J. prakt. Chem. 338 (1996) 337–344

Journal für praktische Chemie
Chemiker-Zeitung

Electroreduction of Organic Compounds. 28 [1]

Partial Hydrogenation of Polycyclic Aromatic Hydrocarbons by Electroreduction in Protic Solvents

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Received October 12th, 1995, respectively January 15th, 1996

Abstract. Polycyclic aromatic hydrocarbons (**PAH**) such as anthracene (**1**), phenanthrene (**5**), acenaphthylene (**15**), pyrene (**17**), chrysene (**22**), and fluoranthene (**28**) are selectively hydrogenated upon electroreduction at a lead cathode in ethanolic solution. The degree of hydrogenation and the structure of the products depend on the reaction conditions, in particular on the applied reduction potential.

Polycyclic aromatic hydrocarbons (PAH) are notorious xenobiotics. They are highly toxic and some of them exhibit pronounced carcinogenicity [2]. Moreover, they are very persistent. Especially the microbial degradation of congeners with a higher number of anellated benzene rings is extremely slow and their mineralization is incomplete [3]. – Partial hydrogenation of the aromatic rings could possibly lead to an increase of the rate of degradation since benzylic positions, which are generated by that process, might be easier attacked during enzymatic reactions. For instance, the degradation of toluene in soils is much faster than that of benzene [4].

The electroreduction of PAH has been studied by electroanalytical methods, and the mechanism of the reaction has been discussed in terms of the polarographic half-wave potentials and MO calculations of the HOMO and LUMO energies [5]. Also preparative electrolyses have been carried out on selected compounds such as anthracene **1**, phenanthrene **5**, and pyrene **17** [5, 6]. These were, however, performed under conditions which are unsuitable if practical applications are envisaged. Especially the use of mercury cathodes and aprotic solvents should be avoided if possible.

We have, therefore, investigated the electrolytic reduction of PAH on a (micro-)preparative scale at lead cathodes in *ethanolic* solution, which procedure supposedly should yield the desired partially hydrogenated derivatives.

Results and Discussion

Our investigation covered the following eight compounds: anthracene **1**, 9-methylanthracene **2**, phenanthrene **5**, acenaphthylene **15**, acenaphthene **16**, pyrene **17**, chrysene **22**, and fluoranthene **28**. Besides **2** these were selected from the 16 compounds compiled in the list of the US American Environmental Protection Agency (EPA). For comparison, some of their reduction products were also studied.

In order to get information on the relative reducibilities we have measured the differential pulse polarographic (DPP) peak potentials of the PAH. The results are shown in Table 1. Three types of PAH can be roughly distinguished. The first ones, **1**, **2**, **15**, and **28**, exhibit first reduction peaks due to the formation of radical anions at –1.71 V to –2.00 V. These can be smoothly reduced to one definite reduction product (see below). The second ones, **5**, **17**, and **22**, are reduced at potentials between –2.10 V and –2.45 V. These tend to take up more than two hydrogen atoms upon electroreduction (see below). The third type, represented by **16** and **30**, contains methylene groups, i.e. sp^3-hybridized carbon atoms, within the framework of aromatic rings. Their reduction peaks appear below –2.60 V and electrochemical hydrogenation in protic solvents is not possible.

In several cases a second reduction peak at more negative potential is observed, which can be assigned to

Table 1 Potentials $E_p^{(1)}$ and $E_p^{(2)}$ (*vs* SCE) of the first and second reduction peak as measured by DPP (solvent/supporting electrolyte: 10 % tetraethylammonium bromide in acetonitrile) and HOMO/LUMO energy differences ΔE

Comp.	$E_p^{(1)}$ [V]	$E_p^{(2)}$ [V]	ΔE [eV] a)
1	-1.91	- 2.36	-7.04
2	-2.00	-2.44	- 7.17
3	b)	b)	-9.98
4	-2.67	b)	-9.52
5	-2.45	-2.67	-8.13
6	-2.61	b)	-8.20
15	-1.80	-2.36	-7.56
16	- 2.64	b)	-8.28
17	-2.10	-2.52	-7.14
18	-2.40	b)	-8.14
22	-2.24	-2.61	-7.58
23	- 2.51	b)	-7.85
28	-1.71	-2.19	-7.50
29	- 2.18	b)	- 8.49
30	-2.65	b)	-8.49

a) E(HOMO) - E(LUMO) from AM1-MO calculations
b) No peak observed

the formation of dianions. On the other hand, also certain dihydro- and tetrahydroderivatives of the PAH exhibit reduction peaks of their own at rather negative potentials (see Table 1), as one would expect.

A fairly good linear correlation (r = 0.948) exists between the DPP peak potentials as measured in dry acetonitrile and LUMO energies, which we calculated using the AM1 method. This is shown in Figure 1. It is in agreement with Streitwieser's results [7] for the polarographic half-wave potentials of PAH in aqueous dioxane, i.e. differences in solvation energies are small.

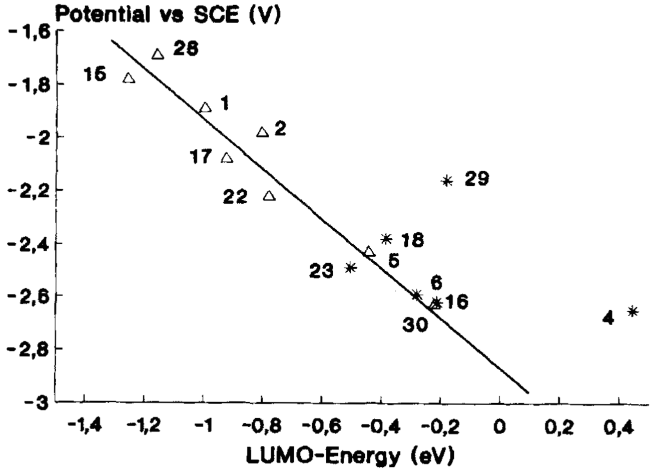


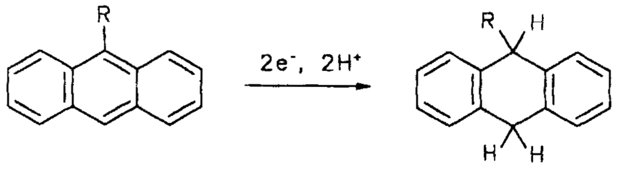
Fig. 1 Correlation of the reduction potentials (*vs.* SCE, 10 % tetraethylammonium bromide in acetonitrile as solvent/supporting electrolyte) of PAH (Δ) and hydrogenated derivatives (*) *versus* LUMO energies from AM1 calculations.

