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Dissolving Metal and Electrochemical Reduction of Polycyclic Aromatic Hydrocarbons

POUL ERIK HANSEN, OLE BLAABJERG * and ARNE BERG

Department of Organic Chemistry, Aarhus University, DK-8000 Aarhus C, Denmark

Pyrene and 2,7-di-*t*-butylpyrene have been subjected to reduction with sodium in isoamyl alcohol and to electrolytic reduction at controlled potential. Structures and yields of reduction products are discussed. Reduction potentials of intermediates, ion-pairing effects and basicity of the solution, leading to isomerizations, seem to be important. All degrees of hydrogenation of pyrene from dihydro- through decahydropyrenes, including a number of isomeric cases, have been observed. Products are characterized by the ^1H and ^{13}C NMR spectra. Convenient procedures for preparing some hydropyrenes from pyrene are given.

While much interest has been given to scrutinizing the metal-ammonia and metal-amine reduction of aromatic hydrocarbons [1–4] no similar efforts have been devoted to the classical method of reduction with alkali metal in an alcoholic medium. Contrary to the former, easily controllable method [4,5] the latter usually yields complex mixtures of products of different degrees of hydrogenation.

Electrochemical reduction of aromatic hydrocarbons has been extensively studied for a long time, especially by polarographic and voltammetric techniques, and electrochemical data have been of particular value for testing theoretical predictions based on quantum mechanical calculations.[6–8]

Coulson [9] in an early examination isolated a series of products from the reduction of pyrene (*1*) with sodium in isoamyl alcohol. Our interest in polycyclic aromatics prompted the present study of the metal-alcohol and electrochemical reduction of pyrene and 2,7-di-*t*-butylpyrene (*1a*), utilizing modern techniques.

RESULTS

Yields of reduction products are shown in Table 1 and structures are presented in Scheme 1.

Reduction with sodium in boiling isoamyl alcohol (Na/i-AmOH). The reduction of pyrene (*1*) was performed using the same proportions of reactants as used by Coulson.[9] The product pattern was found to be independent of reaction time between 0.5 and 2 h. Beside products discussed by Coulson the product mixture contained considerable amounts of two octahydropyrenes, *OH1* and *OH2*.* The former was recognized recently in catalytic hydrogenation of pyrene [10] and in reactions of [2,2]-*meta*-cyclophane.[10,11] One decahydropyrene, *DcH2*, was formed in substantial amounts while only traces of *DcH1* were found. Catalytic hydrogenation of *OH1* and *OH2* yielded *DcH1* and *DcH2*, respectively. Cutting down the relative amount of sodium resulted in small yields of the tetrahydropyrenes *TH2* and *TH3*, which were not observed under the above conditions.

The reduction of 2,7-di-*t*-butylpyrene (*1a*) is much slower than the reduction of pyrene and it is obvious from Table 1 that the presence of the two *t*-butyl groups brings about considerable modifications in the product composition.

* Present address: Department of Clinical Chemistry, Odense University Hospital, DK-5000 Odense, Denmark.

* For abbreviations denoting the compounds discussed, *cf.* Scheme 1.

Table 1. Reduction products [a] of pyrene (*1*) and 2,7-di-*t*-butylpyrene (*1a*).

Substrate	*1*				*1a*				*DH1*			
Method Route [b]	B		A		B		A		B		A	
Sodium in amyl alcohol [c]	*TH1*	2	*(TH2)* [i]		*DH1a*	2	*TH3a*	23	*HH3*	10	*TH1*	18
	OH1	16	*(TH3)* [i]		*TH1a*	12	*HH2a*	17			*OH1*	70
	DcH1	1	*HH2*	43	*HH1a*	6	*HH3a*	27			*DcH1*	2
			HH3	11	*DcH1a*	5	*HH4a*	8				
			OH2	7								
			DcH2	8								
Electrolytic red. TBAI [d,f,g,h]	*DH1*	29	*HH2*	7	*DH1a*	43	*TH2a*	38			*TH1*	79
			HH3	57			*TH3a*	14			*DcH1*	21
							HH3a	5				
Electrolytic red. LiCl [e,f,g,h]			*TH2*	55	*DH1a*	5	*TH2a*	66			*TH1*	100
			HH2	16			*TH3a*	22				
			HH3	29			*HH2a*	2				

