Reactivity of the 1-hydropyrenyl anion towards α,ω-dibromoalkanes

Joost T. M. van Dijk, Johan Lugtenburg and Jan Cornelisse *
Gorlaeus Laboratories, Leiden Institute of Chemistry, PO Box 9502, 2300 RA Leiden, The Netherlands

The reactivity of the 1-hydropyrenyl mono-anion (1^-) towards 1,2-dibromoethane, 1,3-dibromopropane and 1,4-dibromobutane has been examined. Six novel products were isolated from these reactions and characterised: spiro[cyclopropane-1,5'-(1',5'-dihydropyrene)] (**2**), 1,3a-dihydro-1,3a-ethanopyrene (**3**), 9,10,11,11a-tetrahydro-8b*H*-cyclopenta[*e*]pyrene (**4**), 2,3,3a,12a-tetrahydro-1*H*-cyclopenta[*c*]pyrene (**5**), 3a-(3-bromopropyl)-3,3a-dihydropyrene (**6**) and 8b,9,10,11,12,12a-hexahydrobenzo[*e*]pyrene (**7**). The formation of these products could be rationalised by initial attack of the dibromoalkane at positions 3a and 5 of 1^-. Deprotonation of the initial ω-bromoalkyldihydropyrenes leads to intramolecular alkylation, the course of which depends on the length of the alkyl chain. Attempts to aromatize the products resulted, except in the case of **5**, in the fully aromatic pyrene derivatives cyclopenta[*cd*]pyrene, benzo[*e*]pyrene, pyrene and the new cyclopenta-fused pyrene derivative, 10,11-dihydro-9*H*-cyclopenta[*e*]pyrene (**9**).

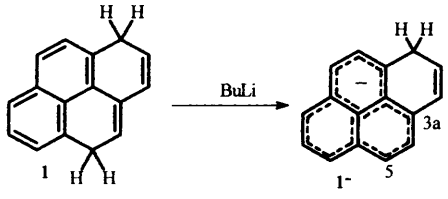
Polycyclic aromatic hydrocarbons (PAH) and their derivatives are a class of widely spread environmental pollutants.[1,2] They are formed during various incomplete combustion processes.[3] Some of these PAHs have been shown to be highly mutagenic and carcinogenic.[4] Because many of these compounds occur only in small amounts in complex mixtures, pure PAHs have to be obtained by synthesis in order to establish their occurrence in the environment and to study their biological properties.[5]

Many environmentally important PAHs such as cyclopenta[*cd*]pyrene, benzo[*a*]pyrene and benzo[*e*]pyrene are derived from pyrene. Reductive alkylation of pyrene with bifunctional reagents is an effective method to prepare new PAHs based on pyrene. The reactive species is the 1-hydropyrenyl anion (1^-),[6] which shows a remarkable selectivity towards electrophiles. Electrophilic attack only takes place at positions 5 and 3a. This is highly selective considering the fact that there are seven charge-bearing carbon atoms in 1^-.

Recently the reactivity of the highly symmetrical phenalenyl anion towards α,ω-dibromoalkanes was studied.[7] The phenalenyl anion reacts with bifunctional alkyl bromides to form first a 1-(ω-bromoalkyl)phenalenyl system. Treatment with a second equivalent of base results in the formation of a substituted phenalenyl anion, which reacts intramolecularly with the C–Br function. It was found that the structure of the products of this reaction depends on the number of carbon atoms in the reagent. From reagents with two, four or five carbon atoms, spiro annelated phenalene derivatives are formed. In the case of three carbon atoms, ring fusion to a pyrene derivative takes place.

The 1-hydropyrenyl anion[6] (1^-) reacts with hard electrophiles at the position bearing the highest charge, *i.e.* position 5. With increasing softness of the electrophile, reaction at the position with the highest HOMO-coefficient, *i.e.* 3a, increases. The 1-hydropyrenyl anion (1^-) can be regarded as an asymmetrically modified phenalenyl anion derivative (Scheme 1). We are therefore interested in its behaviour towards α,ω-dibromoalkanes.

We have studied the reactions of the asymmetric 1-hydropyrenyl anion (1^-) with 1,2-dibromoethane, 1,3-dibromopropane and 1,4-dibromobutane in order to investigate the dependence of the reactivity and the product formation on the number of carbon atoms in the electrophile. After the initial reaction of 1^- with the dibromoalkane, acid-, base- and oxygen-sensitive monoalkylated dihydropyrenes were formed. These were treated with a second equivalent of base, leading, after reaction of the substituted 1-hydropyrenyl anions, to mixtures



Scheme 1 Conversion of 1,5-dihydropyrene (**1**) into the 1-hydropyrenyl anion (1^-)

of pyrene derivatives. These products were separated and analysed. The various products were subsequently heated and treated with DDQ in order to obtain stable, fully aromatic pyrene derivatives.