Two compounds, 9,10-dihydro-9-methyl-anthracene **4** and 1,2,3,10b-tetrahydrofluoranthene **29**, are far off the straight line and are not included in the linear correlation. The structure of these two considerably deviates from planarity, which may cause irregularities of the electron-uptake at the cathode surface.

The electroreduction of anthracene **1** has been studied extensively [6]. Especially the mechanism of the reaction, i.e. the sequence of electron transfer and chemical steps has been established [5b]. It has been shown with **1** as a prototype for PAH molecules that an *ECEH* mechanism is operating in protic media whereas formation of dianions which eventually are protonated (*EEHH* mechanism) is observed in aprotic media. 9,10-dihydroanthracene **3** has been obtained as the only product from controlled-potential electrolyses of **1** at mercury cathodes [6, 8] whereas 1,2,3,4-tetrahydro- and two octahydroanthracenes were formed besides **3** with Raney-Nickel under electrocatalytic conditions [9].

For comparison we have performed electroreductions of **1** under controlled potential (–2.5 V *vs* SCE) in ethanol/tetraethylammonium bromide at a lead cathode in a batch cell („standard conditions") [10]. This method has been chosen with respect to practical applications, in which mercury cathodes cannot be taken into consideration. After optimization of the reaction parameters we obtained a quantitative yield of **3**. Even with sodium hydroxide instead of TEAB as supporting electrolyte the yield of **3** was up to 98%. The current efficiency reached acceptable 25%. – A comparable result was obtained with 9-methylanthracene **2** as starting material. 9,10-Dihydro-9-methylanthracene **4** was formed with 73% yield. The current efficiency was lower (7%) and 23% of a by-product could be isolated. It was identified as ethoxy-9-methylanthracene by its mass spectrum. The position of the ethoxy substituent remains unknown. The ethoxy derivative represents an oxidation product of **2** which obviously was formed at the anode. Varying amounts of ethoxyanthracene were also formed if **1** was electrolysed under non-optimal conditions.

Phenanthrene **5** has also been electroreduced at a mercury cathode in 55% aqueous tetrabutylammonium hydroxide solution, and a complex mixture of oligohydro derivatives was obtained as product [6, 8b, 11]. By electroreduction of **5** under our standard conditions nearly

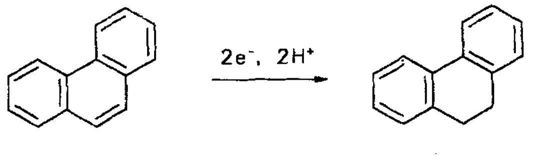


1 R = H
2 R = Me

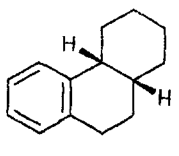
3 R = H ~100%
4 R = Me 73%

quantitative conversion into 9,10-dihydrophenanthrene **6** was achieved. In this case the current efficiency was only about 1% since under these conditions hydrogen evolution was the prevailing process. Further electroreduction with up to 25% current efficiency was possible if more rigorous conditions, i.e. negative potentials, higher current density, higher amounts of electricity and especially a tenfold concentration of **5** were applied. No tetrahydrophenanthrene was detectable but two pairs of each two hexahydro and two octahydrophenanthrenes were isolated by column and gas-liquid chromatography, which could, however, not be further separated. The identification of the products was therefore difficult. Under the reasonable assumption that **6** represents the only intermediate nine different hexahydrophenanthrenes including three pairs of *cis/trans* isomers are possible. One of these, **7**, was excluded by independent synthesis and structural elucidation by NMR-spectroscopy (cf. Experimental). We assign structure **8** to one of the isomers on the basis of its simple and characteristic mass spectrum: besides the molecular ion, m/z = 184 (13%) one prominent fragment ion appears as parent peak with m/z = 130 (100%). This can be explained by *retro*-Diels-Alder reaction, i.e. loss of 1,3-butadiene (C_4H_6, m/z = 54) to form the conjugated 1,2-dihydronaphthalene ion $\mathbf{10}^+$, which is further degraded to the benzylic cation $\mathbf{11}^+$ (m/z = 129, 35%), the naphthalene ion $\mathbf{12}^+$ (m/z = 128, 18%) and finally the indenyl cation, C_9H_7 (m/z = 115, 20%). Hexahydrophenanthrene **7**, on the other hand, exhibits a conjugated double bond. It forms a very stable molecular ion which appears as parent peak. No butadiene elimination takes place but instead ethene, propene, butene, and propyl radicals are eliminated. The mass spectrum of the second unknown hexahydrophenanthrene closely resembles the spectrum of **7** and is completely different from the spectrum of **8**. We therefore provisionally assign another conjugated structure, **9**, to this isomer.

