a quartz vessel with a Coleman Model VII M blue light source for 19 h. Workup as previously indicated gave a clear slightly yellow mobile oil. Overnight drying under vacuum (0.3 torr) gave an off-white solid (139.5 mg), of which 106.7 mg was sublimed, giving 103.6 mg of **2d** (44.7%): mp 85–87 °C; IR (neat) 677, 697, 722, 750, 788, 2874, 2933, 3067 cm^{-1}.

Anal. Calcd for $C_{12}H_5Cl_5$: C, 44.15; H, 1.54; Cl, 54.30. Found: C, 44.30; H, 1.61; Cl, 54.30.

2,2',3,4,5,5'-Hexachlorobiphenyl, 2e. Compound **1e** (122.2 mg, 2.9×10^{-4} mol) was irradiated in 5 mL of benzene solution with a Coleman Model VII M blue light for 12 h. Solvent removal gave a crude residue, mp 85–88 °C, which upon sublimation of 115.9 mg gave 65.5 mg (62%) of **2e**: mp 88–89.5 °C (lit.[5] mp 89–91 °C); IR (neat) 645, 687, 722, 769, 3096 cm^{-1}; NMR (CCl_4) δ 7.42 (m); mass spectrum, *m/e* (relative intensity) 366 (8.9), 364 (35), 362 (80), 360 (100), 358 (53).

Anal. Calcd for $C_{12}H_4Cl_6$: C, 39.94; H, 1.12; Cl, 58.94. Found: C, 39.86; H, 1.19; Cl, 59.02.

(4-Chlorophenyl)acetylene, 4b. Compound **4b** was prepared according to Scheme I. A solution of **5b** (50 g, 0.32 mol) and hydroquinone (0.35 g, 0.003 mol) was frozen in an ice–salt water bath, and PCl_5 (72 g, 0.35 mol) was added to the solid mixture. When the mixture was warmed to 25 °C under a reflux condenser equipped with a $CaCl_2$ tube, evolution of HCl commenced. The reaction mixture was maintained with stirring at 63–75 °C for 75 min, filtered, and distilled in vacuo, giving $POCl_3$ [bp 30–38 °C (17 torr)] and a fraction, bp 121–124 °C (17 torr), which was mixed with a solution of KOH (75 g, 1.34 mol) in 300 mL of 95% ethanol, heated to reflux for 12 h, and steam distilled into ice. Suction filtration and air drying gave crystalline **4b**: 10.6 g (24%); mp 44–45 °C (lit.[6] mp 41–43 °C); IR (neat) 625–700 (br), 780, 825, 2288, 3278 cm^{-1}; mass spectrum, *m/e* (relative intensity) 138 (33), 136 (100), 101.

(3-Chlorophenyl)acetylene, 4d. Compound **4d** was prepared from the corresponding acetophenone **5d** (30 g, 0.19 mol) and hydroquinone (0.40 g, 0.009 mol), as for **4b** above, according to the method of Trompen and Huisman.[6] After steam distillation into ice, the organic distillate separated as a second liquid phase. The entire volume was extracted with ether, and the ethereal solution dried over Na_2SO_4. Fractional distillation of the residue under vacuum gave **4d**, bp 77–79 °C (19 torr) [lit.[11] bp 64–65 °C (12 torr)], pure by gas chromatography: 2.17 g (8.2%); IR (neat) 625–775 (br), 680, 748, 2985, 3400 cm^{-1}; NMR (CCl_4) δ 3.16 (s, 1 H), 7.29–7.58 (m, 4 H); mass spectrum, *m/e* (relative intensity) 138 (40), 136 (100), 101.

(2,4-Dichlorophenyl)acetylene, 4c. Compound **5c** (11.5 g, 0.06 mol), hydroquinone (0.13 g, 0.001 mol), and PCl_5 (12.7 g, 0.06 mol) were reacted as for **4b** above. After treatment with KOH, the reaction mixture was poured over ice with stirring, suction filtered, and washed with water, giving an orange solid. Sublimation gave 3.4 g of white crystalline **4c** (33%): mp 52–55 °C; IR (neat) 676, 698, 707, 824, 862, 2299, 3086, 3300 cm^{-1}; NMR (CCl_4) δ 3.37 (s, 1 H), 7.37 (m, 3 H); mass spectrum, *m/e* (relative intensity) 174 (100), 172 (66), 170 (11), 135, 100.

(2,5-Dichlorophenyl)acetylene, 4e. A solution of **5e** (10.0 g, 0.05 mol) and hydroquinone (0.10 g, 0.009 mol) was reacted as for the preparation of **4b**. Upon steam distillation into ice, the product crystallized. Suction filtration and air drying gave **4e**: 1.22 g (13%); mp 38–41 °C (lit.[12] 40 °C); IR (neat) 625–700 (br), 633, 680, 694, 708, 2262, 3021, 3096, 3300 cm^{-1}; mass spectrum, *m/e* (relative intensity) 174 (100), 172 (47), 170 (11), 135, 100.

