$10^{8.5\pm0.5}$ M^{-1} s^{-1}. However, such an assumption will cause the rate constants to be overestimated because preexponential factors for hydrogen atom abstraction from OH groups by oxygen-centered radicals are always found to be considerably smaller than $10^{8.5\pm0.5}$ M^{-1} s^{-1}.[24-33] Indeed, it is highly unlikely that the preexponential factor for reaction 4 would be as large as 10^8 M^{-1} s^{-1}, a value as low as 10^6 M^{-1} s^{-1} (or even 10^4 M^{-1} s^{-1}) being more in line with values that have been reported for hydrogen atom abstraction by oxygen-centered radicals, XO·, from ArOH and similar hindered phenols and for the reverse reactions between ArO· and XOH.[26,27,29,33,34] Nevertheless, to be on the safe side, we take $k_4 \leq A_4 \leq 10^8$ M^{-1} s^{-1}, which yields $k_2 \leq 1.6 \times 10^7$ M^{-1} s^{-1} and $k_1 \leq 1 \times 10^5$ s^{-1}. In connection with this *upper* limit on k_1 for *thermalized* benzoyloxy radicals at 55 °C in a hydrocarbon solvent we note that *if* the 308-nm photolysis of benzoyl peroxide gave benzoyloxy radicals, these radicals have $k_1 \geq 10^8$ s^{-1} at room temperature.[14a,35] There can be no doubt that the thermolysis and photolysis of benzoyl peroxide do not yield the same chemical species.

Experimental Section

Materials. Benzoyl peroxide, PBN, and ArOH were commercial materials that were purified by recrystallization before use. 4,4′-Dibenzoylbenzoyl peroxide was prepared by literature methods[36] from 4-benzoylbenzoic acid (Aldrich) and was also purified by several recrystallizations, mp 161 °C, lit.[19] mp 159–160 °C. Freon 113 was purified by refluxing for a few hours over $CaCO_3$ and distillation.

Kinetic EPR Procedures. A stock solution containing 0.03 M benzoyl peroxide in Freon 113 was mixed, 3:5 (v/v), with a Freon 113 solution containing a known concentration of PBN in a quartz EPR tube. This solution was degassed on a high vacuum line by several freeze–thaw cycles, filled with nitrogen at 760 torr, sealed, and placed in a 55 °C water bath for ca. 5–10 s and then in the preheated (to 55 °C) cavity of a Varian E-104 EPR spectrometer. Growth of the BA and PA signals was monitored by repetitive scanning of appropriate lines in their spectra and comparison of these spectra with those obtained by simulation for various BA/PA ratios. Absolute radical concentrations were determined by double integration followed by calibration against a solution containing a known concentration of the diphenylpicrylhydrazyl free radical.[37] The experiments with ArOH were carried out in essentially the same manner.

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(34) Although two measurements only 22 °C apart do not define reliable Arrhenius parameters, the results in Table II (viz., $E_2 - E_4 \approx 6.0$ kcal/mol, log $(A_2/A_4) \approx 3.2$) also suggest that A_4 is considerably less than A_2, the latter being expected to have a "normal"[8] value of $10^{8.5\pm0.5}$ M^{-1} s^{-1}.
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Base-Induced Coupling-Condensations of Phenyl *p*-Toluenesulfonate and of *N*-Methyl-*p*-toluenesulfonanilide[1]

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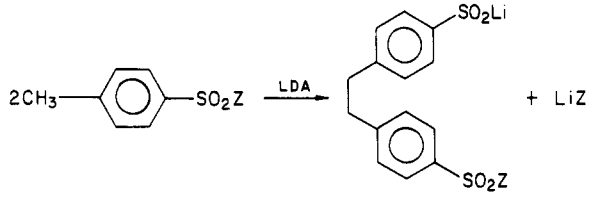
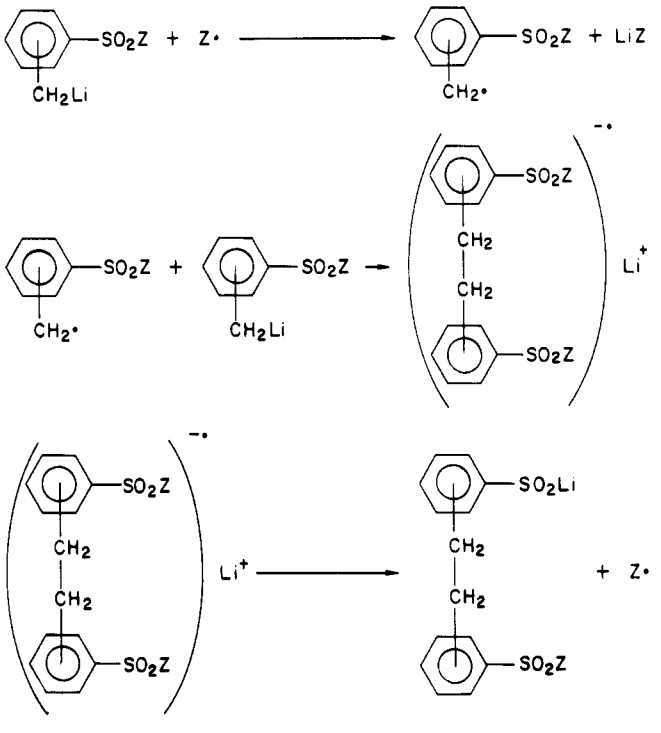
The novel base-induced coupling–condensation reaction[2] of aryl *o*-methylarenesulfonates and of *o*-methylarenesulfonanilides has been extended to para-oriented analogues.



Z = OC_6H_5, $N(CH_3)C_6H_5$

Having discarded several "anionic" mechanisms,[2] and inasmuch as a radical-coupling mechanism is precluded by the absence of symmetrical coupling products, a tentative but highly reasonable sequence for these coupling–condensation reactions is a chain mechanism[3] involving an electron-transfer step and radical and radical-anion intermediates.



Experimental Section

All reactions were carried out under nitrogen atmosphere. The IR spectra were recorded on a Beckmann IR-33. The 60-MHz ^1H NMR spectra were recorded on a Varian A-60A spectrometer and the 90-MHz ^1H NMR spectra on a Perkin-Elmer R32. The 20-MHz ^{13}C NMR spectra were recorded on a Varian CFT-20. All NMR chemical shift data are reported in ppm, employing tetramethylsilane (Me_4Si, δ 0) as an internal standard. Mass

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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.

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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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