[a] Yields (mol %) refer to 100 % conversion. Conversion of substrate into products is 100 % (*i.e.* no pyrene recovered) unless otherwise stated. [b] B, *DH1* is the primary reaction product. A, *DH2* is one of a series of primary products (*cf.* Refs. 16 and 17). [c] 12 % of unidentified products from *1*. [d] 7 % of ketonic products from *1*. By ^{1}H NMR probably 5-oxo-1,2,3,5- and 6-oxo-1,2,3,6-tetrahydropyrene. [e] 5 % of unidentified products from *1a*. [f] TBAI: 4 % *1* and 12 % *1a* were recovered. LiCl: 2 % *1*, 17 % *1a*, and 82.5 % *DH1* were recovered. [g] Solvent: Dimethylformamide with 5 % of water. TBAI is tetrabutylammonium iodide. [h] Potentials, TBAI: *1* (−1.75 V), *1a* (−1.8 V), *DH1* (−1.95 to 2.1 V). LiCl: *1* (−1.8 V), *1a* (−1.8 V), *DH1* (−1.85 to −1.95 V). Small yields of these were found when the amount of sodium was reduced to one third of that otherwise used.

TH1a in a separate experiment proved very reluctant to Na/i-AmOH reduction. According to NMR hardly any reaction took place.

Electrolytic reduction. *1* and *1a* were subjected to controlled potential electrolysis (cpe) on mercury in *N*,*N*-dimethylformamide (DMF) containing 5 % of water as proton donor. It is seen from Table 1 that reduction under the actual conditions does not proceed as far as in the Na/i-AmOH reaction. Octa- and decahydro derivatives are not produced. The di-, tetra- and hexahydro derivates are formed in varying yields depending on the electrolyte used (tetrabutylammonium iodide, TBAI, or LiCl) and whether the pyrene molecule is substituted or not.

When D_2O was substituted for water in the LiCl case the corresponding deuterated products could be isolated. *TH2* (deuterated) was again the most abundant one. However, the mass spectra indicated also the formation of tetra- and hexahydro derivatives, which were deuterated to a higher degree.

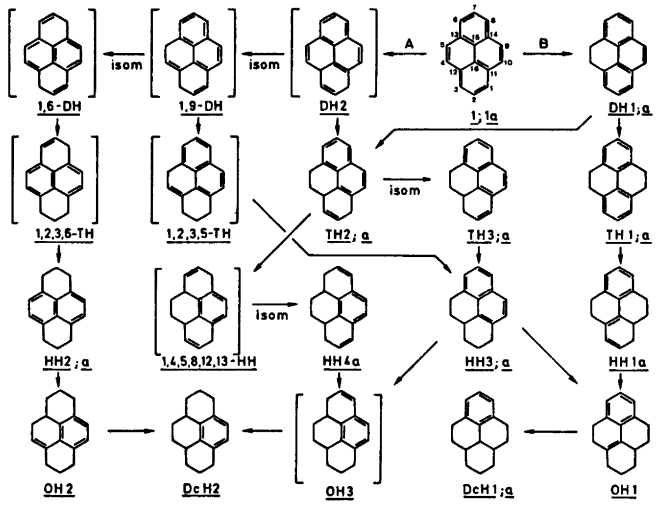
Electrolysis (TBAI) of 4,5-dihydropyrene, *DH1*, at a somewhat lowered potential gave a considerable amount of *DcH1* (m.p. 45 °C) besides the main product *TH1*, and offers a convenient preparative way to these hydropyrenes.

