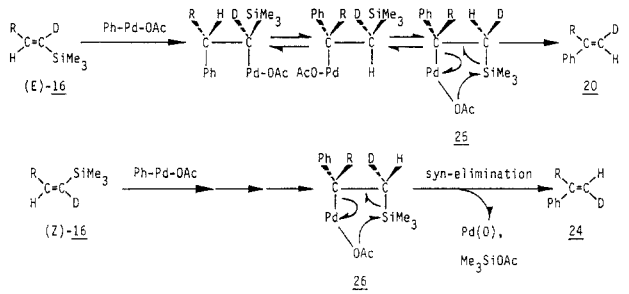
Scheme IV

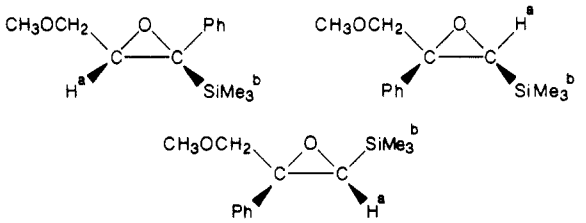


Cl_3) δ H^a 3.27 (s, 3 H), H^b 3.80 (d, J_{bc} = 5.87 Hz, 2 H), H^c 6.14 (t, J_{cb} = 5.87 Hz, 1 H), H^d 0.16 (s, 9 H).

((*E*)-3-Methoxy-2-phenylpropenyl)trimethylsilane ((*E*)-3c) ((*E*)-$Me^aOCH_2{}^bC(Ph)$=$CH^cSiMe_3{}^d$): ^1H NMR ($CDCl_3$) δ H^a 3.42 (s, 3 H), H^b 4.08 (d, J_{bc} = 1.47 Hz, 2 H), H^c 5.90 (t, J_{cb} = 1.47 Hz, 1 H), H^d −0.08 (s, 9 H).

((*Z*)-3-Methoxy-2-phenylpropenyl)trimethylsilane ((*Z*)-3c) ((*Z*)-$Me^aOCH_2{}^bC(Ph)$=$CH^cSiMe_3{}^d$): ^1H NMR ($CDCl_3$) δ H^a 3.42 (s, 3 H), H^b 4.43 (s, 2 H), H^c 6.12 (s, 1 H), H^d 0.36 (s, 9 H).

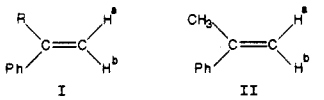
Epoxide of (*E*)-2c: ^1H NMR ($CDCl_3$) δ H^a 3.02 (s, 1 H), H^b −0.20 (s, 9 H). **Epoxide of (*E*)-3c**: ^1H NMR ($CDCl_3$) δ H^a 2.44 (s, 1 H), H^b 0.07 (s, 9 H). **Epoxide of (*Z*)-3c**: ^1H NMR ($CDCl_3$) δ H^a 2.15 (s, 1 H), H^b 0.33 (s, 9 H).



Arylation of Vinyltrimethylsilane. ((*E*)-2-Phenylvinyl)trimethylsilane (8a) and (1-Phenylvinyl)trimethylsilane (9a). The reaction was carried out through method A and employed 5 mmol (0.50 g) of vinyltrimethylsilane (**6**), 5 mmol (0.82 g) of **7a**, 0.5 mmol (0.29 g) of $Pd(dba)_2$, and 50 mL of CH_3CN. After completion of the gas evolution, the mixture was diluted with 100 mL of diethyl ether. The usual workup and purification by column chromatography (silica gel–hexane) gave **8a** and **9a** (0.71 g, 80%, **8a**:**9a** = 94:6). **(*E*)-PhCH=CHSiMe$_3$ (8a)**: Anal. Calcd for $C_{11}H_{16}Si$: C, 74.91; H, 9.16. Found: C, 74.76; H, 9.25. **(*E*)-4-MeC$_6$H$_4$CH=CHSiMe$_3$ (8b)**: Anal. Calcd for $C_{12}H_{18}Si$: C, 75.70; H, 9.55. Found: C, 75.91; H, 7.90. **(*E*)-4-$Me^aOC_6H_4CH^b$=$CH^cSiMe_3{}^d$ (8c)**: ^1H NMR ($CDCl_3$) δ H^a 3.87 (s, 3 H), H^b 6.90 (d, J_{bc} = 19.7 Hz, 1 H), H^c 6.24 (s, J_{cb} = 19.7 Hz, 1 H), H^d 0.40 (s, 9 H). Anal. Calcd for $C_{12}H_{18}OSi$: C, 69.83; H, 8.81. Found: C, 72.00; H, 9.16. **(*E*)-4-$CH_3{}^aCH_2{}^bOCOC_6H_4CH^c$=$CH^dSiMe_3{}^e$ (8g)**: ^1H NMR ($CDCl_3$) δ H^a 1.50 (t, J_{ab} = 6.0 Hz, 3 H), H^b 4.35 (q, J_{ba} = 6.0 Hz, 2 H), H^c 6.92 (d, J_{cd} = 1.87 Hz, 1 H), H^d 6.47 (d, J_{dc} = 18.7 Hz, 1 H), H^e 0.42 (s, 9 H). Anal. Calcd for $C_{14}H_{20}O_2Si$: C, 67.68; H, 8.13. Found: C, 68.20; H, 8.18. **4-EtOCOC$_6$H$_4$(Me$_3$Si)C=CH$_2{}^{a,b}$ (9g)**: ^1H NMR ($CDCl_3$) δ H^a 5.79 (d, J_{ab} = 2.9 Hz, 1 H), H^b 5.60 (d, J_{ba} = 2.9 Hz, 1 H).

