduction using liq ammonia–tetrahydrofuran–ethanol–sodium gave only *dl*-tetrahydro-(**1**),[18)] although a modification of the procedure reported by Marshall *et al.*[19)] gave **18**, but no further reduction products. The cathodic reduction of **18** carried out in the same way as above gave **19** and **20**.



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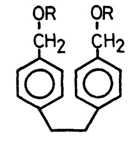

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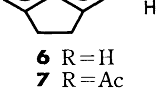
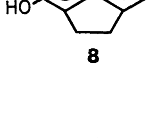
3 R=EtCO
4 R=Me
5 R=Et



6 R=H
7 R=Ac



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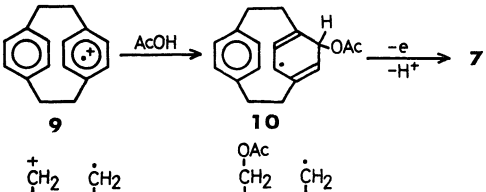
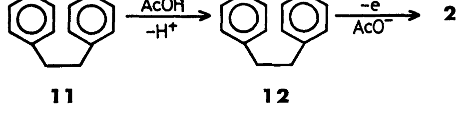
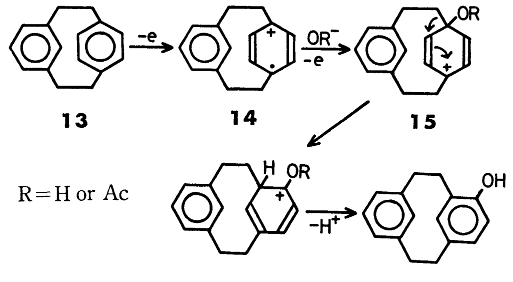
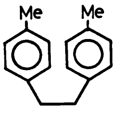


9 **10**



11 **12**





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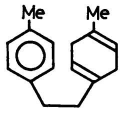

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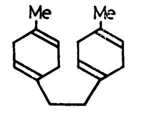

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Experimental

Cyclic Voltammetry. Cyclic voltammetry was performed at room temperature using the combination of a generator, Hokuto HB-107A, and a potentiostat, Hokuto HA-101. The H-type cell used consisted of an anode compartment (20 ml) and a cathode compartment separated by a glass frit. A platinum inlay electrode, Beckman No. 39273, was used as the anode, while platinum wire was inserted to serve as the counter electrode. The reference SCE electrode was connected to the side-arm with the aid of two junction bridges, each fitted with a ceramic plug. These were filled with saturated KCl solution and solution containing anolyte.

Controlled-potential and Controlled-current Electrolyses. A Hokuto potentiostat/galvanostat HA-101 (max. output 30 V, 0.1 A) or HA-105 (max. output 200 V, 1 A) was used as the dc source. Coulometry was performed by a Hokuto digital coulometer, HF-102.

A cylindrical cell is equipped with two side arms for connecting the SCE and a nitrogen bubbler. A ceramic thimble was used as the divider. A punched platinum electrode with an area of 40 cm^2 was used as the anode, while a platinum wire was used as the cathode for the anodic experiments. The electrodes used for solvated-electron reduction (Ti, Pb, and Pt) have an area of 8.5 cm^2.

The reference electrode was connected to the side arm through two junction bridges, each fitted with a ceramic plug and each containing a saturated KCl solution and the reaction medium.

1,2-Bis[4-(acetoxymethyl)phenyl]ethane (2). A mixture of **1** (200 mg, 0.91 mmol) in acetic acid (100 ml) containing TBAF (0.1 M) was electrolyzed at the controlled potential of +1.7—1.9 V. When 2F/mol of the electricity had been consumed, the electrolysis was stopped and the resultant reaction mixture was neutralized with aqueous sodium hydrogen carbonate. The ether extracts were evaporated and passed through a Florisil column, using benzene as the eluent. The products were further purified by liquid chromatography on a prepacked silica gel column (Lobar column from Merck). Compound **2** was obtained as colorless crystals (mp 77—78.5 °C (recrystallized from benzene–hexane)) in a 24% yield. The material recovery was 16%. The rest of the material was a colored, tarry matter. ^{1}H NMR (CDCl$_3$) δ 2.08s (6H), 2.90s (4H), 5.08s (4H), and 7.24s (8H).

Found: C, 73.29; H, 6.75%. Calcd for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79%.

The electrolysis of **1** in acetic acid–sodium acetate also produced **2** in a 15% yield.

