Electrophilic aromatic substitution of 7-*t*-butyl-1,3-dimethylpyrene: preparation of 5-mono- and 5,9-di-substituted 7-*t*-butyl-1,3-dimethylpyrenes

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Formylation and acetylation of 7-*t*-butyl-1,3-dimethylpyrene selectively afforded the 5-mono- and 5,9-di-substitution products depending on the Lewis acid catalyst used, while bromination and nitration afforded the 6-substitution product.

Keywords: pyrenes, electrophilic substitution, regioselectivity, polymethylpyrenes

Pyrenes belong to the class of polycyclic aromatic hydrocarbons (PAHs), and are reported to cause cancer or mutations in living organisms,[1] thus making them the largest class of chemical carcinogens today. Pyrenes are formed when organic materials are burned or strongly heated. They are produced in larger amounts under inefficient combustion conditions. Analysis of the complicated mixtures of polycyclic aromatic compounds in the environment is possible only when pure and well-characterised reference materials are available.[2] Reference materials are essential also for the study of the biological effects of polycyclic aromatic compounds and for the establishment of structure–activity relationships.

Electrophilic substitution of pyrene occurs at the 1, 3, 6, and 8 positions, but not at the other positions (2, 4, 5, 7, 9 and 10).[3–8] Therefore, pyrenes substituted at the latter positions must be prepared in ways other than by direct electrophilic substitution of pyrene itself.[9] For example, 2- and 4-nitropyrene were prepared by dehydrogenation of 2-nitro-4,5,9,10-tetrahydropyrene[10] and 4-nitro-1,2,3,6,7,8,-hexahydropyrene.[11] Moyle and Ritchie[6] prepared 4,9-diethylpyrene in a low total yield from ethylbenzene in 14 steps using Friedel–Crafts intramolecular acylation to construct a pyrene ring. Thus there is substantial interest in investigating the selective introduction of substituents at positions 4, 5, 9 and 10 in ways other than by direct electrophilic substitution of pyrene itself.

We previously reported the convenient preparative route for 7-*t*-butyl-1,3-dimethylpyrene (**1**) from pyrene in 5 steps, which involves formylation of 7-*t*-butyl-1-methylpyrene and Wolff–Kishner reduction.[12,13] This compound is a convenient starting material for preparing a series of 5-mono- and 5,9-di-substituted 1,3-dimethylpyrenes by electrophilic substitution because one of the active positions of pyrene at 6 and 8 positions is protected by the *t*-butyl group. We now report electrophilic aromatic substitution of 7-*t*-butyl-1,3-dimethylpyrene which selectively afforded 5-mono- and 5,9-diformyl and acetyl substitution products depending on the Lewis acid catalyst used, while bromination and nitration afforded the 6-substitution product.

Results and discussion

The preparation of 7-*t*-butyl-1,3-dimethylpyrene (**1**) was carried out according to the reported procedure.[12,13] Bromination of **1** with benzyltrimethylammonium tribromide ($BTMABr_3$)[14] afforded 6-bromo-7-*t*-butyl-1,3-dimethylpyrene (**2**) in 85% yield resulting from bromination at the 6-position of the pyrene ring along with a small amount of 5,8-dibromo-7-*t*-butyl-1,3-dimethylpyrene (**3**). The relatively facile electrophilic substitution *ortho* to a *t*-butyl group (6-position) instead of at the 5- or 9-position on the pyrene ring is remarkable because the steric bulk of the *t*-butyl group usually inhibits the substitution towards 6 and 8 positions on the pyrene ring. No substitution at the 4, 5, 9 and 10 positions was observed.

This result is also attributable to the high reactivity of the 1, 3, 6 and 8-positions. In fact, the further bromination of **2** with equimolar $BTMABr_3$ under the same conditions above afforded 5,8-dibromopyrene (**3**) in quantitative yield. On the other hand, when nitration of **1** with copper(II) nitrate trihydrate in acetic anhydride was carried out at room temperature, the 6-nitro derivative **4** was obtained in 90% yield (Scheme 1). The nitronium ion attacks on the pyrene ring occurred due to the higher π-basicity of the pyrene ring as compared to a benzene ring even under the relatively mild reaction conditions. The present lower positional selectivity may be governed by the stability of π-complex transition state proposed in the normal aromatic nitration being different from that of the σ-complex transition state in formylation or acetylation.[15–17]