If **8** or **9** or any other hexahydrophenanthrene with an intact outer benzene ring is considered as precursor of the two octahydrophenanthrenes the latter should be *cis*- and *trans*-1,2,3,4,4a,9,10,10a-octahydrophenanthrene, **13** and **14**. This is in agreement with their mass spectra, which are very similar to each other as one would expect for diastereomers and to the mass spectrum of an independently prepared sample of **14**. Besides very intense peaks at m/z = 186 (M^+) fragment ions at m/z = 158 ($M^+ - C_2H_4$), 143 ($M^+ - C_3H_7$), 130 ($M^+ - C_4H_8$), 129 ($M^+ - C_4H_9$), 128 ($M^+ - C_4H_{10}$), 115 (C_9H_7, indenyl), and 104 ($M^+ - C_2H_4 - C_4H_6$) are ob-



5 **6** 97%



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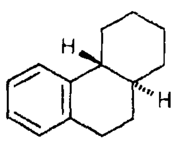

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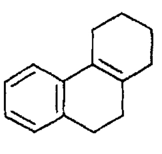

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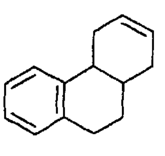

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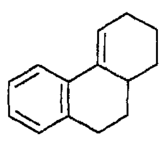

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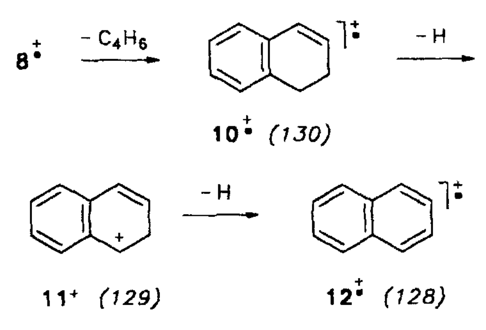


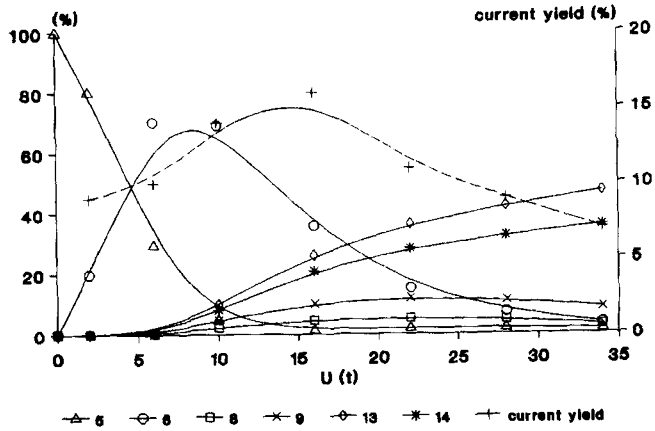
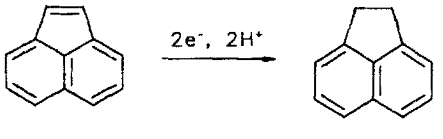


Fig. 2 Formation of hydrogenated phenanthrenes in the course of galvanostatic electroreduction of **5**. The dimensionless parameter $U(t)$ = 2F·E/Q(t) (E = amount of educt [mmol], F = Faraday constant, Q(t) = consumed electrical charge [A·s] at the time t) represents the turn-over of charge and is proportional to t under galvanostatic conditions.

served. Octahydrophenanthrene **13** or **14** were also reported, without consideration of the stereoisomerism, to be products of electrocatalytic reduction of **5** with Raney-Nickel [9,12].

The progress of the electroreduction of **5**, i.e. the subsequent formation of **6** and the higher hydrogenated phenanthrenes **8**, **9**, **13**, and **14** is shown in Figure. 2.

Acenaphthene **16** is the exclusive product of the electroreduction of acenaphthylene **15** under our standard conditions [13]. Quantitative yields of **16** [14] with current efficiences of 50% are achieved and no further reduction occurs under more rigorous conditions (E_{red} = – 2.7 V) or with **16** as starting material.



15 **16** ~100%

Pyrene **17** is very easily reduced to a mixture of five products, four of which could be identified. About 35% of 4,5-dihydropyrene **18** are present in the mixture after intermediate amounts of electricity have been passed (cf. Fig. 3). At the same time two hexahydroderivatives **19** and **20** are formed independently. Finally, however, 4,5,9,10-tetrahydropyrene **21** predominates over all other products. – This strange sequence of products during the electrolysis of **17** is demonstrated in Figure 3. It can be rationalized by the assumption that an undetectable short lived dihydroderivative is primarily formed, which is rapidly further reduced to the detectable fifth product, a tetrahydropyrene of unknown structure. Both **18** and the latter are transformed into **21** via reduction or rearrangement, respectively. A similar result, i.e. formation of **18**–**20** and, independently via another dihydropyrene, **21** was obtained by P. E. Hansen et al. [15] who electroreduced **17** in DMF. – It should be emphasized that the hydropyrenes **18**–**21** exhibit the maximum degree of aromaticity, i.e. phenanthrene, naphthalene, or biphenyl moieties.

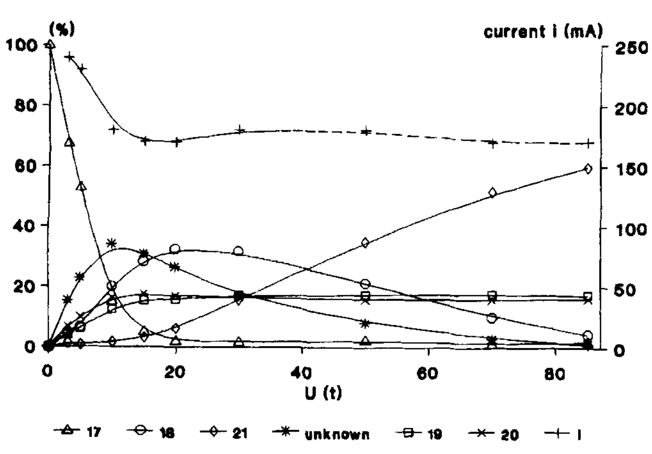
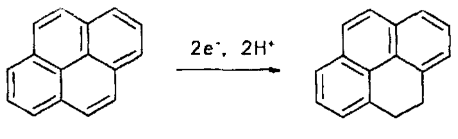
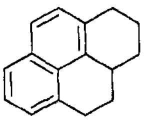


Fig. 3 Formation of hydroderivatives in the course of galvanostatic electroreduction of **17**, cf. Figure 2 for the definition of U(*t*).



