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The Stepwise Cathodic Reduction of [2$_4$]Paracyclophanetetraene

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The reduction of [2$_4$]paracyclophane-1,9,17,25-tetraene at a mercury cathode has been investigated. The hydrogenation of one, two, three, or all four olefinic double bonds in the substrate can be achieved selectively by proper variation of the electrode potential. Two possible dienes having the double bonds in adjacent or opposite positions, respectively, are formed in the ratio 2:1. Voltammetry at a hanging mercury drop electrode has been used both in order to select the proper potentials for preparative electrolyses and to characterize the compounds.

We recently described the reversible two-electron reduction of [2$_4$]paracyclophane-1,9,-17,25-tetraene, *1* (Fig. 1).[1] The dianion formed upon electron transfer could be intercepted by protonation with acetic acid, leading to [2$_4$]-paracyclophane-1,9,17-triene, *2*, as was shown by constant potential electrolysis (CPE). Further reduction of *2* would be expected to lead to progressively more hydrogenated compounds. The number and positions of the double bonds in the bridges between the benzene rings will influence the flexibility and planarity of these molecules. The double bonds always have *cis* configuration and the saturated bridges can attain *gauche*, but not *anti*, orientations of the benzene rings. The interconversion of *gauche*$^+$ and *gauche*$^-$ conformations over a *syn* barrier can be studied by dynamic NMR. The compounds *1*—*4* and *6* are also desired for the investigation of steric effects on the photocyclisation of *cis* stilbenes to dihydrophenanthrenes.[2]

CPE is a good method for partial reduction, and in the present paper, the selective preparation of *2*—*6* by this method will be described. The results demonstrate the usefulness of CPE. It is improbable that the same results could

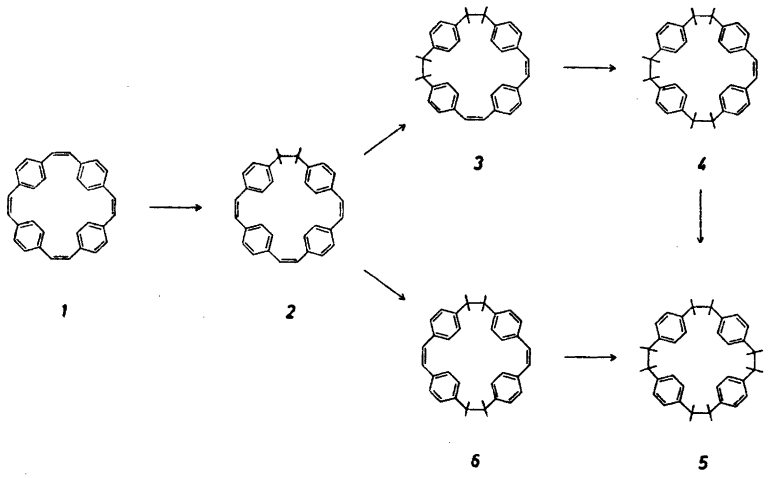

Fig. 1. Hydrocarbons formed in the stepwise cathodic reduction of [2$_4$]paracyclophanetetraene, *1*.

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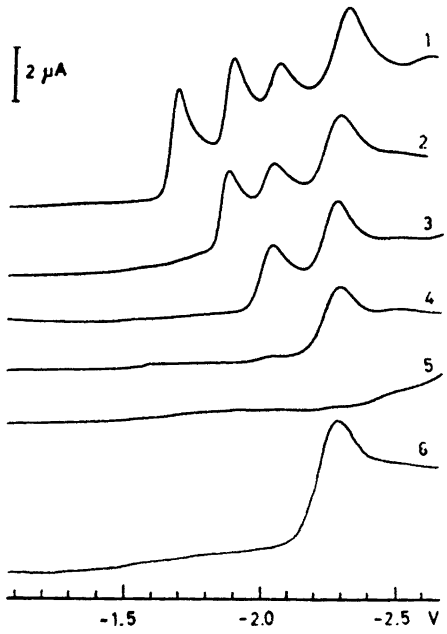

Fig. 2. Hanging mercury drop voltammograms of compounds *1*–*6* in DMF/0.1 M TEAP. Substrate conc. 10^{-3} M, phenol conc. 8×10^{-3} M. Sweep rate 25 mV s^{-1}. Pot. *vs.* SCE.

have been achieved by chemical reducing agents such as dissolving metals.

