Electron-organic Chemistry. Anodic Oxidation of [2.2]Metacyclophanes and Transannular Cation Radical Formation

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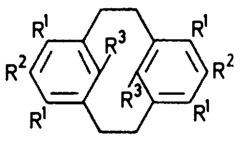
Anodic oxidation of [2.2]metacyclophane gave a transannular dehydrogenation product, 4,5,9,10-tetrahydropyrene, dihydropyrene, and pyrene. Cyclic voltammetry revealed a one-electron transfer mechanism involving a cation radical. Half-wave potentials and ionization potentials of alkylated [2.2]metacyclophanes were compared with those of simple arene models. For the 5,13-dialkyl derivative the half-wave potential was found to be anomalously lower than that of the model suggesting the involvement of a transannular cation radical intermediate.

THE unique structural features, the very short distance between the two inner aryl positions and considerable strain, of [2.2]metacyclophane (1)[1] make it suitable for investigating the generation, stability, and fate of an aryl cation radical situated in close proximity to another aryl ring. We have carried out voltammetry, using both stationary and rotating platinum electrodes, and preparative anodic oxidation of a series of alkylated [2.2]metacyclophanes (2)—(6).



(1) $R^1 = R^2 = R^3 = H$
(2) $R^1 = R^3 = H, R^2 = Me$
(3) $R^1 = R^3 = H, R^2 = Et$
(4) $R^1 = Me, R^2 = R^3 = H$
(5) $R^1 = R^2 = Me, R^3 = H$
(6) $R^1 = R^3 = Me, R^2 = H$

Cyclic Voltammetry and Controlled Potential Electrolysis.—Cyclic voltammetry (c.v.) was carried out in MeCN, with $Bu^n_4NClO_4$ as supporting electrolyte and saturated calomel electrode as reference, using a platinum inlay electrode on a generator–potentiostat combination at various scan rates. For rapid scans the wave-memory technique was employed. The representative curves are shown in Figures 1—3. The data are summarized in Table 1.

TABLE 1

Peak potentials from cyclic voltammetry [a] (V *versus* s.c.e.)

Compound	Scan rate (mV s^{-1})	O_1	O_2	R_2	O_3
(1)	140	1.38	1.80		
(2)	50	1.05	1.36	1.31	1.76
	240	1.04	1.37	1.31	1.74
	500	1.03	1.36	1.31	1.78
(3)	240	1.18	1.37	1.31	1.76
(4)	300	1.16	1.41	1.34	1.80
	600	1.20	1.43	1.37	1.82
(5)	145	0.88	1.16	1.13	
(6)	50	1.16			
	500	1.24			

[a] $MeCN–Bu^n_4NClO_4$ (0.1M).

Compound (2) showed three oxidation peaks, O_1—O_3, at +1.04, 1.37, and 1.74 V, respectively, together with a reduction peak R_2 at +1.31 V on potential reversal at a scan speed of 240 mV s^{-1} (Figure 1a). On increasing the scan rate, the peak potential remained almost constant but the quasi-reversible couple O_2–R_2 become more apparent indicative of a coupled electrochemical mechanism.[2] C.v. at the same speed with potential clipping at +1.5 V showed R_2 as a more distinct peak (Figure 1b). When the potential range was extended to —0.4 V cathodic peaks appeared which increased on repeated scanning suggesting the abstraction of a proton during the reaction.[3]