TH1 was electrolyzed similarly when chromatography yielded two stereoisomeric decahydropyrenes, *DcH1*, with m.p. 45.5 and 118 °C, respectively, the former being identical with the product from *DH1*.

Structure assignments were based on ^{1}H NMR, ^{13}C NMR, UV, IR and MS of the separate compounds or binary mixtures resulting from chromatographic separation of the crude product mixtures. On this basis the ^{1}H NMR spectra of the crude mixtures could be reliably analyzed for product ratios. For details see the experimental section.

DISCUSSION

At the potentials used in electrolysis in this work the anion radical will not be further reduced to the dianion, but will be protonated prior to transfer of the second electron (ECE process).



Scheme 1. Structures and pathways. *1* (pyrene). *DH*, *TH*, *HH*, *OH*, and *DcH* indicate di-, tetra-, hexa-, octa-, and decahydropyrenes, respectively. Compounds carrying *t*-butyl groups in the 2- and 7-positions are represented in the text as *1a*, *DH1a*, *etc.* In the scheme *DH1; a*, *TH1; a*, *etc.* denote that the structure referred to has been encountered as a product in both the unsubstituted and the substituted case. *OH1*, *OH2*, and *DcH2* were found as the unsubstituted compounds, whereas *HH1a* and *HH4a* were found as the substituted compounds only. Structures in brackets are tentative intermediates. 1,9-*DH*,[17] 1,2,3,5-*TH* [26] and 1,2,3,6-*TH* [26] have been described by other workers (*cf.* text); isom = isomerization. For discussion of alternative routes; see text.

A relationship between electrolytic reduction and dissolving metal reduction is well established by studies on product composition,[3,12] polarographic reductions and the ESR and optical spectra of the involved anionic species.[3] Recently Fry and Reed [13] suggested that the reduction of a number of anils by the two methods follows a common mechanism (ECE process). The present results are consistent with this relationship.

Surface phenomena do not seem to be part of the reduction process with alkali metals,[3] and the pyrene anion radical reacts too slowly with water in DMF to do so near the surface.[14]

It is generally assumed that protonation of the aromatic anion takes place preferably at the point of highest electron density as calculated by HMO theory,[3,15] and the detailed reaction path that is, whether the anion radical or the dianion is being protonated, is unimportant at least for alternate hydrocarbons. For the pyrene anion the first proton is predicted to add preferably to the 1-position. The second proton, then, adds to an anion in which a series of alternate positions are predicted to have the highest, and equal, electron density.[3,16,17] This process may give rise to a series of dihydropyrenes as primary reduction products. In Scheme 1 1,12-dihydropyrene (*DH2*) is shown as an example.

It cannot, however, be excluded that the first protonation may take place at the 4-position, leading to 4,5-dihydropyrene (*DH1*). ESR hyperfine splitting constants of the pyrene radical anion,[3,18] lithiation [19] and electrolytic reductive alkylation [20] studies on pyrene reveal a certain reactivity in this position. The two reaction routes are depicted as A and B, respectively (Scheme 1).

Reaction conditions, such as the nature of the supporting electrolyte in electrolysis, can be expected to influence the stability of the radical anion by ion-pair formation [8, 21–23] and thereby change the product composition. According to Table 1 the results for the Na/i-AmOH reaction resemble those for cpe/TBAI more than those for cpe/LiCl. The ion-pairing power of TBA^+ is smaller than that of Li^+ [22] and ion-pairing in i-AmOH solution is reduced due to strong solvation.

Another important factor to be considered is the basicity of the solution, which may cause isomerization of intermediates. This, obviously, can be expected in the strongly alkaline medium of the Na/i-AmOH reduction, but also under electrolytic conditions will isomerizations occur. This is shown by the formation of products deuterated in excess of the degree expected, when D_2O is the proton donor in cpe experiments.