RESULTS

Electroanalytical studies. The cyclic voltammogram of *1* in aprotic DMF is illustrated in Ref. 1. Addition of phenol, an eightfold molar amount with respect to *1*, gives a voltammogram as shown in Fig. 2, which also shows similar recordings for *2*–*6*. In the presence of phenol, no anodic peaks were obtained upon sweep reversal, except that, at insufficient phenol concentration, some reversibility of *1* was observed.

The peak potentials of *1* are: −1.70 V, −1.90 V, −2.07 V, and −2.33 V *vs.* SCE. Correspondingly, they are for *2*: −1.90 V, −2.07 V, and −2.33 V, for *3*: −2.07 V and −2.32 V, for *4*: −2.33 V, and for *6*: −2.33 V. For the completely bridge-saturated *5*, no cathodic reduction was observed under our conditions.

Coulometric and preparative studies. Electrolyses of *1* at the potentials corresponding to the peaks in its voltammogram have been made. Compounds *3* and *6* were also electrolyzed. All results are collected in Table 1. In the cases where mixtures of products resulted, the molar ratios stated are based on ^{1}H NMR analyses of the crude reaction products. Recrystallization and fractional crystallization gave yields of pure compounds which were 50–70 % of the theoretical values. The electrolyses were generally performed on 50–100 mg of substrate.

DISCUSSION

Reduction of *1* at the first peak of its voltammogram is straightforward and leads to *2*. In this work, lithium perchlorate was used instead of tetraethylammonium perchlorate [1] as the supporting salt. This change had no effect on the peak potential, nor on the outcome of the reduction. Acetic acid was used as a proton donor for this particular electrolysis, since it is easier to remove than is phenol in the work-up,

Table 1. Preparative electrolyses of cyclophanes in DMF/0.1 M TEAP.

Substrate [a]	Proton donor	Cathode potential/ *V* vs. SCE	n_{obs} [b]	n_{calc} [c]	Product(s) (molar ratio) [d]
1	AcOH	−1.67	2.09	2.00	*2*
1	PhOH	−1.89	3.80	4.00	*3*+*6* (2:1)
1	PhOH	−2.08	5.59	5.34	*4*+*6* (2:1)
1	PhOH	−2.33	8.19	8.00	*5*
3	PhOH	−2.08	2.13	2.00	*4*
6	PhOH	−2.33	4.07	4.00	*5*

[a] Designations from Fig. 1. [b] Faradays mol^{-1}. [c] Calculated from the product distributions. [d] Determined by ^{1}H NMR spectroscopy on the crude reaction products.

and one is sufficiently far from the background current due to hydrogen ion discharge.

The next step in the reduction leads to a branching, as is seen in Fig. 1 and Table 1. Twice as much *3* is formed compared to *6*. This can be rationalized assuming random protonation of all possible sites in the radical anion of *2*. The mixture of *3* and *6* could be separated by fractional crystallization from ethanol. Pure *6* was also available through an independent synthesis involving a Wittig reaction between two bibenzylic units.[2] The less conjugated isomer, *6*, has the same π electron system as two isolated *cis*-stilbene units and is more difficult to reduce than *3*. Therefore, reduction of *1* at its third peak gives a mixture of *4* and *6* in the ratio 2:1. This mixture is not as easy to separate as the one between *3* and *6*, but pure *4* is available through electrolysis of *3* at its first peak. Finally, reduction of *1* at its fourth peak gives the octahydro compound *5*, as expected. This compound had earlier been prepared *via* catalytic hydrogenation of *1*.[3]

The voltammogram of *6* in phenol-containing DMF displays only one peak, twice the height of that of *4*, which indicates a four-electron process. In the preparative electrolysis of *6*, which yields *5*, no *4* appears as an intermediate, as could be shown by TLC analysis (silica gel/CCl_4) of the catholyte at various times during the electrolysis. On the other hand, in the conversion of *1* to *3* – *6*, *2* did show up in the catholytes before completion of the runs. Presumably, the initial step in the reduction of *6* involves the formation of a dianion with one electron entering each half of the molecule. This species is protonated, and further transfer of two electrons and two protons takes place.