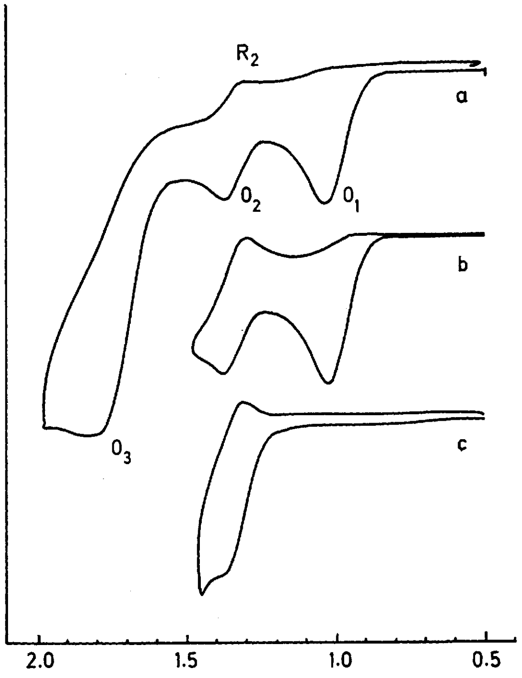


FIGURE 1 Cyclic voltammograms of a, 5,13-dimethyl[2.2]metacyclophane (2) at a scan rate of 240 mV s^{-1}; b, compound (2) at the same scan rate but with potential clipping at +1.50 V; and c, 2,7-dimethyl-4,5,9,10-tetrahydropyrene (7b) at 750 mV s^{-1}

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[1] T. Sato, *Nippon Kagaku Zasshi*, 1971, **92**, 277; F. Vögtle and P. Neumann, *Angew. Chem. Internat. Edn.*, 1972, **11**, 73.

[2] R. S. Nicholson and I. Shain, *Analyt. Chem.*, 1964, **36**, 706.

[3] D. T. Sawer and J. L. Roberts, jun., ' Experimental Electrochemistry for Chemists,' Wiley, New York, 1974, p. 67.

That the O_2–R_2 couple corresponds to the formation of the dimethyltetrahydropyrene (7b) is shown by the c.v. of the latter (Figure 1c), which shows a single anodic peak similar to O_2 for (2). Presumably, one-electron transfer from (2) give the cation radical of (2) (O_1), which is converted to (7b) as evidenced by the preparative electrolysis experiments described below. Whether the peak O_3 corresponds to further oxidation stage, *i.e.* a dication, is not known.

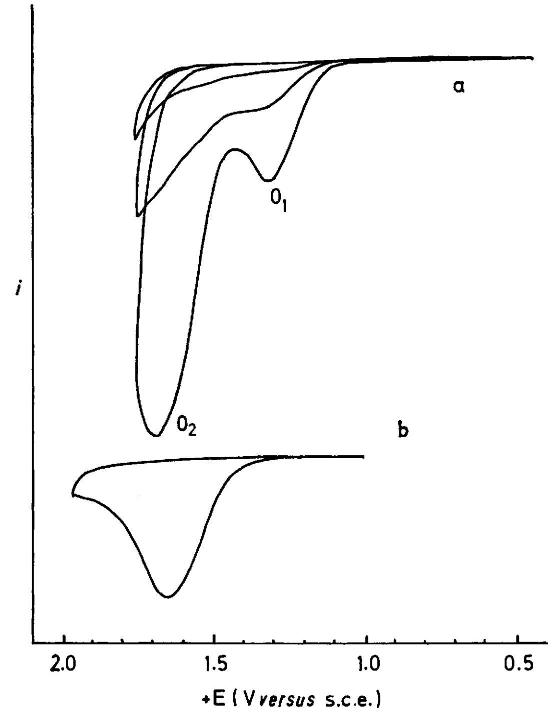
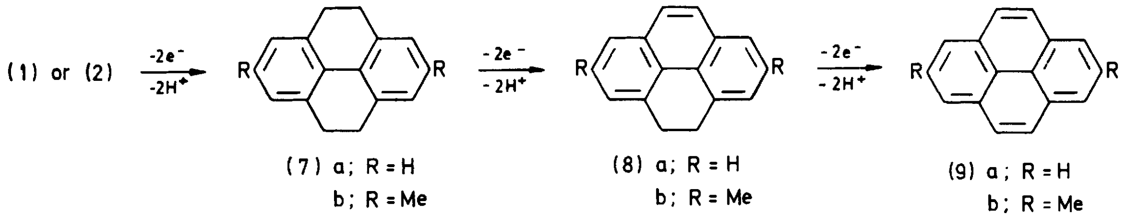


