spectra were recorded on a Hitachi Perkin-Elmer RMU-6A. All melting points and boiling points are uncorrected.

Lithium Diisopropylamide Induced Coupling–Condensation of *N*-Methyl-*p*-toluenesulfonanilide. The sulfonanilide was prepared by treating 21.4 g (0.2 mol) of *N*-methylaniline with 19.0 g (0.1 mol) of *p*-toluenesulfonyl chloride. The product was recrystallized from methanol to give 23 g (88%) of sulfonanilide: IR (KBr) 1345, 1160 and 1140 cm^{-1} (SO_2N); ^1H NMR ($CDCl_3$) 2.40 (s, 3 H), 3.15 (s, 3 H), 7.00–7.60 (m, 9 H). Lithium diisopropylamide (10 mmol) was generated from 4.35 mL of *n*-butyllithium (2.3 M, 10 mmol) and 1.40 mL of diisopropylamine (10 mmol) in 10 mL of dry THF at 0 °C. The sulfonanilide (2.60 g, 10 mmol) was dissolved in 40 mL of dry THF and cooled to −72 °C with an acetone–dry ice bath. The equimolar amount of lithium diisopropylamide was added via syringe while maintaining the temperature at −68 °C or lower. After 4 h, the reaction solution was allowed to warm to room temperature (ca. 40 min) and quenched by pouring onto a mixture of 100 g of ice and 10 mL of concentrated HCl. Ether was added, and the organic layer was separated, washed with an equal volume of water, and then treated with 75 mL of saturated aqueous $NaHCO_3$. The precipitated sodium sulfinate was drawn off with aqueous solution, induced to completely crystallize by cooling, and isolated by filtration. Recrystallization from methanol–water gave 1.25 g (74%) of sodium salt of 4-[(*N*-methyl-*N*-phenylamino)sulfonyl]-4′-sulfinobibenzyl, mp 247–249 °C.

The methyl sulfone derivative was prepared by treating 1.20 g (2.74 mmol) of the sodium sulfinate with an excess of methyl iodide (3 mL) and 1.0 g of anhydrous Na_2SO_4 in 30 mL of absolute ethanol at room temperature for 1 week. The derivative was worked up and recrystallized from methanol: yield 1.05 g (85%); mp 108–109 °C; IR (KBr) 1340, 1170 and 1150 ($SO_2N<$), 1300 and 1145 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 2.98 (s, 7 H), 3.12 (s, 3 H), 6.85–7.50 (m, 11 H), 7.80 (d, 2 H); ^{13}C NMR ($CDCl_3$) δ 37.5 (m), 38.5 (q), 45 (q), 127 (d), 127.5 (d), 127.8 (d), 128.5 (d), 129 (d), 129.5 (d), 135 (s), 139 (s), 143.3 (s), 146.5 (s), 147.5 (s).

The benzyl sulfone derivative was prepared by treating 1.3 g (3 mmol) of the sodium sulfinate with 0.51 g (3 mmol) of benzyl bromide in 30 mL of absolute ethanol at room temperature overnight. The derivative was collected by filtration and recrystallized from methanol: yield 1.20 g (88%); mp 157–158 °C; IR (KBr) 1330, 1160 and 1140 ($SO_2N<$), 1300 and 1140 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 3.00 (s, 4 H), 3.18 (s, 3 H), 4.30 (s, 2 H), 7.00–7.70 (m, 18 H); mass spectral data, *m/e* 505 (M^+), 441, 377, 376, 286, 197, 196, 181, 106, 91.

Lithium Diisopropylamide Induced Coupling–Condensation of Phenyl *p*-Toluenesulfonate. Phenyl *p*-toluenesulfonate (7.44 g, 30 mmol; mp 94–95 °C, lit.[4] mp 94–95 °C) was treated with an equimolar amount of lithium diisopropylamide (30 mmol) as described previously for the analogous sulfonamides to give 5.22 g (82%) of the sodium salt of 4-(phenoxysulfonyl)-4′-sulfinobibenzyl, mp 259–260 °C.[5]

The methyl sulfone derivative was prepared by treating 1.70 g (4 mmol) of the sodium sulfinate with an excess of methyl iodide (2 ml) and 1.0 g of anhydrous Na_2SO_4 in 30 mL of absolute ethanol at room temperature for 1 week. The derivative was worked up and recrystallized from methanol: yield 0.95 g (57%); mp 130–131 °C; IR (KBr) 1360, 1190 and 1170 (SO_3), 1290 and 1135 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 2.98 (s, 7 H), 6.80–9.07 (m, 2 H), 7.15–7.35 (m, 7 H), 7.68 (d, 2 H), 7.81 (d, 2 H); mass spectral data, *m/e* 416 (M^+), 323, 262, 183, 153, 108, 107, 94, 90.