17 **18**



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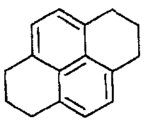

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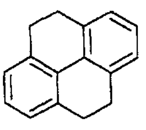

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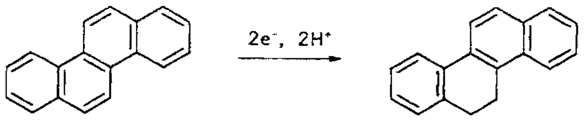
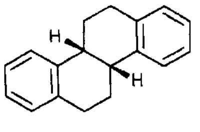
Like phenanthrene **5** and pyrene **17** chrysen **22** is transformed into a mixture of hydroderivatives by electroreduction. The composition of the mixture depends on the reaction conditions. Up to 92% of 5,6-dihydrochrysene **23** are formed under standard conditions. Pure **23** can be isolated by preparative gas-liquid chromatography. Three hexahydrochrysenes can be separated by use of column chromatography: two of them represent the *cis*- and *trans*-isomers **24** and **25**, the NMR spectra of which do not allow an assignment of either compound. The structure of the third one is less certain. Each six quaternary, tertiary, and secondary carbon atoms are identified from its ^{13}C-NMR spectrum. Since no alkene–CH/methylene–CH_2 coupling can be detected from a ^1H-^1H-COSY spectrum only two structures of ten possible ones remain: **26** or **27**. – In addition, a tetrahydrochrysene was formed, which could not be separated from the mixture. The determination of its structure was therefore not possible.

Electroreduction of 5,6-dihydrochrysene **23** at a potential of –2.9 V resulted in the formation of a very similar mixture of **24**, **25**, and **26** or **27**, whereas significantly less of the tetrahydrochrysene was formed as compared with the reduction of **22**.

The complicated fluoranthene **28** was, rather unexpectedly, quantitatively electroreduced to only one single product, 1,2,3,10b-tetrahydrofluoranthene **29**. The current efficiency was 33%. The structure of **29** was elucidated by its mass and ^1H-NMR and, in particular, its ^{13}C-NMR (DEPT-) spectrum, which exhibited signals of three methylene (δ = 22.8, 24.5, 25.4 ppm) and one methine (δ = 44.7 ppm) besides seven tertiary and five quaternary sp^2-hybridized carbon atoms (δ = 116.5 –147.6 ppm).



22 **23**



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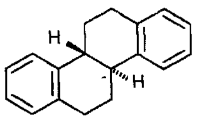

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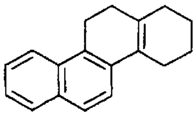

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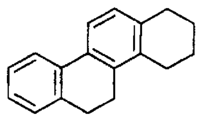

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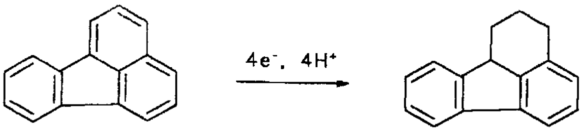
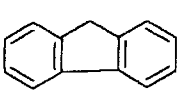
Fluorene **30**, 2-methylnaphthalene **31**, and perylene **32** could not be electroreduced in protic solvents. Both **29** and **30** contain the biphenyl skeleton which is very resistant to reduction. Biphenyl itself exhibits an extremely negative reduction potential of –2.7 V *vs* SCE [7] and we have measured $E_{red} = -2.65$ V in acetonitrile for **30** (see Table 1). – Similarly **31** yields only minor traces of reduced products at a reduction potential of <–3.0 V. Perylene **32**, on the other hand, readily takes up one electron under formation of the corresponding radical anion, which is very persistent [16]. However, neither protonation nor a second electron transfer takes place. Instead, (**32**) is quantitatively recovered upon aqueous work-up of the green coloured catholyte solution [17].



28 **29** -100%



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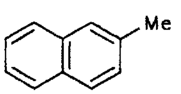

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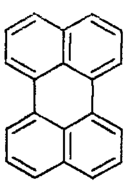

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With regard to practical applications a mixture of **1**, **5**, **15**, and **28** was also subjected to electroreduction. The obtained mixture of products was analysed by gas chromatography. Figure 4 shows the progress of the reaction at a potential of –2.5 V *vs* SCE. The percentages represent the amounts of a product in relation to the corresponding starting compound. Current efficiencies are calculated on the basis of the sum of the products **3**, **6**, **16**, and **29**. Nearly complete reduction of **1**, **15**, and **28** was achieved at a total current efficiency of ca. 51%, whereas the formation of **6** from **5** required much more electricity to be passed and the current efficiency was dropped to 5%.

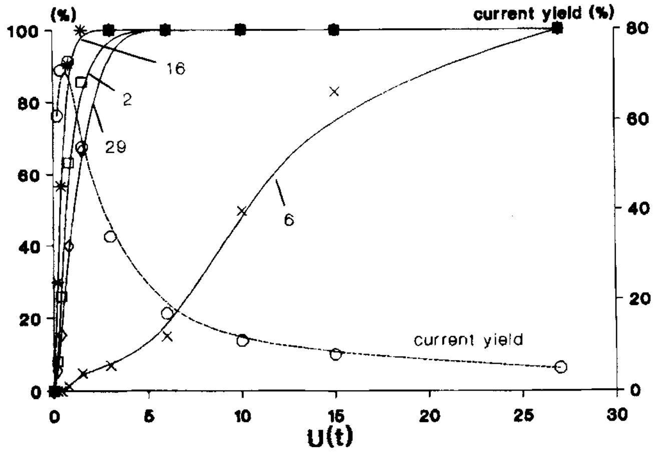

Fig. 4 Galvanostatic electroreduction of a mixture of **1**, **5**, **15**, and **28** in ethanol at -2.6 V *vs*. SCE, cf. Fig. 2 for the definition of U(*t*)

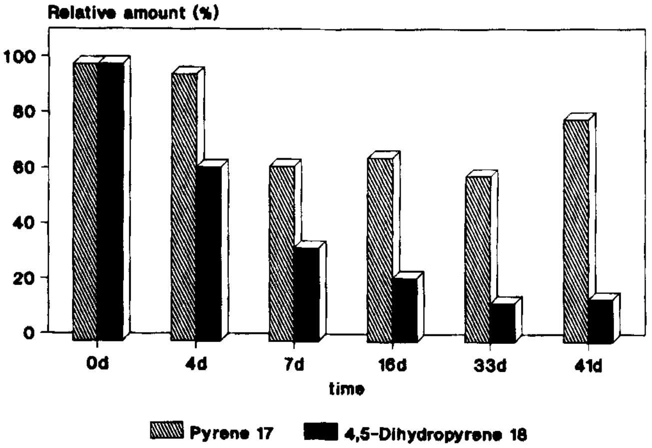

Fig. 5 Extractable amounts of **17** and **18** after different times of *in-vitro* incubation with a suspension of bacteria from soil [18].