FIGURE 2 Cyclic voltammograms of a, [2.2]metacyclophane (1), three scans at 250 mV s^{-1} and b, 4,5,9,10-tetrahydropyrene (7a) at 200 mV s^{-1}

The anodic oxidation of (2) in MeCN, with $Bu^n_4NClO_4$ as supporting electrolyte, was carried out at the constant potential of +1.40 V supplied from a potentiostat in a divided cell using platinum as electrodes. The starting material disappeared when 2.47 F mol^{-1} were passed through (3.5 min for 0.5 mmol), giving (7b)—(9b) as products. The relative yield of (7b) reached 80% and the current efficiency determined from coulometry was 92% assuming each dehydrogenation step required a two-electron oxidation (Scheme 1).



SCHEME 1

The progress of the reaction was followed by g.l.c. of aliquot samples. The results clearly showed that the reaction occurred successively [(1) ⟶ (7a) ⟶ (8a) ⟶ (9a)]. Similar results were obtained for (2). On electrolysis under the same conditions as above (7b) gave 85% (8b) together with a small amount of (9b) (2.66 F mol^{-1}).

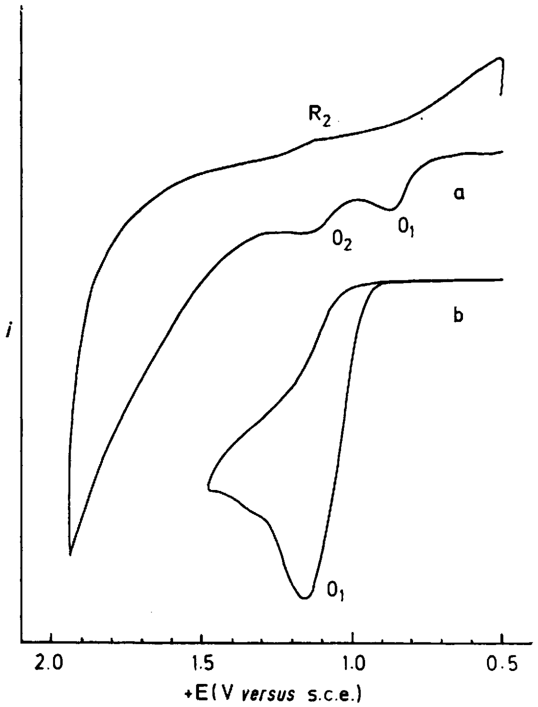


FIGURE 3 Cyclic voltammograms of a, 4,5,6,12,13,14-hexamethyl[2.2]metacyclophane (5) at 154 mV s^{-1} and b, 4,6,8,12,14,16-hexamethyl[2.2]metacyclophane (6) at 50 mV s^{-1}

The anodic dehydrogenation reaction occurred with other metacyclophanes. For example, (1) gave (7a)—(9a) at +1.51 V. Although (1) disappeared within a few minutes on electrolysis the yields of the isolable dehydrogenation products were lower than for (2). This can be attributed to a side reaction to give insoluble matter formed by coupling of the 5- and 13-positions which are blocked in (2).[4] In agreement, the c.v. of (1)

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[4] K. Bechgaad, O. Hammerich, N. S. Moe, A. Ronlan, U. Svanholm, and V. D. Parker, *Tetrahedron Letters*, 1972, 2271; R. Reynolds, L. L. Line, and R. F. Nelson, *J. Amer. Chem. Soc.*, 1974, **96**, 1087; E. T. Seo, R. F. Nelson, J. M. Fritsch, L. S. Marcoux, D. W. Ledy, and R. N. Adams, *ibid.*, 1966, **88**, 3498.

showed a rapid current decrease on multiple scanning (Figure 2, three scans). Similarly the c.v. of (7a) and (8a) showed rapid current decrease on repeated scans.

