IR spectra were recorded on a Perkin-Elmer 727B spectrophotometer. Optical rotations were measured on a JASCO DIP-140 digital polarimeter. Melting points were measured on a Reichert hot stage melting point apparatus. Fast atom bombardment (FAB) mass spectra were obtained on a Finnigan MAT 312 double-focusing mass spectrometer in glycerol-thioglycerol matrix with xenon atom bombardment. High-resolution mass spectra were obtained under similar conditions by peak matching against albuterol.

Preparation of (2*S*,3*R*)-2-Bromo-3-acetoxybutyroyl Chloride (4). Acetyl chloride (6.8 g, 86.9 mmol) was added dropwise to the acid **3** (neat, 15.2 g, 83.1 mmol) with stirring. The reaction mixture was cooled in a bath at 5 °C as exotherm began. After completion of addition, the cooling bath was removed. After 45 min, the mixture was heated at 45–50 °C for 1.5 h. Heating was discontinued, and 10 mL of toluene was added. The mixture was cooled in an ice bath, and oxalyl chloride (11.5 g, 90.4 mmol) was added dropwise. After completion of addition, the mixture was allowed to warm to room temperature, followed by heating at reflux for 30 min. Toluene and excess of reagents were removed by fractonal distillation. The residue was subjected to bulb-to-bulb distillation at 80–90 °C under high vacuum (1 mmHg) to yield 18.4 g (91%) of acid chloride **4**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.44 (d, J = 6.0 Hz, 3 H), 2.11 (s, 3 H), 4.67 (d, J = 6.0 Hz, 1 H), 5.41 (m, 1 H); IR (neat) 1810, 1790, 1740 cm^{-1}.

(2*R*,3*R*)-*N*-[Phenylethoxymethyl]-*N*-(2-oxo-2-phenylethyl)-2,3-epoxybutyramide (6). Generation of 2-Phenyl-2-(trimethylsiloxy)ethylamine. To a solution of 2-amino-1-phenylethanol (Aldrich) (5.1 g, 37.2 mmol) in 25 mL of dichloromethane was added bis(trimethylsilyl)acetamide (6.1 g, 31.1 mmol). The reaction mixture was stirred at room temperature for 3 h. The mixture was diluted with dichloromethane (150 mL) and washed with water (2 × 100 mL). The organic phase was dried over magnesium sulfate and concentrated in vacuo. The crude product thus obtained was directly used for the next step.

Generation of [1-Phenyl-1-(trimethylsiloxy)ethyl]-2-benzaldimine (16). The crude product from above was mixed with benzaldehyde (4.4 g, 42 mmol). The reaction mixture was stirred for 2 min, and benzene (50 mL) was added. The water liberated was removed by addition of anhydrous magnesium sulfate. The mixture was filtered, and the residue was washed with benzene (2 × 10 mL). The solvent was removed under reduced pressure. The product was subjected to high vacuum for 2 h and used immediately for the next step.

Generation of 18. To a stirred solution of the above benzaldimine in 25 mL of dichloromthane, kept cooled in an ice bath, was added a solution of the acid chloride **4** (9.0 g, 37.1 mmol) in 25 mL of dichloromethane. After completion of addition, cooling was discontinued. The reaction mixture was stirred for 25 min, and triethylamine (5.4 g, 53.6 mmol) was added, followed, after 2 min, by anhydrous ethanol (6.9 g, 150.2 mmol). The reaction mixture was stirred at room temperature for 1.5 h. To this was added dichloromethane (25 mL) and water (50 mL). Layers were separated, and the aqueous phase was extracted with dichloromethane (3 × 30 mL). Combined organic phases were washed with water (150 mL), dried over magnesium sulfate, and concentrated in vacuo to give 17.8 g (87%) of crude **18**.

To a solution of 8.9 g (16.2 mmol) of the above crude product in 55 mL of methanol was added anhydrous potassium carbonate (2.2 g, 16.1 mmol). The reaction mixture was stirred at room temperature for 18 h. The suspensions were filtered, and the filtrate was concentrated in vacuo. The residue was dissolved in dichloromethane and washed with water (100 mL). The aqueous phase was extracted with dichloromethane (75 mL). Combined organic phases were washed with water (100 mL), dried over magnesium sulfate, and concentrated under reduced pressure to give the crude alcohol **5**.

