Cleavage of Benzyl Benzoate with Trimethylsilyl Bromide. To a mixture of 11 g (50 mmol) of benzyl benzoate, 0.63 g (2.5 mmol) of iodine, and 0.40 g (2.5 mmol) of bromine was added, with stirring with a magnetic stirrer, 10 g (65 mmol) of trimethylsilyl bromide over a 10-min period. After being stirred for 10 min, the mixture was distilled at reduced pressure to give 6.4 g of a dark liquid [bp 80–90 °C (9 mm)] which appeared to consist of a mixture of iodine monobromide and benzyl bromide, 5.0 g of trimethylsilyl benzoate [bp 95 °C (8.5 mm)], and 3.5 g of a pot residue which solidified on cooling. The pot residue and the fraction which boiled at 95 °C (8.5 mm) were combined and stirred with 20 mL of water at room temperature for 30 min. The solid formed was filtered off and dissolved in 50 mL of ether, and the ether layer was extracted with three 25 mL-portions of saturated aqueous $NaHCO_3$. Acidification of the bicarbonate extract with concentrated HCl gave benzoic acid as a white solid which was filtered and air dried: 5.2 g (85% yield); mp 121–122 °C (lit.[22] mp 122 °C).

Cleavage of Dimethyl Adipate with Trimethylsilyl Bromide. Into a 100-mL, round-bottomed flask were added 8.7 g (50 mmol) of dimethyl adipate, 1.6 g (6.5 mmol) of iodine, 1.1 g (6.8 mmol) of bromine, and 20 g (130 mmol) of trimethylsilyl bromide. The mixture was refluxed for 17 h, cooled to room temperature, and treated with 10 mL of concentrated hydrochloric acid. The solid which formed was filtered, washed with a little aqueous sodium sulfite, dissolved in 100 mL of boiling water, and decolorized with Norite and Celite. Acidification of the resulting light yellow solution to pH 2 with concentrated hydrochloric acid gave adipic acid as a white solid which was allowed to air dry: 5.0 g (68% yield); mp 152–153 °C (lit.[23] mp 151–152 °C).

Cleavage of γ-Butyrolactone with Trimethylsilyl Bromide. A mixture of 4.3 g (50 mmol) of γ-butyrolactone, 0.63 g (2.5 mmol) of iodine, 0.40 g (2.5 mmol) of bromine, and 7.7 g (50 mmol) of trimethylsilyl bromide was allowed to stir overnight at room temperature. The workup and distillation gave 6.0 g (73% yield) of 4-bromobutanoic acid: bp 106–109 °C (3.9 mm); n^{24}_D 1.4825 [lit.[24] bp 124–127 °C (7 mm)]; NMR ($CDCl_3$) δ 2.2 (m, 2 H, $CH_2CH_2CH_2$), 2.5 (m, 2 H, CH_2COOH), 3.4 (t, 2 H, CH_2Br), 11.9 (s, 1 H, COOH).

Cleavage of Benzyl Trimethylsilyl Ether with Trimethylsilyl Chloride. A mixture of 16 g (87 mmol) of benzyl trimethylsilyl ether, 1.3 g (8.1 mmol) of iodine monochloride, and 13 g (120 mmol) of trimethylsilyl chloride was heated at reflux for 30 min. The workup and distillation gave 5.3 g (65% yield) of benzyl chloride: bp 83 °C (29 mm) [lit[25] bp 83.6 °C (29 mm)]; NMR (neat) δ 4.3 (s, 2 H, CH_2Cl), 7.1 (s, 5 H, aromatic).

Acknowledgment. We thank the Committee on Research of the University of California at Davis for a Faculty Research Grant in partial support of this research.