Registry No. **1a**, 22612-94-8; **1b**, 75717-71-4; **1c**, 75717-72-5; **1d**, 75717-73-6; **1e**, 75717-74-7; **2a**, 33284-53-6; **2b**, 74472-37-0; **2c**, 35694-06-5; **2d**, 70424-69-0; **2e**, 52712-04-6; **3b**, 75717-75-8; **3c**, 75731-92-9; **3d**, 75717-76-9; **3e**, 75731-93-0; **4a**, 536-74-3; **4b**, 873-73-4; **4c**, 75717-77-0; **4d**, 766-83-6; **4e**, 38417-89-9; **5a**, 1334-78-7; **5b**, 99-91-2; **5c**, 2234-16-4; **5d**, 99-02-5; **5e**, 2476-37-1; *o*-chloranil, 2435-53-2; pentachlorophenol, 87-86-5.

(11) M. M. Otto, *J. Am. Chem. Soc.*, **56**, 1393 (1934).
(12) C. J. MacDonald, *Can. J. Chem.*, **50**, 2035 (1972).

Six-Membered-Ring Annulation via a Conjugate Addition/Alkylation Sequence Using Functionalized Aryllithium Reagents and Vinyl Sulfones[1]

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A new method, which is a one-flask procedure involving addition of substituted aryllithium reagents **6** to vinyl sulfones **8** and **9** followed by spontaneous intramolecular alkylation of the resulting α-lithio sulfones, has been developed for the annulation of tetrahydronaphthalene moieties onto preexisting carbon frameworks. The aryllithium reagents employed in this study are the previously investigated intermediates obtained by the chemoselective lithium–halogen exchange reactions of simple as well as oxygenated *o*-halo-β-phenethyl halides **5**. The annulation products **11** and **12** may be subjected to various further transformations which should make the overall sequences of considerable utility in the synthesis of steroids and other polycyclic systems.

Because of the widespread occurrence of six-membered carbocyclic rings as structural units of several classes of important natural products, we have been investigating new methods to complement the presently available procedures for the construction of cyclohexane-containing systems.[2] In particular, we have been interested in developing pathways for the annulation of six-membered rings onto preexisting ring systems that would be appli-

(1) This work was described in part at the 179th National Meeting of the American Chemical Society, Houston, TX, Mar 1980, Abstract No. ORGN 128.

(2) For some recent reviews of six-membered ring formation see: (a) Jung, M. E. *Tetrahedron* **1976**, *32*, 3–31. (b) Martin, J. In "International Review of Science: Organic Chemistry, Series Two"; Ginsburg, D., Ed.; Butterworths: London, 1976; Vol. 5, pp 102–106. (c) Kametani, T.; Nemoto, H. *Heterocycles* **1978**, *10*, 349–390. (d) Magnus, P. *Nouv. J. Chim.* **1978**, *2*, 555–557.

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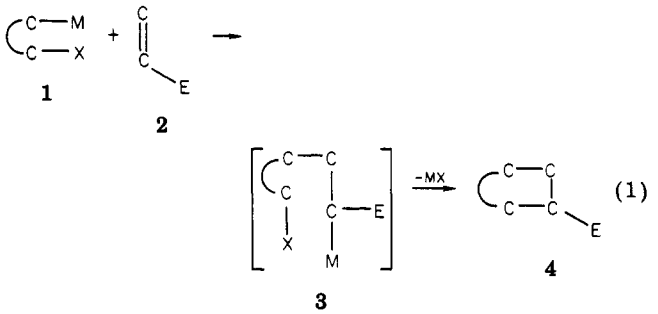
Table I. Cyclization of *o*-Lithiophenethyl Halides with Vinyl Sulfones

dihalide	sulfone	solvent	temp, °C	product	yield, %[a]
5d	8	ether	−100	11	75
5e	9	ether	−78	12a	78
5f	9	ether	−78	12b	81
5g	9	THF	−100	12c	80
5d	9	ether	−100	12d	79
5h	9	ether	−78	12d	71

[a] All yields are for isolated products.

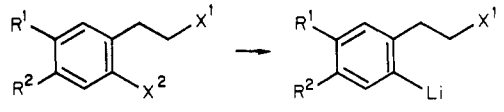
cable to the synthesis of steroids and related polycyclic compounds. The general strategy that we have chosen to study is shown in eq 1. Our approach involves the use



1 2 3 4 (1)

of organometallic reagents 1 bearing a suitable leaving group X as well as containing an appropriate metal M which permits addition of the organometallic portion of the reagent to an electron-deficient olefin, 2 (or an acetylene), bearing an electron-withdrawing, carbanion-stabilizing group (E). Intramolecular alkylation of the adduct 3 would then afford the desired cyclization product 4. Another feature which would increase the synthetic utility of this approach would be the choice of a group, E, which would be useful in various subsequent transformations (e.g., eliminations, addition reactions, etc.). Obviously, the reagents 1 must meet rather stringent requirements of reactivity, not the least of which would be the ability to avoid intramolecular self-coupling of 1.