Interestingly, different regioselectivity was observed for the formylation of 7-*t*-butyl-1,3-dimethylpyrene (**1**) with dichloromethyl methyl ether in the presence of titanium tetrachloride which occurred selectively at the 5-position to afford the corresponding 5-formyl derivative **5a** in 69% yield. The formylation of **1** with a large excess (4.0 equiv.) of dichloromethyl methyl ether in methylene dichloride solution in the presence of $AlCl_3$ afforded regioselectively the diformylated product **6a** in 80% yield arising from the two-fold formylation at the 5,9-positions. This result strongly suggests that the *t*-butyl group on the pyrene ring protects the electrophilic attack at the 6,8-positions as well as the methyl groups at the 1,3-positions inhibiting the electrophilic attack at the 4, 10-positions. Similar results were obtained in the acetylation of **1** with acetyl chloride in the presence of $TiCl_4$ or $AlCl_3$ as a catalyst to afford 5-acetyl-7-*t*-butyl-1,3-dimethylpyrene (**5b**) or 5,9-diacetyl-7-*t*-butyl-1,3-dimethylpyrene (**6b**) in 85 and 95% yields, respectively (Scheme 2).

5-Formyl derivative **5a** was converted into 7-*t*-butyl-1,3,5-trimethylpyrene (**7**) in 86% yield by chlorohydroalane (AlH_2Cl) reduction. (see ref.18 and refs cited therein) Further formylation of **7** carried out with dichloromethyl methyl ether in the presence of $TiCl_4$ afforded the 9-formyl derivative **8** in 90% yield, from which 7-*t*-butyl-1,3,5,9-tetramethylpyrene (**9**) was obtained by chlorohydroalane reduction in 85% yield (Scheme 3). 7-*t*-Butyl-1,3,5,9-tetramethylpyrene (**9**) was also obtained by chlorohydroalane reduction of the 5,9-diformyl derivative **6a** in 85% yield under the same reaction conditions.

Consequently, we have succeeded in preparing a series of methyl substituted pyrene derivatives. The UV spectra of methyl substituted pyrene derivatives **1**, **7** and **9** in CH_2Cl_2 along with those of pyrene and 1-methyl-7-*t*-butylpyrene (**10**)[12,13] are shown in Fig. 1. The spectra were recorded

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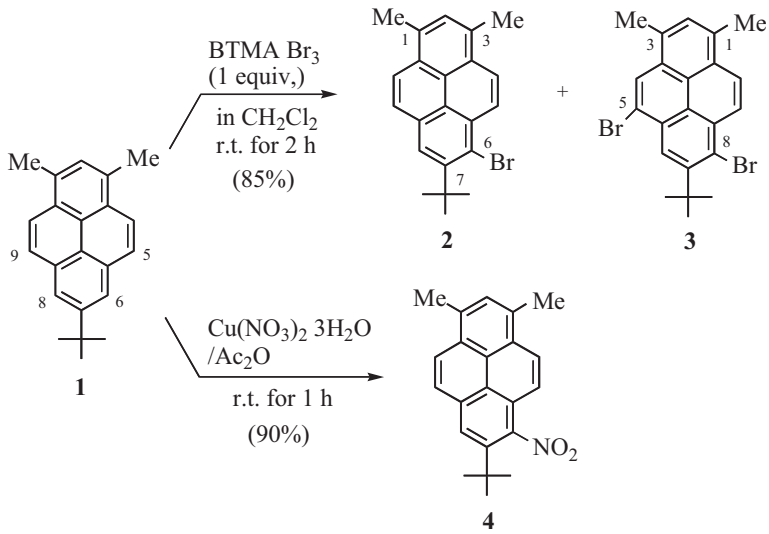
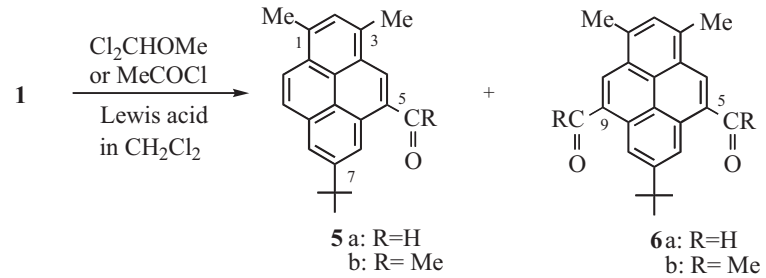


