Synthesis of 1,2-Dimethylpyrene, 1,3-Dimethylpyrene and 1,2,3-Trimethylpyrene

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The title compounds have been prepared, starting from 1*H*-phenalene **1**. The method described in this paper is an efficient procedure for introducing methyl groups into the A-ring of pyrene.

Many polycyclic aromatic hydrocarbons (PAH) and their derivatives are reported to cause cancer or mutations in living organisms,[1] making PAH the largest class of chemical carcinogens known today. PAH are formed when organic material is burned or strongly heated, and they are produced in larger amounts under inefficient combustion conditions.[2] Analysis of the complicated mixtures of polycyclic aromatic compounds in the environment (air, water, sediments, soils) is possible only when pure and well-characterized reference materials are available.[3] Reference materials are essential also for the study of the biological effects of PAH and for the establishment of structure–activity relationships. The presence of methyl groups in PAH may have a profound influence on the biological properties.[4,5] The introduction of a methyl group at a *peri*-position (C-1 or C-9) of phenanthrene changes this compound into a potent mutagen, whereas a methyl group at C-4 does not increase mutagenicity.[4] The nature of the alkyl substituent (methyl, ethyl, ethano bridge) is also an important factor determining the degree of carcinogenicity. 6-Methylbenzo[*a*]pyrene for instance is much more biologically active than 6-ethylbenzo[*a*]pyrene.[5] In studies on the mutagenic activity of methylated pyrenes,[6,7] it was noted that 1-methylpyrene, 1,3-, 1,6- and 1,8-dimethylpyrene have pronounced mutagenic activity relative to other mono- and dimethylated derivatives of pyrene that lack a methyl group at position 1. In this paper we describe an efficient method for selectively introducing methyl groups on the A-ring of pyrene. Our procedure allows the preparation of very pure 1- and 2-methylpyrene, 1,2- and 1,3-dimethylpyrene and 1,2,3-trimethylpyrene and avoids the formation of isomeric impurities.[8] Mono-, di- and tri-methylpyrenes are found in the emission extracts of Diesel vehicles,[9] in sediment trapped material,[10] heavy oils,[11] brown coal[12] and generally are formed in high abundance in low temperature combustion processes.[13]