Registry No. Me_3SiBr, 2857-97-8; c-$C_6H_{11}OCH_3$, 931-56-6; c-$C_6H_{11}OCH_2C_6H_5$, 16224-09-2; $CH_3C(O)OCH_3$, 79-20-9; $CH_3C(O)OCH_2C_6H_5$, 140-11-4; I_2, 7553-56-2; Br_2, 7726-95-6; IBr, 7789-33-5; $C_6H_5CH_2OCH_2CH_3$, 539-30-0; $C_6H_5CH_2OCH_2C_6H_5$, 103-50-4; $CH_3(CH_2)_7OSiMe_3$, 14246-16-3; c-$C_6H_{11}OSiMe_3$, 13871-89-1; $C_6H_5CH_2OSiMe_3$, 14642-79-6; $C_6H_5CH(CH_3)OSiMe_3$, 14856-75-8; $CH_3CH{=}CHCH_2OSiMe_3$, 18269-32-4; $CH_3COOCH_2CH_3$, 141-78-6; $CH_3COOC_6H_{11}$, 622-45-7; $CH_3COOC(CH_3)_3$, 540-88-5; $C_6H_5COOCH_3$, 93-58-3; $C_6H_5COOCH_2C_6H_5$, 120-51-4; $(CH_2CH_2COOCH_3)_2$, 627-93-0; Me_3SiCl, 75-77-4; ICl, 7790-99-0; $Me_3SiSiMe_3$, 1450-14-2; $Me_3SiOSiMe_3$, 107-46-0; $C_6H_5CH_2Br$, 100-39-0; CH_3I, 74-88-4; $C_6H_5CH_2OH$, 100-51-6; tetrahydrofuran, 109-99-9; tetrahydropyran, 142-68-7; γ-butyrolactone, 96-48-0; cyclohexanol sodium salt, 22096-22-6; cyclohexanol, 108-93-0; crotyl alcohol, 6117-91-5.

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Twin Annulation of Naphthalene via a 1,5-Naphthodiyne Synthon. New Syntheses of Chrysene and Dibenzo[*b*,*k*]chrysene

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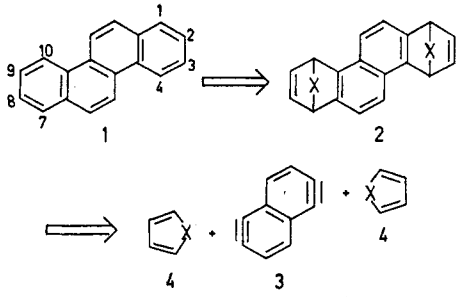
New, efficient syntheses of chrysene (**1**), dibenzo[*b*,*k*]chrysene (**16**), and derivatives are described that feature, as the key step, the formal cycloaddition between 1,5-naphthodiyne (**3**) and a heterocyclic diene (furan, pyrroles, isoindoles). Subsequent manipulation affords the arene in 26–49% overall yield from commercially available 2,6-dibromo-1,5-dihydroxynaphthalene (**5**). The latter is easily converted to ditosylate **6**, which, with phenyllithium, serves as a synthon for **3**.

Chrysene (**1**) and the methylchrysenes are ubiquitous, carcinogenic polycyclic aromatic hydrocarbons[1] (PAH) that are under active investigation by cancer researchers.[2]

Scheme I



These PAH are especially prevalent in tobacco smoke[1a] and various foodstuffs[1c,d] (e.g., spinach, smoked ham), and at least one such derivative, 5-methylchrysene, is highly carcinogenic, having activity comparable to that of ben-

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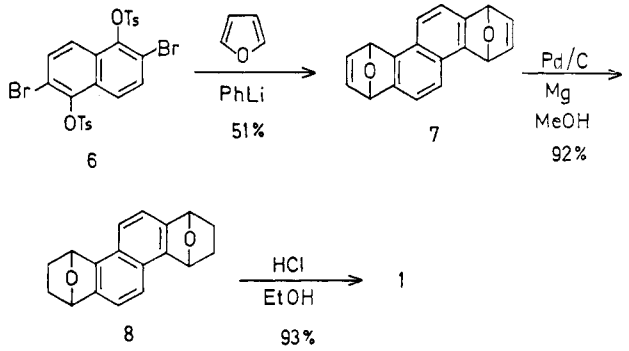
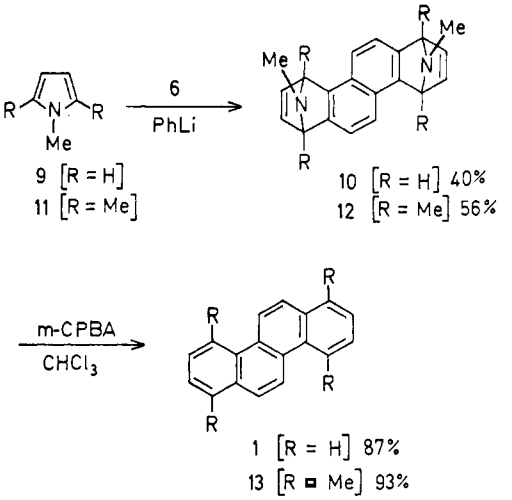
Scheme II