Only three *dihydropyrenes* are reliably described in the literature, *viz.* the long-known and very stable *DH1*, the 1,9-dihydropyrene (1,9-*DH*) of Harvey and Rabideau,[17] and the 15,16-dihydropyrene of Mitchell and Boekelheide,[24] but others have been postulated.[2,25] The less stable dihydropyrenes are subject to isomerizations and further reductions as indicated in Scheme 1. The postulated intermediate tetrahydropyrenes 1,2,3,5-*TH* and 1,2,3,6-*TH* were isolated and described by Paskovitch and Das,[26] who reduced pyrene with lithium in ethylenediamine.

The B-products beyond *DH1* and *DH1a* did not show up in cpe of *1* and *1a*, because the potential used was slightly less negative than that needed for further reduction. When *DH1* was submitted to cpe at a more negative potential, *TH1* and *DcH1* but no A-products were formed. In the Na/i-AmOH reduction of *DH1* the formation of *HH3* may partly be due to a crossing-over of a B-product to the A-route. Even though *DH1* was not found among the reaction products of the Na/i-AmOH reduction of *1*, the presence of *TH1*, *OH1* and *DcH1* strongly indicates its intermediate occurrence. Some of the products (*HH3* and *DcH2*), designated as A-products in Table 1, may have been formed to some extent *via DH1* (crossingover). The situation is more complicated yet, as part of *OH1* may have been formed from *HH3*. This is indicated by the fact that *HH3*, isolated from the product mixture of the reaction of *1*, is reduced under identical conditions to a mixture of *OH1* and *DcH2* with only traces of *DcH1*. *HH2* demands forced conditions when *OH2* and *DcH2* are produced.

The distribution of A-products in cpe of *1* using TBAI and LiCl, respectively, can be explained on the basis of a reaction sequence comprising the isomerization of *TH2* into *TH3*, followed by reduction to *HH3*. The apparent suppression of the isomerization, when LiCl is used as supporting electrolyte, is readily understood as a consequence of the greater ion-pairing power of Li^+ as compared with TBA^+, causing a less basic environment in the former case.

The reduction stops at *HH2* and *HH3*. As naphthalene-type compounds they need a more negative potential than that used, in order to be further reduced. Also, these hydrocarbons are quite stable and not prone to rearrangement. *HH4*, on the contrary, should readily be reduced to *OH3* and *DcH2*. As these compounds are not found, the depicted route *via HH4* does not seem a realistic one.

The occurrence of *TH3a* in all three cases of the reduction of *1a* is perhaps the most prominent feature of these reactions. It presumably demonstrates a decreased reactivity of the conjugated double bond when carrying a *t*-butyl group, as does the formation of *HH1a* and *HH4a* in the Na/i-AmOH reduction. This effect is also encountered in metal-ammonia reductions of aromatic hydrocarbons.[1] Apparently, the migration tendency of the isolated double bond in *TH2a* as compared to that in *TH2* is also reduced, since the ratio of *TH2a*/(*TH3a*+*HH3a*) is only slightly changed in going from TBAI to LiCl, whereas the corresponding ratio in the unsubstituted case changes very much.

Four stereoisomeric *decahydropyrenes* corresponding to formula *DcH1* are possible, *viz.* two *meso*-forms and a *d,l*-pair (Fig. 1).

One of the *meso*-forms, *DcH1-c,c* was isolated by Sato *et al.*[11] as one of a series of products from the reaction of [2,2]*meta*cyclophane with $AlCl_3$, while *DcH1-t,t* was found by Langer and Lehner[10] by catalytic hydrogenation of the same cyclophane.

The decahydropyrene produced by cpe of *DH1* has proved by its melting point (45.5 °C) and the ^{13}C NMR spectrum to be *DcH1-c,c*. The additional decahydropyrene found in cpe

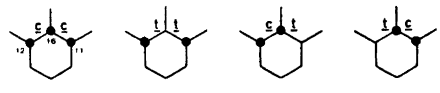


Fig. 1. Stereoisomers of 1,2,3,4,5,9,10,11,12,16-decahydropyrene (*DcH1*).

of *TH1* (m.p. 118 °C) proved similarly to be the *t,t*-isomer. It is noteworthy that *OH1* did not show up in any of these reactions. The exclusive formation of the *c,c*-isomer in the former reaction is a remarkable stereoselective feature.