To a solution of the above product in dichloromethane (25 mL) was added a powdered mixture of pyridinium chlorochromate (13.8 g, 64 mmol) and anhydrous sodium acetate (3 g, 37.6 mmol). The suspension was stirred at room temperature for 1.5 h. The reaction mixture was diluted with dichloromethane (50 mL) and filtered, and the filtrate was concentrated in vacuo. The residue was subjected to chromatography on silica gel with 35% ethyl acetate in hexanes as eluent to give 4.5 g (79% based on crude **18**) of epoxy amido ketone **6**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.12 (t, J = 7.0 Hz, 1 H), 1.2 (t, J = 7.0 Hz, 1.3 H), 1.28 (t, J = 7.0 Hz, 0.7 H), 1.38 (d, J = 6.0 Hz, 1.7 H), 1.55 (d, J = 6.0 Hz, 1.3 H), 4.17–5.92 (m, 6 H), 6.50 (s, 0.2 H), 6.58 (s, 0.2 H), 6.94 (s, 0.3 H), 7.0 (s, 0.3 H), 7.20–7.56 (m, 7 H), 7.71–7.83 (m, 3 H); IR (neat) 1665, 1700 cm^{-1}; MS (FAB), m/e 352 $(M - 1)^+$.

(3*S*,4*S*)-1-[Phenylethoxymethyl]-3-(1(*R*)-hydroxyethyl)-4-benzoyl-2-azetidinone (9). To a solution of epoxy ketone **6** (1.25 g, 3.5 mmol) in 10 mL of dry benzene, cooled in a bath at 8 °C, was added a solution of lithium hexamethyldisilazide in hexanes (Aldrich) (5.3 mL, 5.3 mmol). The reaction mixture was stirred at 8–12 °C for 1.5 h, and 8 mL of 20% aqueous solution of citric acid was added, followed by 20 mL of ethyl acetate. Layers were separated, and the aqueous phase was extracted with ethyl acetate (15 mL). The organic phases were combined, dried over magnesium sulfate, and concentrated under reduced pressure. The residue was subjected to chromatography on silica gel with 30% ethyl acetate in hexanes to give 890 mg (71%) of azetidinone **9**.

Polar diastereomer: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.32 (d, J = 7.0 Hz, 3 H), 1.42 (t, J = 6.0 Hz, 3 H), 3.34–3.46 (m, 1 H), 3.65–3.82 (m, 1 H), 3.94–4.10 (m, 1 H), 4.28–4.50 (m, 1 H), 5.30 (d, J = 2.5 Hz, 1 H), 6.14 (s, 1 H), 7.10–7.28 (m, 3 H), 7.30–7.68 (m, 4 H), 7.72–7.84 (m, 3 H); IR (CH_2Cl_2) 1685, 1760 cm^{-1}; MS (FAB), m/e 352 $(M - 1)^+$.

Less polar diastereomer: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.16 (d, J = 7.0 Hz, 3 H), 1.18 (t, J = 6.0 Hz, 3 H), 3.33–3.46 (m, 1 H), 3.53–3.70 (m, 1 H), 3.88–4.03 (m, 1 H), 4.13–4.28 (m, 1 H), 4.80 (d, J = 2.0 Hz, 1 H), 6.03 (s, 1 H), 7.26–7.48 (m, 7 H), 7.48–7.86 (m, 3 H); IR (CH_2Cl_2) 3550–3650, 3200–3650, 1760, 1685 cm^{-1}; MS (FAB), m/e 352 $(M - 1)^+$.

(3*S*,4*S*)-3-(1(*R*)-Hydroxyethyl)-4-benzoyl-2-azetidinone (10). To a solution of azetidinone **9** (890 mg, 2.5 mmol) in 2 mL of tetrahydrofuran was added 1 mL of 1 N H_2SO_4. The reaction mixture was stirred at room temperature for 24 h. To this was added 10 mL of ethyl acetate and 10 mL of water. Solid sodium bicarbonate was added until the aqueous phase was neutral. Layers were separated, and the aqueous phase was extracted with ethyl acetate (10 mL). Combined organic phases were dried over magnesium sulfate and concentrated in vacuo. The residue was subjected to chromatography over silica gel with 60% ethyl acetate in hexanes to yield 408 mg (74%) of azetidinone **10**, which was crystallized from dichloromethane–ether: mp 134–135 °C; $[\alpha]_D$ –77.5° ($CHCl_3$, c 0.52); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.37 (d, J = 6.3 Hz, 3 H), 2.15 (br s, 1 H), 3.25 (m, 1 H), 4.30–4.50 (m, 1 H), 5.07 (d, J = 2.4 Hz, 1 H), 6.38 (br s, 1 H), 7.46–7.70 (m, 3 H), 8.10–8.20 (m, 2 H); IR (CH_2Cl_2) 3550–3650, 3425, 1770, 1695 cm^{-1}; MS (FAB), m/e 220 $(M + 1)^+$; calcd for $C_{12}H_{14}NO_3$ $(M + H)$ 220.0993, found 220.0974.