Scheme III



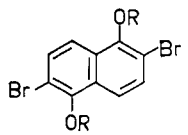
zo[*a*]pyrene.

In continuation of our studies[3] on new syntheses of PAH using Diels–Alder arene annulation methodology, we describe herein a convenient and efficient construction of the chrysene ring system and its dibenzo homologue, dibenzo[*b*,*k*]chrysene (**16**), using the strategy shown in Scheme I.[4] We projected that a twin Diels–Alder cycloaddition between a formal 1,5-naphthodiyne (**3**) and a heterocyclic diene (**4**) would afford bis(adduct) **2** and that subsequent removal of the bridging atom (X = O or NR) would yield the chrysene skeleton.

Although bis(aryne) synthons have been sporadically described in the literature,[5-7] it has only been the recent, elegant work of Hart and co-workers,[8] reported during the course of our own studies in this area, that has demonstrated the synthetic utility of bis(aryne) Diels–Alder methodology.

Results and Discussion

Our first choice for a 1,5-naphthodiyne synthon was 2,6-dibromo-1,5-bis[(*p*-tolylsulfonyl)oxy]naphthalene (**6**)



5 [R = H]
6 [R = Ts]

for two reasons. The requisite 2,6-dibromo-1,5-dihydroxynaphthalene (**5**) is commercially available and Tochtermann[9] has generated 1,2-naphthalyne from 1-bromo-2-naphthyl *p*-toluenesulfonate and *n*-butyllithium. Another logical precursor to **3**, 1,2,5,6-tetrabromonaphthalene, would be difficult to synthesize in pure form and may be highly toxic.[10] A third feasible synthon, 1,5-bis[(phenylsulfonyl)oxy]naphthalene, would be a less efficient source of **3**, based on the relatively poor generation of benzyne from phenyl benzenesulfonate and strong base[11] (because of competing metalation ortho to the sulfonyl group).

When **5** was treated with 2 equiv of *p*-toluenesulfonyl chloride (acetone, aqueous NaOH, 0 °C),[12] it gave **6** in 94% yield. Recrystallization from CH_2Cl_2 afforded pure **6**, mp 259–260 °C, which was used in the following syntheses.

Chrysenes. Our new synthesis of chrysene (**1**) is summarized in Scheme II. When a tetrahydrofuran (THF) solution of **6** and excess furan was treated at 10 °C with 2 equiv of phenyllithium, it gave the bis(adduct) **7**, mp >400 °C, in 51% yield after column chromatography. This material is presumed to be a mixture of syn and anti isomers, but evidence of this fact was not revealed by ^1H and ^{13}C NMR spectroscopy or by TLC behavior. The structure of **7** was established by mass spectrometry and NMR spectroscopy. Hydrogenation of **7** was conveniently performed by using Olah's procedure[13] (Pd/C, Mg, MeOH) to give **8**, mp 258–259 °C, in 92% yield after recrystallization. This was dehydrated under the usual conditions[14] (HCl/EtOH) to give chrysene (**1**), mp 254–255 °C, in 93% yield, identical with a commercial sample. The overall yield of **1** from commercially available **5** is 41%.