EXPERIMENTAL

Chemicals. The preparations and spectral data have been described for *1*,[3] *2*,[1] *5*,[3] and *6*.[2] The solvent, DMF, was distilled from calcium hydride at reduced pressure, stored in the dark and used within two weeks after distillation. The supporting salt, TEAP, was prepared from the bromide and sodium perchlorate, recrystallized three times from water, and dried in a vacuum oven at 40 – 50 °C for several days. Lithium perchlorate was dried in vacuum at room temperature for two days.

Cyclic voltammetry. The equipment has been described in a previous paper.[4] The hanging mercury drop electrode was made by sealing a 1 mm diameter platinum wire in glass, grinding the surface flat and attaching a mercury drop onto the exposed platinum. In the course of this work, it was found that a reference electrode based on the system Ag/0.01 M $AgNO_3$, 0.1 M TEAP in DMF[5] is more convenient and has better reproducibility than the arrangement involving a commercial, aqueous SCE previously used.[4] Potentials *vs.* Ag/0.01 M $AgNO_3$ in DMF appear 0.43 V more negative than those *vs.* SCE. All potentials reported here are calculated *vs.* SCE.

Voltammograms were recorded in 0.1 M TEAP in DMF at a substrate concentration of 10^{-3} M and phenol, 8×10^{-3} M. The sweep rate was 25 mV s^{-1}. Since the same mercury drop was used for all the recordings in Fig. 2, one is entitled to compare peak heights (*cf.* Discussion).

Preparative electrolyses. An H-type cell with a cathode surface of 20 cm^2 and a catholyte volume of 100 ml was used. An Amfion^R C-311 ion exchange membrane was used as separator. A constant speed paddle stirrer was positioned just above the surface of the mercury cathode. The potentiostat and coulometer were the same as in previous work.[6] The initial amount of substrate was 50 – 100 mg, and phenol, 10 – 20 times the molar amount of substrate, was present as a proton donor. Both catholyte and anolyte were 0.1 M TEAP in DMF. The electrolyses were run to completion, 3 h for each run. The catholyte was diluted with 300 ml of ice-water and extracted repeatedly with ether. The ether extracts were combined and washed several times with 2 M aqueous sodium hydroxide in order to remove phenol, washed with water and saturated sodium chloride solution, and dried over sodium sulfate. Evaporation of the ether at reduced pressure gave a solid residue which was subjected to 270 MHz ^1H NMR analysis. Recrystallization or fractional crystallization from ethanol gave pure compounds. For those compounds not previously reported, the melting points and spectral data are:

[2$_4$]Paracyclophane-1,9-diene (*3*), m.p. 142 – 145 °C. ^1H NMR (270 MHz, $CDCl_3$): δ 7.10 (4 H, s), 7.10 (4 H, d, J 8 Hz), 6.82 (4 H, d, J 8 Hz), 6.72 (4 H, s), aromatic protons, 6.55 (2 H, d, J 12 Hz), 6.48 (2 H, d, J 12 Hz), olefinic protons, 2.88 (8 H, s), methylene protons. UV (ethanol): 270 nm (ε 15 600) and 310 (ε 9 800). MS (65 eV): *m/e* 412 (100 %, M^+), 206 (29.1 %, M^{2+}). Abs.mass. 412.214; calc. for $C_{32}H_{28}$ 412.219.

[2$_4$]Paracyclophanemonoene (*4*), m.p. 153 – 155 °C. ^1H NMR (270 MHz, $CDCl_3$): δ 7.03 (4 H, d, J 8 Hz), 6.74 (4 H, d, J 8 Hz), 6.74 (8 H, s), aromatic protons, 6.54 (2 H, s), olefinic protons, 2.85 (4 H, s), 2.83 (8 H, s), methylene protons. UV (ethanol): 269 nm (ε 10 600). MS (65 eV): *m/e* 414 (100 %, M^+), 207 (38 %, M^{2+}), 206 (86 %), 205 (32 %), 191 (27 %),

104 (28 %, C_8H_8). Abs. mass 414.237; calc. for $C_{32}H_{30}$ 414.235.

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