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Synthesis of *cis*-1,2,3,4,4a,9,10,10a-Octahydrophenanthrene

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cis-1,2,3,4,4a,9,10,10a-Octahydrophenanthrene (**3a**) was first synthesized in 1933 via the well-known Bogert[1a]–Cook[1b] acid-catalyzed cyclization of 1-phenethylcyclohexanol (**1**), shown in Scheme I. Hydrocarbon **3a** is of

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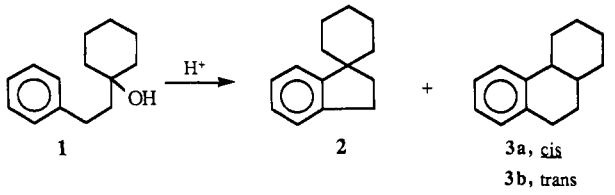
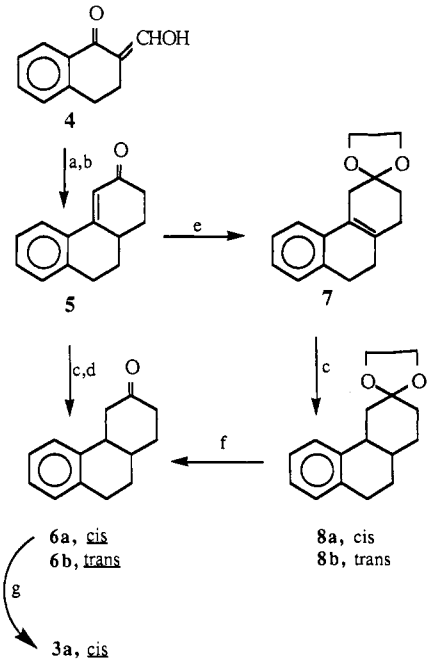
0022-3263/88/1953-0452$01.50/0

Scheme I



Scheme II[a]



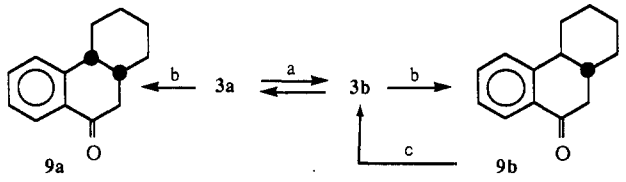
[a] (a) Methyl vinyl ketone, triethylamine; (b) aqueous KOH, CH_3OH; (c) H_2, Pd/C, ethyl acetate; (d) Li, NH_3, H_2O; H_3O^+; (e) $HOCH_2CH_2OH$, *p*-toluenesulfonic acid, benzene, Δ; (f) H_2O, CH_3OH, H_2SO_4; (g) *p*-toluenesulfonohydrazide, $NaCNBH_3$, $ZnCl_2$, CH_3OH.

current interest as a tricyclic hydroaromatic model for use in precise thermodynamic and spectroscopic studies of fossil-fuel constituents.[2a] These studies required a large sample of rigorously pure (99.9+%) **3a**.

The cyclization of **1**, shown in Scheme I, was initially used in the hope that spinning-band distillation and/or preparative high-pressure liquid chromatography (HPLC) could be used to obtain pure **3a**. These methods, however, failed. In the preparation of **3a** (Scheme I) both 85% sulfuric acid at 5 °C[1b] and Amberlyst 15 (A-15)[2b] in refluxing benzene provided complete consumption of **1** with little distillation residue. However, the product composition differed. With A-15, the ratio of **2**/**3a**/**3b** arranged in order of emergence from the GC column, was 39:250:1. With 85% sulfuric acid, at 5 °C for 30 min, a new product was formed having a 16.17-min GC retention time immediately preceded **2** at 16.30 min.[7] The GC peak ratio for the unknown/**2**/**3a** was 1:1:6.4 with no detectable **3b**. The mechanism of the Bogert–Cook cyclization has recently been reviewed.[1c]