The benzyl sulfone derivative was prepared by treating 1.27 g (3 mmol) of the sodium sulfinate with 0.513 g (3 mmol) of benzyl bromide and 1.0 g of anhydrous Na_2SO_4 in 30 mL of absolute ethanol at room temperature overnight. The derivative was collected by filtration and recrystallized from methanol: yield 1.30 g (88%); mp 171–172 °C; IR (KBr) 1360, 1190 and 1170 (SO_3), 1300 and 1140 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 3.00 (s, 4 H), 4.30 (s, 2 H), 6.90–7.45 (m, 14 H), 7.55 (d, 2 H), 7.75 (d, 2 H); mass spectral data, *m/e* 474 (M^+ − 18), 401, 399, 335, 183, 181, 91.

(4) Otto, R. *Ber.* **1886**, *19*, 1833.
(5) Phenyl *o*-toluenesulfonate was converted to its analogous coupling–condensation product by means of *n*-butyllithium: methyl sulfone derivative mp 116–118 °C; 2-hydroxy-3,5-dichlorobenzyl sulfone derivative mp 173–175 °C.

Registry No. PhNHMe, 100-61-8; *p*-$MeC_6H_4SO_2N(Me)Ph$, 599-62-2; $PhN(Me)SO_2$-*p*-$C_6H_4(CH_2)_2$-*p*-$C_6H_4S(O)ONa$, 99355-45-0; $PhN(Me)SO_2$-*p*-$C_6H_4(CH_2)_2$-*p*-$C_6H_4SO_2Me$, 99355-46-1; $PhN(Me)SO_2$-*p*-$C_6H_4(CH_2)_2$-*p*-$C_6H_4SO_2CH_2Ph$, 99355-47-2; *p*-$MeC_6H_4SO_2OPh$, 640-60-8; $PhOSO_2$-*p*-$C_6H_4(CH_2)_2$-*p*-$C_6H_4S(O)ONa$, 99355-48-3; $PhOSO_2$-*p*-$C_6H_4(CH_2)_2$-*p*-$C_6H_4SO_2Me$, 99355-49-4; $PhOSO_2$-*p*-$C_6H_4(CH_2)_2$-*p*-$C_6H_4SO_2CH_2Ph$, 99355-50-7.

Acephenanthrylene

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We report a convenient synthesis for the title compound **5**. The potential mutagenicity and the peculiar properties of cyclopenta-annelated polycyclic aromatic hydrocarbons have brought increasing attention to such substances in recent years.[1-4] Curiously, many compounds of this class have been mentioned in the chemical literature as the subjects of molecular orbital calculations or as suspected components of combustion effluents even prior to their availability through synthesis.[1,5] Our need for samples of the title compound coupled with the absence of published procedures for its preparation prompted us to develop a reliable synthesis for this hydrocarbon. The only prior publication on the synthesis of acephenanthrylene is very brief and provides no experimental details.[1] Herein we report the first detailed experimental procedure for preparation of acephenanthrylene.

Scheme I outlines our synthesis of acephenanthrylene (**5**). The old procedure of Fieser[6] for cyclization of 4-(5-acenaphthenyl)butyric acid (**1**) to ketone **2** was replaced by a new one that uses P_2O_5 in methanesulfonic acid. Reduction of **2** with sodium borohydride yields alcohol **3**, which can be dehydrated conveniently over acid-washed alumina. Dehydrogenation of the resulting tetrahydroacephenanthrylene (**4**) with DDQ gives the fully unsaturated product **5**.

Experimental Section

General Methods. Melting points were determined on a Thomas Hoover melting point apparatus and are uncorrected. ^1H NMR spectra (100-MHz) and ^{13}C NMR spectra (25 MHz) were recorded on a JEOL FX 100 FT NMR. ^1H NMR (60-MHz) spectra were recorded on an Hitachi Perkin-Elmer R-24B. ^1H NMR spectra (500 MHz) were recorded at the University of California Medical Facility, Davis, CA. Chemical shifts are reported from tetramethylsilane on the δ scale. Infrared spectra were recorded on a Perkin-Elmer 599 spectrophotometer. Ultraviolet and visible spectra were recorded with a Beckman Model 25 spectrophotometer. Microanalysis were performed by Spang.