Scheme 1

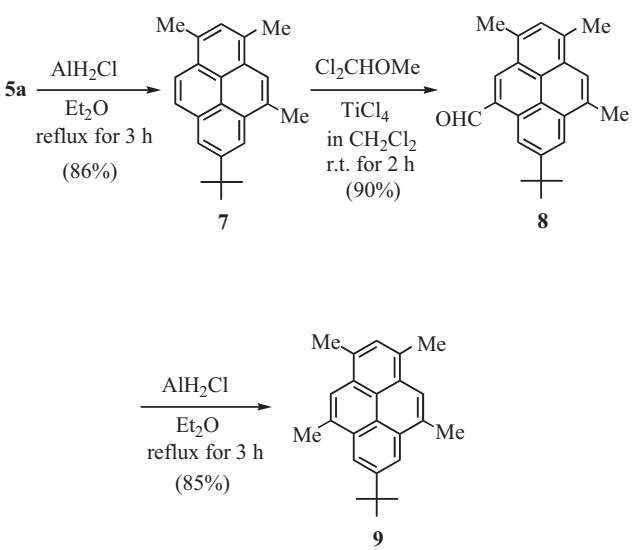


Scheme 2

Table 1 Formylation and acetylation of 7-*t*-butyl-1,3-dimethylpyrene (**1**)[a]

Run	Reagents	Lewis acids	Reaction time/h	Product yields/%[b]	
				5	**6**
1	Cl_2CHOMe	$TiCl_4$	2	93 [69][c]	0
2	Cl_2CHOMe	$AlCl_3$	6	0	89 [80]
3	MeCOCl	$TiCl_4$	2	95 [85][c]	0
4	MeCOCl	$AlCl_3$	3	0	100 [95]

[a]Yields are determined by GLC analyses. [b]Isolated yields are shown in square parentheses. [c]The starting compound **1** was recovered in 7 and 5% yields, respectively.



Scheme 3

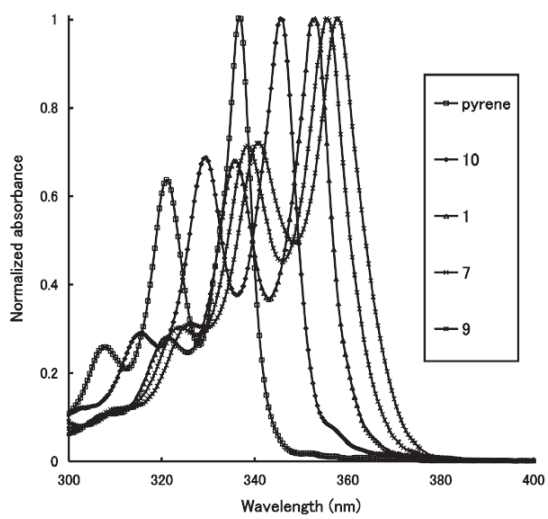


Fig. 1 UV-vis absorption spectra of **1, 7, 9, 10** and pyrene in dichloromethane in the range of 10^{-5} –10^{-6} M concentration at room temperature.

in CH_2Cl_2 in the range of 10^{-5}–10^{-6} M concentration. For these methyl substituted pyrene derivatives, the spectra are almost identical and three absorption bands were observed in the range of 310–380 nm. The longest wavelength π–π* bands of these methyl substituted pyrene derivatives are bathochromically shifted by 9–22 nm in comparison with that of pyrene itself[19] due to the introduction of the methyl group. On the other hand, systematically increasing bathochromic shifts of **1**, **7** and **9** (*e.g.* 18 nm) in comparison with 1-methyl-7-*t*-butylpyrene **10** were observed depending on the number of methyl group introduced. These bathochromic shifts are ascribed to the increased π-electron density on the pyrene ring arising from methyl groups.