Since the attempts at direct purification of **3a** failed to give acceptable material, the synthesis in Scheme II was adopted. This selection was made because the crystalline penultimate product, *cis*-**6a**, is a purifiable intermediate

Scheme III[a]



[a] (a) $AlCl_3$; (b) CrO_3, CH_3CO_2H/H_2O; (c) H_2, Pd/C, CH_3CO_2H, Δ.

and because the carbonyl group of **6a** is remote from epimerizable centers. However, the requirement of regiospecificity in the conversion of **6a** to **3a** remained. The reaction sequence in Scheme II has been used[3-5] to prepare the intermediates **5**, **6a**, **7**, and **8a** but not for the preparation of **3a**. The preparation of **5** proceeded as previously described.[3] Catalytic hydrogenation (Pd/C, ethyl acetate) and Li/NH_3/THF reduction of **5** gave **6a**/**6b** in the ratio 55:45 and 65:35, respectively.[4]

To improve the ratio of *cis*-**6a** to *trans*-**6b**, ketals **7** and **8** were prepared. The catalytic hydrogenation (Pd/C, ethyl acetate) of ketal **7** to ketal **8** is highly regioselective since HPLC studies (silica/CH_2Cl_2) of the reaction mixture showed the ratio of **8a**/**8b** to exceed 99/1. Li/NH_3/THF reduction of **7**, was less selective and gave a 20:80 ratio of **8a**/**8b** as established by ^{13}C NMR and HPLC (silica/$CHCl_2$) studies.

Cis ketone **6a** (**5** → **7** → **8a**) was purified by recrystallization from ether/hexane to give pure (99.97%) **6a**. Once purified, **6a** was deoxygenated to **3a** through reduction of the tosylhydrazone of **6a** with sodium cyanoborohydride in the presence of $ZnCl_2$ in refluxing methanol.[6] The ratio of **3a**/**3b** was 99.95:0.05.[7] Use of sodium cyanoborohydride with sulfolane/DMF[8] at 105 °C gave a generally less pure product containing 0.18% **3b**. Earlier studies using Wolff–Kishner[9a] (NH_2NH_2, H_2O, NaOH, diethylene glycol, 245 °C) and Clemmensen[9b] (Zn(Hg), aqueous HCl, reflux) reductions gave **3a** contaminated with **3b** in 3.8% and 0.38%, respectively. That some of the epimerization, in the case of Clemmensen reduction, took place after deoxygenation was established by treating pure **3a** under the same conditions and for the same time period.[9b] This treatment showed the formation of 0.13% **3b**.[7]

The preparation of cis ketone **9a** by chromic acid oxidation[1b] of **3a**, from Scheme I, was explored with the intent of isolating and purifying **9a** and converting it to pure **3a**. However, the yield of **9a** was low (ca. 30%). Further, ketone **9a** is not a solid and did not form a semicarbazone but did provide a crystalline (2,4-dinitrophenyl)hydrazone (2,4-DNP), mp 210–212 °C. Hydrolysis of this 2,4-DNP using $TiCl_3$[10] gave ketone **9a**, which was used to obtain spectral data and as a GC and HPLC reference compound in the study of mixtures.[7]

(2) (a) The results of the thermodynamic and spectroscopic studies of **3a** will be reported by personnel of the National Institute for Petroleum and Energy Research. (b) Amberlyst-15, sulfonated, bead-from resin, was a gift from Rohm and Haas Co., Philadelphia, PA 19105.

(3) Turner, R. B.; Nettleton, D. E.; Ferebee, R. *J. Am Chem. Soc.* **1956**, *78*, 5923.
(4) Gesson, J.-P.; Jacquesy, J.-C.; Jacquesy, R. *Nouv. J. Chim.* **1977**, *1*, 511.
(5) Boyakhchyan, A. P.; Tatevosyan, G. T. *Arm. Khim. Zh.* **1969**, *22*, 955; *Chem. Abstr.* **1970**, *72*, 42922U.
(6) Kim, S.; Oh, C. H.; Ko, J. S.; Ahn, K. H.; Kim, Y. J. *J. Org. Chem.* **1985**, *50*, 1927.
(7) Hewlett-Packard 5890 GC/FID using 30 M × 0.25 mm i.d., 0.25-μm film thickness, Supelcowax 10 Column. Program: 50 to 350 °C at 8 °C/min. Emergence order was **2** > **3a** > **3b**.
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(9) (a) Minlow, H. *J. Am. Chem. Soc.* **1946**, *68*, 2487. (b) Martin, E. L. *Organic* Syntheses; Wiley: New York, 1943; Collect. Vol. 2, p 499.
(10) McMurray, J. E.; Silvestri, M. *J. Org. Chem.* **1975**, *40*, 1502.