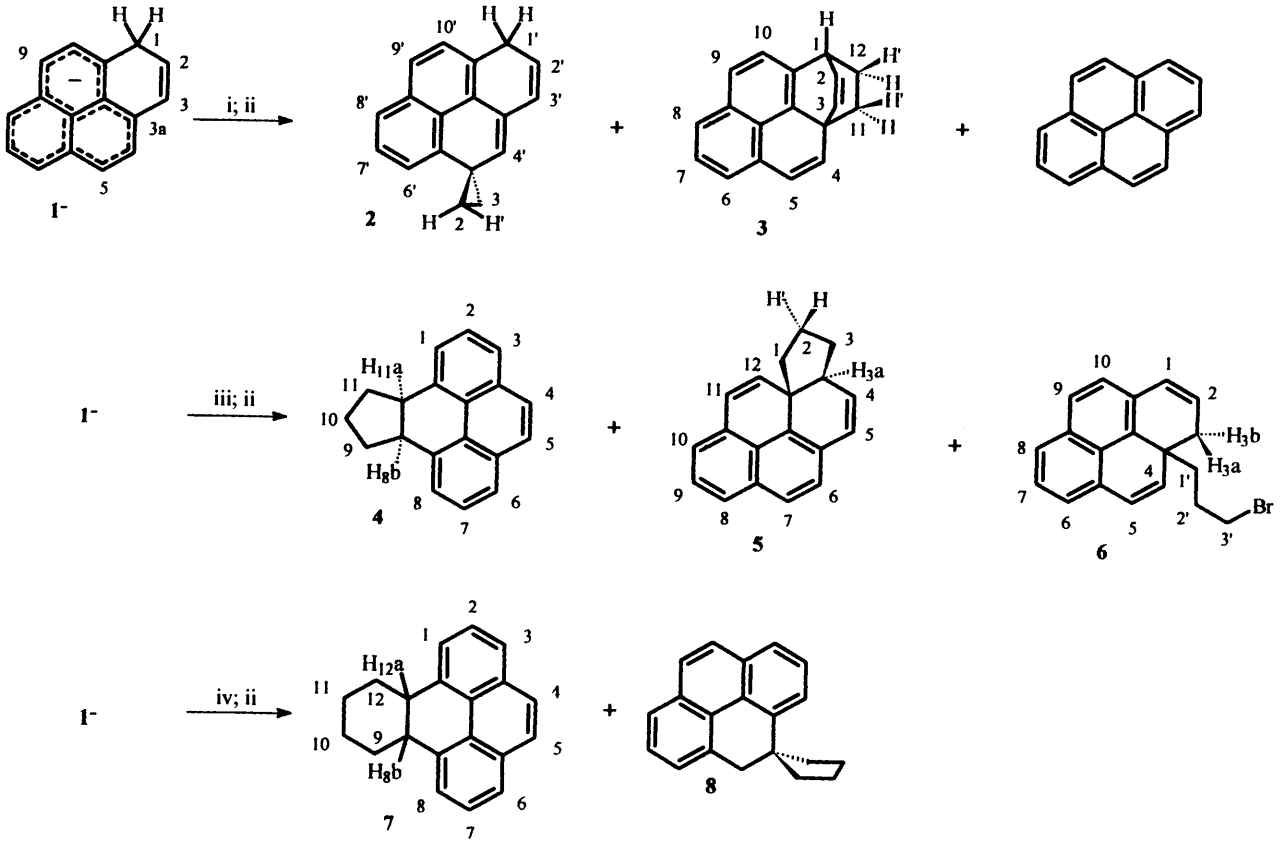
The characterisation of the products of the reactions of 1^- with three α,ω-dibromoalkanes will be described and the influence of the number of carbon atoms in the electrophile on the course of the reaction will be discussed.

Results

Reaction of the 1-hydropyrenyl anion with α,ω-dibromoalkanes

The 1-hydropyrenyl anion (1^-) was obtained by deprotonation of 1,5-dihydropyrene (Scheme 1), which can be obtained in 90% yield by Birch reduction of pyrene.[6] Deprotonation of 1,5-dihydropyrene in tetrahydrofuran with n-butyllithium at −60 °C, gave a deep red-coloured solution. The temperature was raised to −20 °C and subsequent addition of the α,ω-dibromoalkane and stirring for 1 h resulted in the formation of mono-alkylated dihydropyrenes. Upon addition of a second equivalent of n-butyllithium, the solutions again became deep red. After stirring for 3 h the red colour disappeared, indicating completion of the reaction. The products were isolated by means of column chromatography using silica gel or silica gel impregnated with 10% (w/w) of caffeine as the stationary phase. The isolated products are shown in Scheme 2. Six of the seven products have not been characterised before.

The reaction with 1,2-dibromoethane yielded three products which could be isolated by means of column chromatography. A first separation, using silica gel and light petroleum, yielded two fractions, one of which consists of spiro[cyclopropane-1,5'-(1',5'-dihydropyrene)] (**2**, 10%). The structure of **2** is confirmed by mass spectrometry and by comparing its ^{1}H NMR spectrum with that of 1,5-dihydropyrene. In the spectrum of **2** the protons



Scheme 2 Alkylation of 1^- with dibromoalkanes; (i) 1,2-dibromoethane; (ii) n-butyllithium; (iii) 1,3-dibromopropane; (iv) 1,4-dibromobutane

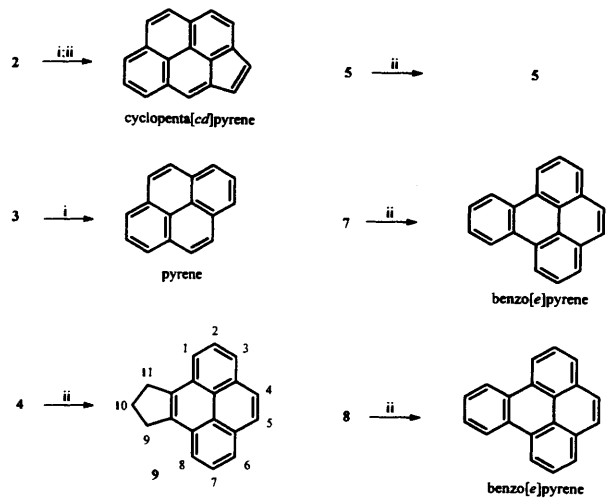
at position 5 are no longer present and the signals of 4-H and 6-H are shifted to a higher field owing to the shielding effect of the cyclopropane ring. The two compounds in the other fraction were separated using silica impregnated with 10% (w/w) of caffeine. This yielded 1,3a-ethano-1,3a-dihydropyrene (**3**, 10%), and pyrene (62%). The structure of **3** is confirmed by mass spectrometry, NOE-difference spectroscopy and by the fact that upon heating **3** undergoes a retro-Diels–Alder reaction, yielding pyrene quantitatively (*vide infra*).

After reaction of 1^- with 1,3-dibromopropane and a second equivalent of base, three products were isolated, none of which have been described before. Column chromatography using silica gel yields pure 9,10,11,11a-tetrahydro-8b*H*-cyclopenta[*e*]pyrene (**4**, 13%), 2,3,3a,12a-tetrahydro-1*H*-cyclopenta[*c*]pyrene (**5**, 19%) and a small amount of 3a-(3-bromopropyl)-3,3a-dihydropyrene (**6**), together with a trace of pyrene. The structures of **4**, **5** and **6** are confirmed by UV–VIS spectroscopy, mass spectrometry and NMR spectroscopy. The UV–VIS spectrum of **4** clearly shows the presence of a phenanthrene moiety. This, together with the presence of eight aromatic protons in the 300 MHz ^{1}H NMR spectrum, proves the presence of a 4,5-dihydropyrene moiety. In the high field region of the ^{1}H NMR spectrum we observe two benzylic protons and six aliphatic protons. From the APT spectrum it is clear that the two benzylic signals in the ^{1}H NMR spectrum originate from two methine protons. This leaves a *cis* or a *trans* structure for **4**. The fact that 10-CH_2 appears as an unsymmetrical multiplet proves the *cis*-structure of **4**. From the UV–VIS and ^{1}H NMR spectra it is evident that compound **5** has a naphthalene moiety conjugated with two double bonds. A ^{13}C APT spectrum and a H–H COSY spectrum prove the structure of **5**. This structure is confirmed by NOE-difference spectroscopy. The exact mass of **6** shows that its molecular formula is $C_{19}H_{17}Br$. The aromatic and olefinic parts of the 300 MHz ^{1}H NMR spectrum of **6** are almost identical to those of 3a-benzyl-3,3a-dihydropyrene as reported by Tintel and co-workers.[8] In the high field region of the spectrum we observe the protons belonging to a bromopropyl chain. This proves the structure of **6** as depicted in Scheme 2.