Results and Discussion

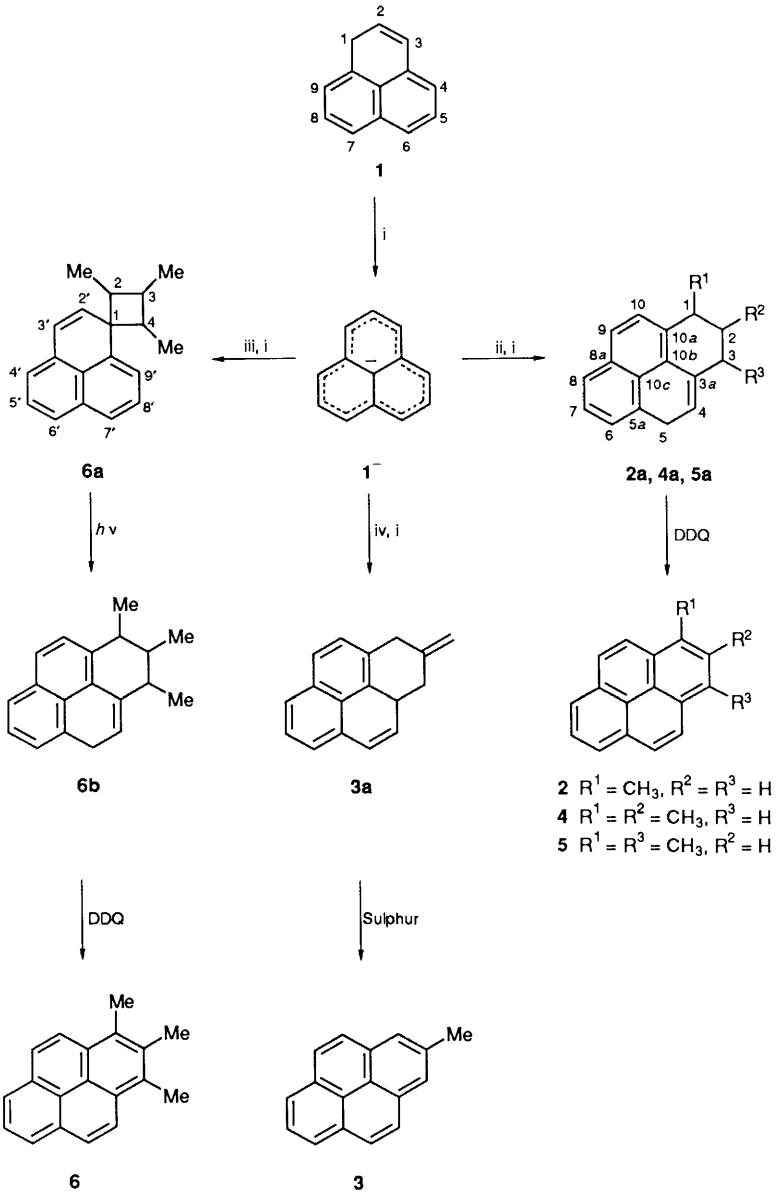
In a previous paper[14] we have described an improved synthesis of 1*H*-phenalene **1** and we have demonstrated its use in the synthesis of fused polycyclic aromatic compounds. When phenalenyl anion $\mathbf{1}^-$ is allowed to react with 1,3-dibromopropane, 1-(3-bromopropyl)phenalene results which can be deprotonated with a second equivalent of butyllithium to 1-(3-bromopropyl)phenalenyl anion. Intramolecular ring closure then affords a 1:1 mixture of 1,2,3,5-tetrahydropyrene and 1,2,3,6-tetrahydropyrene (60%, based on **1**) which can be dehydrogenated to pyrene. We therefore expected that the use of methyl-substituted 1,3-dibromoalkanes might lead to specifically methyl-substituted derivatives of pyrene which are very difficult to prepare in other ways. The availability of 1*H*-phenalene and its anion has been a problem for many years but a few modifications of known procedures[15] enabled us to prepare 1*H*-phenalene easily in gram quantities. We have improved the cyclization of 1-naphthylpropionic acid to 2,3-dihydro-1*H*-phenalen-1-one, the dehydration of 2,3-dihydro-1-hydroxy-1*H*-phenalene to 1*H*-phenalene and the isolation of 1*H*-phenalene.[14] The dibromoalkanes were obtained from the corresponding diols. The purity of the diols and of the dibromides was checked by ^{1}H and ^{13}C NMR spectroscopy and by GCMS. The syntheses of 1-methylpyrene **2**, 2-methylpyrene **3**, 1,2-dimethylpyrene **4**, 1,3-dimethylpyrene **5** and 1,2,3-trimethylpyrene **6** are summarized in Scheme 1. The preparation of 1,2-dimethylpyrene **4** illustrates our method. 1*H*-Phenalene **1** was converted into its anion $\mathbf{1}^-$ with butyllithium. Addition of 1,3-dibromo-2-methylbutane at −15 °C followed by a second equivalent of butyllithium gave a mixture of 1,2-dimethyltetrahydropyrenes **4a** which was dehydrogenated with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) to 1,2-dimethylpyrene **4**. The same procedure was followed for the preparation of 1-methylpyrene **2** and 1,3-dimethylpyrene **5**. 2-Methylpyrene was accessible through reaction of $\mathbf{1}^-$ with the commercially available 3-chloro-2-chloromethylprop-1-ene. The resulting unstable intermediate 2-methylene-1,2,3,3*a*-tetrahydropyrene **3a** could not be dehydrogenated with DDQ but heating **3a** with sulphur in oleic acid did result in 2-methylpyrene **3**. Reaction of the sterically hindered 2,4-dibromo-3-methylpentane with $\mathbf{1}^-$ was only observed at room temperature. After addition of butyllithium, surprisingly, 2,3,4-trimethylspiro[cyclobutane-1,1′-(1*H*)phenalene] **6a** was isolated as the major product, as a mixture of at least four stereoisomers (according to ^{13}C NMR spectroscopy). Spiro ring formation[14] occurs when $\mathbf{1}^-$ reacts with 1,2-dibromoethane, 1,4-dibromobutane and 1,5-dibromopentane, but not with 1,3-dibromopropane. Presumably, the three methyl groups in 2,4-dibromo-3-methylbutane sterically favour the formation of the spiro four-membered ring instead of the fused six-membered ring. Spiro[cyclopropane-1,1′-(1*H*)phenalene] and spiro[cyclopentane-1,1′-(1*H*)phenalene] can be converted photochemically[14] into fused phenalene derivatives and therefore a photochemical ring opening of the cyclobutane ring of **6a** was attempted. Irradiation ($\lambda > 350$ nm) of compound **6a** in its longest wavelength absorption band gave a mixture of 1,2,3-trimethyltetrahydropyrenes **6b** which was dehydrogenated to 1,2,3-trimethylpyrene **6**. The overall yields of the compounds, based on 1*H*-phenalene **1**, are summarized in Table 1.