Historically, the evidence for the stereochemistry of **3a** and **3b** rests on **3a** being equilibrated with $AlCl_3$ to a mixture of **3a** and **3b**, with the latter predominating, and their chromic acid oxidation to **9a** and **9b**[11] (Scheme III). Our findings confirm this. However, the $AlCl_3$ isomerization results in a complex mixture [bp 95–100 °C (0.8 mm)], which contains numerous minor products and at least two new ones in substantial yields. The product distribution and peak areas in order of emergence at 15.18, 16.29, 17.91, 18.02, and 18.26 min from the GC column were first unknown/**2**/second unknown/**3a**/**3b** (26.5:5.4:12:31.7).[7] It should be noted that **1** and **2** were absent from the starting material which was **3a**/**3b** (96:4) prepared via Scheme II.

Experimental Section

Proton NMR spectra were obtained from a Varian XL-300 spectrometer at 299.944 MHz. The ^{13}C NMR data were obtained at 75.429 MHz in the FT mode. Tetramethylsilane was used as internal standard.

Cyclization of 1-Phenethylcyclohexanol (1). Tertiary alcohol 1 (20 g) prepared from phenethylmagnesium bromide and cyclohexanone[1b] was treated with 5 g of A-15 in refluxing benzene for 24 h. Accumulated water was removed as the azeotrope. The reaction mixture was filtered, concentrated under reduced pressure, and distilled at 75–85 °C (0.02 mm) to give 16.2 g of a mixture of **2**/**3a**/**3b** (39:250:1)) as determined by GC analysis.[7]

2-(Hydroxymethylene)-1-tetralone (4) and Its Conversion to 1,2,3,9,10,10a-Hexahydrophenanthren-3-one (5). Compound **4**, prepared[3] in 70% yield from 1-tetralone, showed the following: bp 110–115 °C (0.2 mm) [lit.[3] bp 125–127 °C (1.0 mm)]; ^1H NMR ($CDCl_3$) δ 8.123 (s, 1 H), 7.90 (d, 1 H), 7.40–7.10 (m, 4 H), 2.76 (5, 2 H), 2.40 (t, 2 H); ^{13}C NMR ($CDCl_3$) δ 182.1, 176.7, 141.4, 132.6, 131.3, 128.0, 126.8, 126.0, 108.5, 28.6, 22.6.

Treatment of **4** with methyl vinyl ketone and triethylamine catalyst followed by alkali-catalyzed cyclization gave ketone **5** in 92% crude yield.[4] Recrystallization from ether/hexane gave **5**: mp 77–78 °C (lit.[4] mp 78 °C); ^1H NMR ($CDCl_3$) δ 7.72 (d, 1 H), 7.36–7.15 (m, 3 H), 6.62 (d, 1 H), 2.98–1.44 (m, 9 H); ^{13}C NMR ($CDCl_3$) δ 199.8, 157.9, 139.5, 131.0, 130.3, 129.4, 126.3, 124.8, 120.0, 37.1, 36.8, 30.2, 30.0, 29.7; 85% crude yield. The red 2,4-DNP, mp 204–206 °C dec (lit.[12] mp 204–206 °C dec) was prepared.

Reduction of Ketone 5 to 1,2,3,4,4a,9,10,10a-Octahydrophenanthren-3-ones 6a,b. A. Hydrogenation of 5 with Pd/C in Ethyl Acetate to 6a,b. A 5-g sample of **5** in 100 mL of ethyl acetate containing 0.5 g of 10% Pd/C was hydrogenated at 50 psi at 25 °C for 2 h. The filtered solution was stripped to give 5 g of colorless oil, which was distilled to give 3.5 g (70%) of **6a**/**6b** (55:45).