Reactions of (*E*)- and (*Z*)-*n*-C$_6$H$_{13}$CH=CDSiMe$_3$ with PhN(NO)COCH$_3$. The same procedure with that described above was employed with 2.4 mmol (0.45 g) of (*E*)-**16**, 1.5 mmol (0.25 g) of **7a**, 0.6 mmol (0.35 g) of $Pd(dba)_2$, and 10 mL of CH_3CN, or with 2.4 mmol (0.45 g) of (*Z*)-**16**, 2.0 mmol (0.33 g) of **7a**, 0.4 mmol (0.23 g) of $Pd(dba)_2$, and 10 mL of CH_3CN. The ordinary workup and Kugelrohr distillation gave arylated alkenylsilanes and *n*-octenes in 51% (0.20 g) yield from (*E*)-**16** and in 40% (0.21 g) yield from (*Z*)-**16**. The stereochemistries of **17**–**20** and **21**–**24** were confirmed by NMR spectra of them and by their retention times on GC with those products from entries 7 and 10, respectively. Deuterium contents of products were estimated by NMR spectra of mixtures of them. **(*E*)-*n*-C$_6$H$_{13}$(Ph)C=CDH^a (20)**: ^1H NMR ($CDCl_3$) δ H^a 5.14(s).[22] **(*Z*)-*n*-C$_6$H$_{13}$(Ph)C=CH^{a}D (24)**: ^1H NMR ($CDCl_3$) δ H^a 5.02 (t, J = 1.3 Hz).[22]

(22) The NMR spectra were compared with those of I (R = *n*-C_6H_{13}) prepared from the palladium-catalyzed reaction of (*E*)-RCH=CHSiMe$_3$ with PhN_2BF_4: ^1H NMR ($CDCl_3$) δ H^a 5.09 (m), H^b 5.27 (m). Cf. the spectra were in fair agreement with those of α-methylstyrene (II): H^a 5.02, H^b 5.28; Jackman, L. M.; Wiley, R. H. *J. Chem. Soc.* **1960**, 2881.



I II

Synthesis and Base-Induced Methylation Reactions of *cis*-7a-Hydroxy-3a-(phenylsulfenyl)-3a,4,5,6,7,7a-hexahydro-4-indanone[1a,b]

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Received October 22, 1986

cis-7a-Hydroxy-3a-(phenylsulfenyl)-3a,4,5,6,7,7a-hexahydro-4-indanone (**2**) was prepared by reaction of 10-oxatricyclo[4.3.1.0]decan-2-one with sodium thiophenoxide in THF. Reaction of **2** with potassium hydride in THF/HMPA and an excess of a methylating agent gave *cis*-7a-methoxy-3a-(phenylsulfenyl)-3a,4,5,6,7,7a-hexahydro-4-indanone (**8**) and 1-methyl-7-(phenylsulfenyl)bicyclo[4.3.0]-6(7)-nonen-2-one (**9**), which apparently arose by a retroaldol reaction followed by recyclization, formation of a dienolate, and C-alkylation. The ratio of **8** and **9** was dependent upon the reaction conditions. When DME rather than THF was used as a solvent in some runs, **2** apparently underwent a 1,3-sigmatropic rearrangement of the phenylsulfenyl group because 3-(phenylsulfenyl)bicyclo[4.3.0]-1(6)-nonen-2-one (**14**) and its C-3 methylation product **15** were isolated.

We recently reported that upon base treatment monocyclic β-hydroxy α-phenylsulfenyl ketones undergo retroaldol reactions to generate acyclic keto (or aldehydo) enolates that can be trapped with electrophilic or nucleophilic reagents.[4] The possibility also existed that

(1) (a) This research was supported by Grant R01 CA 28355 (Georgia Institute of Technology) and 7R01 CA 36537 (University of Alabama) awarded by the National Cancer Institute for which we are grateful. (b) Taken in part from the Ph.D. dissertation of C.J.M., Georgia Institute of Technology, 1985.

(2) The University of Alabama.

(3) (a) Georgia Institute of Technology. (b) Present address: Chemistry Department, Georgia State University, Atlanta, GA 30303.

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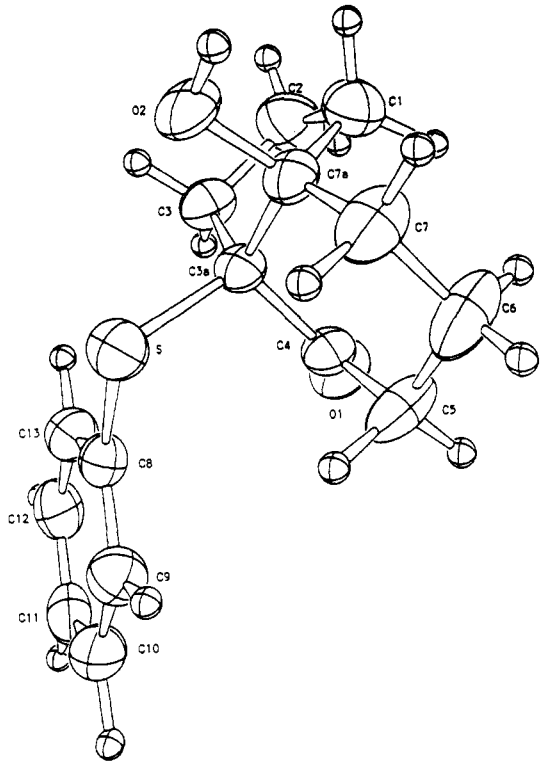