A few years ago, Parham and co-workers reported the conversion of 2-bromo-β-phenethyl bromide (**5a**) into the corresponding aryllithium reagent **6a** through use of *n*-butyllithium at −100 °C (eq 2). When the mixture was

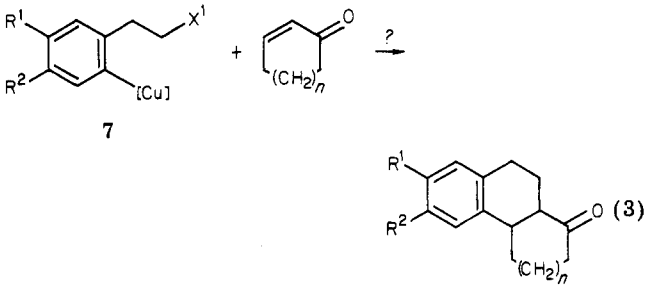


5 6 (2)

a, $R^1 = R^2 = H$; $X^1 = X^2 = Br$
b, $R^1 = OCH_3$; $R^2 = H$; $X^1 = Br$; $X^2 = I$
c, $R^1 = R^2 = OCH_3$; $X^1 = Br$; $X^2 = I$
d, $R^1, R^2 = OCH_2O$; $X^1 = Br$; $X^2 = I$
e, $R^1 = R^2 = H$; $X^1 = Cl$; $X^2 = Br$
f, $R^1 = OCH_3$; $R^2 = H$; $X^1 = Cl$; $X^2 = Br$
g, $R^1 = R^2 = OCH_3$; $X^1 = Cl$; $X^2 = Br$
h, R^1; $R^2 = OCH_2O$; $X^1 = Cl$; $X^2 = Br$

warmed, **6a** was found to undergo intramolecular coupling to afford benzocyclobutene, or it could be trapped with a ketone to produce an isochroman.[3] The aryllithium **6a** appeared to us to have considerable potential in organic synthesis, and, indeed, we developed a general, high-yield synthesis of benzocyclobutenes[4] and isoquinolines[5] based upon the use of **6a–d** as intermediates derived from **5a–d**. More recently, Bradsher's group has reported some very similar reactions.[6]

Our main interest in using the aryllithium intermediates was to develop a new annulation procedure for carbocyclic systems. For example, we had hoped to convert the intermediates into organocopper species **7** which would undergo a conjugate addition/alkylation sequence of reactions with cyclic α,β-unsaturated ketones (eq 3). This pathway



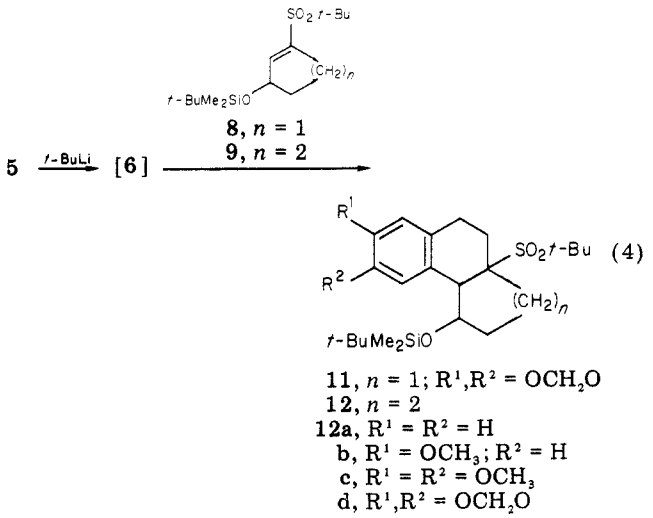
7 (3)

would have many obvious applications in the synthesis of ring-A aromatic steroids and other important natural products. However, under none of the usual conditions nor through use of various types of organocopper intermediates (**7** = monoarylcopper, diarylcuprates or mixed cuprates)[7] nor with a variety of substituents X^1 (Br, Cl, OR, O^-, SR, S^-, NR_2) were we able to find any evidence for the occurrence of conjugate addition, although other reactions typical of arylcopper complexes (e.g., alkylation with alkyl halides and coupling to give biaryls) could be performed.

In concurrent studies in one of our laboratories, we observed that alkyllithium reagents undergo direct addition to the carbon–carbon double bonds of certain vinyl sulfones and that the carbanionic centers of the resulting adducts react with various electrophilic reagents.[8,9] We therefore postulated that our original proposed approach to carbocyclic annulation could be modified by using vinyl sulfones **8** and **9** in place of α,β-unsaturated ketones. We were pleased to find that this modification does indeed provide a very useful annulation procedure (eq 4). A summary of our results is given in Table I. In these cyclizations, the sulfone is simply added to a solution of the aryllithium **6** at −78 or −100 °C generated in situ from the corresponding dihalide (**5**). After 30 min, the resulting reaction mixture is allowed to warm to 25 °C over a 1-h period. The tricyclic products **11** or **12** are then isolated in good yields by standard techniques. Because of subsequent reactions (vide infra) in which the relevant chiral centers are lost, the stereochemistry of the cyclization products was not determined.