A preliminary study has shown that microbial degradation of the hydroderivatives **3**, **18**, and **29** seems to occur faster as compared with the corresponding PAH

1, **17**, and **28** (see Fig. 5), whereas no significant effects could be observed so far in the case of the pairs **5/6** or **22/23** [18].

Support of this work by the „Bundesministerium für Forschung und Technologie“ and the „Deutsche Forschungsgemeinschaft“ is gratefully acknowledged. – We thank Dr. M. Kästner and Mrs. M. Breuer-Jammali, Technische Universität Hamburg-Harburg, who performed the microbiological experiments, and Prof. Dr. W. Francke, Universität Hamburg, for fruitful discussions.

Experimental

Melting points (corrected): Electrothermal. – NMR spectra: Bruker WH 270 and WH 400. – TLC: silica on Al-foil (Merck); detection by quenching of the fluorescence or spraying with salicylaldehyde solution. – Column chromatography: ICN silica 63-100/60 A and ICN alumina NI; eluents: hexane, ethyl acetate or hexane/trichloromethane mixtures. – Preparative GC: Shimadzu GC-8A; steel column (3 m), 10% SE 30 in chromosorb WAW, heat conductivity detector, carrier gas: He. – Analytical GC: Carlo Erba 4200, fused silica capillary column SE 54 (50 m, 0.32 mm) Macherey & Nagel, FID. – GC/MS-coupling: HP-GC 5970, MSD; fused silica capillary column SE 54 (50 m) Chrompak. – MS (70 eV): VG 70–270 SE with HP 5980 split/splitless injector. – Polarography: Metrohm VA 663 with Polarecord 620 and VA scanner E 612. – Potentiostat: Bank Electronic ST 72, integrator SS I/70. Potentials are related *vs.* SCE as reference.

Calculation of HOMO- and LUMO-energies, heats of formation, electron density distributions: QCPE programs. – GC-data processing: Bruker Chromstar 3 X [19]; PARADOX 4.5 WIN; EXCEL 5.0 WIN.

The PAH used were commercially available. We thank Prof. Dr. M. Zander, Rütgers Werke, Castrop-Rauxel, who provided acenaphthylene **15** and chrysene **17** to us and Dr. G. Mann, Dresden, for samples of 1,2,3,3a,4,5- **19** and 1,2,3,6,7,8-hexahydropyrene **20**.

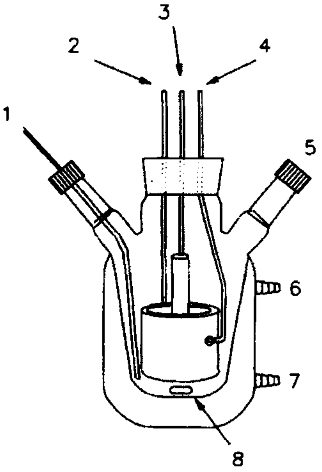

Fig. 6 Batch cell with N_2-inlet (1), lead cathode (2), carbon anode (3), Ag-reference electrode (4), connection for the reflux condenser (5), water heating (6), (7), and magnetic stirring bar (8).

Electrolyses were performed galvanostatically in a batch cell [17] of 50 ml volume (see Fig. 6) at 60 °C under N_2 atmosphere. A solution (10% by weight) of tetraethylammonium bromide (Merck, Darmstadt) in ethanol (96%, synthetic grade, no further pretreatment, and a lead cathode (45 cm^2 active area) were used as solvent supporting electrolyte and working electrode. The progress of the reduction was controlled by taking 1 ml portions of the electrolyte, diluting with dichloromethane, washing with 10% HCl, drying with $MgSO_4$, and determining the composition by GC/MS.

Anthracene **1**: 45 mg (0.25 mmol) **1** were electrolysed at –2.5 V/0.2 A (24 $A{\cdot}m^{-2}$, $Q = 4$ $F{\cdot}mol^{-1}$). Yield: ≈ 100% *9,10-dihydroanthracene* **3** (current efficiency: 25%), identical with an authentic sample. – ^1H-NMR (250 MHz, $CDCl_3$): $\delta = 3.87$ (s, 4H, 9-H, 10-H), 7.18 (m, 4H, ArH), 7.25 (m, 4H, ArH). – MS: *m/z* (%) = 180 (81, M^+), 179 (100), 178 (63), 177 (10), 176 (16), 165 (22), 152 (18), 151 (10), 89 (22).

9-Methylanthracene **2**: 480 mg (2.5 mmol) **2** were electrolysed at –2.5 V/0.18 A (22 $A{\cdot}m^{-2}$, $Q = 3$ $F{\cdot}mol^{-1}$). Yield: 73% *9,10-dihydro-9-methylanthracene* **4** (current efficiency: 25%). – ^1H-NMR (400 MHz, C_6D_6): $\delta = 1.28$ (d, J = 7.1 Hz, 3H, CH_3), 3.62 (d, J = 18.3 Hz, 1H, 10-H), 3.84 (q, J = 7.1 Hz, 1H, 9-H), 3.91 (d, J = 18.2 Hz, 1H, 10-H), 7.12 (m, 4H, ArH), 7.15 (m, 4H, ArH). – MS: *m/z* (%) = 194 (8, M^+), 180 (15, M^+-CH_2), 179 (100, M^+-CH_3), 178 (46), 176 (11), 152 (11), 89 (16). – By-product: *ethoxy-9-methylanthracene*, 25%. – MS: *m/z* (%) = 236 (28, M^+), 208 (13), 207 (36), 195 (12), 194 (26), 193 (67), 192 (100), 190 (80), 189 (15), 188 (46), 179 (17), 178 (43), 176 (15), 165 (48), 163 (14), 152 (13), 96 (10), 95 (16), 82 (10), 63 (12), 45 (12), 43 (15).