A similar sequence was employed with *N*-methylpyrrole (**9**) as the diene, as shown in Scheme III. Thus, treating a THF solution of **6** and excess **9** with phenyllithium gave bis(imine) **10** in 40% yield, presumably as a mixture of syn and anti isomers although preliminary attempts to separate or even to distinguish two isomers were unsuccessful. Oxidative deamination with 2 equiv of *m*-chloroperbenzoic acid[3a] (*m*-CPBA) afforded **1** in 87% yield (33% overall yield from **5**). An identical sequence utilizing 1,2,5-trimethylpyrrole (**11**) gave a new chrysene derivative, 1,4,7,10-tetramethylchrysene (**13**), in 49% overall yield from **5**.

We found that the use of phenyllithium at 0–20 °C was superior to alkyllithium reagents (*n*-butyllithium, *tert*-

(3) (a) Gribble, G. W.; Allen, R. W.; Anderson, P. S.; Christy, M. E.; Colton, C. D. *Tetrahedron Lett.* **1976**, 3673. (b) Gribble, G. W.; Holubowitch, E. J.; Venuti, M. C. *Ibid.* **1977**, 2857. (c) Gribble, G. W.; Allen, R. W.; LeHoullier, C. S.; Eaton, J. T.; Easton, N. R. Jr.; Slayton, R. I.; Sibi, M. P. *J. Org. Chem.* **1981**, *46*, 1025. (d) Gribble, G. W.; Kelly, W. J.; Sibi, M. P. *Synthesis* **1982**, 143.

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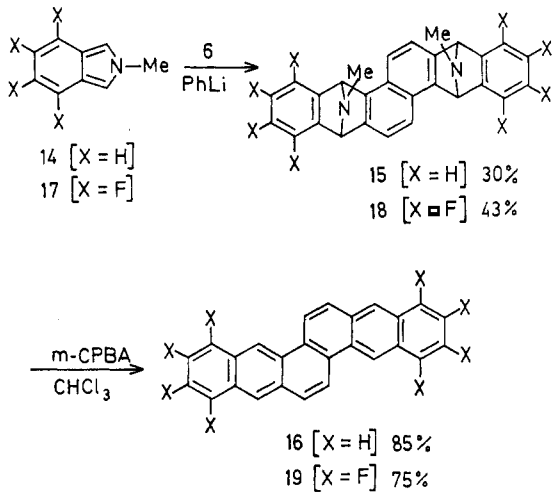
(14) Wittig, G.; Pohmer, L. *Chem. Ber.* **1956**, *89*, 1334.

Scheme IV



butyllithium) and to magnesium, all of which resulted in lower yields of bis(adduct) and/or to butylated products.

Dibenzo[*b*,*k*]chrysenes. An obvious extension of this methodology (vide supra) is to employ an isoindole (or isobenzofuran) as the diene component in the 1,5-naphthodiyne twin cycloaddition in order to prepare the relatively rare and little-studied[15] PAH, dibenzo[*b*,*k*]-chrysene (**16**).

In the event, when a THF solution of **6** and 2-methylisoindole (**14**) was treated with phenyllithium, it gave **15** (30% yield), which, upon exposure to *m*-CPBA, gave **16** (85% yield), mp 402–403 °C, whose UV spectrum matched that reported.[15] The same sequence (Scheme IV) carried out with 2-methyl-4,5,6,7-tetrafluoroisoindole (**17**) provided 1,2,3,4,9,10,11,12-octafluorodibenzo[*b*,*k*]chrysene (**19**) in 32% yield from **5**.

In summary, we have demonstrated that a readily available 1,5-naphthodiyne synthon (ie., **6**) in a Diels–Alder arene annulation strategy provides an efficient and convenient means with which to synthesize chrysenes and dibenzo[*b*,*k*]chrysenes. An inherent limitation of this methodology, as presently formulated, is that the central naphthalene ring will be unsubstituted in the final product.