The c.v. for other compounds are compiled in Table 1. The curves for (3) and (4) are essentially similar to that for (2) exhibiting three oxidation and one reduction peak. Compound (5) showed O_1 at an extremely low potential (0.88 V at 140 mV s^{-1}). It showed the O_2–R_2 couple, though the latter is not distinct, attributed to the formation of the transannular product. Beyond O_2 the anodic current increased sharply and no peak appeared between O_2 and +2.0 V (Figure 3a). With (6) the coupling positions are blocked. The material was largely recovered on electrolysis. The c.v. showed an irreversible curve as shown in Figure 3b. No new oxidation peak appeared on further increase of potential.

TABLE 2

Oxidation half-wave [a] and ionization potentials [b] (V *versus* s.c.e.)

Cyclophane	$E_{1/2}$	Arene	$E_{1/2}$	$\Delta E_{1/2}$	$IP_{cyclophane}$	IP_{arene}	ΔIP
(1)	1.62	*m*-Xylene	2.15	0.53	8.41	8.71	0.30
(2)	1.40	Mesitylene	2.18	0.78	8.26	8.57	0.31
(3)	1.38	Mesitylene			8.20		
(4)	1.49	Durene	1.71	0.22	8.14	8.45	0.31
(5)	1.22	Pentamethylbenzene	1.66	0.44	8.0	8.23	0.23
(6)	1.28	Pentamethylbenzene	1.66	0.38	7.82	8.23	0.41

[a] $MeCN$–$Bu^n{}_4NClO_4$ (0.1M). [b] Calculated from the charge transfer bands of tetracyanoethylene complexes.[7]

Half-wave and Ionization Potentials.—Half-wave potentials for (1)—(6), determined in $MeCN$–$Bu^n{}_4NClO_4$ by using a rotating platinum electrode on a three-electrode device, are compared with those for the corresponding arene models, *e.g.* *m*-xylene for (1) and mesitylene for (2), *etc.* (Table 2). The oxidation potentials of the metacyclophanes are much more cathodic than those of the simple arenes. For example, $E_{1/2}$ for (1), ±1.62 V, is lower than that of *m*-xylene by 0.53 V and is almost the same as those of related compounds having biphenyl and phenanthrene systems, such as (7a) and (8a) (Table 3). For (2), $\Delta E_{1/2}$ from mesitylene reaches almost 0.8 V. Surprisingly the reduction potential of (2) is more cathodic than that of (7b) which has biphenyl structure. It is remarkable that the dialkyl derivatives (2) and (3) are more easily oxidized than the tetramethyl derivative (4). This is contrary to expectation since durene has a lower $E_{1/2}$ than mesitylene. Alkyl substitution at the 5- and 13-positions appears to be responsible for the lowering of $E_{1/2}$. In agreement, (5) has a very low $E_{1/2}$.

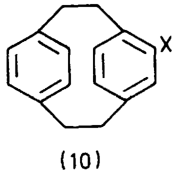
TABLE 3

Oxidation half-wave potentials [a] for compounds (7a and b), (8a), and (9a) (V *versus* s.c.e.)

Compound	$E_{1/2}$
(7a)	1.58
(7b)	1.39
(8a)	1.59
(9a)	1.40

[a] $MeCN$–$Bu^n{}_4NClO_4$ (0.1M).

The lowering of $E_{1/2}$ appears to be dependent on the specific substitution pattern and cannot be explained by simple π-assistance as observed for [2.2]paracyclophanes (10). Shono and his co-workers[5] observed a linear relation between the oxidation potentials and $\sigma_p{}^+$ for (10) as well as several non-conjugated dienes. Transannular assistance from the opposing π-system substituted with electronegative substituents toward the π-cation radical centre is responsible for the phenomena. The $E_{1/2}$ of (10; X = H) is +1.52 V, which is considerably more cathodic than that of the arene model, *p*-xylene (+1.92 V). This can be attributed to increased π-basicity due to the transannular interaction.[6] For the metacyclophanes, however, the deviation from the corresponding arenes is less systematic as shown in Table 2.