4,5,7,8,9,10-Hexahydroacephenanthrylen-7-one (2). To a mixture of P_2O_5 (15 g, 106 mmol) in CH_3SO_3H (150 g, 1.6 mol) was added 10 g (42 mmol) of 4-(5-acenaphthenyl)butyric acid (**1**).[6] The solution was stirred at room temperature for 6 h and then

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(3) Becker, H.-D.; Hansen, L.; Andersson, K. *J. Org. Chem.* **1985**, 277–279.
(4) Sangaiah, R.; Gold, A. *Org. Prep. Proced. Int.* **1985**, *17*, 53–56.
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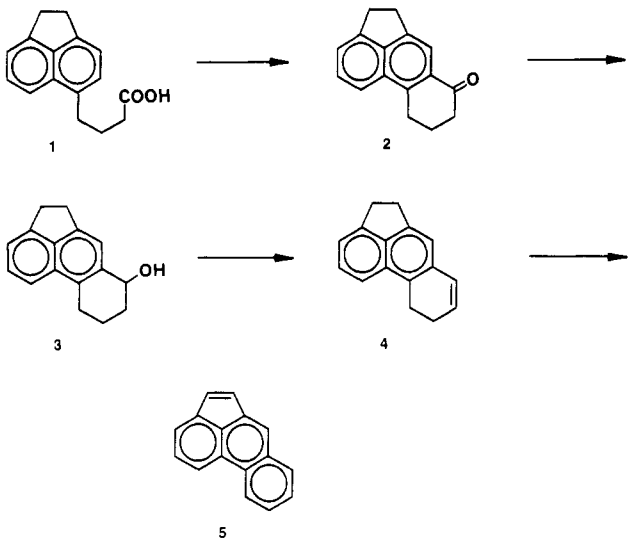
Scheme I



poured over 500 g of ice. This mixture was extracted with CH_2Cl_2 (3 × 200 mL), and the combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure to yield 8.2 g (88%) of **2** as pale yellow crystals: mp 146–147 °C (lit.[6] 147 °C); ^1H NMR ($CDCl_3$) δ 7.7–7.0 (m, 4 H), 3.14 (s, 4 H), 3.10 (m, 2 H), 2.62 (m, 2 H), 2.12 (m, 2 H); IR (KBr) 2940, 2910, 2860, 2810, 1655, 1390, 1340, 1175, 765, 758 cm^{-1}.

4,5,7,8,9,10-Hexahydro-7-hydroxyacephenanthrylene (3). To a solution of 500 mL of tetrahydrofuran and 250 mL of methanol was added ketone **2** (9.0 g, 40 mmol). This solution was cooled to 0 °C in an ice bath, and $NaBH_4$ (5 g, 140 mmol) was added in several portions over a 2-h period. Upon completion of the addition, the solution was stirred for 5 h and allowed to warm to room temperature. The solution was then poured on 1 kg of ice, and the mixture was extracted with CH_2Cl_2 (3 × 300 mL). The combined organic layers were washed with water (2 × 200 mL), dried over Na_2SO_4, and concentrated under reduced pressure to yield 9.0 g (99%) of **3** as a white crystalline solid: mp 112–113 °C; ^1H NMR ($CDCl_3$) δ 7.5–6.9 (m, 4 H), 4.65 (m, 1 H), 3.18 (m, 4 H), 2.82 (m, 2 H), 2.12 (s, 1 H), 1.83 (m, 4 H); IR (KBr) 3340, 2930, 2915, 2850, 1605, 1163, 1065, 1055, 770 cm^{-1}. Anal. Calcd for $C_{16}H_{16}O$: C, 85.67; H, 7.19. Found: C, 85.55; H, 7.19.

4,5,9,10-Tetrahydroacephenanthrylene (4). To a slurry of Al_2O_3 (2 g, washed with concentrated hydrochloric acid, dried 16 h at 180 °C (0.1 mm)) in 30 mL of dry toluene was added alcohol **3** (290 mg, 1.3 mmol). The mixture was refluxed for 1 h and filtered, and the Al_2O_3 was washed with toluene (2 × 20 mL). The combined organic layers were concentrated under reduced pressure, and the product was recrystallized from hexane to yield 257 mg (96%) of **4** as a white crystalline solid: mp 99–100 °C; ^1H NMR ($CDCl_3$) δ 7.7–7.2 (m, 3 H), 7.0 (s, 1 H), 6.56 (dt, J = 9 Hz, J = 1 Hz, 1 H), 6.08 (dt, J = 9 Hz, J = 4 Hz, 1 H), 3.34 (s, 4 H), 3.12 (t, J = 8 Hz, 2 H), 2.45 (m, 2 H). Anal. Calcd for $C_{16}H_{14}$: C, 93.16; H, 6.84. Found: C, 93.15; H, 6.85.