Figure 1. ORTEP drawing of *cis*-7a-hydroxy-3a-(phenylsulfenyl)-3a,4,5,6,7,7a-hexahydro-4-indanone (**2**).

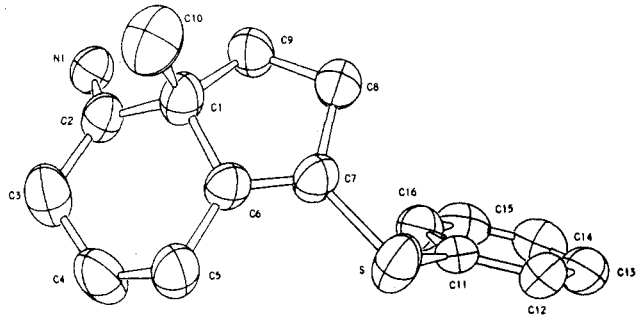
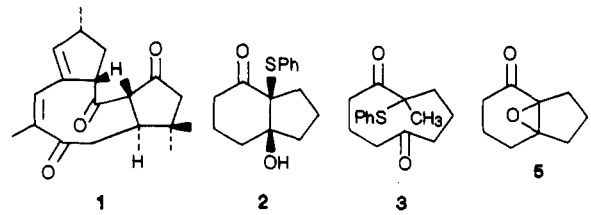


Figure 2. ORTEP drawing of 2-(2,4-dinitrophenylhydrazono)-1-methyl-7-(phenylsulfenyl)bicyclo[4.3.0]-6(7)-nonene with the 2,4-dinitrophenylhydrazone group deleted.

appropriately substituted bicyclic β-ketols might undergo the retroaldol reaction to produce keto enolate intermediates that could be trapped to give larger ring functionalized monocyclic systems.

Our interest in the synthesis of the antileukemic tricyclic diterpene jatrophatrione (**1**)[5] in which the nine-membered B ring contains an enedione system led us to prepare the title cis 6/5-fused β-ketol **2** and to investigate its reactions with bases and methylating agents under a variety of conditions. We were unsuccessful in isolating the desired

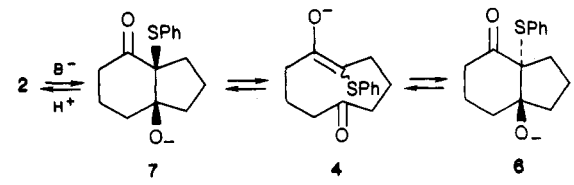


1 **2** **3** **5**

(4) (a) Caine, D.; Crews, E.; Salvino, J. M. *Tetrahedron Lett.* **1983**, *24*, 2083. (b) Caine, D.; Crews, E. *Ibid.* **1984**, *25*, 5359. (c) See also: Caine, D.; Procter, K.; Cassell, R. A. *J. Org. Chem.* **1984**, *49*, 2647.

(5) Torrance, S. J.; Wiedhopf, R. M.; Cole, J. R.; Arora, S. K.; Bates, R. B.; Beavers, W. A.; Cutler, R. S. *J. Org. Chem.* **1976**, *41*, 1855.

Scheme I

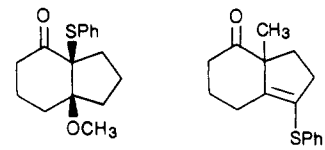


7 **4** **6**

cyclononadione **3**, a potential precursor for a nine-membered ring enedione system, but certain runs yielded a product that apparently arose via the monocyclic keto enolate **4** (Scheme I).

β-Ketol **2** was produced as the major product upon treatment of the 6/5-fused epoxy ketone **5**[6] with sodium thiophenoxide in THF. The structure of **2** was verified by a single-crystal X-ray analysis. The molecular structure as generated by ORTEP is shown in Figure 1.[7] Presumably, initial attack of the thiophenoxide anion upon the epoxide ring took place at the position α to the carbonyl group to yield the trans alkoxy ketone **6**,[8] but this was followed by retroaldol cleavage to the keto enolate **4** and ring closure to the more stable cis alkoxy ketone **7**. Upon workup, protonation of **7** then yielded the cis ketol **2** (Scheme I).