Table 1 Yields, based on 1*H*-phenalene **1**, of the methylated pyrenes

Pyrene derivative	Yield (%)
1-Me **2**	45
2-Me **3**	33
1,2-Me_2 **4**	32
1,3-Me_2 **5**	30
1,2,3-Me_3 **6**	1

The low overall yield of 1,2,3-trimethylpyrene **6**, partly caused by the reluctance of 1*H*-phenalene **1** to react with the sterically hindered 2,4-dibromo-3-methylpentane, is disappointing. There is, however, to our knowledge, no other procedure for the preparation of this compound.

Double focus Electron Impact mass spectra of **4**, **5**, **6a** and **6**



Scheme 1 *Reagents:* i, BuLi; ii, 1,3-dibromobutane (for **2a**), 1,3-dibromo-2-methylbutane (for **4a**), 2,4-dibromopentane (for **5a**); iii, 2,4-dibromo-3-methylpentane; iv, 3-chloro-2-chloromethylprop-1-ene

were recorded. ^{1}H NMR (300 MHz) spectra of compounds **2**, **3**, **4**, **5**, **6a** and **6** were recorded in $CDCl_3$ at low concentrations (0.01 mol dm^{-3}). All signals could be assigned using NOE and homonuclear decoupling techniques. We also recorded ^{13}C NMR (100 MHz) and 2D ^{1}H–^{13}C correlated spectra in order to assign the ^{13}C signals of the methylpyrenes. The use of a *J*-pass filter made it possible to identify the quaternary signals in the 2D ^{1}H–^{13}C spectrum of **4**, the quaternary signals of **5** and **6** were assigned based on **4**. The ^{1}H and ^{13}C NMR spectra of **2**, **3**, **4**, **5** and **6**, and the high resolution mass spectra recorded after silica gel chromatography and recrystallization clearly show the high purity of the compounds. The absence of isomeric impurities may also be due to the relatively mild dehydrogenation conditions.

The NMR spectra of compounds **4**, **5** and **6** display some interesting substituent effects on chemical shifts (compared to pyrene[16]) of protons and carbon atoms at *peri* positions. The steric interaction between 1-Me and 10-H, and between 3-Me and 4-H (**5**, **6**) results in a shift of charge density[17] from 10-H to 10-C (**4**, **5**, **6**) and from 4-H to 4-C (**5**, **6**). In 1,3-dimethylpyrene **5** 4-H and 10-H, are therefore, shifted downfield by +0.14 ppm (0.18 ppm in 1-methylpyrene[16,18]). In 1,2-dimethylpyrene **4** and 1,2,3-trimethylpyrene **6** the presence of a 2-Me increases the steric interaction between 1-Me and 10-H (and between 3-Me and 4-H in **6**) resulting in a larger downfield shift of +0.26 ppm for 10-H (and 4-H in **6**). Carbon atoms 10-C and 4-C in **2**, **4**, **5** and **6** are shifted upfield, as could be expected, by 3–3.5 ppm (compared to pyrene[17]).

In 1,2-dimethylpyrene **4** the *ortho* proton 3-H is shifted −0.16 ppm compared to 3-H in pyrene (−0.15 ppm for 1-H in 2-methylpyrene[18]). In 1,3-dimethylpyrene **5** the *ortho* proton 2-H is shifted upfield by −0.26 ppm. Each methyl group causes a shift of −0.13 ppm which agrees well with the substitution shift of 2-H in 1-methylpyrene (−0.13 ppm[16,18]). The *ortho* protons in the ^{1}H NMR spectra of **2**, **3**, **4** and **5** are not only easily recognized by their upfield shift but also by their H–H coupling over four bonds with an adjacent methyl group. An *ortho* benzylic[18] coupling constant of 0.7 Hz was observed.