DcH1, as formed from *1* (Na/i-AmOH), is by the ^{13}C NMR spectrum different from the two *meso*-isomers and is probably the *d,l*-pair. Tiny amounts of both *meso*-forms were also present.

Two diastereoisomers will correspond to formula *DcH2*, a *cis*- and a *trans*-form as regards the relative position of the hydrogens at C-12 and C-13. The two isomers were formed in equal amounts in the Na/i-AmOH reduction of *1* as well as *HH3*.

EXPERIMENTAL

Compounds. All substrates were purified by crystallization and chromatography prior to reduction. Pyrene (*1*) and symmetric hexahydropyrene (*HH2*) were supplied by Rütgerswerke. 4,5-Dihydropyrene (*DH1*) and 4,5,9,10-tetrahydropyrene (*TH1*) were obtained by chromatographic separation from ostensible dihydropyrene (Koch-Light and Aldrich) that appeared to be a 2:2:1 mixture of *DH1*, *TH1* and *1*, respectively. Asymmetric hexahydropyrene (*HH3*) was obtained from the Na/i-AmOH reduction of *1*. 2,7-Di-*t*-butylpyrene was prepared as previously described.[27]

Column chromatographic separations were performed on silica gel (Merck, 0.05 – 0.2 mm) mixed with 10 % of caffeine.[28] Light petroleum (b.p. < 50 °C) was used as the eluent. A little benzene (1 – 5 %) may profitably be added towards the end of a separation. Fractionation was monitored by TLC and UV, and fractions were further characterized by NMR (^1H and ^{13}C) and MS.

^1H NMR spectra were recorded at 60 MHz on a Varian A-60 spectrophotometer and ^{13}C NMR spectra at 20 MHz on a Varian CFT-20 instrument. Chemical shifts in ppm are downfield from TMS as internal standard.

Reduction with Na/i-AmOH. The procedure was that of Coulson except for mechanical stirring that was used instead of "frequent shaking". In case the crude product was separated into its components this was not achieved *via* their picrates, as done by Coulson, but by column chromatography.

Pyrene (1) (Table 1). Pyrene (1 g, 4.9 mmol), isoamyl alcohol (20 ml), and sodium (1.7 g, 70 mmol) in small cuts (added during 20 min) were reacted for 30 min in all. In two similar experiments the reaction time were 1 and 2 h, respectively. Only in the last case was all the sodium used up. Separation was performed in all three cases with almost identical results. Rechromatography of fractions was performed as needed. 80 – 85 % of the material could be recovered from the column (3.5 × 110 cm; 220 – 230 fractions of 25 ml each). The order of appearance of the products from the column was: *DcH2*, *DcH1*, *OH1*, *OH2*, *TH1*, *HH2*, *HH3*. There was a heavy overlap of consecutive components and most fractions were binary mixtures. Small amounts of further purified components could be obtained by repurification, *e.g.* by means of preparative TLC. They were, however, in most cases not pure enough for elemental analysis or melting points to be quoted.

4,5-Dihydropyrene, DH1 (Table 1) was reduced under conditions as used for *1*. Reaction time 3 h. Separation followed as for *1*.

4,5,9,10-Tetrahydropyrene, TH1 (1 g, 4.9 mmol), isoamyl alcohol (70 ml), and sodium (4 g, 0.17 mmol, added during 25 min) were reacted for 3.5 h. Crystallization from ethanol of the crude product gave 0.5 g (m.p. 68.5 – – 70 °C) containing 90 % *OH1*. M.p. of *OH1*, litt. 68 °C. Hydrogenation (Raney-Ni, 3 atm., room temp., cyclohexane, 5 h) of this product gave *DcH1*, 85 % pure and perhydrogenated products. Further hydrogenation only increased the percentage of the latter.