The reaction of a pyrene anion with a 1,4-dihalobutane was first described by Tintel *et al.*[9] They reported the formation of 8b,9,10,11,12,12a-hexahydrobenzo[*e*]pyrene (**7**). Later Hempenius *et al.*[6] showed that the product did not contain a fused six-membered ring, but rather a spiro five-membered ring (**8**). The isolation of a fused product after reaction of 1^- with 1,3-dibromopropane prompted us to reinvestigate the reaction of 1^- with 1,4-dibromobutane. Addition of a second equivalent of base to the reaction mixture obtained after the reaction of 1^- with 1,4-dibromobutane resulted in two products together with a trace of pyrene. Separation of the products over a silica column results in spiro[cyclopentane-1,4′-(4′,5′-dihydropyrene)] (**8**, 12%), the product which was reported by Hempenius *et al.*, and the new product 8b,9,10,11,12,12a-hexahydrobenzo[*e*]pyrene (**7**, 18%). The UV–VIS spectrum and the aromatic and benzylic parts of the ^{1}H and ^{13}C APT NMR spectra of **7** are almost identical to those of **4**. The aliphatic parts of the ^{1}H and ^{13}C NMR APT spectra prove the presence of a saturated six-membered ring, thus confirming the structure of **7**. However, in this product we cannot assign a *cis* or *trans* configuration unambiguously.

Transformation to pyrene derivatives

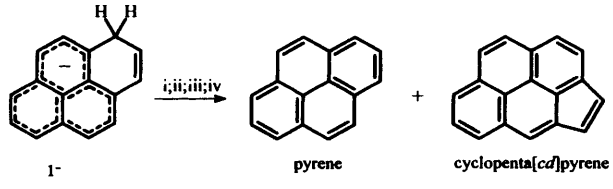
Most of the isolated products can be transformed into fully aromatic pyrene derivatives (Scheme 3). With compound **3** this transformation is achieved by refluxing a solution in toluene for 30 min, yielding pyrene quantitatively. Refluxing a solution of **2** in toluene for 30 min, addition of DDQ and heating at reflux temperature for 1 h gave a 60% yield of cyclopenta[*cd*]pyrene



Scheme 3 Transformation to pyrene derivatives: (i) 110 °C, 30 min; (ii) DDQ

(CPP). In a similar procedure **4** was transformed into **9** (83%), a new cyclopenta-fused derivative of pyrene, the structure of which was proven by means of mass spectrometry, UV–VIS spectroscopy and ^{1}H NMR spectroscopy. The UV–VIS spectrum of **9** clearly shows the presence of a pyrene moiety. The four different signals belonging to eight protons in the aromatic part of the 300 MHz ^{1}H NMR spectrum appearing as an ABX pattern and a singlet prove that we are dealing with a 4,5-disubstituted pyrene skeleton. The remaining six aliphatic protons appear as a triplet and a quintet, which proves the structure of **9** as depicted in Scheme 3. Product **5** remained unchanged upon heating together with DDQ in toluene. 8b,9,10,11,12,12a-Hexahydrobenzo[*e*]pyrene (**7**) was aromatized to benzo[*e*]pyrene in 56% yield by refluxing for 6 h in toluene in the presence of DDQ. As was reported before, **8** can also be transformed into benzo[*e*]pyrene in 50% yield.

Cyclopenta[*cd*]pyrene can be synthesized in a two-pot procedure starting from 1,5-dihydropyrene (Scheme 4). This



Scheme 4 Synthesis of cyclopenta[*cd*]pyrene: (i) 1,2-dibromoethane; (ii) n-BuLi; (iii) toluene reflux; (iv) DDQ

transformation was achieved by allowing **1**$^-$ to react with 1,2-dibromoethane and a second equivalent of base, and refluxing the crude mixture in toluene for 30 min. Addition of DDQ to this mixture and refluxing for another hour resulted in a mixture of 60% pyrene and 6% CPP, which could be separated by means of column chromatography.

Discussion

In a previous study[6] the highest charge density in **1**$^-$ was found at C-5 and a high charge and a large HOMO coefficient at C-3a. Reactions of **1**$^-$ with various electrophiles agree with positions 5 and 3a being the most reactive sites. Hard electrophiles react at C-5, whereas with increasing softness of the electrophile the amount of reaction at position 3a increases. A bromoalkane is intermediate on the hardness scale of electrophiles and reaction of the spiro[cyclopentane-1,1′-[1*H*]pyrenyl] anion with 1,4-dibromobutane has confirmed this.[6] A small amount of product arising from attack at a position equivalent to position 3a was detected, but the 5-substituted isomer was reported to be the major product. Reaction of **1**$^-$ with 1,4-dibromobutane was, however, reported to yield exclusively compound **8**, resulting from initial attack at C-5. The question arises whether initial attack at position 3a does indeed occur in the reaction of **1**$^-$ with α,ω-dibromoalkanes.