We conclude that phenalene is a valuable synthon in the preparation of methyl-substituted pyrenes and we are now investigating its use in the synthesis of cyclopenta-fused PAH.

Experimental

Double focus Electron Impact mass spectra were recorded on a Kratos MS 9/50 mass spectrometer (source 70 eV, temperature 70 °C). ^{1}H NMR spectra were recorded at 300 MHz on a Bruker WM-300 spectrometer at low concentrations (1 mg/0.5 cm^3) and chemical shifts are reported in δ(ppm) downfield from Me_4Si. *J* Values are given in Hz. ^{13}C NMR spectra were recorded at 100 MHz with a Bruker WM-400 instrument using the solvent peak ($CDCl_3$, δ 77.0) as reference **4**, **5** and **6a**: 60 mg/0.5 cm^3, **6**: 13 mg/0.5 cm^3). Melting points were determined on a Büchi hot-stage microscope and are uncorrected. THF (tetrahydrofuran) was freshly distilled from $LiAlH_4$. Toluene was distilled from $CaCl_2$. DDQ was recrystallized from $CHCl_3$ before use. Butyllithium (1.6 mol dm^{-3} in hexane), 4-hydroxy-3-methylbutan-2-one (85%), pentane-2,4-dione (99+%), 3-methylpentane-2,4-dione (90%), (±)-1,3,dibromobutane (98%) and 3-chloro-2-chloromethylprop-1-ene (99+%) were purchased from Aldrich. Column chromatography was carried out on Merck (230–400 mesh) silica gel with light petroleum (60–80 °C) on hexane. Yields were determined before recrystallization of the compounds.

2,4-*Dibromopentane*.—Pentane-2,4-dione was reduced with $NaBH_4$ in a methanol–water mixture.[19] After distillation, pentane-2,4-diol was obtained as a mixture of stereoisomers[22,23] in 86% yield (*meso*:(±) = 1:0.8), b.p. 110 °C (17 mmHg) [lit.,[19] 65 °C (2 mmHg)]. Pentane-2,4-diol was converted into 2,4-di(methylsulphonyl)pentane[20] in 83% yield. Treatment of the dimesylate with LiBr in refluxing acetone[21] for 8 h afforded 2,4-dibromopentane in 50% yield, after distillation (*meso*:(±)[24] = 0.6:1), b.p. 70–75 °C (15 mm) [lit.,[19] 40 °C (4 mmHg)].

1,3-*Dibromo*-2-*methylbutane*.—4-Hydroxy-3-methylbutan-2-one was reduced with $NaBH_4$.[19] After distillation, 2-methylbutane-1,3-diol was obtained as a mixture of stereoisomers[25,26] in 76% yield (*threo*:*erythro* = 0.55:1), b.p. 74 °C (0.4 mmHg) [lit.,[25] *threo* 110 °C (15 mmHg); lit.,[26] *erythro* 110–120 °C (10 mmHg)]. The dimesylate was prepared in 86% yield. Treatment with LiBr[21] gave 1,3-dibromo-2-methylbutane (*threo*:*erythro*[27] = 1:0.6) in 50% yield b.p. 75–83 °C (17 mmHg) [lit.,[27] 50–52 °C (4 mmHg)].

2,4-*Dibromo*-3-*methylpentane*.—3-Methylpentane-2,4-dione was reduced with $NaBH_4$.[19] After distillation, 3-methylpentane-2,4-diol was obtained in 80% yield (±:*S*-*meso*:*R*-*meso*[28,29] = 0.5:0.4:1), b.p. 71.5–73 °C (0.4 mmHg) or 116 °C (17 mmHg) [lit.,[29] 91–93 °C (2.4 mmHg)]. The dimesylate was prepared[20] in 85% yield; treatment with LiBr in acetone afforded 2,4-dibromo-3-methylbutane in 26% yield after distillation (±:*S*-*meso*:*R*-*meso*[28,29] = 0.9:0.3:1), b.p. 85–90 °C (17 mmHg) [lit.,[29] 67–70 °C (4.5 mmHg)].