When a solution of the ketol **2** in THF was added to a slurry of 1.5 equiv of potassium hydride in THF containing 8 equiv of hexamethylphosphoramide (HMPA) and 3 equiv of methyl iodide at room temperature and the reaction mixture stirred for 1.25 h, two methylated products and the starting material were isolated in a ca. 2:2:1 ratio, as shown by thin-layer chromatography and NMR analysis. One of the methylation products was easily identified as the *O*-methyl derivative of **2**, i.e., **8**, on the basis of its NMR



8 **9**

spectral properties (a three-proton singlet at δ 3.27 for the methoxyl group and other absorptions similar to those of **2**). The other methylation product was conclusively identified as the enone **9** by a single-crystal X-ray analysis on its (2,4-dinitrophenyl)hydrazone derivative. The ORTEP generated molecular structure of this compound with the 2,4-dinitrophenyl group deleted is shown in Figure 2.[7]

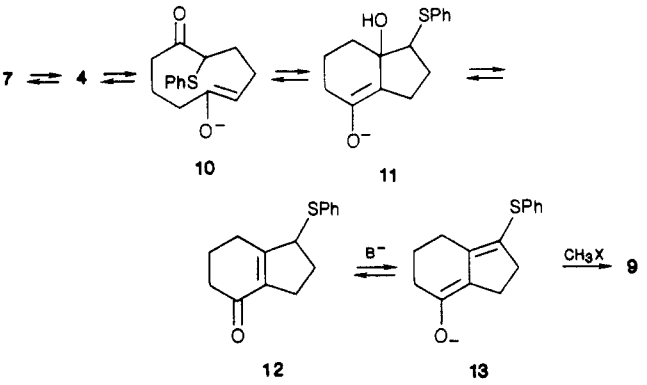
A variety of conditions were explored in an effort to trap the keto enolate **4** by methylation, but use of potassium hydride (or sodium hydride) as the base in THF under several sets of conditions gave only mixtures of the ether **8** and the enone **9** along with small quantities of compounds believed to be di- or trimethyl derivatives of the parent ring systems. In general, the formation of **8** was favored by lower reaction temperatures and the generation of the alkoxide **7** in the presence of an excess of the me-

(6) Lange, G. L.; Hall, T. *J. Org. Chem.* **1974**, *39*, 3819.

(7) The space group (No.) and unit cell parameters for the compounds whose X-ray crystal structure were determined were as follows. Compound **2**: *Pbca* (61); a = 8.380 Å, b = 13.780 Å, c = 23.693 Å; α, β, and γ = 90°; V = 2735.98 Å^3. (2,4-Dinitrophenyl)hydrazone derivative of compound **9**: *Pbca* (61); a = 7.024 Å, b = 15.828 Å, c = 39.170 Å; α, β, and γ = 90.00°; V = 4354.68 Å^3. Compound **14**: $P2_12_12_1$ (19); a = 7.570 Å, b = 9.260 Å, c = 18.292 Å; α, β, and γ = 90.00°; V = 1282.31 Å.^{3}

(8) Upon reaction of epoxy ketone **6** with thiophenol and triethylamine in acetonitrile,[4] a new compound believed to be the trans isomer of **2** was isolated. However, attempted purification of this material by column chromatography on silica gel led to its isomerization into **2**, which was the only product recovered.

Scheme II



thylating agent. Higher reaction temperatures, treatment of the substrate with the base for longer periods of time prior to the addition of the methylating agent, and addition of cation-complexing additives (e.g., HMPA or 18-crown-6) favored the formation of enone **9**.

The ether **8** obviously arose via simple Williamson reaction of the alkoxide **7** with the methylating agent. A possible pathway for the production of enone **9** is shown in Scheme II. Retroaldol cleavage of **7** could give the monocyclic keto enolate **4**, which could undergo proton transfer to the new keto enolate **10**, which could undergo aldol cyclization and proton transfer to the 6/5-fused β-hydroxy enolate **11**. Loss of hydroxide ion from **11** by β-elimination could produce the enone **12**, and further deprotonation could give the linearly conjugated dienolate **13**. Finally, methylation at the α-position of **13** could yield **9**. The equilibrium depicted in Scheme II would be expected to be forced to the right by the ability of enolate **11** to undergo loss of hydroxide ion. A similar reaction was observed by DeGroot and Jansen[9] when 2,3-dimethyl-3-hydroxy-2-(phenylsulfenyl)cyclohexanone was treated with base.

No evidence was obtained in any of the runs for the formation of the cyclononane derivative **3** or products of its intramolecular aldol reaction. The above results strongly suggest that the monocyclic keto enolate **4**, produced by retroaldol reaction of **2**, is in equilibrium with the bicyclic alkoxides **6** and **7**. However, the concentration of this species must be too low and/or proton transfer to the isomeric enolate **10** too fast to permit its trapping by methylation.

When 1,2-dimethoxyethane (DME) was substituted for THF in some runs involving deprotonation and methylation of **2**, the reaction took a somewhat different course. For example, treatment of **2** with 1 equiv of potassium hydride in DME containing 2 equiv of 18-crown-6 and an excess of methyl bromide at −25 °C for 1 h gave the ether **8**, recovered starting material, the α-phenylsulfenyl enone **14**, and is methylation product **15** in a ca. 1:1:2:2 ratio. The enone **9** was apparently not formed in this reaction, but in an experiment conducted under the same conditions but with THF for the solvent, ether **8** and enone **9** were produced in a ca. 3:1 ratio. The structure of **14** was established by a single-crystal X-ray analysis. The ORTEP generated molecular structure is shown in Figure 3.[7] The structure of the α-methyl α-phenylsulfenyl enone **15** was easily established from its spectral properties and also from its preparation by methylation of **14** which, in addition, was also obtained independently by phenylsulfenylation of the kinetic lithium dienolate of bicyclo[4.3.0]-1(6)-nonen-2-one.