Phenanthrene **5**: a) 45 mg (0.25 mmol) **5** were electrolysed at –2.5 V/0.29 A (35 $A{\cdot}m^{-2}$, $Q = 130$ $F{\cdot}mol^{-1}$). Yield: 97% *9,10-dihydrophenanthrene* **6** (current efficiency 0.7%), identical with an authentic sample. – ^1H-NMR (250 MHz, D_6-acetone): $\delta = 2.84$ (s, 4H, 9-H, 10-H), 7.18 – 7.32 (m, 6H, ArH), 7.80 (d, 2H, ArH). – MS: *m/z* (%) = 180 (100, M^+), 179 (77), 178 (51), 176 (14), 165 (37), 152 (14), 89 (35), 88 (14), 76 (23), 63 (11). – b) 445 mg (2.5 mmol) **5** were electrolysed at –3.3 V/0.34 A (41 $A{\cdot}m^{-2}$, $Q = 340$ $F{\cdot}mol^{-1}$). The products were separated by first column (SiO_2) and subsequent preparative gas chromatography. Yield: 3% *1,4,4a,9,10,10a-hexahydrophenanthrene* **8**; MS: *m/z* (%) = 184 (13, M^+), 131 (11), 130 (100, $M^+-C_4H_6$), 129 (35, $M^+-C_4H_7$), 128 (18, $M^+-C_4H_8$), 115 (20, $C_9H_7^+$); together with 9% *1,2,3,9,10,10a-hexahydrophenanthrene* **9**; MS: *m/z* (%) = 184 (100, M^+), 169 (27, M^+-CH_3), 165 (10), 156 (52, $M^+-C_2H_4$), 155 (30, $M^+-C_2H_5$), 154 (11), 153 (14), 152 (13), 143 (57, $M^+-C_3H_5$), 142 (59, $M^+-C_3H_6$), 141 (93, $M^+-C_3H_7$), 130 (34), 129 (45), 128 (89, $M^+-C_4H_8$), 127 (23), 116 (13), 115 (55), 91 (27), 89 (14), 78 (14), 77 (13), 76 (18), 65 (11), 63 (18), 51 (18), 41 (14), 39 (14). Only traces (< 1%) of *1,2,3,4,9,10-hexahydrophenanthrene* **7** were formed.

A sample of **7** was prepared independently: 8.9 g (50 mmol) **5** were heated to reflux in 300 ml pentanol. 20.5 g Na were added portionwise and the solution kept boiling for 1 h. After cooling the dark reaction mixture was acidified with a few drops of aqu. HCl and washed with water (3 x 600 ml). Evaporation *i.vac.* yielded 8 g oil, which according to its GC consisted of five main products and contained 15% **7**. Distillation (spinning band column) provided two fractions, from the second of which (b.p. 110 °C/30 Torr) **7** was obtained by column chromatography (SiO_2, hexane/ethyl acetate). – ^{1}H-NMR (400 MHz, C_6D_6): δ = 1.51 (m, 2H, 2-H, 3-H), 1.62 (m, 2H, 2-H, 3-H), 1.94 (m, 4H, 1-H, 4-H), 2.25 (m, 2H, 10-H), 2.60 (t, J = 8.1 Hz, 2H, 9-H), 7.0 – 7.1 (m, 4H, ArH); – ^{13}C-NMR (100 MHz, C_6D_6): δ = 23.10 (CH_2), 23.17 (CH_2), 25.55 (CH_2), 28.36 (CH_2), 29.12 (CH_2), 30.93 (CH_2), 121.61 (CH), 126.01 (CH), 126.57 (C_{ar}H), 127.08 (C_{quart}), 127.28 (C_{ar}H), 134.25 (C_{quart}), 135.39 (C_{quart}), 136.90 (C_{quart}). – MS: *m/z* (%) = 184 (100, M$^+$), 182 (16), 169 (19), 167 (14), 165 (18), 156 (39, M$^+$– C_2H_4), 155 (30, M$^+$– C_2H_5), 154 (14), 153 (19), 152 (19), 143 (32), 142 (61), 141 (95), 129 (21), 128 (53), 127 (12), 115 (40), 91 (12), 77 (12), 76 (11), 63 (11), 51 (12), 41 (11), 39 (16). – *cis-1,2,3,4,4a,9,10,10a-Octahydrophenanthrene* **13**, 47 %. – MS: *m/z* (%) = 186 (79, M$^+$), 158 (18), 144 (14, M$^+$– C_3H_6), 143 (81, M$^+$– C_3H_7), 141 (11), 130 (32), 129 (100, M$^+$–C_4H_9), 128 (56), 127 (14), 117 (12), 116 (11), 115 (46), 105 (12), 104 (37), 91 (25), 77 (12), 41 (16), 39 (14); together with 36% *trans-1,2,3,4,4a,9,10,10a-octahydrophenanthrene* **14**. – MS: *m/z* (%) = 186 (100, M$^+$), 158 (33), 144 (15), 143 (82, M$^+$– C_3H_7), 141 (15), 130 (35), 128 (82, M$^+$– C_4H_9), 128 (62), 127 (16), 117 (44), 116 (15), 115 (58), 105 (15), 104 (42), 95 (24), 94 (11), 91 (38), 77 (16). 65 (11), 41 (22), 39 (18), identical with an authentic sample [20].

Acenaphthylene **15** [14]: 38 mg (0.25 mmol) **15** were electrolysed at –1.90V/3 mA (0.36 A·m^{-2}, Q = 2 F·mol^{-1}). Yield: ≈ 100% *acenaphthene* **16** (current efficiency 50%), identical with an authentic sample.