1-*Methyltetrahydropyrene* **2a** *and Dimethyltetrahydropyrenes* **4a**, **5a**.—1*H*-Phenalene **1** (360 mg, 2.17 mmol) in THF (100 cm^3) was converted into the phenalenyl anion **1**$^-$[14] at −65 °C under argon. The appropriate dibromide (1.05 equiv.) was added and the temperature was raised to −15 °C. After the mixture had been stirred for 2.5 h BuLi (1.0 equiv.) was added at −65 °C and stirring was continued for 5 h at −15 °C. NH_4Cl was added and the reaction mixture was poured on water and extracted with diethyl ether. The organic layer was dried (Na_2SO_4), filtered and concentrated under reduced pressure. The residues were not purified but immediately dehydrogenated to **2**, **4** and **5**.

1-*Methylpyrene* **2**, 1,2-*Dimethylpyrene* **4** *and* 1,3-*Dimethylpyrene* **5**.—The appropriate (di)methyltetrahydropyrene was diluted with toluene (2 cm^3) and added dropwise through a septum to a solution of DDQ (1.48 g, 6.51 mmol, 3 equiv. based on **1**) in dry toluene (25 cm^3) under argon. After 5 h, excess of DDQ was removed with saturated aqueous Na_2SO_3 and the organic layer was dried (Na_2SO_4), filtered and concentrated under reduced pressure. Compounds **2**, **4** and **5** were purified by silica gel column chromatography and recrystallized (*ca.* 90% recovery) from methanol containing a little water.

2: Yield 211 mg, 0.97 mmol, 45% based on **1**; ^{1}H NMR spectrum in accordance with the literature.[16]

4: Yield 160 mg, 0.69 mmol, 32% based on **1**; m.p. 108 °C (Found: $M^{+\cdot}$, 230.1100. $C_{18}H_{14}$ requires M, 230.1095); λ_{max}(cyclohexane)/nm 237, 246, 267, 279, 303, 314, 328 and 344 (log ε 4.65, 4.87, 4.39, 4.62, 3.70, 4.06, 4.43 and 4.58): λ_{min}(cyclohexane)/nm 216, 260, 272, 293, 335 and 356 (log ε 3.63, 4.06, 4.18, 3.52, 4.15 and 3.30); δ_H(400 MHz) 2.74 (3 H, s, 2-CH_3), 2.86 (3 H, s, 1-CH_3), 7.92 (1 H, d, *J* 9.0, 5-H), 7.92 (1 H, m, *J* 7.6, 7-H), 7.95 (1 H, m, *J* 0.7, 3-H), 7.95 (1 H, d, *J* 9.0, 4-H), 8.04 (1 H, d, *J* 9.3, 9-H), 8.10 (1 H, dd, *J* 7.6, 1.2, 6-H or 8-H), 8.11 (1 H, dd, *J* 7.6, 1.2, 8-H or 6-H), 8.29 (1 H, d, *J* 9.3, 10-H); δ_C(100 MHz) 15.11 (1-CH_3), 21.52 (2-CH_3), 123.48 (10*b*-C), 123.68 (10-C), 124.44 (6-C or 8-C), 124.66 (8-C or 6-C), 124.83 (10*c*-C), 125.35 (7-C), 126.39 (4-C), 126.59 (3-C), 127.05 (9-C), 127.14 (5-C), 129-15 (3*a*-C), 129.21 (10*a*-C), 130.49 (8*a*-C), 130.88 (5*a*-C), 131.15 (1-C), 134.52 (2-C); *m*/*z* 230 (M^+, 47%), 145 (3), 133 (4), 113 (32), 101 (12), 51 (100) and 28 (23).