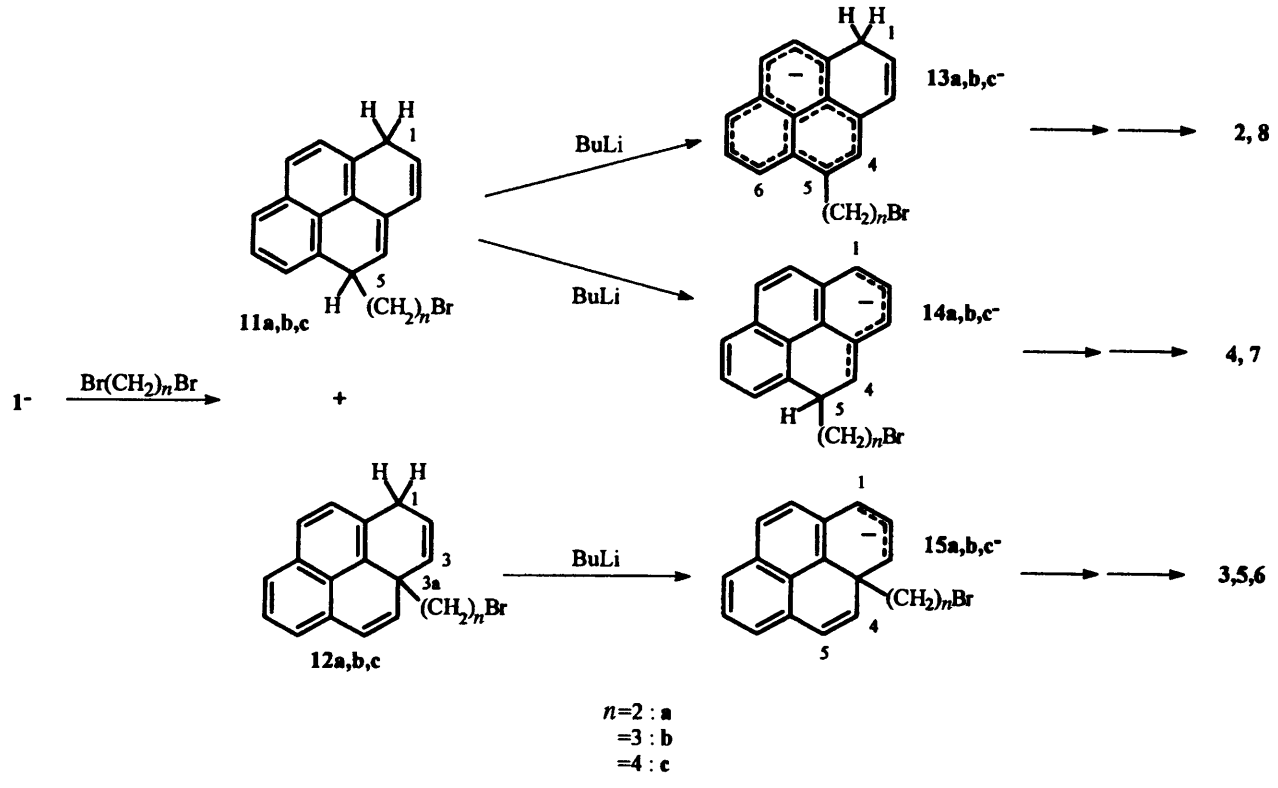
After reaction of **1**$^-$ with 1,2-dibromoethane three products are isolated: pyrene, **2** and **3**. Compound **2** results from initial attack at C-5 of **1**$^-$ by 1,2-dibromoethane. Addition of a second equivalent of base transforms the primary 5-bromoalkyl-1,5-dihydropyrene intermediate **11a** into an anion containing a phenalenyl moiety (**13a**$^-$; Scheme 5). The formation of a spiro three-membered ring is favoured over ring closure at C-6, which would result in a five-membered ring. This is in accordance with the observation that only a spiro three-membered ring is formed in the reaction of the phenalenyl anion with 1,2-dibromoethane.[7] Compound **3** is formed by initial attack at C-3a (Scheme 5), followed by deprotonation of 3a-(1-bromoethyl)-1,3a-dihydropyrene (**12a**) at C-1, resulting in an allylic anion (**15a**$^-$). An intramolecular reaction can then take place at C-1 or C-3, the charge-bearing carbon atoms. The only product detected is **3**, indicating that ring closure to form a six-membered ring is favoured over formation of a four-membered ring. A large amount of pyrene is formed as a result of electron transfer between **1**$^-$ and 1,2-dibromoethane. Oxidation–reduction reactions of this type have been observed earlier in interactions between 1,2-dibromoethane and aromatic radical-anions or dianions.[10]

Reaction of **1**$^-$ with 1,3-dibromopropane affords three products together with a trace of pyrene. The formation of the products can again be rationalised by assuming initial attack at C-5 and C-3a of **1**$^-$ by the dibromoalkane (Scheme 5). The formation of compound **4** starts with attack at position 5. Deprotonation of the ω-bromoalkyl intermediate **11b** at C-5 would result in **13b**$^-$, containing a phenalenyl moiety which does not bear charge at C-4. Owing to steric hindrance at C-5 in **11b**, as a result of the presence of an ω-bromopropyl chain, deprotonation may instead take place at C-1, yielding a pentadienylic anion (**14b**$^-$), which does bear charge at C-4 (Scheme 5). An intramolecular reaction, leading to **4**, can now easily take place. An anion with a structure similar to **14**$^-$ was also suggested by Tintel and co-workers[8] as an intermediate in the reductive alkylation of pyrene with 1,4-diiodobutane.

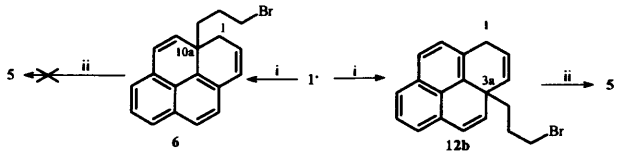
The formation of **5** can only be rationalised by assuming initial attack by 1,3-dibromopropane at C-3a of **1**$^-$. The ω-bromoalkyl-dihydropyrene intermediate **12b**, is deprotonated at C-1, yielding an allylic anion (**15b**$^-$). This anion apparently prefers closure of a five-membered ring over the formation of a seven-membered ring.

A small amount of 3a-(3-bromopropyl)-3,3a-dihydropyrene **6** is the third product from the reaction of **1**$^-$ and 1,3-dibromopropane. Its formation can be explained by assuming a base-catalysed [1,3] H-shift of the initially formed intermediate **12b** to the thermodynamically more stable **6**. The second possibility is attack of the dibromoalkane at position 10a of **1**$^-$ leading directly to **6**. Exposure of **6** to one equivalent of base under the same conditions as in the di-alkylation experiments, did not give any reaction. Even after stirring at room temperature for 16 h with a strong base, only the starting material is isolated. Since **6** cannot be converted into **5**, we have to assume that **5** arises from **12b** and is thus formed *via* initial attack at C-3a (Scheme 6). Likewise, compound **3** will be formed *via* initial attack at C-3a by 1,2-dibromoethane.