Conclusions

We conclude that the electrophilic substitutions of 7-*t*-butyl-1,3-dimethylpyrene **1** lead to the first-reported direct introduction of one and two substituents such as formyl and acetyl group at the 5- or 9-position depending on the Lewis acid catalyst used, while bromination and nitration afforded 6-substitution product. The preparative routes of **1** → **5a** → **7** and **1** → **6a** → **9** should be useful for the preparation of 7-*t*-butyl-1,3,5-tri- and 7-*t*-butyl-1,3,5,9-tetramethylpyrene. Further application of the present method is currently under study in our laboratory.

Experimental

All melting points are uncorrected. ^{1}H NMR spectra were recorded at 300 MHz on a Nippon Denshi JEOL FT-300 NMR spectrometer in deuteriochloroform with Me_4Si as an internal reference. IR spectra were measured as KBr pellets on a Nippon Denshi JIR-AQ2OM spectrometer. UV-vis spectra were recorded on a Perkin Elmer Lambda 19 UV/VIS/NIR spectrometer. Mass spectra were obtained on a Nippon Denshi JMS-HX110A Ultrahigh Performance Mass Spectrometer at 75 eV using a direct-inlet system. Elemental analyses were performed by Yanaco MT-5.

Materials

Preparation of 7-*t*-butyl-1,3-dimethylpyrene (**1**) was previously described.[12,13]

CAUTION: Appropriate care was taken in handling all pyrenes due to the established carcinogenicity.

*Bromination of 7-*t*-butyl-1,3-dimethylpyrene* (**1**): To a solution of **1** (1.82 g, 6.36 mmol) in a mixture of CH_2Cl_2 (75 cm^3) and MeOH (25 cm^3) was added a solution of BTMA Br_3 (2.5 g, 6.36 mmol) at 0°C. After the reaction mixture was stirred for 2 h at room temperature, it was poured into water (100 cm^3). The organic layer was extracted with CH_2Cl_2 (2 × 50 cm^3). The extract was washed with 10% aqueous sodium thiosulfate (50 cm^3) and water (50 cm^3), dried (Na_2SO_4), and concentrated. The residue was column chromatographed over silica gel (Wako, C-300; 200 g) with hexane as an eluent to afford a mixture of **2** and **3** in the ratio of 95: 5 (determined by ^{1}H NMR spectrum) as a colourless solid. Recrystallisation from hexane–$CHCl_3$ (1:1) gave 6-bromo-7-*t*-butyl-1,3-dimethylpyrene (**2**) (1.97 g, 85%) as colourless plates, m.p. 255–257°C (dec.); ν_{max}(KBr)/cm^{-1}: 2960, 1600, 1580, 1450, 1380; δ_H ($CDCl_3$): 1.80 (9H, s, *t*Bu), 2.92 (6H, s, *Me*), 7.71 (1H, s, ArH_2), 7.97 (1H, d, J = 9.2 Hz, ArH_9), 8.18 (1H, d, J = 9.2 Hz, ArH_{10}), 8.24 (1H, d, J = 9.7 Hz, ArH_4), 8.25 (1H, s, ArH_8), 8.68 (1H, d, J = 9.7 Hz, ArH_5); *m/z*: 364, 366 (M^+). Anal. calcd. for $C_{22}H_{21}Br$ (365.31): C, 72.3; H, 5.7. Found: C, 72.2; H, 5.9.

Bromination of **2** *to afford* **3**: To a solution of **2** (234 mg, 0.64 mmol) in a mixture of CH_2Cl_2 (8 cm^3) and MeOH (3 cm^3) was added a solution of BTMA Br_3 (250 mg, 0.64 mmol) at 0°C. After the reaction mixture was stirred for 2 h at room temperature, it was poured into water (10 cm^3). The organic layer was extracted with CH_2Cl_2 (2 × 5 cm^3). The extract was washed with 10% aqueous sodium thiosulfate (5 cm^3) and water (5 cm^3), dried (Na_2SO_4), and concentrated. The residue was column chromatographed over silica gel (Wako, C-300; 50 g) with hexane as an eluent to afford crude **3** as a colourless solid. Recrystallisation from hexane gave 5,8-dibromo-7-*t*-butyl-1,3-dimethylpyrene (**3**) (276, mg, 97%) as colourless prisms, m.p. 265–267°C (dec.); ν_{max}(KBr)/cm^{-1}: 2950, 1605, 1460, 1360, 1080; δ_H ($CDCl_3$): 1.83 (9H, s, *t*Bu), 2.90 (3H, s, *Me*), 2.93 (3H, s, *Me*), 7.72 (1H, s, ArH_2), 8.27 (1H, d, J = 9.9 Hz, ArH_{10}), 8.53 (1H, s, ArH_4), 8.72 (1H, s, ArH_6), 8.73 (1H, d, J = 9.9 Hz, ArH_9); *m/z*: 442, 444, 446 (M^+). Anal. calcd. for $C_{22}H_{20}Br_2$ (444.18): C, 59.5; H, 4.5. Found: C, 59.5; H, 4.5.