B. Li/NH_3/THF Reduction of 5 to 6a,b. A solution of 19.8 g (0.1 mol) of **5** in 100 mL of dry THF was added dropwise at −75 °C to 1.8 g (0.25 mol) of Li, dissolved in 450 mL of condensed ammonia, during 30 min. The mixture was stirred 1 h, and solid NH_4Cl was used to discharge the blue color. The reaction mixture was evaporated, acidified with 10% HCl, and extracted with ether and the extract dried ($MgSO_4$), filtered, concentrated, and distilled [Kugelrohr, 115–120 °C (0.3 mm)] to give 16.2 g (85%) of colorless **6a,b**, which partially crystallized. HPLC analysis (silica/CH_2Cl_2) showed **6a**/**6b** (65:35), based on the ratio of quaternary peaks in the ^{13}C NMR.

Separation of 6b from 6a and 6b. The 55:45 mixture of **6a**/**6b** obtained from Pd/C hydrogenation of **5** was subjected to preparative HPLC[13] (silica/CH_2Cl_2) to give **6b**/**6a** (98:2) with **6b** preceding **6a**. After recrystallization this method gave **6b**: mp 69–70 °C (lit.[4] mp 73–74 °C); ^1H NMR ($CDCl_3$) δ 7.18 (d, 4 H), 3.20–1.40 (m, 12 H); ^{13}C NMR ($CDCl_3$) δ 210.6, 138.1, 136.2, 129.0, 126.0, 125.8, 125.0, 46.1, 43.1, 41.2, 39.1, 32.7, 29.8, 29.3. This material was converted to the yellow 2,4-DNP and colorless semicarbazone, mp 196–197 °C and 212–214 °C dec, respectively.

3,3-(Ethylenedioxy)-1,2,3,4,9,10-hexahydrophenanthrene (7). A 100-g (0.5 mol) sample of **5** was treated with 90 mL of ethylene glycol in 1 L of refluxing benzene containing 0.6 g of *p*-toluenesulfonic acid for 48 h until formation of water (Dean–Stark trap) ceased. The benzene layer was washed with water, dried ($MgSO_4$), filtered, and concentrated to give 125 g of pale yellow **7**: bp 120–130 °C (0.3 mm) (Kugelrohr); ^1H NMR ($CDCl_3$) δ 7.10 (m, 4 H), 3.98 (m, 4 H), 2.74 (t, 2 H), 2.62 (s, 2 H), 2.38 (t, 2 H), 2.18 (m, 2 H), 1.82 (t, 2 H); ^{13}C NMR ($CDCl_3$) δ 135.7, 135.0, 132.9, 127.0, 126.2, 126.0, 124.5, 121.2, 108.6, 64.3, 35.6, 31.1, 29.8, 28.3, 28.0.

Reduction of 7 to *cis*-3,3-(Ethylenedioxy)-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (8a). A. Pd/C Hydrogenation of 7 in Ethyl Acetate to 8a. A 118-g sample of **7** in 800 mL of ethyl acetate containing 8.0 g of 10% Pd/C was hydrogenated at 50 psi at 25 °C for 30 min. The filtered solution was stripped to give 116 g of colorless crystalline **8a**. Recrystallization from hexane gave mp 78–79 °C (lit.[5] mp 98 °C): ^1H NMR ($CDCl_3$) δ 7.10 (m, 4 H), 3.90 (m, 4 H), 3.10–2.80 (m, 3 H), 2.00–1.60 (m, 9 H); ^{13}C NMR δ ($CDCl_3$) 141.0, 135.7, 129.0, 128.8, 125.7, 125.5, 109.4, 64.2, 64.0, 40.4, 38.2, 32.3, 29.8, 29.7, 28.9, 22.4.

B. Reduction of 7 to 8a,b with Li/NH_3/THF. Ketal **7** (4.84 g, 0.02 mole) was reduced in stirred ammonia (100 mL)/THF (50 mL) with lithium (0.35 g, 0.05 g atom) for 1 h. Solid NH_4Cl was added to discharge the blue color. The reaction mixture was evaporated, acidified with 10% HCl, and extracted with ether and then dried ($MgSO_4$), filtered, and concentrated to 5 g of colorless viscous oil. HPLC analysis (silica, CH_2Cl_2) showed **8a**/**8b** (20:80).