The trace of pyrene isolated from this reaction mixture was probably already present in the starting material, 1,5-dihydropyrene. Although this compound is stable at −80 °C



Scheme 5



Scheme 6 Formation of 5: (i) 1,3-dibromopropane; (ii) n-BuLi

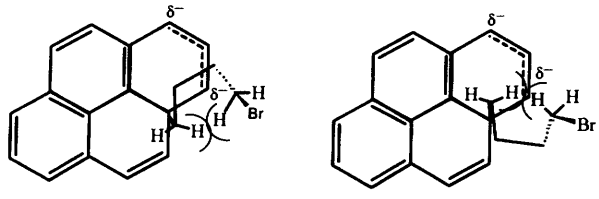


Fig. 1 Two possible boat-like transition states for ring closure of $15c^-$

for a few months, it still contains about 5% of pyrene after purification and slowly oxidises to pyrene at room temperature. Much of the deficit in the material balance in these reactions can be accounted for by assuming the formation of polymers during the process. Polymers are known to be formed during several reductive alkylations, *e.g.* in the reductive alkylation of anthracene with 1,3-dibromopropane.[11]

As mentioned before, the isolation of a 4,5 fused product in the reaction of 1^- with 1,3-dibromopropane inspired us to reinvestigate the reaction of 1^- with 1,4-dibromobutane. After allowing 1^- to react with 1,4-dibromobutane and a second equivalent of base, we identified 18% of 8b,9,10,11,12,12a-hexahydrobenzo[*e*]pyrene **7**, together with 12% of the spiro compound **8**. From the ^{1}H NMR spectrum of **7** we can immediately confirm the conclusion that Tintel *et al.*[9] did not isolate **7** from their reaction mixture.[6] Both isolated products are derived from the intermediate **11c** (Scheme 5) formed after initial attack at C-5 of 1^- by 1,4-dibromobutane. Deprotonation of **11c** at position 5 yields an anion containing a phenalenyl moiety ($13c^-$). Ring closure at C-5 followed by a base-catalysed H-shift, results in the formation of **8**, as reported by Hempenius *et al.*[6] Deprotonation of **11c** at C-1 results in a pentadienylic anion ($14c^-$). This anion reacts intramolecularly at position 4 yielding **7**, confirming the existence of a competition in deprotonation between positions 1 and 5 due to steric hindrance at position 5.

The 1-hydropyrenyl anion thus reacts with each of the three dibromoalkanes in a similar manner, forming the 5-(ω-bromoalkyl)-1,5-dihydropyrenes **11a–c** and the 3a-(ω-bromoalkyl)-1,3a-dihydropyrenes **12a–c** (Scheme 5). From **11a–c** two types of anion are formed: **13a–c** by deprotonation at C-5 and **14a–c** by deprotonation at C-1. Compounds **12a–c** are deprotonated only at C-1, leading to anions **15a–c**. The pathways followed by each of the anions 13^-, 14^- and 15^- depend on the length of the alkyl chain. Anions $13a^-$ and $13c^-$ both react *via* attack of the bromide at the *ipso* position C-5. *Ipso* attack in the case of $13b^-$ would lead to a spiro four-membered ring which is known to be very unfavourable.[12] The other possible mode of attack, at C-6, is not found either, in contrast with the corresponding phenalene derivative,[7] probably because the charge density at C-6 is too low. Intramolecular alkylation of anions 14^- can only take place at position 4, a reaction that does indeed occur with $14b^-$ and $14c^-$. Reaction at C-4 of $14a^-$ is disfavoured because a four-membered ring would result. The same reasoning applies to $15a^-$ as far as the reaction at C-3 is concerned. This anion however has another possibility to undergo alkylation, namely at C-1, and this indeed occurs. From $15b^-$ compound **5** is formed as mentioned above, whereas $15c^-$ does not undergo intramolecular reaction. Closure of $15c^-$ to C-1, forming an eight-membered ring, is, for reasons of entropy, unfavourable. The formation of a six-membered ring from $15c^-$ *via* closure to C-3 is likely to be inhibited by the large amount of steric crowding in the only two possible boat-like transition states, which would lead to the product (Fig. 1). When the intramolecular reaction is disfavoured as in $13b^-$, $14a^-$ and

15c$^-$, intermolecular alkylations may take place instead, leading to polymers.

A remarkable difference is observed in the reactions with 1,2-dibromoethane and 1,4-dibromobutane leading to spiro annelated products **2** and **8** (Scheme 2). The initial product formed after ring closure of **13c**$^-$ has a structure similar to that of **2**. Under the reaction conditions a base-catalysed H-shift leads to the more stable product **8**, containing a phenanthrene moiety. Such a shift is not observed in compound **2**. In this molecule, the orbitals of the double bond, the naphthalene nucleus and the cyclopropyl group interact, forming a conjugated phenalene-like moiety which is the thermodynamically most stable structure.

Almost all products can be converted into aromatic pyrene derivatives. 1,3a-Dihydro-1,3a-ethanopyrene **3** can be considered as a Diels–Alder adduct from ethene and pyrene. Upon heating of **3** in toluene for 30 min, a retro-Diels–Alder reaction occurs, yielding pyrene quantitatively. Heating of **2** in toluene and subsequent dehydrogenation with DDQ results in the environmentally widespread mutagen cyclopenta[*cd*]pyrene in 60% yield. The first step of the reaction is the well known thermal vinylcyclopropane–cyclopentene rearrangement,[13] resulting in a less strained, fused five-membered ring. Dehydrogenation then leads to the fully aromatic CPP. If these conditions are applied to the crude mixture of products obtained after reaction of **1**$^-$ with 1,2-dibromoethane and an additional equivalent of base, **2** rearranges and **3** yields pyrene by a retro-Diels–Alder reaction. Thus a mixture of CPP (6%) and pyrene (65%) is obtained after reaction with DDQ. This two-pot procedure is, together with the flash vacuum thermolysis procedure of Sarobe *et al.*,[14] the shortest and most facile known synthesis of CPP.

Dehydrogenation of **4** results in a new cyclopentapyrene derivative, 10,11-dihydro-9*H*-cyclopenta[*e*]pyrene (**9**) in 10% yield.

Compound **5** cannot be further aromatized because of its quaternary carbon atom.

As reported, **8** can be transformed into benzo[*e*]pyrene *via* cationic rearrangement of the spiro five-membered ring to the desired benzo[*e*]pyrene skeleton.[6] Tintel and co-workers reported the dehydrogenation of **7** to benzo[*e*]pyrene,[8] but it was later proven that **8** instead of **7** was their starting material. Dehydrogenation of a pure sample of **7** to benzo[*e*]pyrene is, as expected, indeed possible. Dehydrogenation of the crude reaction mixture transforms both products into benzo[*e*]-pyrene.