*Nitration of 7-*t*-butyl-1,3-dimethylpyrene* (**1**): To a solution of **1** (182 mg, 0.636 mmol) in acetic anhydride (50 cm^3) was added copper(II) nitrate trihydrate (184 mg, 0.762 mmol) at room temperature. After the reaction mixture was stirred for 1 h at room temperature, it was poured into a large amount of ice water (200 cm^3) and extracted with CH_2Cl_2 (2 × 50 cm^3). The CH_2Cl_2 extract was washed with water, dried (Na_2SO_4), and concentrated. The residue was chromatographed over silica gel (Wako, C-300; 100 g) with hexane as eluent to give as a pale yellow solid **4** (211 mg, 100%). Recrystallisation from hexane gave 7-*t*-butyl-1,3-dimethyl-6-nitropyrene (**4**) (190 mg, 90%) as pale yellow prisms, m.p. 290–292°C; ν_{max}(KBr)/cm^{-1}: 3000, 2980, 1530, 1370, 1260; δ_H ($CDCl_3$): 1.64 (9H, s, *t*Bu), 2.94 (3H, s, *Me*), 2.95 (3H, s, *Me*), 7.70 (1H, d, J = 9.5 Hz, ArH_9), 7.77 (1H, s, ArH_2), 7.98 (1H, d, J = 9.5 Hz, ArH_{10}), 8.24 (1H, s, ArH_8), 8.26 (1H, d, J = 9.2 Hz, ArH_4), 8.29 (1H, d, J = 9.2 Hz, ArH_5); *m/z*: 331 (M^+). Anal. calcd. for $C_{22}H_{21}NO_2$ (331.39): C, 79.7; H, 6.4; N, 4.2. Found: C, 80.0; H, 6.5; N, 4.4.

*Preparation of 7-*t*-butyl-5-formyl-1,3-dimethylpyrene* (**5a**): To a stirred solution of **1** (106 mg, 0.37 mmol) and dichloromethyl methyl ether (74 mg, 0.64 mmol) in CH_2Cl_2 (4 cm^3) was added at 0°C a solution of titanium tetrachloride (0.1 cm^3, 0.91 mmol) in CH_2Cl_2 (1 cm^3). This mixture was stirred for 2 h at room temperature. The reaction mixture was poured into a large amount of ice-water and extracted with CH_2Cl_2 (2 × 10 cm^3). The organic layer was washed with water (2 × 5 cm^3), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was recrystallised from hexane to afford **5a** (80 mg, 69%) as pale yellow prisms, m.p. 268–269°C; ν_{max}(KBr)/cm^{-1}: 3050, 2950, 1670, 1570, 1470; δ_H ($CDCl_3$): 1.62 (9H, s, *t*Bu), 2.93 (3H, s, *Me*), 2.95 (3H, s, *Me*), 7.69 (1H, s, ArH_2), 8.02 (1H, d, J = 9.2 Hz, ArH_9), 8.12 (1H, d, J = 9.2 Hz, ArH_{10}), 8.25 (1 H, d, J = 2.0 Hz, ArH_8), 8.61 (1H, s, ArH_4), 9.73 (1H, d, J = 2.0 Hz, ArH_6), 10.49 (1H, s, C*H*O); *m/z*: 314 (M^+). Anal. calcd. for $C_{23}H_{22}O$ (314.4): C, 87.9; H, 7.1. Found: C, 88.1; H, 7.1.