Experimental Section

Melting points were determined with a Mel-Temp Laboratory Devices apparatus and are uncorrected. Elemental analyses were performed by Atlantic Microlabs, Atlanta, GA. Infrared spectra were recorded on a Perkin-Elmer 599 instrument. ^{1}H NMR spectra were obtained with a Hitachi Perkin-Elmer R-24 spectrometer, and ^{13}C NMR spectra were measured on a JEOL-FX60Q Fourier transform NMR spectrometer. Tetramethylsilane was the internal reference. Low-resolution mass spectra were determined at 70 eV on a Finnigan 4023 GC/MS system by A. Barefoot. Woelm alumina was used for column chromatography, and thin-layer chromatography was performed on precoated (0.2 mm) Silica Gel 60 F_{254} plastic sheets (E. Merck). Phenyllithium and the alkyllithium reagents were standardized by titration against 2,5-dimethoxybenzyl alcohol.[16] Tetrahydrofuran was distilled from sodium/benzophenone. All reactions were performed in oven-dried (130 °C) glassware under nitrogen.

2,6-Dibromo-1,5-bis[(*p*-tolylsulfonyl)oxy]naphthalene (6). To a mechanically stirred solution of 2,6-dibromo-1,5-dihydroxynaphthalene (**5**) (ICN; 5.5 g, 0.017 mol), *p*-toluenesulfonyl chloride (8.3 g, 0.043 mol), and acetone (100 mL) at 0 °C was added dropwise 10% aqueous NaOH (80 mL).[12] The resulting yellow suspension was stirred for 30 min, after which time the resulting solid was collected by filtration, washed with Et_2O, and dried (80 °C/0.1 torr) to afford 10.2 g (94%) of **6** as a green solid, mp 250 °C. Recrystallization from CH_2Cl_2 gave 8.3 g (74%) of pure **6** as large pale green prisms: mp 259–260 °C; ^{1}H NMR ($CDCl_3$) δ 2.5 (s, 6 H), 7.2–8.0 (m, 12 H); IR (KBr) 1605 (s), 1590 (s), 1380 (s), 1315 (s), 1205 (s), 1190 (s), 935 (s), 850 (s), 820 (s), 740 (s), 710 (s) cm^{-1}.

Anal. Calcd for $C_{24}H_{18}Br_2S_2O_6$: C, 46.02; H, 2.90; Br, 25.52; S, 10.24. Found: C, 46.00, H, 2.96; Br, 25.48; S, 10.22.

1,4:7,10-Diepoxy-1,4,7,10-tetrahydrochrysene (7). A magnetically stirred suspension of **6** (3.0 g, 0.0048 mol) and THF (250 mL) under N_2 was refluxed for 1 h to effect dissolution. To the resulting greenish solution at 10 °C were added furan (25 mL, 0.34 mol) and then dropwise phenyllithium (1.70 M in cyclohexane; 5.65 mL, 0.0098 mol). The resulting orange solution was stirred at room temperature overnight and then evaporated in vacuo. The resulting yellow residue was dissolved in CH_2Cl_2 (50 mL), washed with H_2O (3 × 50 mL), dried (Na_2SO_4), and then preadsorbed onto activity III basic Al_2O_3. Column chromatography over activity III basic Al_2O_3 (1:1 Et_2O–hexane) gave 0.63 g (51%) of **7** as a colorless solid. Recrystallization from 1:1 CH_2Cl_2–Et_2O afforded an analytical sample: mp >400 °C (evacuated tube); ^{1}H NMR ($CDCl_3$) δ 5.95 (m, 2 H), 6.25 (m, 2 H), 7.20 (s, 4 H), 7.55 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 148.9, 147.5, 147.8, 142.9, 126.2, 119.8, 119.6, 83.4, 81.4; IR (KBr) 3010 (m), 1280 (s), 1150 (m), 1028 (s), 870 (s), 800 (s), 740 (s), 715 (m), 670 (m) 655 (m) cm^{-1}.

Anal. Calcd for $C_{18}H_{12}O_2$: C, 83.06; H, 4.65. Found: C, 83.04; H, 4.74.