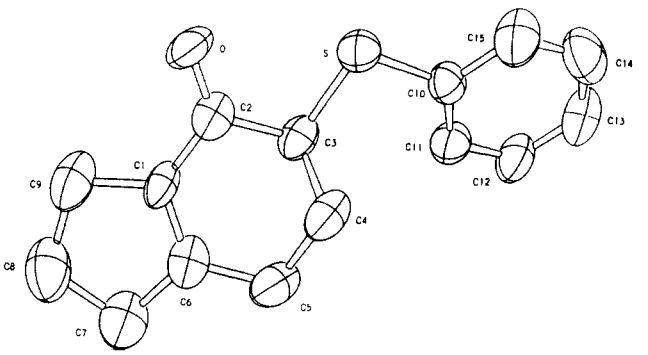
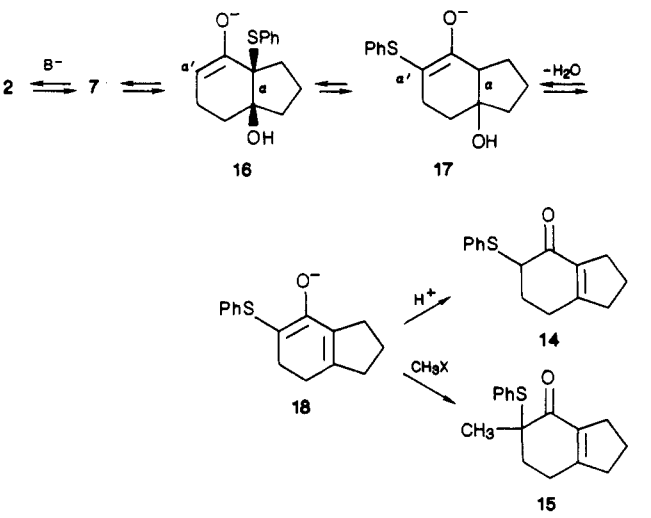


Figure 3. ORTEP drawing of 3-(phenylsulfenyl)bicyclo[4.3.0]-1-(6)-nonen-2-one (**14**).

Scheme III



By analogy with the known base-promoted 1,3-sigmatropic rearrangements of sterically crowded α-phenylselenenyl ketones,[10] we postulate that **14** and **15** are formed from **2** by the pathway shown in Scheme III. The hydroxy enolate **16**, which could be formed from **7** via proton transfer could undergo intermolecular α,α'-rearrangement[10a] of the phenylsulfenyl group to produce the more stable enolate **17** which could lose water to produce the stabilized cross-conjugated dienolate **18**. Methylation of **18** could yield **15**, and upon workup unmethylated **18** could undergo protonation to produce **14**. The role of the solvent in altering the course of the reaction of **2** with potassium hydride to give either the linearly conjugated dienolate **13** (leading to **9** in THF) or the cross-conjugated dienolate **18** (leading to **14** or **15** in DME) is unclear at this time.

Experimental Section

General Procedures. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 299 spectrophotometer. Mass spectra were obtained with a Varian MAT Model 112S spectrometer operating at 70 eV. Ionization was effected by electron impact. Reported masses are due to peaks of intensity greater than 30% of the base peak except where noted. Proton NMR spectra of 60 MHz were recorded on a Varian T-60A NMR spectrometer. Proton NMR spectra at 300 MHz and ^{13}C NMR spectra at 75 MHz were recorded on a Bruker Aspect 2000 NMR spectrometer. ^1H NMR spectra at 200 MHz were recorded on a Nicolet Model 293A spectrometer. Spectra were recorded as solutions in $CDCl_3$ with tetramethylsilane as

(9) DeGroot, A.; Jansen, J. M. *Recl. Trav. Chim. Pays-Bas* **1979**, *98*, 487.

(10) (a) Liotta, D.; Saindane, M.; Brothers, D. *J. Org. Chem.* **1982**, *47*, 1598. (b) Falcone, S. J.; Munk, M. E. *Synth. Commun.* **1979**, *9*, 719.

internal reference; signals are reported in ppm. The following abbreviations are used: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad absorption.

Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, GA 30366.