5: Yield 149 mg, 0.64 mmol, 30% based on **1**; m.p. 152 °C (Found: $M^{+\cdot}$, 230.1107. $C_{18}H_{14}$ requires M, 230.1095); λ_{max}(cyclohexane)/nm 236, 245, 258, 268, 279, 307, 319, 333 and 350 (log ε 4.60, 4.80, 4.02, 4.40, 4.70, 3.65, 4.08, 4.47 and 4.65): λ_{min}(cyclohexane)/nm 216, 238, 253, 272, 290, 323 and 341 (log ε 3.80, 4.58, 3.88, 4.21, 3.36, 4.00 and 4.14); δ_H(300 MHz) 2.93 (6 H, s, 1-CH_3 + 3-CH_3), 7.72 (1 H, m, *J* 0.7, 2-H), 7.95 (1 H, m, *J* 7.6, 7-H), 8.02 (2 H, d, *J* 9.2, 5-H + 9-H), 8.13 (2 H, d, *J* 7.6, 6-H + 8-H), 8.18 (2 H, d, *J* 9.2, 4-H + 10-H); δ_C(100 MHz) 19.52 (1-CH_3 + 3-CH_3), 123.59 (4-C + 10-C), 123.59 (?) (10*b*-C), 124.47 (6-C + 8-C), 124.93 (10*c*-C), 125.53 (7-C), 125.96 (5-C + 9-C), 127.61 (3*a*-C + 10*a*-C), 129.93 (2-C), 131.19 (5*a*-C + 8*a*-C) and 131.60 (1-C + 3-C); *m*/*z* 230 (M^+, 23%), 194 (3), 145 (2), 133 (4), 113 (30), 101 (10), 51 (100) and 28 (27).

2-*Methylene*-1,2,3,3a-*tetrahydropyrene* **3a**.—This compound was prepared in the same way as **2a**, **4a** and **5a**. The reactive 3-chloro-2-chloromethylprop-1-ene requires shorter reaction times (1 h for the first alkylation step, 3 h for the second). Compound **3a** readily polymerizes and was therefore dehydrogenated immediately after isolation.

2-*Methylpyrene* **3**.—Compound **3a** was dissolved in oleic acid (2 cm^3). Sulphur (210 mg, 6.55 mmol, 3 equiv. based on **1**) was added and the mixture was heated under an argon atmosphere at 180 °C for 15 min. Extraction with dichloromethane and purification by silica gel column chromatography yielded 155 mg **3** (0.72 mmol, 33% based on **1**). 2-Methylpyrene **3** was recrystallized from methanol containing a little water; δ_H(300 MHz) 2.80 (3 H, s, 2-CH_3), 7.96 (1 H, m, *J* 7.7, 7-H), 8.00 (2 H, m, *J* 0.7, 1-H + 3-H), 8.00 (2 H, d, *J* 9.0, 4-H + 10-H), 8.05 (2 H, d, *J* 9.0, 5-H + 9-H) and 8.15 (2 H, m, *J* 7.7, 6-H + 8-H); δ_C(100 MHz) 21.98 (2-CH_3), 122.80 (10*b*-C), 124.59 (10*c*-C), 124.77 (6-C + 8-C), 125.34 (7-C), 125.60 (1-C + 3-C), 127.01 (4-C + 10-C), 127.30 (5-C + 9-C), 130.78 (3*a*-C + 10*a*-C), 131.10 (5*a*-C + 8*a*-C) and 135.60 (2-C). ^{1}H NMR spectrum was in accordance with the literature.[18]

2,3,4-*Trimethylspiro*[*cyclobutane*-1,1′-(1H)*phenalene*] **6a**.—The preparation of **6a** was similar to that of **2a**, **4a** and **5a** with the following exceptions. 1*H*-Phenalene (1.11 g, 6.0 mmol) was converted into **1**$^-$ in THF (200 cm^3). After addition of 2,4-dibromo-3-methylpentane stirring was continued for 4 h at 20 °C. Cyclization occurred overnight at 20 °C. Compound