1,2,3,6,7,8-Hexahydropyrene, HH2, was reduced in conditions as used for *TH1*, when a mixture of unreacted *HH2* (40 %), *OH2* (10 %), and *DcH2* (50 %) resulted. Removing *HH2* by chromatography and hydrogenation (conditions as for *OH1*) yielded almost pure *DcH2*, m.p. 33 – 34 °C (litt. 34 °C [29]).

1,2,3,4,5,12-Hexahydropyrene, HH3, was reduced as described for *TH1*. ^1H and ^{13}C NMR spectra showed the presence of *OH1* (*ca.* 30 %) and *DcH2* (*ca.* 70 %). The two diastereomeric forms, *DcH2-c* and *DcH2-t* were present in equal amounts ($\Delta\delta$(arom. H) *ca.* 1.5 Hz). Only traces of *DcH1* were indicated.

^{13}C NMR chemical shift (δ). Solvent $CDCl_3$. *DcH1*-c,c: 135.98 (C-15), 135.78 (C-13, C-14), 126.21 (C-6, C-8), 125.44 (C-7), 47.98 (C-16), 38.17 (C-11, C-12), 34.35 (C-5, C-9), 30.79, 29.14 (C-1, C-3; C-4, C-10), 25.76 (C-2). These values deviate 1.2 – 1.5 ppm from the values given by Sato *et al.*[11] (Formation of *DcH1*, see a following paragraph).

DcH1-t,t: 136.22 (C-13, C-14), 134.12 (C-15), 126.22 (C-6, C-8), 125.00 (C-7), 39.75 (C-16), 35.68 (C-11, C-12), 28.47 (C-5, C-9), 26.06, 25.74, 25.24 (C-1, C-3; C-4, C-10; C-2). These values agree with those of Langer and Lehner.[10]

DcH2-c, DcH2-t: 138.14, 136.23, 134.14, 133.58, 125.89, 125.75, 37.46, 32.83, 31.50, 31.33, 30.69, 29.94, 29.15, 28.57, 22.72, 22.54.

OH1: 135.01, 134.54, 131.39, 131.01, 128.51, 126.81, 125.39, 124.94, 35.95, 31.84, 31.59, 31.22, 29.80, 29.29, 28.03, 22.18. These values agree with those of Sato *et al.*[11]

HH3: 136.18, 134,42, 132.22, 131.58, 127.68, 125.68, 125.58, 124.41, 124.28, 37.79, 31.20, 31.00, 30.72, 29.96, 22.91. One of the aromatic signals was not observed.

TH1: 135.38, 127.04, 125.93, 28.49. One of the aromatic signals was not observed.

2,7-di-t-butylpyrene, 1a (Table 1). *1a* (10 g, 31 mmol), isoamyl alcohol (125 ml), and sodium (10.5 g, 0.46 mol, added during 20 min). A quarter of the initial volume was withdrawn after 2, 4, and 5 h, respectively. More sodium (2 g, 0.09 mol) was added to the remaining portion that was reacted for one additional hour. The four parts yielded 1.8, 2.4, 2.8, and 3.0 g of product, respectively. The second product was subjected to chromatography (column 2.5 × 110 cm), and data obtained for the components were used to analyze the four product mixtures. Only minor differences appeared. The compounds identified are described in the following in order of appearance in the eluate. Percentages in parentheses refer to the total product mixture.

2,7-Di-t-butyl-1,2,3,4,5,9,10,11,12,16-decahydropyrene (DcH1a) (5 %). ^{1}H NMR (CS_2:) δ 0.89 (s, 9 H), 1.23 (s, 9H), 1.70 – 2.90 (m, 16H), 6.72 (broad s, 2H). *DcH1a* was only obtained 60 % pure mixed with *HH1a*.