Preparation of *cis*-7a-Hydroxy-3a-(phenylsulfenyl)-3a,4,5,6,7,7a-hexahydro-4-indanone (2). Sodium hydride (1.5 g, 0.037 mol) in a 60% oil dispersion was washed with hexane under nitrogen to remove the hydrocarbon oil. Dry THF (60 mL) was added, and 4.07 g of benezenethiol was added dropwise with stirring. When the evolution of hydrogen ceased, the solution was cooled to 0 °C, and a solution of 5.35 g (0.035 mol) of 10-oxatricyclo[4.3.1.0]decan-2-one (**5**)[6] in 20 mL of THF was added dropwise with stirring over 30 min. The reaction mixture was then stirred at room temperature overnight then treated with 20 mL of water. The layers were separated, and the water layer was extracted with five 20-mL portions of ether. The combined ethereal solutions were washed with 25-mL portions of water and brine and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure to give a yellow oil, which partially crystallized on standing in a freezer overnight. Filtration and washing of the crystals gave a total of 3.3 g (36%) of **2**, mp 105–106 °C; IR ($CHCl_3$) 3680, 3600, 3580–3400, 3070, 2960, 2890, 1702, 1460, 1435, 1360, 1345, 1340, 1315, 1300, 1265, 1200, 1157, 1100, 1040, 1030, 1010, and 850 cm^{-1}; 300-MHz ^1H NMR ($CDCl_3$) δ 1.50–2.00 (m, 9 H), 2.27–2.33 (m, 2 H), 2.75 (br s, 1 H, OH), 3.22 (ddd, J = 14.7, 14.7, 7.4 Hz, 1 H, C-5 axial H), and 7.30–7.40 (m, 5 H); 25-MHz ^{13}C NMR ($CDCl_3$) δ 19.11, 20.39, 30.82, 32.28, 34.22, 35.98, 71.05, 83.78, 128.26, 129.77, 134.99, and 204.76; MS, m/e (relative intensity) 264 (2.6), 263 (9.6), 262 (58.0, M^+), 153 (60.1), 135 (90.7), 110 (100), 107 (48.6), 93 (57.8), 76 (62.5), 55 (68.5), and 41 (32.2). Anal. Calcd for $C_{15}H_{18}O_2S$: C, 68.67; H, 6.92; S, 12.22. Found: C, 68.68; H, 6.93; S, 12.18.

Reaction of the Cis β-Ketol 2 with Potassium Hydride in THF Containing HMPA and Methyl Iodide. Potassium hydride (0.87 g, 7.6 mmol) in a 35% oil dispersion was washed with hexane under nitrogen to remove the inert oil. Dry THF (40 mL), 2.2 g (15.2 mmol) of methyl iodide, and 7.3 g (41 mmol) of HMPA were then added with stirring to produce a slurry. Then, a solution of 1.4 g (5.3 mmol) of the ketol **2** in 30 mL of THF was added dropwise over 15 min at room temperature, and the reaction mixture was stirred for 60 min. The reaction mixture was then treated with 10 mL of water, and the layers were separated. The water layer was saturated with sodium chloride and extracted with three 50-mL portions of ether. The combined ethereal solutions were washed with water and brine and dried over anhydrous magnesium sulfate. After filtration, removal of the solvent under reduced pressure gave 1.58 g of a yellow oil, whose NMR spectrum and TLC analysis indicated that it was composed of a 2:2:1 mixture of *cis*-7a-methoxy-3a-(phenylsulfenyl)-3a,4,5,6,7,7a-hexahydro-4-indanone (**8**), 7-(phenylsulfenyl)-1-methylbicyclo-[4.3.0]-6(7)-nonen-2-one (**9**), and the starting material, respectively. The estimated yields of **8** and **9** were 35–40% each. Preparative TLC of a portion of the reaction mixture on Merck 20 × 20 cm, 0.5-mm thickness precoated silica gel plates using 30% ether–hexane as the eluting solvent allowed the isolation of pure **8** and **9**.

Compound **8**: IR ($CHCl_3$) 3060, 2950, 2890, 2830, 1700, 1585, 1475, 1465, 1460, 1440, 1390, 1365, 1260, 1180, 1100, 1090, 1050, 1030, 975, 920, 875, and 695 cm^{-1}; 60-MHz ^1H NMR ($CDCl_3$) 1.1–2.9 (m, 9 H), 3.27 (m, 1 H, C-5 axial H), 3.27 (s, 3 H, OCH_3), and 7.2 (br s, 5 H, aromatic ring); MS, m/e (relative intensity) 278 (2.3), 277 (6.9), 276 (39.7, M^+), 167 (69.5), 135 (100), 109 (30.1), 107 (63.5), 93 (52.3), 79 (71.4), 59 (44.7), 55 (39.2), 45 (38.5), and 41 (35.5); exact mass calcd for $C_{16}H_{20}O_2S$ 276.1185, found 276.1227.

Comound **9**: IR (CCl_4) 3070, 2960, 2900, 2860, 1715, 1475, 1450, 1440, 1420, 1365, 1330, 1305, 1230, 1140, 1120, 1020, 940, 910, 860, and 685 cm^{-1}; 300-MHz ^1H NMR ($CDCl_3$) δ 1.24 (s, 3 H, CH_3), 1.47–2.54 (m, 8 H), 2.60 (ddd, J = 14.5, 13.5, 6 Hz, 1 H, probably axial H at C-5), 2.84 (d, of m, J = 14.5 Hz, 1 H, probably equatorial H at C-5), and 7.10–7.20 (m, 5 H, aromatic ring); MS, m/e (relative intensity) 260 (0.6), 259 (1.1), 258 (6.1, M^+), 153 (57.8), and 149 (100). Anal. Calcd for $C_{16}H_{18}OS$: C, 74.38; H, 7.02. Found: C, 74.15; H, 7.07.

The (2,4-dinitrophenyl)hydrazone derivative of **9** was prepared in the usual manner.[11] Recrystallization of this material from ethanol gave orange crystals, mp 143–144 °C, which were suitable for X-ray diffraction analysis.