1,4:7,10-Diepoxy-1,2,3,4,7,8,9,10-octahydrochrysene (8). To a magnetically stirred suspension of **7** (0.15 g, 0.58 mmol), 10% Pd/C (10 mg), and MeOH (20 mL) under N_2 was added oven-dried, crushed Mg turnings (0.14 g, 5.8 mmol). The resulting suspension was stirred at 25 °C overnight and then poured into cold 3 N HCl (20 mL) and extracted with CH_2Cl_2 (3 × 50 mL). The extract was dried (Na_2SO_4) and evaporated in vacuo to afford **8** as a colorless solid. Recrystallization from 1:1 benzene–Et_2O gave 0.14 g (92%) of **8** as colorless needles: mp 258–259 °C; ^{1}H NMR ($CDCl_3$) δ 1.3 (m, 4 H), 2.15 (m, 4 H), 5.52 (m, 2 H), 5.86 (m, 2 H) 7.60 (m, 4 H); IR (KBr) 3000 (m), 1450 (m), 1360 (s), 1180 (s), 1165 (s), 940 (s), 870 (s), 845 (s), 805 (s), 715 (s), 630 (s) cm^{-1}; MS, *m/e* 264.1180 (calcd for $C_{18}H_{16}O_2$: 264.1150).

Chrysene (1) from 8. A magnetically stirred solution of **8** (0.05 g, 0.189 mmol) and absolute EtOH was saturated with HCl gas for 10 min and then refluxed for 2 h. The resulting suspension was poured into H_2O (50 mL) and extracted with CH_2Cl_2 (2 × 50 mL). The organic extract was dried (Na_2SO_4) and evaporated in vacuo to afford 0.04 g (93%) of **1** as a colorless solid, mp 254–255 °C, which was identical with a commercial sample (IR, TLC, UV, mmp = 254–255 °C).

13,14-Dimethyl-1,4,7,10-tetrahydrochrysene-1,4:7,10-diimine (10). A magnetically stirred suspension of **6** (2.5 g, 4.0 mmol) and THF (200 mL) under N_2 was refluxed for 1 h to effect dissolution. To the resulting greenish solution at 10 °C were added *N*-methylpyrrole (**9**) (25 mL, 0.34 mol) and then dropwise phenyllithium (1.70 M in cyclohexane; 4.8 mL, 8.0 mmol). The resulting brown solution was stirred at room temperature overnight and then evaporated in vacuo. The resulting brown residue was dissolved in CH_2Cl_2 (20 mL) and treated with Et_2O (10 mL). The resulting yellow precipitate was collected by filtration and dried to afford 0.45 g (40%) of **10** as a light yellow solid: mp 253–254 °C; ^{1}H NMR ($CDCl_3$) δ 2.20 (s, 6 H), 4.70 (m, 2 H), 5.00 (m, 2 H), 7.10 (m, 4 H), 7.50 (s, 4 H); IR (KBr) 2870 (m), 1295 (m), 1110 (m), 1010 (m), 900 (m), 850 (s), 827 (s), 800 (s), 770 (s), 685 (m) cm^{-1}; MS, *m/e* 286.1504 (calcd for $C_{20}H_{18}N_2$: 286.1470).

Chrysene (1) from 10. To a magnetically stirred solution of **10** (0.13 g, 0.45 mmol) in CH_2Cl_2 (20 mL) at 25 °C was added *m*-CPBA (0.13 g, 0.91 mmol). The resulting yellow solution was stirred at 25 °C for 3 h and then preadsorbed onto activity III basic Al_2O_3. Chromatography over activity III basic Al_2O_3 (hexane) gave 0.090 g (87%) of **1**, mp 254–255 °C.

1,4,7,10,13,14-Hexamethyl-1,4,7,10-tetrahydrochrysene-1,4:7,10-diimine (12). To a magnetically stirred solution of **6** (2.0 g, 0.003 mol) and 1,2,5-trimethylpyrrole (**11**) (25.0 g, 0.23 mol) in THF (200 mL) at 10 °C was added dropwise phenyllithium

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(16) Winkle, M. R.; Lansinger, J. M.; Ronald, R. C. *J. Chem. Soc., Chem. Commun.* **1980**, 88.