2,7-Di-t-butyl-1,4,5,9,10,11-hexahydropyrene (HH1a) (6 %), m.p. (ethanol) 149.5 – 151 °C. (Found: C 89.69; H 10.28. Calc. for $C_{24}H_{32}$: C 89.94; H 10.06). UV (ethanol): 324 (4.04), 338 (4.12), 353 (3.96) nm (log ε). ^{1}H NMR (CS_2): δ 1.09 (s, 9H), 1.24 (s, 9H), 1.7 – 2.9 (m, 11H), 5.62 (d, J = 2.1 Hz, 1H), 6.77 (broad s, 2H).

2,7-Di-t-butyl-4,5,9,10-tetrahydropyrene (TH1a) [30] (12 %). *TH1a* was not isolated in a pure state. M.p. (from Ref. 28) 229 – 230 °C.

2,7-Di-t-butyl-1,8,9,10,11,14-hexahydropyrene (HH4a) (8 %). ^{1}H NMR (CS_2): δ 1.11 (s, 18 H), 1.8 – 3.1 (m, 10 H), 6.10 (d, J = 2.1 Hz, 2H), 6.63 (s, 2H). *HH4a* was obtained 20 % pure mixed with *HH3a*.

2,7-Di-t-butyl-1,2,3,4,5,12-hexahydropyrene (HH3a) (27 %), m.p. (ethanol) 129.5 – 131 °C. (Found: C 89.63; H 10.33. Calc. for $C_{24}H_{32}$: C 89.94; H 10.06). UV (ethanol): 230 (4.68), 235.5 (4.89), 282 (3.72), 292 (3.68), 314 (3.28), 328 (3.28) nm (log ε). ^{1}H NMR (CS_2): δ 0.96 (s, 9 H), 1.33 (s, 9 H), 1.7 – 3.1 (m, 10 H), 6.88 – 7.43 ppm (q, J = 8.4 Hz, 2 H; two broad singlets, 2 H).

2,7-Di-t-butyl-1,2,3,6,7,8-hexahydropyrene (HH2a) (17 %), m.p. (ethanol) 174.5 – 175 °C. (Found: C 89.80; H 10.23. Calc. for $C_{24}H_{32}$: C 89.94; H 10.06). UV (ethanol): 228.5 (4.63), 235 (4.80), 288 (3.96), 297.5 (4.06), 310 (3.90), 316 (3.81), 330 (3.54) nm (log ε). ^{1}H NMR (CS_2): δ 1.02 (s, 18 H), 1.7 – 3.1 (m, 10 H), 6.95 (s, 4 H). ^{13}C NMR ($CDCl_3$): δ 27.47, 32.41, 32.71, 44.84, 123.63, 129.72, 134.85; CS_2 + $(CD_3)_2CO$: δ 27.48, 32.13, 32.86, 44.97, 123.83, 129.84, 134.38 (CH_3, Me_3C, C-1, C-2, C-4, C-15, and C-11, respectively).

2,7-Di-t-butyl-1,9,10,11-tetrahydropyrene (TH3a) (23 %), m.p. (ethanol) 176 °C. UV (ethanol): 250 (4.38), 258 (4.67), 267.5 (4.73), 303 (3.86), 316 (3.98), 329 (3.86), 350 (2.80) nm (log ε). ^{1}H NMR (CS_2): δ 1.16 (s, 9 H), 1.33 (s, 9 H), 1.7 – 3.1 (m, 7 H), 6.23 (d, J = 2.6 Hz, 1 H), 6.88 – 7.50 (q, 2 H; two broad singlets, 2 H). The double bond in *TH3a* is conjugated in a phene orientation with the naphthalene nucleus, and accordingly the UV spectrum resembles that of *DH1a*.[31]

2,7-Di-t-butyl-4,5-dihydropyrene (DH1a) [30] (2 %). *DH1a* was not isolated in a pure state. M.p. (from Ref. 28) 187 – 187.5 °C.

Electrolytic reduction. The electrolytic cell described by Iversen [32] was used.