Pyrene **17**: 50.5 mg (0.25 mmol) **17** were electrolysed at –2.6 V/0.17 A (20 A·m^{-2}, Q = 20 F·mol^{-1}). Yield: 33% *4,5-Dihydropyrene* **18**, identical with an authentic sample. – ^{1}H-NMR (250 MHz, D_6-acetone): δ = 3.27 (s, 4H, 4-H, 5-H), 7.43 (d, J = 4.7 Hz, 2H, 3-H, 6-H), 7.52 (t, J = 4.7 Hz, 2H, 2-H, 7-H), 7.78 (d, J = 4.7 Hz, 2H, 1-H, 8-H), 7.78 (s, 2H, 9-H, 10-H). – MS: *m/z* (%) = 204 (89, M$^+$), 203 (100), 202 (79), 201 (16), 200 (21), 101 (79), 100 (35), 89 (11), 88 (12), 87 (11). – 6% (60% if F·mol^{-1} are passed) *4,5,9,10-Tetrahydropyrene* **21**. – ^{1}H-NMR (250 MHz, D_6-acetone): δ = 2.64 (s, 8H, 4-H, 5-H, 9-H, 10-H), 6.95 (d, J = 4.8 Hz, 4H, 1-H, 3-H, 6-H, 8-H), 7.05 (t, J = 4.6 Hz, 2H, 2-H, 7-H). – ^{13}C-NMR (100 MHz, C_6D_6): δ = 28.63 (CH_2), 126.31 (C_{ar}H), 127.34 (C_{ar}H), 128.27 (C_{quart}), 128.51 (C_{quart}), in accordance with ref. [15]. – MS: *m/z* (%) = 206 (100, M$^+$), 205 (76), 204 (15), 203 (42), 202 (62), 201 (13), 191 (15), 190 (22), 189 (27), 178 (29), 165 (29), 152 (11), 103 (11), 101 (64), 100 (24), 95 (27), 89 (42), 88 (27), 76 (22), 44 (13), 40 (15), 39 (13). – 27% *Tetrahydropyrene* (unknown structure). – MS. *m/z* (%) = 206 (100, M$^+$), 205 (82), 204 (19), 203 (46), 202 (61), 201 (14), 200 (12), 191 (25), 190 (26), 189 (32), 178 (21), 165 (21), 152 (11), 101 (65), 100 (28), 95 (12), 89 (40), 88 (25), 87 (11), 76 (19), 75 (14), 63 (11), 39 (11). – 16% *1,2,3,3a,4,5-Hexahydropyrene* **19**, identical with an authentic sample [21]. – ^{1}H-NMR (400 MHz, C_6D_6): δ = 1.12 (m, 1H), 1.27 (m, 1H), 1.39–1.53 (m, 1H), 1.58–1.70 (m, 3H), 2.44 (t, 1H), 2.52–2.64 (m, 2H), 2.66–2.88 (m, 2H), 6.90 (d, J = 8.2 Hz, 1H), 6.95 (d, J = 8.2 Hz, 1H), 7.09 (t, J = 8.2 Hz, 1H), 7.35–7.42 (m, 2H). – ^{13}C-NMR (100 MHz, C_6D_6): δ = 23.39 (CH_2), 30.38 (CH_2), 31.13 (CH_2), 31.40 (CH_2), 31.69 (CH_2), 38.17 (CH, 3a-H), 124.81 (C_{ar}H), 126.28 (C_{ar}H), 126.40 (C_{ar}H), 128.15 (C_{ar}H), 128.49 (C_{ar}H), 130.57 (C_{quart}), 131.77 (C_{quart}), 133.18 (C_{quart}), 134.85 (C_{quart}), 136.54 (C_{quart}), in accordance with ref. [13]. – MS: *m/z* (%) = 208 (96, M$^+$), 207 (44), 202 (13), 189 (11), 181 (13), 180 (73), 179 (36), 178 (29), 166 (18), 165 (100, M$^+$– C_3H_7), 152 (18), 101 (11), 94 (15), 89 (55), 88 (16), 83 (18), 76 (18). – 17 % *1,2,3,6,7,8-Hexahydropyrene* **20**, identical with an authentic sample [21]. – ^{1}H-NMR (400 MHz, D_6-acetone): δ = 1.95 (qui, J = 6 Hz, 4H, 2-H, 7-H), 2.99 (t, J = 6 Hz, 8H, 1-H, 3-H, 6-H, 8-H), 7.05 (s, 4H, 4-H, 5-H, 9-H, 10-H). – MS: *m/z* (%) = 208 (100, M$^+$), 207 (21), 202 (13), 193 (11), 189 (13), 180 (23), 179 (29), 178 (23), 166 (10), 165 (63, M$^+$– C_3H_7), 152 (13), 101 (13), 94 (16), 90 (16), 89 (45), 88 (12), 76 (14).