Hydrolysis of 8a to 6a. A mixture of 116 g (0.47 mol) of **8a**, 650 mL methanol, and 155 mL of 3M sulfuric acid was heated at reflux for 3 h. The reaction mixture was diluted with water and extracted with ether, and the extract was washed with 10% sodium bicarbonate solution, dried ($MgSO_4$), filtered, and concentrated to yield 91 g (95%) of **6a** as a pale yellow solid. Distillation at 130–140 °C (0.2 mm) (Kugelrohr) and two recrystallizations from ether/isohexane gave 68 g of colorless crystals: mp 68–69 °C (lit.[4] mp 69–70 °C); ^1H NMR ($CDCl_3$) δ 7.14–7.04 (m, 4 H), 3.20–1.74 (m, 12 H); ^{13}C NMR ($CDCl_3$) δ 211.0, 139.2, 135.4, 129.2, 128.3, 126.3, 126.0, 46.7, 41.3, 37.4, 32.7, 30.8, 29.2, 23.2. The yellow 2,4-DNP and the colorless semicarbazone melted at 173–175 (lit.[12] mp 175–177 °C) and 228–230 °C dec (lit.[12] mp 229–231 °C), respectively.

Sodium Cyanoborohydride Reduction of 6a to 3a. To a stirred solution of purified ketone **6a** (91 g, 0.45 mol) and *p*-toluenesulfonohydrazide (94 g, 0.5 mol) in 1.2 L of methanol at 25 °C, was added a solution of sodium cyanoborohydride (32 g, 0.5 mol) and $ZnCl_2$ (33 g, 0.25 mol) in 800 mL methanol over a period of 20 min.[6] The mixture was stirred at 25 °C for 15 min and then heated at reflux for 25 h. The reaction mixture was cooled and 3 L of 0.1 N NaOH was added. The product was extracted with ether and washed with 10% HCl and then with saturated brine. The ether extract was dried ($MgSO_4$), filtered, and concentrated to 85 g of yellow oil. This was placed on a 1-in. diameter glass column containing a bed of 3 in. of alumina covered with 6 in. of silica and eluted with hexane. The eluted material was concentrated and distilled to give 65 g (77%) of **3a**, bp 78 °C (0.1 mm). GC analysis[7] showed this to be 99.95% pure: ^{13}C NMR ($CDCl_3$) δ 142.0, 135.9, 128.9, 128.6, 125.5, 125.4, 40.3, 33.9, 31.9, 31.5, 29.6, 26.3, 23.9, 21.6.

Chromic Acid Oxidation of 3a to *cis*-1,2,3,4,4a,9,10,10a-Octahydrophenanthren-3-one (9a). To 20 g (0.11 mol) of **3a**/**3b** (96:4 from Scheme II) in 200 mL acetic acid was added a solution of CrO_3 (22.2 g, 0.22 mol) in 45 mL of 80% acetic acid over 30 min. The reaction mixture was stirred at 25 °C for 5 days, diluted with water (3 L), and extracted with ether and the extract washed first with 10% sodium bicarbonate and then with saturated brine. The extract was dried ($MgSO_4$), filtered, and concentrated to 13.8 g of yellow viscous oil. It was Kugelrohr distilled, and 6.0 g of **9a**, bp 100–110 °C (0.1 mm), was collected as an impure (GC) yellow viscous oil. The mixture was converted to a red 2,4-DNP. This product was purified by Soxhlet extraction through a column (1 in. diameter × 2 in. bed) of neutral alumina using toluene as the eluant. Toluene was distilled off, and the residual red solid

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(8.3 g) was crystallized from boiling nitroethane to give 4.6 g of red crystals, mp 210–212 °C. TL chromatography on silica (toluene) showed a single spot. The 2,4-DNP (4.5 g) was treated with 120 mL of 20% aqueous $TiCl_3$ in 600 mL of 1,2-dimethoxyethane at reflux for 45 min under nitrogen.[10] The reaction mixture was cooled, diluted with water, and extracted with ether. The ether extract was washed with water, dried ($MgSO_4$), filtered, and concentrated to give 2.5 g of a dark yellow oil, which was placed on a column of silica gel (1 in. diameter × 6 in.) and eluted with a 1:1 mixture of ether/hexane. Concentration gave 1.5 g of nearly colorless **9a** (GC retention time 24.64 min): ^{13}C NMR ($CDCl_3$) δ 198.8, 148.5, 133.6, 131.5, 129.0, 127.2, 126.4, 40.4, 39.7, 33.6, 30.0, 25.2, 20.8.