1,2-Bis[4-(propionyloxymethyl)phenyl]ethane (3). A mixture of **1** (208 mg, 1.0 mmol) in propionic acid (50 ml) and dichloromethane (150 ml) containing TBAF (0.1 M) was electrolyzed until 1.8 F/mol of electricity had been consumed. Subsequent chromatography on Florisil eluted with benzene–hexane gave **3** as a viscous oil in a 9% yield; this substance solidified on long standing; mp 29—30 °C. The starting material was recovered in a 70% yield. ^{1}H NMR (CDCl$_3$) δ 1.17t (6H), 2.23q (4H), 5.03s (4H), and 7.20s (8H); MS *m/e* 297 [M$^+$−57 (COC$_2$H$_5$)].

Found: C, 73.76; H, 7.26%. Calcd for $C_{22}H_{26}O_4$: C, 74.55; H, 7.39%.

1,2-Bis[4-(methoxymethyl)phenyl]ethane (4). A mixture of **1** (500 mg, 2.4 mmol) and TBAF (1.1 g, 33 mmol) in methanol (500 ml) was electrolyzed at the constant potential of +1.39 V. A usual work-up, followed by chromatography on silica gel, gave **4** as colorless needles; mp 69—72 °C (recrystallized from hexane); ^{1}H NMR (CDCl$_3$) δ 2.83s (4H), 3.38s (6H), 4.43s (4H), and 7.16s (8H).

Found: C, 79.98; H, 8.26%. Calcd for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20%.

Cathodic Reduction of 1. The constant-current cathodic reduction of **1** was carried out in hexamethylphosphoric triamide containing lithium chloride (0.3 M), using acetic acid as a proton source, at the current density of 12 mA/cm^2. The results are summarized in Table 3.

The typical reaction was carried out as follows: a mixture of **1** (610 mg, 2.9 mmol), hexamethylphosphoric triamide (75 ml) containing lithium chloride (0.3 M), and acetic acid (2 g) was electrolyzed until 7.4 F/mol of electricity had been consumed, using a titanium cathode and a platinum anode. The voltage between the working and reference electrodes was −2.66——3.2 V. The ether extract was passed through a column packed with Wakogel C-200 containing 20% silver nitrate. The column was then eluted with hexane–benzene.

Compounds **18** (17%), **19** (21%), and **20** (7.5%) were successively eluted. Compound **18** was obtained as colorless needles; mp 80—81.5 °C; ^{1}H NMR (CDCl$_3$) δ 2.28s (6H), 2.82s (4H), and 7.06s (8H).

Compound **19** was obtained as colorless needles; mp 48—49.5 °C; ^{1}H NMR δ 1.67s (3H), 2.28s (3H), 2.10—2.40m (4H), 2.57m (4H), 5.40m (2H), and 7.04s (4H); MS *m/e* 212.

Found: C, 89.93; H, 9.39%. Calcd for $C_{16}H_{20}$: C, 90.50; H, 9.50%.

Compound **20** was obtained as colorless needles; mp 57—58 °C; ^{1}H NMR δ 1.67s (6H), 2.08s (4H), 2.56m (8H), and 5.40m (4H); MS *m/e* 214.

Found: C, 88.54; H, 10.06%. Calcd for $C_{16}H_{22}$: C, 89.65; H, 10.35%.

When **18** was subjected to similar reaction conditions, **19** (13%) and **20** (42%) were obtained.

Anodic Rearrangement of 13. A solution of **13** (52 mg, 0.25 mmol) in acetic acid (50 ml) containing sodium acetate (0.2 M) was electrolyzed at +1.80 V. After 2.8F/mol of electricity had been passed through the reaction mixture was handled as usual and was analyzed by column chromatography on silica gel. In addition to the recovered **13** (36%), 4-hydroxy[2.2]metacyclophane (**17**) (mp 161—164 °C) was obtained in a 20% yield. It was identical with the authentic material prepared according to the literature.[19]

The Reaction of 1 with Lead Tetraacetate. Compound **1** was treated with lead tetraacetate in acetic acid–dichloromethane or in trifluoroacetic acid–dichloromethane.

The reaction in trifluoroacetic acid–dichloromethane is summarized in Table 2. A typical run was carried out as follows: to a solution of **1** (625 mg, 3.0 mmol) in dichloromethane (80 ml), a solution of lead tetraacetate (670 mg, 1.5 mmol) in TFA (10 ml) was added at 0 °C. After 9 h the reaction mixture was worked-up as usual. Column chromatography on Florisil eluted by benzene gave **1** (50%), **6** (15%) (mp 184—193 °C),11) and a trace amount of **8**. Compound **8** was obtained in a 39% yield when an excess amount of lead tetraacetate was employed; mp 229—231 °C.13)

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