Conclusions

This study on the reactivity of the 1-hydropyrenyl anion (**1**$^-$) towards α,ω-dibromoalkanes, confirms that positions 5 and 3a are the reactive positions of **1**$^-$. Addition of one equivalent of α,ω-dibromoalkane to **1**$^-$ results in a mixture of two isomeric ω-bromoalkyl-dihydropyrenes. Owing to steric hindrance, the 5-alkylated dihydropyrenes can be deprotonated both at positions 1 and 5 and addition of one equivalent of base thus results in the formation of three different anions. The fate of each of these anions strongly depends on the length of the bromoalkyl chain. In the case of the intramolecular reaction, the entropically favoured and thermodynamically most stable products are formed. When the intramolecular reaction is inhibited by strain or steric factors, the intermolecular reaction, resulting in oligomers and polymers is most likely to occur.

Experimental

Pyrene (96%) and butyllithium were purchased from Janssen Chimica (Belgium). Pyrene was used without further purification. Xylene, toluene (both distilled from P_2O_5 and stored over sodium wire), 1,2-dibromoethane, 1,3-dibromopropane and 1,4-dibromobutane were obtained from Merck. Tetrahydrofuran from Janssen Chimica was distilled from $LiAlH_4$ directly before use. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) was purchased from Aldrich. Column chromatography was performed on silica gel 60 (230–400 mesh) obtained from Merck. The 300 MHz ^1H NMR, 75 MHz ^{13}C NMR, COSY, NOESY, NOE-difference and ^{13}C–^1H correlated spectra were recorded on a Bruker WM-300 spectrometer. All chemical shifts (δ) are given in ppm relative to tetramethylsilane (TMS); the coupling constants (J) are given in Hz. Observed NOE effects from NOE difference experiments are printed as: NOE: irradiated proton (observed correlation proton). UV–VIS spectra were recorded on a Varian DMS 200 spectrophotometer. Mass spectra were recorded using a Finnigan MAT 900 with a direct insertion probe, in EI mode. Accurate masses in EI mode were measured with perfluorokerosine as the standard compound.

1,5-Dihydropyrene

1,5-Dihydropyrene was prepared according to the method of Hempenius *et al.*[6] except for the fact that we allowed the reduction to proceed for 3 h. The ^1H and ^{13}C NMR spectra were identical to those reported by Hempenius *et al.*[6]

1-Hydropyrenyl mono-anion and its dialkylation with 1,2-dibromoethane

1,5-Dihydropyrene (934 mg, 4.62 mmol), was dissolved in 100 cm^3 THF under an atmosphere of argon. The solution was cooled to −60 °C and 1.0 equivalent of n-butyllithium (2.89 cm^3, 4.62 mmol) was syringed into the solution. A deep red solution of the 1-hydropyrenyl anion was obtained. Quickly the solution was warmed to −20 °C and after stirring for 5 min 398 μl (1 μl = 1 mm^3) (868 mg; 4.62 mmol) of 1,2-dibromoethane in 2 cm^3 THF was added dropwise to the solution. After stirring at −20 °C for 1 h the colour of the reaction mixture changed to lemon-yellow. At −70 °C a second equivalent of butyllithium was added and stirring was continued at −20 °C until the deep red colour disappeared indicating completion of the reaction. Work-up was accomplished by adding water and light petroleum to the reaction mixture and washing the light petroleum layer until neutral. Drying ($MgSO_4$) resulted in a lemon-yellow solid. Product **2** could be isolated by column chromatography over silica gel using light petroleum as the eluent. This yielded 86 mg (0.37 mmol; 8%) **2** as a very viscous oil. Compound **3** could be separated from pyrene by column chromatography over silica gel impregnated with 10% caffeine by weight. This yielded 577 mg (2.86 mmol; 62%) pyrene as a white solid and 105 mg (0.46 mmol; 10%) of product **3** as a white solid, mp 75.8–76.4 °C (Found: C, 93.8; H, 6.2. $C_{18}H_{14}$ requires C, 93.9; H, 6.1%).

Product **2**: UV–VIS (hexane): λ_{max} 217.6 nm. Other maxima at 244.0 and 335 nm (exact mass calc. for $C_{18}H_{14}$: 230.1096; Found: 230.1095); δ_H(300 MHz, $CDCl_3$) 1.27 (2 H, m, 2-H + 3-H), 1.37 (2 H, m, 2-H′ + 3-H′), 3.83 (2 H, m, 1′-CH_2), 5.13 (1 H, t, $^6J_{1,4}$ 2.2, 4′-H), 5.88 (1 H, dt, J 9.9, 4.0, 2′-H), 6.30 (1 H, dt, J 9.9, 2.1, 3′-H), 6.68 (1 H, dd, J 7.5, 1.1, 6′-H), 7.14 (1 H, d, J 8.4, 10′-H), 7.31 (1 H, dd, J 8.0, 7.5, 7′-H), 7.49 (1 H, dd, J 8.0, 1.1, 8′-H) and 7.57 (1 H, d, J 8.4, 9′-H); δ_C(75 MHz, $CDCl_3$): 23.3 (C-5′), 28.2 (C-2 + C-3), 32.1 (C-1′), 117.0 (C-6′), 124.3 (C-8′), 124.6 (C-2′), 125.8 (C-7′), 126.6 (C-9′), 127.2 (C-10′), 127.3 (C-3′), 130.3 (C-4′), 128.9, 132.1, 133.6, 134.6, 137.0 and 139.9 (C-3a′, C-5a′, C-8a′, C-10a′, C-10b′ and C-10c′).