(10)

Table 2 summarizes ionization potential data determined from the charge-transfer spectra of tetracyanoethylene complexes.[7] The potential for the metacyclophane is lower than that of the corresponding arene. The simple parallelism observed between these two figures indicates a π-assistance mechanism. A good deal of evidence has been accumulated[8] to suggest a linear free energy relationship between half-wave and ionization potentials. The data in Table 2, however, reveal no such simple relation exists in the case of metacyclophanes. An alternative explanation other than π-assistance is needed to account for the anomalous $E_{1/2}$ of these molecules.

Metacyclophanes are highly strained molecules due to

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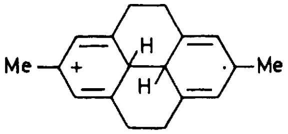
[5] T. Shono, A. Ikeda, J. Hayashi, and S. Hakazaki, *J. Amer. Chem. Soc.*, 1975, **97**, 4261.

[6] M. Sheehan and D. J. Cram, *J. Amer. Chem. Soc.*, 1969, **91**, 3553.

[7] T. Sato and T. Takemura, *J.C.S. Perkin II*, 1976, 1195, S. Hayashi and T. Sato, *Nippon Kagaku Zasshi*, 1970, **91**, 950; *Bull. Chem. Soc. Japan*, 1972, **45**, 2360.

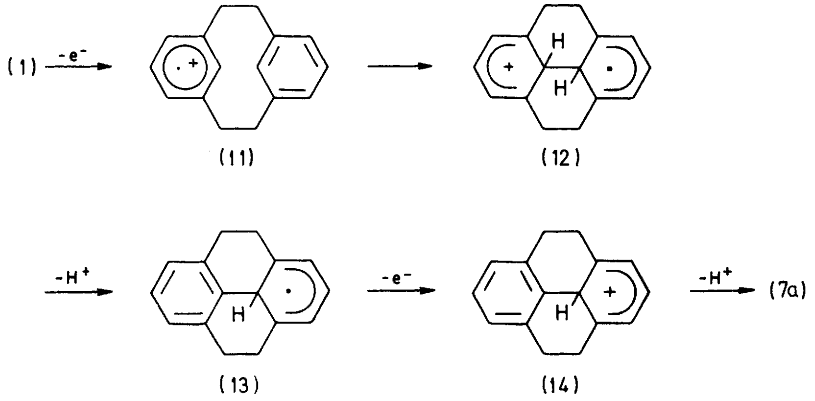
[8] P. Zuman, *Progr. Phys. Org. Chem.*, 1967, **5**, 81.

the close proximity of the two π-systems within a ten-membered ring. The strain energy for (1), for example, was found from combustion analysis to 12 kcal mol^{-1} compared with two *m*-xylene molecules.[9] We assume the one-electron oxidation of metacyclophane involves σ-bond formation to give the transannular cation radical (2′). On going to (2′) from (2) strain is released together with a partial loss of aromatization energy. The large $\Delta E_{1/2}$ found for (2) reflects the stability of the canonical form (2′) in which two methyl groups stabilize the radical and cation centres by hyperconjugation.



(2′)

As support for σ-bond assistance we have found enhanced reactivity of (2) toward copper(II) chloride, iron(III) chloride, and lead tetra-acetate to give (7b).[10] Competitive experiments showed that (2) is 160 times more reactive than (1). While (3) has reactivity comparable with (2) compound (4) is only 40 times as reactive as (1) and is less reactive than the dialkyl derivatives although the ionization potential is the lowest for these.



SCHEME 2

The ECEC mechanism formulated in Scheme 2 explains all the experimental evidence. The cation radical (11) is converted into (12), which is deprotonated to give (13) followed by a second electron transfer. Compound (7b) results from deprotonation of (14).