Aromatic hydrocarbon (1 g) and lithium chloride (0.5 M) or tetrabutylammonium iodide (TBAI, 0.1 M) in dimethylformamide (175 ml, 5 % H_2O or D_2O) was electrolysed overnight (15 – 20 h). External cooling was arranged. The potentials and currents were as follows: *1* (TBAI), −1.75 to −1.8 V/0.3 A; *1* (LiCl), −1.8 V/0.45 A; *1* (LiCl, D_2O), −1.75 to −1.8 V/0.3 A; *1a* (TBAI), −1.8 V/0.4 A; *1a* (LiCl), −1.8 V/0.4 A; *DH1* (TBAI), −1.95 to −2.1 V/0.25 A; *DH1* (LiCl), −1.85 to −1.95 V/0.3 A. Current consumption was 3 – 6 times that calculated for transfer of two electrons (for *DH1* (TBAI) only 1.4). Some evolution of hydrogen occurred. Colour changes were observed. Work-up upon addition of water gave crude products which were analyzed by ^{1}H NMR and separated by column chromatography as described (Table 1).

1,2,3,4,5,9,10,11,12,16-Decahydropyrene (DcH1-c,c) from *DH1*/TBAI (21 %), m.p. 45 – 46 °C (litt. 54 °C [11]). (Found: C 90.64; H 9.35. Calc. for $C_{16}H_{20}$: C 90.51; H 9.49. Mw. found (MS): 212). ^{1}H NMR (CS_2): δ 1.0 – 2.1 (m, 12 H), 2.5 – 3.0 (m, 5 H), 6.6 – 7.0 (A_2B-m, 3 H). ^{13}C NMR, see a previons paragraph. In addition to this isomer the other *meso*-form, *DcH1-t,t*, was formed from *TH1*/TBAI, m.p. 118 °C (litt. 129 °C [10]). ^{13}C NMR, see a previous paragraph.

1,4,5,12-Tetrahydropyrene (TH2) from *1*/LiCl (55 %), m.p. 115 °C. (Found: C 92.82; H 7.16. Calc. for $C_{16}H_{14}$: C 93.16; H 6.84. Mw. found (MS): 206. According to ^{1}H NMR and MS *TH2* contained about 10 % of hexahydrocompound that will account for the slight deviation in the analysis). ^{1}H NMR (CS_2): δ 1.5 – 2.2 (m, 2 H), 2.9 – 3.2 (m, 2 H), 3.2 – 3.5 (m, 3 H), 5.6 – 6.1 (AB-q (J = 9.5 Hz) with further splitting, 2 H), 6.9 – 7.7 (m + AB-q (J = 8 Hz), 5H).

1,4,5,12-Tetradeuterio-1,4,5,12-tetrahydropyrene (TH2-d_4), m.p. 115 °C. ^{1}H NMR (CS_2): δ-values as for *TH2*, but each of the first three multiplets now integrates only 1, as was to be expected.

2,7-Di-t-butyl-1,4,5,12-tetrahydropyrene (TH2a) from *1a*/LiCl (66 %). Not isolated in a pure state. ^{1}H NMR (CS_2): δ 1.12 (s, 9 H), 1.34

(s, 9 H), 1.5–3.5 (m, 7 H), 5.57 (broad s, 1 H), 6.9–7.6 (m, 4 H). *TH2a* autoxidized slowly in the air.

A survey of the proton chemical shifts due to the *t*-butyl groups and to olefinic protons follows. *t*-Butyl protons (δ): *DcH1a* (0.89, 1.23), *DcH2a* (0.92), *HH3a* (0.96, 1.33), *HH2a* (1.02), *HH1a* (1.09, 1.24), *HH4a* (1.11), *TH2a* (1.12, 1.34), *TH3a* (1.16, 1.33), *TH1a* (1.28), and *DH1a* (1.40). Olefinic protons (δ): *OH2* (5.55), *TH2a* (5.57), *TH2* (5.83–5.87), *HH1a* (5.62), *HH4a* (6.10), *TH3* (6.02, 6.23), and *TH3a* (6.23).

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