6a (probably a mixture of stereoisomers) was isolated as a yellow oil (179 mg, 12% based on **1**) (Found: $M^{+\bullet}$, 248.1568. $C_{19}H_{20}$ requires M, 248.1565); λ_{max}(cyclohexane)/nm 215, 238, 318, 330 and 348 (log ε 4.23, 4.52, 3.96, 4.03 and 3.98): λ_{min}(cyclohexane)/nm 210, 219, 272, 339, 383 (log ε 4.21, 4.20, 3.31, 3.80 and 1.95); δ_H(300 MHz) 0.74 (3 H, d, *J* 7.4, CH_3), 1.00 (3 H, d, *J* 6.6, CH_3), 1.03 (3 H, d, *J* 6.4, CH_3), 2.33–2.58 (3 H, m, cyclobutane), 6.54 (1 H, d, *J* 10, 2′-H), 6.70 (1 H, d, *J* 10, 3′-H), 7.08 (1 H, dd, *J* 6.9, 1.3, 4′-H), 7.33 (1 H, dd, *J* 8.3, 6.9, 5′-H), 7.50 (1 H, m, 9′-H), 7.51 (1 H, m, 8′-H), 7.61 (1 H, dd, *J* 8.3, 1.3, 6′-H) and 7.65 (1 H, m, 7′-H); δ_C(100 MHz) 10.51, 13.73, 14.42 (CH_3), 31.89 (1-C) 33.86, 46.16, 46.41, 48.62 (cyclobutane), 122.24 (4′-C), 124.41 (3′-C), 125.40 (9′-C), 125.70 (7′-C), 125.75 (5′-C), 125.94 (8′-C), 126.76 (6′-C), 128.39 (9′*b*-C), 131.32 (3′*a*-C), 133.23 (6′*a*-C), 135.83 (2′-C) and 136.12 (9′*a*-C); *m*/*z* 249 (5%), 248 (21), 202 (6), 193 (21), 192 (100), 191 (71), 190 (10), 189 (17), 178 (7), 166 (6), 165 (4), 113 (7) and 51 (22).

1,2,3-*Trimethyltetrahydropyrene* **6b**.—A solution of **6a** (179 mg, 0.72 mmol) in cyclohexane (850 cm^3) under argon was irradiated in a Pyrex photoreaction vessel with a Hanau TQ 81 medium pressure mercury arc through a Corning OS-52 glass filler ($\lambda > 350$ nm). The course of the photoreaction was monitored using UV-spectrometry. After 5 h, the absorption of **6a** at $\lambda = 348$ nm no longer decreased. The cyclohexane was removed under reduced pressure and after silica gel column chromatography **6b** (80 mg, 0.32 mmol, 44% based on **6a**) was isolated.

1,2,3-*Trimethylpyrene* **6**.—Compound **6b** (80 mg, 0.32 mmol) was added, under argon, to a solution of DDQ (1 mmol) in toluene (25 cm^3) and the mixture stirred for 1.5 h. Saturated aqueous Na_2SO_3 was added and after work-up and purification compound **6** was isolated (15 mg, 0.06 mmol, 19% based on **6b**), m.p. 185 °C (Found: $M^{+\bullet}$, 244.1249. $C_{19}H_{16}$ requires M, 244.1252); λ_{max}/nm 239, 248, 270, 282, 320, 334 and 350 (log ε 4.63, 4.81, 4.39, 4.62, 4.05, 4.41 and 4.56); λ_{min}/nm 217, 242, 257, 263, 275, 298, 323, 341 and 397 (log ε 3.86, 4.61, 4.08, 4.06, 4.22, 3.53, 4.03, 4.20 and 2.68); δ_H(300 MHz) 2.70 (3 H, s, 2-CH_3), 2.91 (6 H, s, 1-CH_3 + 3-CH_3), 7.92 (1 H, m, *J* 7.6, 7-H), 8.01 (2 H, d, *J* 9.3, 5-H + 9-H), 8.10 (2 H, d, *J* 7.6, 6-H + 8-H) and 8.30 (2 H, d, *J* 9.3, 4-H + 10-H); δ_C(100 MHz) 16.11 (1-CH_3 + 3-CH_3), 17.64 (2-CH_3), 123.42 (10*b*-C), 123.97 (4-C + 10-C), 124.27 (6-C + 8-C), 124.93 (10*c*-C), 125.27 (7-C), 126.14 (5-C + 9-C), 127.43 (3*a*-C + 10*a*-C), 130.77 (5*a*-C + 8*a*-C), 130.84 (1-C + 3-C) and 133.46 (2-C); *m*/*z* 244 (M^+, 47%), 229 (21), 202 (5), 149 (10), 133 (3), 113 (26), 101 (11), 71 (4), 51 (100) and 28 (30).

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