Parker and his co-workers have carried out the anodic oxidation of unsymmetrically substituted methoxybibenzyl[11] and homologues[12] to distinguish between two mechanisms for bridged biphenyl formation, cation radical coupling and electrophilic cation radical attack on an unoxidized aromatic ring. Bridged biphenyls with a favourable ring size were shown to be formed by radical coupling while intermolecular arylation occurred by attack of a cationic species on the neutral aromatic ring. The radical coupling reaction was also shown to occur in related cases.[4,13]

With [2.2]metacyclophanes aryl coupling occurred during one-electron abstraction as shown by c.v. This implies that the intramolecular reaction is greatly assisted by internal strain and the close proximity of an aromatic carbon atom to the radical centre.

EXPERIMENTAL

Voltammetry.—Cyclic voltammetry was performed at room temperature under nitrogen using the combination of a generator (NF Circuit Block FG-121B or Hokuto Denko HA-101) and a potentiostat (Hokuto Denko HB-107A). For rapid scans exceeding 2 V s^{-1} the output was stored in a wave-memory (NF Circuit Block WM-812A) and reproduced on an oscilloscope or an *X–Y* recorder by converting the time scale. The *H* type cell was used consisting of an anode compartment (20 ml) and a reference compartment separated by a glass frit. A platinum inlay electrode (Beckman No. 39273) was used as the anode while platinum wire was inserted as the counter electrode. The reference saturated calomel (s.c.e.) electrode was connected to the main compartment through a side-arm with the aid of two junction bridges each fitted with a ceramic plug. These were saturated KCl solution and MeCN solution containing anolyte.

The half-wave potential was recorded on a Shimadzu RP-50 polarograph connected to an AIC-50 automatic potential corrector using an RE-50 rotating platinum electrode. The cell used was similar to that above.

Controlled Potential Electrolyses.—The preparative cell was a cylinder with the active volume of 70 ml and was equipped with a nitrogen bubbler at the bottom and a side-arm for the reference electrode. The punched platinum electrode (Tokuriki) had an area of 54 cm^2. The counter

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[9] C. Shieh, D. C. McNally, and R. H. Boyd, *Tetrahedron*, 1969, **25**, 3653.

[10] K. Nishiyama, K. Hata, and T. Sato, *J.C.S. Perkin II*, 1974, 577; *Tetrahedron*, 1975, **31**, 239.

[11] V. D. Parker and A. Ronlan, *J. Amer. Chem. Soc.*, 1975, **97**, 4714.

[12] A. Ronlan, D. Hammerich, and V. D. Parker, *J. Amer. Chem. Soc.*, 1973, **95**, 7132.

[13] J. R. Falck, L. L. Miller, and F. R. Stermitz, *J. Amer. Chem. Soc.*, 1974, **96**, 2981.

electrode, a platinum wire, was contained in a ceramic thimble which served as a divider. For stirring a magnetic bar was inserted. The required potential was supplied from a Shimadzu PS-2 potentiostat and coulometry was performed by inserting in series a Hokuto Denko HF-102 digital coulometer.

A typical run was carried out as follows. A solution of compound (2) (12 mg, 0.05 mmol) in acetonitrile (50 ml) containing Bu^n_4NClO (0.1M) was electrolysed at a constant potential of +1.4 V *versus* s.c.e. for 3.5 min when 11.9 C of electricity were consumed, giving (7b)—(9b) as products. These were characterised by comparison with authentic samples.[10] The maximum yield of (7b) was 80% and current efficiency was 92%.

We thank Professor G. Sato, Sophia University, for advice on instrumentation. We also thank Professors T. Osa, Tohoku University, and T. Shono, Kyoto University, for helpful discussions. This work was supported by a grant-in-aid for scientific research from the Ministry of Education.

[6/844 *Received*, 3*rd May*, 1976]