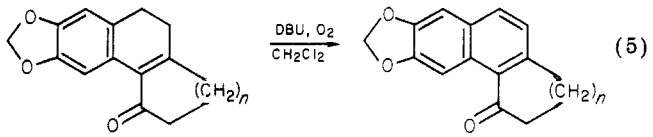
Ether was found to be the solvent of choice for these reactions except for the use of the dimethoxy substrate **5g** which was largely insoluble at low temperature in this solvent. Instead, THF was used for this case, but a temperature of −100 °C for the lithium–halogen exchange and

(3) Parham, W. E.; Jones, L. D.; Sayed, Y. A. *J. Org. Chem.* **1976**, *41*, 1184–1186.
(4) Brewer, P. D.; Tagat, J.; Hergrueter, C. A.; Helquist, P. *Tetrahedron Lett.* **1977**, 4573–4574.
(5) Hergrueter, C. A.; Brewer, P. D.; Tagat, J.; Helquist, P. *Tetrahedron Lett.* **1977**, 4145–4148.
(6) Bradsher, C. K.; Hunt, D. A. *Org. Prep. Proced. Int.* **1978**, *10*, 267–272.
(7) Posner, G. H. *Org. React.* **1972**, *19*, 1–113; **1975**, *22*, 253–400.
(8) (a) Conrad, P. C.; Fuchs, P. L. *J. Am. Chem. Soc.* **1978**, *100*, 346–348. (b) Saddler, J. C.; Conrad, P. C.; Fuchs, P. L. *Tetrahedron Lett.* **1978**, 5079–5082. (c) Barton, D. L.; Conrad, P. C.; Fuchs, P. L. *Ibid.* **1980**, *21*, 1811–1814.
(9) Some related addition reactions have been reported in: (a) Tanikaga, R.; Sugihara, H.; Tanaka, K.; Kaji, A. *Synthesis* **1977**, 299–301. (b) Eisch, J. J.; Galle, J. E. *J. Org. Chem.* **1979**, *44*, 3277–3279. (c) Isobe, M.; Kitamura, M.; Goto, T. *Tetrahedron Lett.* **1979**, 3465–3468; *Chem. Lett.* **1980**, 331–334.



subsequent reaction with the vinyl sulfone was necessary because of the enhanced tendency for benzocyclobutene formation to occur in this solvent.[4] Also, for most of this work, we have employed the bromo chlorides **5e–h** rather than the previously reported dibromide **5a** or iodo bromides **5b–d** because again of a decreased tendency of the *o*-lithiophenethyl chlorides **6e–h** to undergo benzocyclobutene formation relative to the corresponding lithio bromides (**6a–d**).

The particular vinyl sulfones 8 and 9 were chosen for these studies because of the quite useful transformations to which the initial tricyclic products (11 and 12) may be subjected. For example, by a three-step sequence of reactions (Scheme I), the products may be converted into the α,β-unsaturated ketones 13 and 14. The results of these transformations are summarized in Table II. The reactions leading to 13 and 14 are performed sequentially without purification of the intermediates shown in Scheme I. Care must be taken with the final products because of their high tendency to undergo aromatization. As a result, their complete purification is difficult. Alternatively, we have taken advantage of this reactivity; for example, treatment of 13 and **14d** with DBU and molecular oxygen leads to formation of the naphthocycloalkenones **15** and **16** in yields of 80% and 77%, respectively (eq 5).



In conclusion, we have developed a very efficient, one-step annulation procedure which permits the fusion of hydronaphthalene ring systems onto preexisting carbon frameworks. The resulting products may conveniently be transformed into other systems which have many obvious applications in the synthesis of steroids and other polycyclic compounds.

Experimental Section

All reactions of air- and water-sensitive materials were performed in flame-dried glassware under nitrogen by using double-manifold techniques.[10] Syringes were used to transfer air-sensitive solutions. Commercially obtained reagents were purified by distillation or recrystallization before use. *tert*-Butyllithium was obtained as a pentane solution from Alfa or Aldrich and was titrated by the diphenylacetic acid method.[11] Low temperatures were maintained through use of liquid nitrogen/methanol (−100 °C) or dry ice/acetone (−78 °C) baths or through use of a bath equipped with a Neslab Cryo-Cool Model CC-100F low-temperature unit, a Cole-Parmer Versa-Therm Model 2158 temperature controller, and a 500-W immersible heating coil. The ^{1}H NMR spectra were recorded at 60 MHz with a Varian EM-360 spectrometer or at 80 MHz with a Varian HFT-80 spectrometer. The ^{13}C NMR spectra were recorded at 20 MHz with a Varian CFT-20 spectrometer. The NMR spectra were obtained from $CDCl_3$ solutions containing tetramethylsilane, methylene chloride, or chloroform as the internal standard. The chemical shifts are expressed in parts per million (δ) downfield from Me_4Si, and the ^{1}H NMR peak areas are expressed as the number of hydrogen atoms (H). Mass spectra were recorded with Hewlett-Packard Model 5982A and AEI Model MS-30 mass spectrometers by using electron-impact ionization at 70 eV. The IR spectra were obtained with a Pye-Unicam Model SP-1000 or a Perkin-Elmer Model 727 spectrophotometer as neat liquid films or solutions in chloroform and were calibrated with a polystyrene standard. Elemental analyses were performed by Galbraith Laboratories, Inc. For the reasons mentioned in the text, accurate analyses were often difficult to obtain. Therefore, the analytical results are given only when they agree with the calculated values within ±0.3%. In all other cases, the homogeneity of the compounds was demonstrated by careful GLC and TLC, and molecular formulas were determined by high-resolution mass spectroscopy. For separations by high-performance liquid chromatography, a Waters dual-pump chromatograph equipped with a 1 ft × 1/4 in. μ-Porasil column was employed.