(2.0 M in cyclohexane; 4.0 mL, 0.008 mol). The resulting orange solution was allowed to warm to room temperature overnight and then was evaporated in vacuo. The resulting oily residue was dissolved in CH_2Cl_2 (50 mL), washed with H_2O (2 × 50 mL), dried (Na_2SO_4), and then preadsorbed onto activity III basic Al_2O_3. Column chromatography over activity III basic Al_2O_3 (95:5 EtOAc–Et_3N) gave 0.62 g (56%) of **12** as a pale yellow solid: mp 204–205 °C; ^1H NMR ($CDCl_3$) δ 1.75 (s, 6 H), 2.0 (s, 6 H), 2.05 (s, 6 H), 6.9 (m, 4 H), ~7.6 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 149.2, 148.9, 148.6, 148.3, 129.9, 120.2 (2), 78.2, 75.2, 30.3, 17.4, 12.8; IR (KBr) 2990 (m), 1460 (m), 1380 (m), 1320 (s), 1200 (s), 1155 (s), 1090 (s), 830 (s), 800 (s), 780 (s), 750 (s) cm^{-1}; MS, *m/e* 342.2087 (calcd for $C_{24}H_{26}N_2$: 342.2076.

Anal. Calcd for $C_{24}H_{26}N_2$: C, 84.17; H, 7.65; N, 8.18. Found: C, 84.07; H, 7.69, N, 8.17.

1,4,7,10-Tetramethylchrysene (13). To a magnetically stirred solution of **12** (0.13 g, 0.38 mmol) and CH_2Cl_2 (25 mL) at 25 °C was added *m*-CPBA (0.11 g, 0.76 mmol). The resulting yellow solution was stirred for 2 h and then preadsorbed onto activity III neutral Al_2O_3. Chromatography over activity III neutral Al_2O_3 (hexane) gave 0.10 g (93%) of **13** as colorless crystals. Recrystallization from hexane–EtOH gave an analytical sample: mp 165–166 °C; ^1H NMR ($CDCl_3$) δ 2.75 (s, 6 H), 3.05 (s, 6 H), 7.35 (s, 4 H), 8.35 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 132.7, 131.9, 131.3, 130.9, 129.9, 128.2, 126.8, 126.0, 120.7, 26.0, 19.8; IR (KBr) 2980 (w), 1470 (m), 1460 (m), 1270 (m), 1240 (w), 1100 (w), 1040 (m), 830 (s), 815 (s), 745 (s), cm^{-1}.

Anal. Calcd for $C_{22}H_{20}$: C, 92.91; H, 7.09. Found: C, 92.62; H, 7.34.

17,18-Dimethyl-5,8,13,16-tetrahydrodibenzo[*b*,*k*]chrysene-5,16:8,13-diimine (15). This reaction was carried out as described for **10** by employing the following materials; **6** (2.5 g, 4.0 mmol), 2-methylisoindole[17] (**14**) (2.1 g, 16.0 mmol), THF (250 mL), and phenyllithium (1.70 M in cyclohexane, 4.80 mL, 7.98 mmol). The usual workup and chromatography gave 0.45 g (30%) of **15** as a light brown solid: mp 172–175 °C (dec); ^1H NMR ($CDCl_3$) δ 2.15 (s, 6 H), 5.00 (m, 2 H), 5.30 (m, 2 H), 6.90–7.70 (m, 12 H); IR (KBr) 2960 (m), 1420 (s), 1380 (s), 1185 (s), 1090 (s), 1010 (m), 940 (m), 820 (s), 735 (s), 695 cm^{-1}; UV (EtOH) λ_{max} 326, 302, 290, 253, 235 nm; MS, *m/e* 386.1783 (calcd for $C_{28}H_{22}N_2$: 386.1783).