Reaction of the Cis β-Ketol 2 with Potassium Hydride in DME Containing 18-Crown-6 and Methyl Bromide. Potassium hydride (0.21 g, 2.0 mmol) in a 36% oil dispersion was washed with hexane under nitrogen to remove the oil. Dry DME (30 mL) and 1.0 g (4 mmol) of dry 18-crown-6 were added, and the flask was cooled to −25 °C in a carbon tetrachloride–dry ice bath. Methyl bromide (ca. 1.0 mL, ca. 10 mmol) was condensed from a cylinder into a collector tube at −78 °C and then transferred to the flask. A solution of 0.5 g (2.0 mmol) of the ketol **2** in 15 mL of dry DME was added dropwise with stirring over 30 min, and the reaction mixture was stirred at −25 °C for 40 min prior to the addition of 20 mL of a saturated aqueous solution of ammonium chloride. The layers were separated, and the aqueous layer was extracted with three 20-mL portions of ether. The combined ethereal extracts were washed with 25-mL portions of water and brine and dried over anhydrous magnesium sulfate. After filtration, the solvent was removed under reduced pressure to give ca. 1.0 g of a yellow oil, which was shown by NMR and TLC analysis to contain 3-(phenylsulfenyl)bicyclo[4.3.0]-1(6)-nonen-2-one (**14**), 3-methyl-3-(phenylsulfenyl)bicyclo[4.3.0]-1-(6)-nonen-2-one (**15**), the ether **8**, and the starting material in a 2:2:1:1 ratio. The estimated yields of **14** and **15** were 35–40% each, and the estimated yield of **8** was 15–20%.

Compounds **14** and **15** were purified by preparative TLC on silica gel using 50% ether–hexane as the eluting solvent. Compound **14**, mp 91.0–92.5 °C, gave suitable crystals for the determination of its structure by X-ray analysis.

Compound **14**: IR ($CHCl_3$) 3060, 2950, 2920, 2890, 2860, 2830, 1660, 1630, 1580, 1475, 1440, 1430, 1390, 1350, 1325, 1300, 1265, 1205, 1090, 1070, 1025, 950, and 850 cm^{-1}; 200-MHz ^1H NMR ($CDCl_3$) δ 1.76–2.56 (m, 10 H), 3.78 (t, J = 4 Hz, 1 H), 7.17–7.27 (m, 3 H), and 7.39–7.44 (m, 2 H); MS, m/e (relative intensity) 246 (2.1), 245 (6.1), 244 (34.6, M^+), 136 (35.8), 135 (73.3), 134 (62.4), 108 (100), and 79 (40.4); exact mass calcd for $C_{15}H_{16}OS$ 244.1123, found 244.0941. Anal. Calcd for $C_{15}H_{16}OS$: C, 73.73, H, 6.60. Found: C, 73.82; H, 6.60.

Compound **15**: IR ($CHCl_3$) 3070, 3060, 2960, 2920, 2830, 1655, 1635, 1470, 1445, 1430, 1390, 1370, 1350, 1260, 1245, 1100, 1090, 1075, 1020, 860, and 800 cm^{-1}; 200-MHz ^1H NMR ($CDCl_3$) δ 1.27 (s, 3 H, CH_3), 1.77–2.64 (m, 10 H), and 7.17–7.35 (m, 5 H); MS, m/e (relative intensity) 260 (0.8), 259 (3.5), 258 (17.9, M^+), 149 (100), 148 (91.4), and 108 (56.8); exact mass calcd for $C_{16}H_{18}O$ 258.1079; found 258.0995.

Synthesis of 3-(Phenylsulfenyl)bicyclo[4.3.0]-1(6)-nonen-2-one (14) from Bicyclo[4.3.0]-1(6)-nonen-2-one. A flask containing a few crystals of 2,2′-bipyridine was charged with 12.6 mL (20 mmol) of a 1.6 M solution of *n*-butyllithium in hexane and 7.0 mL of dry THF under nitrogen. The solution was cooled to −78 °C, and a solution of 2.8 mL of freshly distilled diisopropylamine in 10 mL of dry THF was added dropwise with stirring over 15 min. The mixture was stirred for an additional 30 min at −78 °C to ensure the complete formation of lithium diisopropylamide, and a solution of 2.5 g (18 mmol) of bicyclo-[4.3.0]-1(6)-nonen-2-one[6] in 15 mL of THF was added. The solution was stirred at −78 °C for 30 min, warmed to 0 °C, and stirred for an additional 20 min. The solution was transferred via a syringe to a solution containing 4.63 g (10 mmol) of phenylbenzenethiosulfonate[12] in 25 mL of THF at 25 °C. The mixture was stirred for 5 min and then poured into a mixture of 50 mL of ether and 50 mL of 1 M hydrochloric acid. The layers were separated, and the water layer was extracted with three 50-mL portions of ether. The combined ethereal extracts were washed with 50 mL of a saturated aqueous solution of sodium bicarbonate and 50 mL of brine and dried over anhydrous magnesium sulfate. After filtration, the solvent was removed to give a dark yellow oil. This oil was subjected to column chromatography on silica gel. Elution with 10% ether–hexane gave 440 mg (7%) of 3,3-bis(phenylsulfenyl)bicyclo[4.3.0]-1(6)-nonen-2-one [mp 117–118 °C; IR (CCl_4) 3085, 3070, 3030, 3010, 2970, 2930, 2870, 2840, 1670,