*Preparation of 5-acetyl-7-*t*-butyl-1,3-dimethylpyrene* (**5b**): To a stirred solution of **1** (106 mg, 0.37 mmol) and acetyl chloride (44 mg, 0.56 mmol) in CH_2Cl_2 (5 cm^3) was added at 0°C a solution of titanium tetrachloride (0.05 cm^3, 0.46 mmol) in CH_2Cl_2 (1 cm^3). This mixture was stirred for 2 h at room temperature. The reaction mixture was poured into a large amount of ice-water and extracted with CH_2Cl_2 (2 × 10 cm^3). The organic layer was washed with water (2 × 5 cm^3), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was recrystallised from hexane to afford **5b** (103 mg, 85%) as pale yellow prisms, m.p. 156–158°C; ν_{max}(KBr)/cm^{-1}: 3051, 2952, 1670, 1570, 1475; δ_H ($CDCl_3$): 1.59 (9H, s, *t*Bu), 2.94 (3H, s, *Me*), 2.95 (3H, s, *Me*), 2.98 (3H, s, *Me*), 7.74 (1H, s, ArH_2), 8.03 (1H, d, J = 9.3 Hz, ArH_9), 8.15 (1H, d, J = 9.3 Hz, ArH_{10}), 8.22 (1H, d, J = 1.8 Hz, ArH_8), 8.71 (1H, s, ArH_4), 9.17 (1H, d, J = 2.0 Hz, ArH_6); *m/z*: 328 (M^+). Anal. calcd. for $C_{24}H_{24}O$ (328.43): C, 87.8; H, 7.4. Found: C, 87.9; H, 7.2.

*Preparation of 7-*t*-butyl-5,9-diformyl-1,3-dimethylpyrene* (**6a**): To a stirred mixture of **1** (286 mg, 1.0 mmol) and dichloromethyl methyl ether (463 mg, 4.0 mmol) in CH_2Cl_2 (10 cm^3), was added aluminum chloride (534 mg, 4.0 mmol) at 0°C. After this addition, this mixture was stirred for 6 h at room temperature. The reaction mixture was poured into a large amount of ice-water and extracted with CH_2Cl_2 (2 × 100 cm^3). The organic layer was washed with water (3 × 50 cm^3) and brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was column chromatographed with hexane: chloroform (1 : 3) as eluent to give an orange solid. Recrystallisation from hexane to afford **6a** (273 mg, 80%) as orange–yellow prisms, m.p. 256–258°C; δ_H ($CDCl_3$): 1.64 (9H, s, *t*Bu), 3.05 (6H, s, *Me*), 7.82 (1H, s, ArH_2), 8.68 (2H, s, Ar$H_{4,10}$), 9.84 (2H, s, Ar$H_{6,8}$), 10.56 (2H, s, *CHO*); *m/z*: 342 (M^+). Anal. calcd. for $C_{24}H_{22}O_2$ (342.44): C, 84.2; H, 6.5. Found: C, 84.2; H, 6.4.

*Preparation of 5,9-diacetyl-7-*t*-butyl-1,3-dimethylpyrene* (**6b**): To a stirred solution of **1** (106 mg, 0.37 mmol) and acetyl chloride (44 mg, 0.56 mmol) in CH_2Cl_2 (5 cm^3) was added at 0°C, a solution of titanium tetrachloride (0.05 cm^3, 0.46 mmol) in CH_2Cl_2 (1 cm^3). This mixture was stirred for 3 h at room temperature. The reaction mixture was poured into a large amount of ice-water and extracted with CH_2Cl_2 (2 × 10 cm^3). The organic layer was washed with water (3 × 5 cm^3), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was recrystallised from hexane to afford **6b**

(130 mg, 95%) as yellow prisms, m.p. 233–235°C; δ_H ($CDCl_3$): 1.58 (9H, s, *t*Bu), 2.93 (6H, s, *Me*), 2.97 (6H, s, *Me*), 7.75 (1H, s, ArH_2), 8.60 (2H, s, Ar$H_{4,10}$), 9.17 (2H, s, Ar$H_{6,8}$); *m/z*: 370 (M^+). Anal. calcd. for $C_{26}H_{26}O_2$ (370.49): C, 84.3; H, 7.1. Found: C, 84.4; H, 7.1.