Vinyl Sulfones 8 and 9. A detailed procedure is given for the cyclohexenyl sulfone 9. A solution of sodium ethoxide was prepared from sodium metal (0.034 g, 41 mmol) and ethanol (77 mL) and was then allowed to react at 0–25 °C with *tert*-butyl mercaptan (4.8 mL, 43 mmol). To the resulting solution was added 3-bromocyclohexene (6.54 g, 41 mmol). After 3 h at 25 °C, the

Scheme I

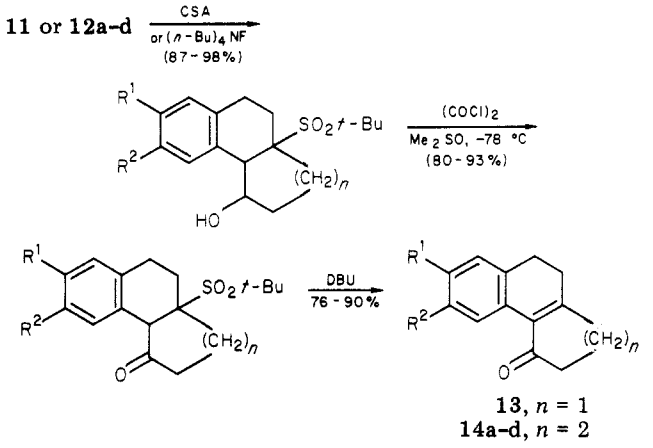


Table II. Conversion of Cyclization Products into α,β-Unsaturated Ketones

starting matl	product	yield,[a] %
11	13, n = 1; R^1,R^2 = OCH_2O	68
12a	14a, n = 2; R^1 = R^2 = H	47 (53)[b]
12b	14b, n = 2; R^1 = OCH_3; R^2 = H	(77)[b]
12c	14c, n = 2; R^1 = R^2 = OCH_3	69
12d	14d, n = 2; R^1,R^2 = OCH_2O	70 (75)[b]

[a] Isolated overall yields (except as noted) for the three-step sequence. [b] Determined by ^{1}H NMR integration.

(10) (a) Shriver, D. F. "The Manipulation of Air-Sensitive Compounds"; McGraw-Hill: New York, 1969. (b) Burlitch, J. M. "How to Use Ace No-Air Glassware"; Ace Glass: Vineland, NJ, 1971.

(11) Kofron, W. G.; Baclawski, L. M. *J. Org. Chem.* **1976**, *41*, 1879–1880.

mixture was filtered, and isolated from the filtrate was 5.10 g (74%) of 3-(*tert*-butylthio)cyclohexene, bp 69–71 °C (3 torr). A solution of this material (4.4 g, 20 mmol) and methylene chloride (100 mL) was added to *m*-chloroperbenzoic acid (14.2 g, 66 mmol) in methylene chloride (150 mL) at 0 °C. After 1 h at 0 °C and 23 h at 25 °C, 2,3-epoxycyclohexyl *tert*-butyl sulfone was isolated from the reaction mixture as a white solid which was recrystallized from chloroform–hexane to give 5.3 g (94%) of colorless crystals, mp 95–99 °C. A solution of this product (2.18 g, 10.0 mmol), DMF (25 mL), and DBU (0.15 mL, 1 mmol) was heated at 80 °C for 5 h. After the mixture was cooled to 25 °C, imidazole (1.49 g, 22 mmol) and *tert*-butyldimethylchlorosilane (1.73 g, 11.5 mmol) were added. After 2 h at 25 °C, the product was isolated as a white solid which was recrystallized from ether–hexane to give 2.93 g (88%) of the vinyl sulfone **9** as colorless crystals: mp 72–73 °C; IR ($CHCl_3$) 3.35, 7.7, 7.8, 8.8, 8.9 μm; ^1H NMR ($CDCl_3$) 6.7 (m, 1 H), 4.4 (br m, 1 H), 2.4 (br m, 2 H), 1.7–2.0 (br m, 4 H), 1.35 (s, 9 H), 0.9 (s, 9 H), 0.1 (s, 6 H); ^{13}C NMR ($CDCl_3$) 144.68 (d), 138.23 (s), 66.61 (d), 60.21 (s), 31.22 (t), 26.33 (s), 25.74 (q), 23.79 (q), 19.65 (t), 18.02 (t), −4.68 (q); mass spectrum (70 eV), *m/e* 332.183 (M^+, 332.184 calcd for $C_{16}H_{32}O_3SSi$).

An analogous series of reactions was employed in the preparation of the cyclopentenyl sulfone (**8**). The yields of the three steps in order were 67%, 92%, and 92%. The physical data for **8** were as follows: mp 81–82 °C; IR ($CHCl_3$) 3.4, 6.8, 7.8, 9.0 μm; ^1H NMR ($CDCl_3$) 6.75 (m, 1 H), 5.0 (br m, 1 H), 1.8–2.9 (br m, 4 H), 1.4 (s, 9 H), 0.9 (s, 9 H), 0.1 (s, 6 H); ^{13}C NMR ($CDCl_3$) 148.70 (d), 142.70 (s), 77.08 (d), 59.60 (s), 35.14 (t), 32.25 (t), 25.79 (q), 23.56 (q), 18.10 (s), −4.70 (s); mass spectrum (70 eV), *m/e* 318.165 (M^+, 318.168 calcd for $C_{15}H_{30}O_3SSi$).