Dibenzo[*b*,*k*]chrysene (16). To a magnetically stirred solution of **15** (0.10 g, 0.27 mmol) and CH_2Cl_2 (25 mL) at 25 °C was added *m*-CPBA (0.075 g, 0.54 mmol), resulting in an immediate bright yellow precipitate. The suspension was stirred for 1 h and then was filtered to afford 0.075 g (85%) of **16** as a bright yellow solid: mp 402–403 °C (lit.[15] mp 400 °C); IR (KBr) 3060 (m), 1280 (m), 960 (m), 900 (s), 885 (s), 820 (s), 740 (s), 720 (m) cm^{-1}. The UV spectrum was identical with that reported.[15]

17,18-Dimethyl-1,2,3,4,9,10,11,12-octafluoro-5,8,13,16-tetrahydrodibenzo[*b*,*k*]chrysene-5,16:8,13-diimine (18). This reaction was carried out in the same manner as for the preparation of **10** by employing the following materials: **6** (2.0 g, 0.0032 mol), 2-methyl-4,5,6,7-tetrafluoroisoindole[18] (**17**) (3.0 g, 0.015 mol), THF (200 mL), and phenyllithium (1.70 M in cyclohexane, 3.80 mL, 0.0064 mol). the usual workup and chromatography gave 0.73 g (43%) of **18** as a yellow solid: mp 305–306 °C; ^1H NMR ($CDCl_3$) δ 2.30 (s, 6 H), 5.25 (m, 2 H), 5.70 (m, 2 H), 7.60 (s, 4 H); IR (KBr) 2990 (m), 1500 (s), 1490 (s), 1270 (s), 1100 (s), 1040 (s), 925 (m), 800 (s), 755 (s), 730 (s) cm^{-1}; UV (EtOH) λ_{max} 323, 298, 255 nm; MS, *m/e* 530.0987 (calcd for $C_{28}H_{14}N_2F_8$: 530.1029).

1,2,3,4,9,10,11,12-Octafluorodibenzo[*b*,*k*]chrysene (19). To a magnetically stirred solution of **18** (0.18 g, 0.339 mmol) and CH_2Cl_2 (25 mL) at 25 °C was added *m*-CPBA (0.094 g, 0.678 mmol), resulting in an immediate bright yellow precipitate. The suspension was stirred for 1 h and then was filtered to afford 0.12 g (75%) of **19** as a bright yellow solid. Recrystallization from xylene gave the analytical sample, mp >400 °C (evacuated tube sublimed at 400 °C); IR (KBr) 1685 (s), 1600 (s), 1505 (s), 1495 (s), 1425 (s), 1385 (m), 1355 (s), 1325 (m), 1000 (s), 890 (s), 810 (m), 675 (m) cm^{-1}; UV (EtOH) λ_{max} 310, 300, 289, 285 nm.

Anal. Calcd for $C_{26}H_8F_8$: C, 66.12; H, 1.71. Found: C, 66.08; H, 1.74.

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Preparation of Benzenetetracarboxylic Acids by the Cobalt-Catalyzed Carbonylation of Schiff Bases from Benzenedicarbaldehydes and Subsequent Oxidation

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Schiff bases (**3a–d** and **4a–c**), synthesized from benzenedicarbaldehydes (terephthalaldehyde and isophthalaldehyde) and primary amines (methylamine, ethylamine, butylamine, and aniline), were carbonylated in the presence of $Co_2(CO)_8$ under an elevated pressure at 200–290 °C to give dicarbonylated products, benzodipyrrolediones (**5a–d**, **10a–c**, and **11a–c**), in high yields. 1,2,3,4-Benzenetetracarboxylic acid (prehnitic acid) and 1,2,4,5-benzenetetracarboxylic acid (pyromellitic acid) were prepared selectively by the oxidation of the benzodipyrrolediones with nitric acid. Structural analysis of the benzodipyrrolediones by NMR spectra and the mechanism of the carbonylation reaction are discussed.

Transition-metal carbonyl-catalyzed carbonylation reactions of organic compounds with nitrogen containing multiple bonds such as nitrile,[2] oxime[3], Schiff base,[4] hydrazone,[5] azo compound,[6] and nitro compound[7] have been

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