*Preparation of 7-*t*-butyl-1,3,5-trimethylpyrene* (**7**): To a stirred solution of AlH_2Cl [prepared from $AlCl_3$ (670 mg, 5.0 mmol) and $LiAlH_4$ (190 mg, 5.0 mmol) in diethyl ether] was gradually added a solution of 7-*tert*-butyl-5-formyl-1,3-dimethylpyrene (**5a**) (314 mg, 1.0 mmol) in diethyl ether (25 cm^3) while stirring at room temperature. After the reaction mixture had been refluxed for 3 h, it was poured into a large amount of ice-water and extracted with ethyl acetate. The organic layer was washed with water and brine, dried over Na_2SO_4, and the solvent evaporated under reduced pressure. The residue was column-chromatographed over silica gel (Wako, C-300; 50 g) with hexane:chloroform (4 : 1) as eluent to give a colourless solid. Recrystallisation from hexane to afford **7** (258 mg, 86%), m.p. 124–126°C; δ_H ($CDCl_3$): 1.62 (9H, s, *t*Bu), 2.93 (9H, s, *Me*), 7.68 (1H, s, ArH_2), 8.02 (1H, d, J = 9.2 Hz, ArH_9), 8.03 (1H, s, ArH_4), 8.17 (1H, d, J = 9.2 Hz, ArH_{10}), 8.21 (1H, d, J = 1.8 Hz, ArH_8), 8.31 (1H, d, J = 1.8 Hz, ArH_6); *m/z*: 300 (M^+). Anal. calcd. for $C_{23}H_{24}$ (300.24): C, 91.95; H, 8.05. Found: C, 92.0; H, 8.1.

*Preparation of 7-*t*-butyl-9-formyl-1,3,5-trimethylpyrene* (**8**): Formylation of **7** (300 mg, 1.0 mmol) with dichloromethyl methyl ether in the presence of titanium tetrachloride under the same reaction conditions as preparation of **5a** described above afforded 7-*t*-butyl-9-formyl-1,3,5-trimethylpyrene **8** (297 mg, 90%) as pale yellow prisms, m.p. 218–220°C; ν_{max}(KBr)/cm^{-1}: 3055, 2950, 1670, 1560, 1460; δ_H ($CDCl_3$): 1.63 (9H, s, *t*Bu), 2.92 (3H, s, *Me*), 2.98 (3H, s, *Me*), 2.98 (3H, s, *Me*), 7.70 (1H, s, ArH_2), 7.98 (1H, s, ArH_4), 8.39 (1H, d, J = 2.1 Hz, ArH_6), 8.67 (1H, s, ArH_{10}), 9.78 (1H, d, J = 2.1 Hz, ArH_8) 10.52 (1H, s, C*H*O); *m/z*: 328 (M^+). Anal. calcd. for $C_{24}H_{24}O$ (328.43): C, 87.86; H, 7.37. Found: C, 87.9; H, 7.2.

*Preparation of 7-*t*-butyl-1,3,5,9-tetramethylpyrene* (**9**): To a stirred solution of AlH_2Cl [prepared from $AlCl_3$ (0.67 g, 5.0 mmol) and $LiAlH_4$ (190 mg, 5.0 mmol) in diethyl ether] was gradually added a solution of 7-*t*-butyl-5,9-diformyl-1,3-dimethylpyrene (**6a**) (342 mg, 1.0 mmol) in diethyl ether (25 cm^3) while stirring at room temperature. After the reaction mixture had been refluxed for 3 h, it was poured into a large amount of ice-water and extracted with ethyl acetate. The organic layer was washed with water and brine, dried over Na_2SO_4, and the solvent evaporated under reduced pressure. The residue was column-chromatographed over silica gel (Wako, C-300; 50 g) with hexane:chloroform (9 : 1) as eluent to give a colourless solid. Recrystallisation from hexane afforded the *title compound* **9** (270 mg, 85%) as colourless prisms, m.p. 182–184°C; δ_H ($CDCl_3$): 1.62 (9H, s, *t*Bu), 2.91 (6H, s, *Me*), 2.92 (6H, s, *Me*), 7.64 (1H, s, ArH_2), 8.02 (2H, s, Ar$H_{4,10}$), 8.31 (2H, s, Ar$H_{6,8}$); *m/z*: 314 (M^+). Anal. calcd. for $C_{24}H_{26}$ (314.24): C, 91.7; H, 8.3. Found: C, 91.75; H, 8.4.

Similarly, compound **9** was prepared by the chlorohydroalane reduction of **8** in 85% yield.

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