Product **3**: UV–VIS (hexane): λ_{max} 240.7 nm. Other maxima at 229.4 and 327.8 nm (exact mass calc. for $C_{18}H_{14}$: 230.1096; Found: 230.1094); δ_H(300 MHz, $CDCl_3$): 1.18–1.34 (2 H, m, 11-H + 12-H), 1.57 (1 H, m, 12-H′), 1.76 (1 H, m, 11-H′), 4.26

(1 H, m, 1-H), 6.40–6.45 (2 H, m, 2-H + 3-H), 6.50 (1 H, d, *J* 9.8, 4-H), 6.88 (1 H, d, *J* 9.8, 5-H), 7.17 (1 H, dd, *J* 6.9, 1.1, 6-H), 7.32 (1 H, dd, *J* 6.9, 8.3, 7-H), 7.42 (1 H, d, *J* 8.1, 10-H), 7.57 (1 H, d, *J* 8.1, 9-H) and 7.65 (1 H, dd, *J* 8.3, 1.1, 8-H). NOE: 2-H + 3-H (11'-H + 12'-H); 11'-H (4-H); δ_C(75 MHz, $CDCl_3$): 22.9 (C-12), 33.4 (C-11), 40.7 (C-1), 45.6 (C-3a), 122.3 (C-6), 122.4 (C-10), 123.5 (C-9), 125.0 (C-7), 126.6 (C-8), 127.3 (C-5), 131.0 (C-2 or C-3), 133.7 (C-4), 140.2 (C-2 or C-3), 124.6, 129.7, 130.6, 138.3 and 139.6 (C-5a, C-8a, C-10a, C-10b and C-10c); *m/z* 230 (M^+, 7%) and 202 ($M^+ - 28$, 100%).

1-Hydropyrenyl mono-anion and its dialkylation with 1,3-dibromopropane

Similarly, as in the previous reaction, 439 mg (2.44 mmol) 1,5-dihydropyrene was treated with 1.52 cm^3 (2.44 mmol) n-butyllithium, 259 μl (514 mg; 2.44 mmol) 1,3-dibromopropane and again with 1.52 cm^3 n-butyllithium. After column chromatography over silica gel using light petroleum as the eluent four products were isolated: 59 mg pyrene (0.29 mmol, 12%), 113 mg product **4** (0.46 mmol, 19%), 78 mg product **5** (0.32 mmol, 13%) and 21 mg product **6** (0.09 mmol, 4%). Product **4** mp 94.6–95.8 °C and **5** mp 117.6–119.7 °C (Found: C, 93.7; H, 6.3. $C_{19}H_{16}$ requires C, 93.4; H, 6.6%) are white solids, and **6** is a very viscous oil.

Product **4**: UV–VIS (hexane): λ_{max} 260.4 nm. Other maxima at 217.9, 281.9 and 300.0 nm (exact mass calc. for $C_{19}H_{16}$: 244.1253; Found: 244.1278); δ_H(300 MHz, $CDCl_3$): 1.63–1.81 (2 H, m, 10-CH_2), 1.99 (2 H, m, 9-H + 11-H or 9-H' + 11-H'), 2.25 (2 H, m, 9-H and 11-H or 9-H' + 11-H'), 3.66 (2 H, m, 8b-H and 11a-H), 7.49 (2 H, dd, *J* 1.2, 7.5, 1-H and 8-H), 7.53 (2 H, dd, *J* 7.2, 7.5, 2-H + 7-H), 7.71 (2 H, s, 4-H + 5-H) and 7.71 (2 H, dd, *J* 1.2, 7.2, 3-H + 6-H); NOE: 11a-H (H-1); δ_C(75 MHz, $CDCl_3$): 23.4 (C-10), 34.6 (C-9 + C-11), 42.3 (C-11a + C-8b), 125.0 (C-1 + C-8), 125.6 (C-4 + C-5 or C-3 + C-6), 126.5 (C-2 + C-7), 126.7 (C-4 + C-5 or C-3 + C-6), 137.7, 131.1 and 126.2 (C-3a + C-5a, C-11c + C-11d and C-11b + C-8a); *m/z* 244 (M^+, 75%), 215 ($M^+ - 29$, 100%) and 202 ($M^+ - 42$, 83%).

Product **5**: UV–VIS (hexane): λ_{max} 272.7 nm. Other maxima at 215.6 and 263.1 nm (exact mass calc. for $C_{19}H_{16}$: 244.1253; Found: 244.1245); δ_H(300 MHz, $CDCl_3$): 1.52–1.70 (2 H, m, 1-H or 1-H' + 2-H or 2-H'), 1.77–1.90 (2 H, m, 1-H or 1-H' + 2-H or 2-H'), 2.16 (1 H, m, 3-H), 2.46 (1 H, m, 3-H'), 3.09 (1 H, m, 3a-H), 5.64 (1 H, dd, *J* 9.7, 2.5, 4-H), 6.16 (1 H, d, *J* 9.7, 12-H), 6.52 (1 H, dd, *J* 9.7, 2.7, 5-H), 6.67 (1 H, d, *J* 9.7, 11-H), 7.16 (1 H, dd, *J* 6.9, 1.2, 10-H), 7.27 (1 H, d, *J* 8.2, 6-H), 7.34 (1 H, dd, *J* 6.9, 8.3, 9-H), 7.62 (1 H, d, *J* 8.2, H-7) and 7.63 (1 H, dd, *J* 8.3, 1.2, 8-H); NOE: 11-H (10-H); 6-H (5-H); δ_C(75 MHz, $CDCl_3$): 21.7 (C-2), 31.8 (C-3), 44.9 (C-3a), 45.1 (C-1), 46.9 (C-12a), 122.9 (C-10), 124.4 (C-11), 125.2 (C-7), 125.5 (C-9), 125.9 (C-6), 126.1 (C-5), 126.7 (C-8), 131.4 (C-4), 135.2 (C-12), 127.4, 128.7, 131.3, 132.3 and 134.3 (C-5a, C-7a, C-10a, C-12b and C-12c); *m/z* 244 (M^+, 51%), 215 ($M^+ - 29$, 98%) and 202 ($M^+ - 42$, 100%).

Product **6**: (exact mass calc. for $C_{19}H_{17}{}^{79}Br$: 324.0514; Found: 324.0514); δ_H(300 MHz, $CDCl_3$): 1.18 (1 H, m, 2'a-H), 1.31 (1 H, m, 1'a-H), 1.74 (1 H, m, 2'b-H), 2.15 (1 H, m, 1'b-H), 2.41 (1 H, m, 3a-H), 2.76 (1 H, m, 3b-H), 3.08 (2 H, m, 3'-CH_2), 5.85 (1 H, d, *J* 9.7, 4-H), 5.88 (1 H, ddd, *J* 9.6, 6.2, 2.4, 2-H), 6.60 (1 H, dd, *J* 9.6, 3.0, 1-H), 6.76 (1 H, d, *J* 9.7, 5-H), 7.11 (1 H, dd, *J* 6.9, 0.9, 6-H), 7.24 (1 H, d, *J* 8.2, 10-H), 7.31 (1 H, dd, *J* 8.3, 6.9, 7-H), 7.58 (1 H, dd, *J* 8.3, 0.9, 8-H) and 7.61 (1 H, d, *J* 8.2, 9-H).