2-Halo-β-phenethyl Halides (5). The preparations of these dihalides were based upon the previously reported procedures.[3,6,12] A representative preparation is given for 2-(2-bromo-5-methoxyphenyl)ethyl chloride (**5f**). To a suspension of lithium aluminum hydride (11.77 g, 310 mmol) and THF (500 mL) at 0 °C was added a solution of commercial 3-methoxyphenylacetic acid (25.0 g, 150 mmol) and THF (250 mL). After 22 h at 25 °C, treatment of the reaction mixture with aqueous sodium hydroxide and partitioning between ether and water led to isolation of 16.68 g (73%) of 2-(3-methoxyphenyl)ethanol as an oil which was used without further purification. To a solution of this product (1.18 g, 7.8 mmol), methylene chloride (10 mL), and pyridine (0.75 mL, 9.3 mmol) at 25 °C was added neat bromine (0.47 mL, 18 mmol). After 16 h at 25 °C, 1.58 g (88%) of 2-(2-bromo-5-methoxyphenyl)ethanol was isolated as a yellow oil. Finally, reaction of this material with 1.5 equiv each of *N,N*-dimethylaniline and thionyl chloride in chloroform at reflux for 12 h provided **5f** (77%) as a pale yellow liquid: bp 90–95 °C (0.01 torr); IR (neat) 3010, 2950, 1595, 1570, 1480, 805 cm^{-1}; ^1H NMR ($CDCl_3$) 7.6 (d, J = 9 Hz, 1 H), 6.9 (dd, J = 6, 3 Hz, 1 H), 6.73 (d, J = 3 Hz, 1 H), 3.83 (s, 3 H), 3.8 (t, J = 7 Hz, 2 H), 3.2 (t, J = 7 Hz, 2 H); mass spectrum (70 eV), *m/e* 249.9561 (M^+, 249.9574 calcd for $C_9H_{10}BrClO$).

Preparation of (Tetrahydronaphtho)cycloalkanes. A detailed representative example of the cyclization procedure is given as follows for the preparation of **12d**. To a solution of **5h** (0.132 g, 0.0500 mmol) and ether (2.5 mL) at −78 °C was added a solution of *tert*-butyllithium (1.05 mmol) in pentane over a 5-min interval. The reaction mixture was allowed to stir at −78 °C for 1 h and then a solution (1 mL of THF) of the vinyl sulfone **9** (0.166 g, 0.500 mmol) precooled to −78 °C was added with a double-ended needle. This mixture was allowed to stir at −78 °C for 0.5 h, and then it was warmed to 25 °C over a 1-h period. Workup was accomplished by dilution with ether, washing the ethereal solution with saturated aqueous ammonium chloride (buffered at pH 8), and extracting the aqueous phase with ether. Obtained from the organic extracts was 0.211 g (81%) of a yellow oil which was purified by column chromatography (silica gel, 20% THF/hexane) to give **12d** as colorless oil which was spectroscopically pure (71% yield). Alternatively, the crude product could be crystallized from CH_3CN to give a light yellow solid: mp 127–130 °C; ^1H NMR ($CDCl_3$) 6.65 (s, 1 H), 6.55 (s, 1 H), 5.85 (m, 2 H), 3.5–1.8 (m, 12 H), 1.45 (s, 9 H), 0.8 (s, 9 H), −0.24 (s, 3 H), −0.30 (s, 3 H); IR ($CHCl_3$) 3010, 2950, 1500, 1485, 1275, 1110, 860, 840 cm^{-1}; mass spectrum (70 eV), *m/e* 480.2397 (M^+, 480.2366 calcd for $C_{25}H_{40}O_5SSi$).

For the other entries in Table I, the same basic procedure was followed with the exceptions noted in the table. All reactions were performed on approximately the same scale as in the sample procedure above. Relevant data for each of the cyclization products are given in the following summaries.

11. The reaction of the dibromide **5d** with *tert*-butyllithium was performed at −100 °C for 1 h followed by addition of a precooled (−78 °C) solution of the vinyl sulfone **8**. The mixture was allowed to warm to −78 °C over a 30-min period and then to 25 °C over a 1-h period. The usual workup and chromatographic purification provided a 75% yield of **11** as a white foam: TLC (silica gel, 20% THF/hexane) R_f 0.23 (one spot); ^1H NMR ($CDCl_3$) 6.73 (s, 1 H), 6.67 (s, 1 H), 5.92 (s, 2 H), 3.55 (m, 2 H), 1.8–3.0 (m, 8 H), 1.45 (s, 9 H), 0.85 (s, 9 H), −0.15 (s, 3 H), −0.20 (s, 3 H).