Acephenanthrylene (5). To a solution of dichlorodicyanoquinone (4.9 g, 21.6 mmol) dissolved in 150 mL of dioxane was added hydrocarbon **4** (1.5 g, 7.20 mmol). This solution was heated to reflux for 2 h, cooled to room temperature, and filtered. The organic layer was concentrated and chromatographed on a 2 × 30 cm silica gel column with benzene. The product was recrystallized from methanol with rapid cooling to yield 1.112 g (75%) of **5** as a yellow[7] crystalline solid: mp 141–142 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 8.64 (d, J = 8 Hz, 1 H), 8.38 (d, J = 7.5 Hz, 1 H), 8.00 (d, J = 5.5 Hz, 1 H), 7.99 (s, 1 H), 7.75 (m, 3 H), 7.60 (dd, J = 7.5 Hz, J = 7.0 Hz, 1 H), 7.20 (d, J = 5 Hz, 1 H), 7.10 (d, J = 5 Hz, 1 H); ^{13}C NMR ($CDCl_3$) 139.58, 138.27, 134.17, 132.17, 131.20, 130.52, 128.60, 128.37, 127.84, 127.30, 126.47, 126.13, 125.89, 123.16, 122.33, 121.35; IR (KBr) 3070, 2920, 1605, 905, 830, 755, 720 cm^{-1}; UV λ_{max} (MeOH) 362 nm (ε 12 000), 359 (8800), 344 (11 000), 328 (11 000), 317 (10 000), 298 (13 000), 287 (10 000), 258 (30 000), 228 (33 000); MS (70 eV), m/z (rel abund) 203 (18), 202 (M^+, 100), 201 (15), 200 (20), 101 (33), 100 (22), 88 (15). Anal. Calcd for $C_{16}H_{10}$: C, 95.02; H, 4.98. Found: C, 94.89; H, 5.04.

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Note added in proof: An alternative synthesis of the title compound has recently been reported.[8]

Registry No. 1, 38036-08-7; 2, 7467-80-3; 3, 76170-18-8; 4, 76170-19-9; 5, 201-06-9.

(7) Slow crystallization and slow sublimation give crystals that are more red, but the solution spectra of the two crystalline forms are the same.

(8) Neumann, G.; Müllen, K. *Chimia* **1985**, *39*, 275–276.

A Convenient Synthesis of Vinyl Spiro Epoxides from α,β-Unsaturated Ketones

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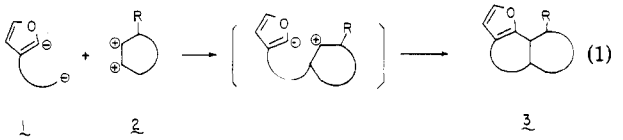
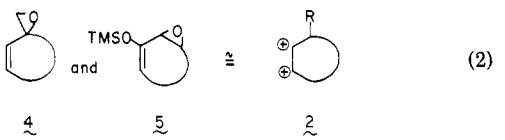
During the course of another study,[2] we became interested in developing bis electrophile equivalents for the annulation shown in eq 1. Our major concern in this



(1)

sequence is the selectivity of the initial carbon–carbon bond formation. To ensure selectivity, we envisioned employing bis electrophile equivalents in which the second reactive site is produced as a result of the first C–C bond formation.

As a result of this analysis, we selected cyclic vinyl spiro epoxides **4**[2,3] and epoxy enol silyl ethers **5**[2,4] as the operational equivalents of **2** (eq 2). Vinyl epoxides have been



(2)

widely employed as electrophiles in S_n2' type of addition reactions providing allylic alcohols as products.[3] Enol silyl ethers of α,β-epoxy ketones have been used by Marino[4a] and Wender[4b] as electrophiles, yielding α′-alkyl α-β-unsaturated cycloalkenones as products. Both sequences allow the construction of a C–C bond and provide a potential electrophilic center at the adjacent carbon.

Numerous variants of **5** have been prepared; however, few cycloalkenone spiro epoxides have been reported.[5]

(1) Recipient of a Camille and Henry Dreyfus Foundation Grant for Young Faculty in Chemistry, 1980–1984.

(2) Tanis, S. P.; Herrinton, P. M. *J. Org. Chem.* **1985**, *50*, 3988.

(3) For recent examples of the reaction of cuprates with vinyl epoxides, see: (a) Marino, J. P.; Abe, H. *J. Am. Chem. Soc.* **1981**, *103*, 2907. (b) Ziegler, F. E.; Cady, M. A. *J. Org. Chem.* **1981**, *46*, 122. (c) Marino, J. P.; Abe, H. *Synthesis* **1980**, *11*, 892. (d) Marino, J. P.; Hatanaka, N. *J. Org. Chem.* **1979**, *44*, 4467. (e) Marino, J. P.; Floyd, D. M. *Tetrahedron Lett.* **1979**, 675.

(4) For reactions of cuprates with enol ethers of α,β-epoxy kjetones, see: (a) Marino, J. P.; Jaen, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 3165. (b) Wender, P. A.; Erhardt, J. M.; Letendre, L. J. *J. Am. Chem. Soc.* **1981**, *103*, 2114.

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