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1645, 1580, 1475, 1440, 1435, 1420, 1390, 1350, 1265, 1100, 1070, 1045, 1030, 950, and 860 cm^{-1}; 60-MHz ^1H NMR ($CDCl_3$) δ 1.6–2.7 (m, 10 H), and 7.1–7.6 (m, 10 H); MS, *m/e* (relative intensity) 353 (1.3), 352 (5.9, M^+), 243 (89.7), 215 (100), 109 (38.8), 105 (35.3), 91 (31.3), 79 (31.4), and 77 (31.9). Anal. Calcd for $C_{21}H_{20}OS_2$: C, 71.55, H, 5.72, S, 18.19. Found: C, 71.54; H, 5.77; S, 18.08], and elution with 30% ether–hexane gave 700 mg (16%) of crude 3-(phenylsulfenyl)bicyclo[4.3.0]-1(6)-nonen-2-one (**14**), which, after purification by preparative TLC, showed identical spectral properties with those reported above.

Preparation of 3-Methyl-3-(phenylsulfenyl)bicyclo-[4.3.0]-1(6)-nonen-2-one (15). Sodium hydride (0.04 g, 1.0 mmol) in a 60% oil dispersion was washed with hexane under nitrogen to remove the oil. Dry THF (20 mL) was added, and the slurry was cooled to 0 °C. A solution of 0.25 g (1.02 mmol) of enone **14** in 5 mL of THF was added dropwise with stirring over 5 min. The mixture was stirred at 0 °C for 45 min, and then 2.7 g (3.2 mmol) of methyl iodide was added. The mixture was stirred for 5 min and treated with 5 mL water. The layers were separated and the water layer was washed with three 20-mL portions of ether. The combined ethereal extracts were washed with 20 mL of water and 20 mL of brine and dried over anhydrous magnesium sulfate. After filtration, the solvent was removed under reduced pressure to give 0.21 g (81%) of 3-methyl-3-(phenylsulfenyl)bicyclo[4.3.0]-1(6)-nonen-2-one (**15**) as an oil. The oil was purified by preparative TLC on silica gel plates using 50% ether–hexane as the eluting solvent to give **15** as a pale yellow oil with identical spectral properties with those reported above.

Supplementary Material Available: Information on data collection and structure solutions, tables of positional parameters, anisotropic temperature factors, bond angles, and interatomic distances for compounds **2**, **9**, and **14** (18 pages). Ordering information is given on any current masthead page.

Syntheses of Cyclopentene-Fused Polynuclear Aromatic Hydrocarbons

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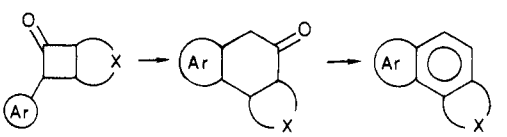
Regioselective α or β ring opening of bicyclic α-arylcyclobutanones permits the synthesis of linear and angular cyclopentene-fused polynuclear aromatic hydrocarbons (PAH), respectively. The syntheses of the cyclopentene-fused PAHs, aceanthrylene, acephenanthrylene, benz[*a*]aceanthrylene, and benz[*e*]acephenanthrylene are detailed utilizing this novel methodology.

Current interest in the environmental presence and toxicological properties of cyclopenta[*cd*]pyrene has stimulated work on the synthesis and chemical and biological properties of related cyclopentene-fused polynuclear aromatic hydrocarbons (PAHs).[1-3] Recently aceanthrylene (**1**) and acephenanthrylene (**4**), two non-bay-region PAHs, have been found to exhibit mutagenic activity[4,5] and along with the interest in their excited-state properties,[6] at least five reports of their synthesis have appeared.[4,7-10] Several years ago we developed a method for the preparation of PAHs incorporating cyclopentenes and heterocyclic rings via α-arylcyclobutanones substituted at the β-position with charge-stabilizing groups.[11,12] The method is based on the selective acid-catalyzed β ring opening (Scheme I) and lead to angular fused PAH derivatives. α-Arylcyclobutanones **2** are readily obtained from the cycloaddition of aryl ketenes with the appropriate olefin.

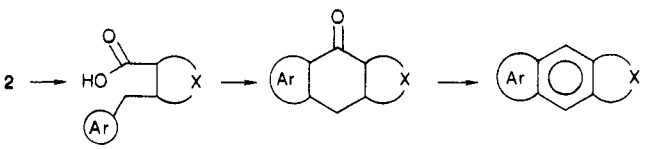
In addition to acid-catalyzed β ring opening, selective α ring opening reactions of cyclobutanones are known to occur under basic conditions[13] and reaction of **2** under these conditions would provide α-arylbutanoic acids **3**. Cyclization of **3** would result in α-tetralones which could be readily converted to linear fused PAHs (Scheme II). Therefore, the use of the bicyclic α-arylcyclobutanones, **2**, in such schemes would provide divergent syntheses of angular and linear fused polycyclics from common intermediates. In this study we report the syntheses of aceanthrylene (**1**), acephenanthrylene (**4**), and the benzoannelated derivatives benz[*a*]aceanthrylene (**5**) and benz[*e*]acephenanthrylene (**6**) using the above methodology.

Scheme I



2

Scheme II



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Results and Discussion

The key intermediates in these syntheses are the cyclobutanones **7** and **8**, which are readily prepared from cycloaddition of the corresponding ketenes with a 4- to 5-fold excess of 1,3-cyclohexadiene in benzene solution.

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