12a. The crude product was purified by column chromatography (silica gel, methylene chloride followed by ether) to give a 78% yield of **12a** as a viscous oil: ^1H NMR ($CDCl_3$) 6.95 (s, 4 H), 1.3–3.3 (br m, 12 H), 1.25 (s, 9 H), 0.65 (s, 9 H), −0.50 (s, 3 H), −0.25 (s, 3 H); IR (neat) 2950, 1490, 1450, 1280, 100 cm^{-1}.

12b. Column chromatography (silica gel, 5% ether/chloroform) provided an 80% yield of **12b** as colorless crystals: mp 126–128 °C; TLC (silica gel, 5% ether/chloroform) R_f 0.43 (single spot); ^1H NMR ($CDCl_3$) 6.5–7.2 (br m, 3 H), 3.65 (s, 3 H), 1.4–3.20 (br m, 12 H), 1.27 (s, 9 H), 0.65 (s, 9 H), −0.52 (s, 3 H), −0.36 (s, 3 H); IR ($CHCl_3$) 3010, 2950, 1840, 1500, 1450, 1270, 1110 cm^{-1}; mass spectrum (70 eV), *m/e* 466.2548 (M^+, 466.2573 calcd for $C_{25}H_{42}O_4SSi$).

12c. The reaction of **5g** with *tert*-butyllithium was performed in THF at −100 °C for 1 h followed by addition of a precooled solution (−78 °C) of **9** in THF. After the mixture was warmed to −78 °C over a 30-min period, the product was isolated and purified in the usual manner to afford an 82% yield of **12c** as colorless crystals which were recrystallized from hexane: mp 52–55 °C; ^1H NMR ($CDCl_3$) 6.6 (s, 1 H), 6.55 (s, 1 H), 3.73 (s, 6 H), 1.6–3.4 (br m, 12 H), 1.32 (s, 9 H), 0.70 (s, 9 H), −0.4 (s, 3 H), −0.65 (s, 3 H); IR (neat) 2950, 1510, 1465, 1440, 1280, 1100 cm^{-1}; mass spectrum (70 eV), *m/e* 496.2697 (M^+, 496.2678 calcd for $C_{26}H_{44}O_5SSi$).

Preparation of (Dihydronaphtho)cycloalkenones. A sample procedure is given for the conversion of **12c** into **14c**.

14c. To a suspension of **12c** (0.198 g, 0.4 mmol) in MeOH (3.3 mL) was added solid camphorsulfonic acid (CSA; 0.4640 g, 2.0 mmol). The mixture was allowed to react for 2 h at 25 °C, after which time it was diluted with water. Saturated aqueous sodium chloride (2 mL) was added to prevent emulsions, and the phase was extracted with methylene chloride. From the combined extracts was obtained the crude product which was purified by column chromatography (silica gel, ether) to give 0.139 g (92%) of 1,2,3,4,4a,9,10,10a-octahydro-6,7-dimethoxy-10a-[(1,1-dimethylethyl)sulfonyl]-4-phenanthrenol as a yellow solid: TLC (silica gel, 20% acetone/methylene chloride) R_f 0.48 (single spot); mp 160 °C dec; ^1H NMR ($CDCl_3$) 6.54 (br m, 2 H), 3.60 (s, 6 H), 1.5–3.1 (br m, 13 H), 1.25 (s, 9 H); IR ($CHCl_3$) 3565, 3010, 2950, 1510, 1465, 1445, 1280, 910 cm^{-1}; mass spectrum (70 eV), *m/e* 382.1810 (M^+, 382.1814 calcd for $C_{20}H_{30}O_5S$). To a solution of oxalyl chloride (0.034 mL, 0.39 mmol) in CH_2Cl_2 (0.65 mL) under N_2 at −78 °C, was added dimethyl sulfoxide (0.055 mL, 0.78 mmol) dropwise over a 3-min period. After 15 min a solution of the previous product (0.100 g, 0.26 mmol) in methylene chloride (1.3 mL) was added with a double-ended needle. After 30 min, triethylamine (0.22 mL, 1.56 mmol) was added, and then after an additional 15 min, the mixture was warmed to 25 °C and quenched with 5% hydrochloric acid (0.65 mL). A standard workup provided 0.0970 g (93%, as estimated by ^1H NMR integration) of the ketone as a yellow solid which was used without further purification: TLC (silica gel, THF) R_f 0.55; ^1H NMR ($CDCl_3$) 6.60 (s, 2 H), 4.15 (br s, 1 H), 3.67 (s, 3 H), 3.60 (s, 3 H), 1.6–3.0 (br m, 10 H), 1.49 (s, 9 H); IR ($CHCl_3$) 3540, 3015, 2950, 1710, 1610, 1520, 1465, 1445, 1285, 1260, 910 cm^{-1}. To a solution of this

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product (0.097 g, 0.26 mmol) in methylene chloride (1.3 mL) at 25 °C under nitrogen was added DBU (0.072 mL, 0.51 mmol) dropwise. After 1.5 h, the mixture was diluted with methylene chloride and 5% hydrochloric acid. The crude product was isolated from the organic layer and was purified under nitrogen by flash chromatography (silica gel, 3% acetone/methylene chloride)[13] to give 0.071 g (81%) of **14c** as a yellow solid: mp 105–106 °C; TLC (3% acetone/methylene chloride) R_f 0.27 (single spot); ^{1}H NMR ($CDCl_3$) 7.71 (s, 1 H), 6.60 (s, 1 H), 3.80 (s, 3 H), 3.71 (s, 3 H), 1.6–2.8 (br m, 10 H); IR ($CHCl_3$) 3010, 2950, 1660, 1610, 1515, 1465 cm^{-1}; mass spectrum (70 eV), m/e 258.1248 (M^+, 258.1256 calcd for $C_{16}H_{18}O_3$).