1-Hydropyrenyl mono-anion and its dialkylation with 1,4-dibromobutane

Similarly, as in the previous reaction, 541 mg 1,5-dihydropyrene was treated with 1.52 cm^3 (2.44 mmol) n-butyllithium, 259 μl (514 mg; 2.44 mmol) 1,3-dibromopropane and again with 1.52 cm^3 n-butyllithium. After column chromatography over silica gel using light petroleum as the eluent, two products were isolated: 113 mg product **7** (0.44 mmol, 18%) and 75 mg product **8** (0.29 mmol, 13%) both as very viscous oils.

The ^1H NMR spectrum of **8** was identical to that reported by Hempenius *et al.*[6]

Product **7**: UV–VIS (hexane): λ_{max} 259.2 nm. Other maximum at 220.3 nm (exact mass calc. for $C_{20}H_{18}$: 258.1409; Found: 258.1387); δ_H(300 MHz, $CDCl_3$): 1.52–1.82 (8 H, m, 9, 10, 11 and 12-CH_2), 3.44 (2 H, m, 8b-H + 12a-H), 7.50 (2 H, dd, *J* 7.3, 1.5, 1-H + 8-H), 7.56 (2 H, dd, *J* 7.6, 7.3, 2-H + 7-H), 7.73 (2 H, dd, *J* 7.7, 1.5, 3-H + 6-H) and 7.73 (2 H, s, 4-H + 5-H). NOE: 12a-H (1-H); δ_C(75 MHz, $CDCl_3$): 23.9 (C-10 + C-11), 28.9 (C-9 + C-12), 40.2 (C-8b + C-12a), 124.1 (C-1 + C-8), 125.5 (C-3 + C-6 or C-4 + C-5), 126.7 (C-3 + C-6 or C-4 + C-5), 126.7 (C-2 + C-7); *m/z* 258 (M^+, 100%), 215 ($M^+ - 43$, 58%) and 202 ($M^+ - 56$, 42%).

Retro-Diels–Alder reaction of 1,3a-dihydro-1,3a-ethanopyrene 3

20 mg **3** was refluxed for 30 min in 10 cm^3 toluene, yielding pyrene quantitatively, after evaporation of the solvent *in vacuo*.

Cyclopenta[*cd*]pyrene from 2

50 mg of **2** was refluxed in toluene for 30 min, after which 100 mg DDQ was added. Refluxing was continued for another hour. Work-up was performed by washing with saturated aqueous sodium thiosulfate solution. Drying (magnesium sulfate), evaporation of the solvent under reduced pressure and column chromatography yielded 30 mg CPP (60%). The ^1H NMR spectrum was equal to that reported by Jans *et al.*[15]

Cyclopenta[*cd*]pyrene from 1,5-dihydropyrene (1)

A lemon-yellow product mixture was obtained after dialkylation of 980 mg 1,5-dihydropyrene with 393 μl (857 mg; 4.56 mmol) 1,2-dibromoethane and two times 2.85 cm^3 (4.56 mmol) n-butyllithium (*vide supra*). The crude mixture obtained after washing with water, saturated sodium chloride solution, drying (magnesium sulfate) and evaporation of the solvents, was dissolved in 50 cm^3 toluene and refluxed for 1 h under an argon atmosphere. After cooling to room temperature, 621 mg (2.74 mmol) DDQ was added and the mixture was again refluxed for 1 h. After cooling to room temperature, work-up was performed by filtration over hyflo and washing with 50 cm^3 saturated Na_2SO_3. After addition of light petroleum and extraction with water, the organic layer was dried ($MgSO_4$). The solvent was removed under reduced pressure and the product was purified by column chromatography over silica gel using light petroleum as the eluent. This resulted in 60 mg CPP (0.27 mmol; 6%) and 553 mg pyrene (2.74 mmol; 60%). The ^1H NMR spectrum of CPP is identical to that reported by Jans *et al.*[15]

10,11-Dihydro-9*H*-cyclopenta[*e*]pyrene 9

To a solution of 67 mg of **4** (0.27 mmol) in 15 cm^3 toluene, 68 mg of DDQ (0.30 mmol) was added. This mixture was refluxed for 1 h. Work-up was accomplished by filtration over hyflo, washing with saturated sodium thiosulfate and drying (magnesium sulfate). Evaporation of the solvent *in vacuo* and purification over silica gel with light petroleum as the eluent, yielded 37 mg (0.15 mmol; 56%) of 10,11-dihydro-9*H*-cyclopenta[*e*]pyrene (**9**) as a white waxy solid (Found: C, 94.1; H, 5.9. $C_{19}H_{14}$ requires C, 94.2; H, 5.8%).

UV–VIS (hexane): λ_{max} 242.3 nm. Other maxima at 267.4, 278.6, 325.5 and 342.0 nm (exact mass calc. for $C_{19}H_{14}$: 242.1096; Found: 242.1091); δ_H(300 MHz, $CDCl_3$): 2.48 (2 H,

quint, J 7.7, 10-CH_2), 3.52 (4 H, t, J 7.7, 9-CH_2 + 11-CH_2), 8.02 (2 H, dd, J 7.9, 7.2, 2-H + 7-H), 8.08 (2 H, s, 4-H + 5-H), 8.14 (2 H, dd, J 7.9 + 1.4, 3-H + 6-H) and 8.16 (2 H, dd, J 7.2 + 1.4, 1-H + 8-H); NOE: 4-H (1-H).

Dehydrogenation of 7

A sample of 50 mg (0.20 mmol) **7** was refluxed with 177 mg DDQ (0.80 mmol; 6 equiv.) for 6 h in toluene. After dehydrogenation 28 mg benzo[*e*]pyrene (0.11 mmol; 56%) was obtained. The ^{1}H NMR spectrum of benzo[*e*]pyrene was identical to that of Tintel *et al.*[9]

Dehydrogenation of 8

A sample of 60 mg (0.23 mmol) **8** was refluxed with 211 mg DDQ (0.92 mmol; 4 equiv.) for 6 h in toluene. After dehydrogenation 35 mg benzo[*e*]pyrene (0.14 mmol; 60%) was obtained. The ^{1}H NMR spectrum of benzo[*e*]pyrene was identical to that of Tintel *et al.*[9]

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