Chromic Acid Oxidation of 3a and 3b to 9a and *trans*-1,2,3,4,4a,9,10,10a-Octahydrophenanthren-3-one (9b). A 2.5-g sample of $AlCl_3$-isomerized mixture prepared from **3a/3b** (96:4, Scheme I) and containing **3a/3b** (1:2.65) was oxidized with chromic acid as described above. The crude reaction product was Kugelrohr distilled to give 1.5 g of yellow oil, bp 110–140 °C (1.5 mm). This partially solidified on standing. The GC ratio of **9a/9b** was 1:2.3 at 24.69 and 25.82-min retention times. Two crystallizations from petroleum ether gave colorless crystals of **9b**: mp 92.5–93.5 °C (lit.[14] mp 95–96 °C); ^{13}C NMR ($CDCl_3$) δ 198.0, 147.1, 133.4, 132.4, 127.0, 126.2, 125.0, 46.5, 42.6, 40.5, 33.5, 29.6, 26.1, 25.4.

Pd/C Hydrogenation of 9b to 3b. A 1-g sample of **9b** in 50 mL of acetic acid containing 0.2 g of 10% Pd/C was hydrogenated at 50 psi and 40–45 °C. The filtered solution was concentrated, and the residue was dissolved in ether and washed with 10% $NaHCO_3$ and then water. The ether extract was dried ($MgSO_4$), filtered, and concentrated to a yellow oil, whih was distilled (Kugelrohr) to give 0.6 g of **3b** as a colorless oil: ^{13}C NMR $CDCl_3$) δ 140.1, 136.5, 128.7, 125.2, 125.1, 125.0, 43.6, 40.4, 34.2, 30.7, 30.5, 29.7, 26.8, 26.1.

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Communications

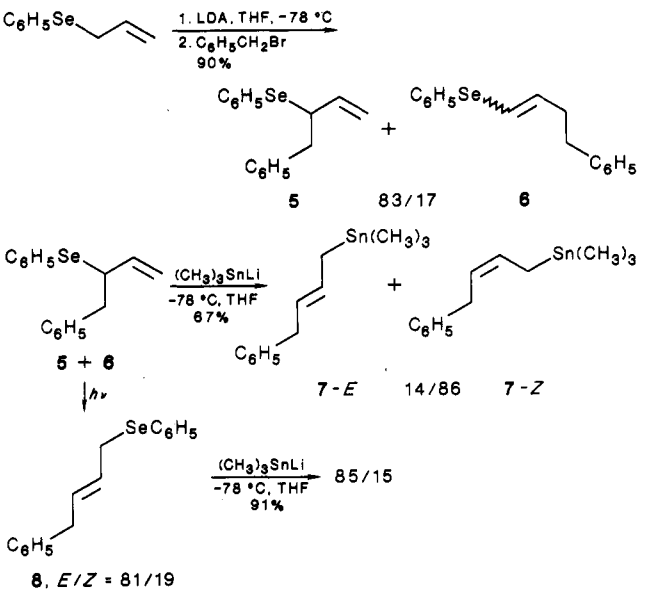
Organoselenium Chemistry.[1] Preparation of Allyl, Allenyl, and Propargyl Stannanes by Substitution of Phenylseleno with Trimethylstannyl

Summary: Allyl and otherwise activated phenylseleno groups are replaced by trimethylstannyl on reaction with (trimethylstannyl)lithium.

Sir: Organotin compounds have many applications in organic synthesis as mild anion equivalents.[2a] Important uses have been found in Lewis acid[2b] or palladium[2c] catalyzed condensations with electrophiles, free radical coupling reactions,[2d] and conversion to organolithium reagents by Li/Sn exchange.[3] While traditional methods for the formation of carbon–tin bonds such as the reaction of triorganostannyl lithium, magnesium, or copper reagents with alkyl halides and the reaction of lithium and Grignard reagents with triorganostannyl halides have served well for the preparation of simple tin compounds, they are not always effective for more complex systems.

We report here that allyl, benzyl, allenyl, and propargyl selenides, as well as selenoacetals and selenoketals, react with (trimethylstannyl)lithium at −78 °C to give trimethylstannyl compounds (Table I).[1b,4] The advantage of this procedure over most others is that the chemistry of α-lithioallyl (**1a,b**),[1a–d,7a] -benzyl (**2**)[1e,7b] -allenyl (**3**),[1f] and

Scheme I



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