Chrysene **22**: a) 57 mg (0.25 mmol) **22** were electrolysed at –2.4 V/0.06 A (7 A·m^{-2}; Q = 20 F·mol^{-1}). Yield: 92% *5,6-dihydrochrysene* **23**, identical with an authentic sample [22], m.p. 221°C. – ^{1}H-NMR (400 MHz, $CDCl_3$). δ = 2.99 (t, J = 7.4 Hz, 2H, CH_2), 3.29 (t, J = 7.4 Hz, 2H, CH_2), 7.22–7.38 (m, 3H, ArH), 7.42–7.55 (m, 2H, ArH), 7.76–7.86 (m, 3H, ArH), 7.93 (d, J = 8.6 Hz, 1H, ArH), 8.13 (d, J = 8.1 Hz, 1H, ArH). – MS: *m/z* (%) = 280 (100, M$^+$), 229 (96), 228 (47), 227 (16), 226 (32), 215 (12), 202 (14), 115 (19), 114 (46), 113 (33), 112 (12), 107 (16), 101 (35), 100 (18), 88 (12). b) 57 mg (0.25 mmol) **22** were electrolysed at –2.7 V/0.56 A (67 A·m^{-2}; Q = 300 F·mol^{-1}). Yield: 21 % **23** together with 13% *trans-* or *cis-4b,5,6,10b,11,12-hexahydrochrysene* **25** or **24**. – ^{1}H-NMR (400 MHz, C_6, D_6): δ = 1.60 –1.70 (m, 4H, CH_2), 2.44 (dd, J = 16/3.6 Hz, 1H, CH_2), 2.52 – 2.68 (m, 2H, CH_2), 2.72 (m, 2H, CH), 6.80–6.98 (m, 8H, ArH). – ^{13}C-NMR (100 MHz, C_6D_6): δ = 29.96 (CH_2), 30.59 (CH_2), 38.59 (CH), 126.24 (C_{ar}H), 126.36 (C_{ar}H), 129.33 (C_{ar}H), 129.98 (C_{ar}H), 136.44 (C_{quart}), 141.29 (C_{quart}). – MS: *m/z* (%) = 234 (60, M$^+$), 143 (51, M$^+$– C_7H_7), 130 (100), 129 (73), 128 (42), 127 (11), 117 (20), 115 (35), 104 (16), 103 (11), 91 (25), 78 (11), 77 (13); and 10% **24** or **25**, respectively. – ^{1}H-NMR (400 MHz, C_6D_6): δ = 1.33–1.55 (m, 2H, CH_2), 2.25 (m, 2H, CH_2), 2.45 (m, 2H, CH_2), 2.55–2.65 (m, 4H, CH_2, CH), 6.75–7.00 (m, 8H, ArH). – ^{13}C-NMR (100 MHz, C_6D_6): δ = 27.87 (CH_2), 30.25 (CH_2), 41.51 (CH), 125.99 (C_{ar}H), 126.36 (C_{ar}H), 128.88 (C_{ar}H), 129.32 (C_{ar}H), 137.16 (C_{quart}), 140.89 (C_{quart}): – MS: *m/z* (%) = 234 (84, M$^+$), 206 (19), 203 (12), 202 (11), 144 (12), 143 (100, M$^+$– C_7H_7), 142 (21), 141 (14), 130 (37), 129 (91), 128 (74), 127 (14), 117 (33), 116 (11), 115 (51), 105 (11), 104 (12), 103 (11), 102 (11), 101 (17), 91 (45), 89 (11), 77 (16), 65 (12), 39 (10); and 40% *1,2,3,4,11,12-hexahydrochrysene* **26** or *1,2,3,4,5,6-hexahydrochrysene* **27**. – ^{1}H-NMR (400 MHz, C_6D_6): δ = 1.53–1.62 (m, 4H, CH_2), 2.40 (t, J = 5.6 Hz, 2H, CH_2), 2.51 (q, 2H, CH_2), 2.61–2.68 (m, 4H, CH_2), 6.97 (d, J = 7.6 Hz, 1H, ArH), 7.05 –7.25 (m, 3H, ArH), 7.57 (d, J = 7.6 Hz, 1H, ArH), 7.70 (d, J = 7.6 Hz, 1H, ArH). – ^{13}C-NMR (100 MHz, C_6D_6): δ = 23.26 (CH_2), 23.98 (CH_2), 24.53 (CH_2), 27.11 (CH_2), 29.32 (CH_2), 30.71 (CH_2), 121.80 (C_{ar}H), 124.30 (C_{ar}H), 127.21 (C_{ar}H), 127.43 (C_{ar}H), 128.20 (C_{ar}H), 128.48 (C_{ar}H), 132.61 (C_{quart}), 134.33 (C_{quart}), 135.96 (C_{quart}), 136.10 (C_{quart}), 136.92 (C_{quart}), 137.21 (C_{quart}). – MS: *m/z* (%) = 234 (100, M$^+$), 233 (13), 206 (29,

$M^+–C_2H_4$), 205 (15), 203 (15), 202 (18), 193 (11), 192 (18), 191 (64, $M^+–C_3H_7$), 190 (15), 189 (18), 178 (18), 165 (13), 101 (18), 95 (13), 89 (13).

5,6-Dihydrochrysene **23**: 27 mg (0.25 mmol) **23** were electrolysed galvanostatically at 1 A (120 A·m^{-2}; Q = 150 F·mol^{-1}). After work-up a mixture of 19% **23**, 20% **24**, 22% **25**, and 34% **26** or **27** was obtained (GC-MS analysis).

Fluoranthene **28**: 51 mg (0.25 mmol) **28** were electrolysed at –2.3 V/0.08 A (10 A·m^{-2}; Q = 6 F·mol^{-1}). Yield: 98% *1,2,3,10b-tetrahydrofluoranthene* **29** (current efficiency: 33 %). – ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.10–1.23 (m, 1H), 2.05–2.14 (m, 2H), 2.50 (m, 1H), 2.71 (m, 1H), 2.99 (m, 1H), 3.59 (dd, 1H, 10b-H), 7.00 (d, J = 7.7 Hz, 1H, ArH), 7.24 (m, 2H, ArH), 7.78 (d, J = 7.7 Hz, 1H, ArH). – ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 22.78 (CH_2), 24.50 (CH_2), 25.37 (CH_2), 44.72 (CH, C-10b), 116.50 ($C_{ar}H$), 119.87 ($C_{ar}H$), 122.50 ($C_{ar}H$), 124.50 ($C_{ar}H$), 125.10 ($C_{ar}H$), 126.06 ($C_{ar}H$), 126.35 ($C_{ar}H$), 134.33 (C_{quart}), 138.76 (C_{quart}), 141.06 (C_{quart}), 145.41 (C_{quart}), 147.55 (C_{quart}). – MS: *m/z* (%) = 206 (40, M^+), 205 (12), 203 (12), 202 (14), 178 (100, $M^+–C_2H_4$), 101 (16), 89 (32), 88 (14), 76 (27). Compound **29** was identical with the product of chemical reduction (sodium/pentanol, see above).

Electrolysis of a mixture of 45 mg (0.25 mmol) **1**, 45 mg (0.25 mmol) **5**, 38 mg (0.25 mmol) **15**, and 51 mg (0.25 mmol) **28** was performed at a): –2.5 V/0.17 A (20 A·m^{-2}; Q = 2 F·mol^{-2}) to yield each ≈ 100% **3**, **16**, and **29**, and 5% **6**, respectively (total current efficiency: 51%) or b): at –2.7 V/0.57 A (68 A·m^{-2}; Q = 27 F·mol^{-1}) to yield each ≈ 100% **3**, **6**, **16**, and **29**, respectively (total current efficiency: 5%).

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