The remaining compounds of this series were prepared by similar procedures on similar scales.

13. The crude product was purified by column chromatography (silica gel, 2% ethyl acetate/methylene chloride) or by recrystallization from 40% THF/hexane to give yellow crystals: mp 206–207 °C; TLC (silica gel, 5% ether/chloroform) R_f 0.40 (single spot); IR ($CHCl_3$) 5.9 μm; ^{1}H NMR ($CDCl_3$) 7.85 (s, 1 H), 6.3 (s, 1 H), 5.9 (s, 2 H), 3.25 (m, 8 H); ^{13}C NMR ($CDCl_3$) 205.9 (s), 172.78 (s), 146.16 (s), 147.5 (s), 134.75 (s), 128.57 (s), 122.98 (s), 108.40 (d), 105.15 (d), 100.88 (t), 35.84 (t), 28.98 (t), 27.91 (t), 27.14 (t); mass spectrum (70 eV), m/e 228.080 (M^+, 228.078 calcd for $C_{14}H_{12}O_3$).

14a. Purification was accomplished with high-performance LC (μ-Porasil, methylene chloride), affording a 67% yield of **14a** as a yellow solid: mp 64–66 °C; TLC (silica gel, methylene chloride) R_f 0.31 (single spot); ^{1}H NMR ($CDCl_3$) 7.90 (m, 1 H), 7.05 (m, 1 H), 1.70–2.80 (m, 10 H); IR ($CHCl_3$) 3010, 2950, 1660, 1595, 1485, 1450, 820 cm^{-1}; mass spectrum (70 eV), m/e 198.1047 (M^+, 198.1044 calcd for $C_{14}H_{14}O$). An analytically pure sample was obtained by repeating the high-performance LC purification as described above.

Anal. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.78; H, 7.30.

14b. The usual isolation procedure provided a 90% yield (^{1}H NMR) of **14b** as a yellow solid which could be recrystallized (albeit with low recovery) from 40% THF/hexane at −25 °C to give yellow crystals: mp 100–102 °C; TLC (silica gel, 10% acetone/methylene chloride) R_f 0.59 (single spot); ^{1}H NMR 7.91 (d, J = 8.5 Hz, 1 H), 6.70 (m, 2 H), 3.61 (s, 3 H), 1.6–2.8 (br m, 10 H); IR ($CHCl_3$) 3010, 2950, 1660, 1605, 1495 cm^{-1}; mass spectrum (70 eV), m/e 228.1133 (M^+, 228.1151 calcd for $C_{15}H_{16}O_2$).

14d. The same procedure afforded an 83% yield (^{1}H NMR) of **14d** as a deep yellow solid which could be recrystallized (low recovery) from 40% THF/hexane to give yellow crystals: mp 80–81 °C; TLC (silica gel, 2% ethyl acetate/methylene chloride) R_f 0.45 (single spot); ^{1}H NMR ($CDCl_3$) 7.7 (s, 1 H), 6.65 (s, 1 H), 5.95 (s, 2 H), 2.8–2.2 (br m, 8 H), 2.05 (m, 2 H); IR ($CHCl_3$) 3010, 2950, 1660, 1590, 1500, 1480 cm^{-1}; mass spectrum (70 eV), m/e 242.0960 (M^+, 242.0943, calcd for $C_{15}H_{14}O_3$).

Preparation of Naphthocycloalkenones. The following sample procedure is given for one of these dehydrogenations.

15. Through a solution of **13** (0.143 g, 0.63 mmol), methylene chloride (3 mL), and DBU (0.192 g, 1.26 mmol) at 25 °C was bubbled oxygen for 4 h. After an additional 24 h at 25 °C, the solution was subjected to a standard workup to yield 0.114 g (80%) of **15** as yellow crystals: mp 168–170 °C; TLC (silica gel, 5% ether/chloroform) R_f 0.45 (single spot); IR ($CHCl_3$) 5.85 μm; ^{1}H NMR ($CDCl_3$) 8.6 (s, 1 H), 7.9–7.3 (AB, 2 H), 7.15 (s, 1 H), 6.08 (s, 2 H), 3.3–2.7 (A_2B_2, 4 H); ^{13}C NMR ($CDCl_3$) 207.44 (s), 156.06 (s), 150.26 (s), 147.82 (s), 134.50 (d), 130.90 (s), 130.48 (s), 129.75 (s), 122.31 (d), 104.36 (d), 101.42 (d), 101.23 (t), 36.92 (t), 25.75 (t, CH_2); mass spectrum (70 eV), m/e 226.061 (M^+, 226.063 calcd for $C_{14}H_{10}O_3$).

16. The application of the same procedure as above converted **14d** into **16** in 77% yield as yellow crystals: mp 98–100 °C; TLC (silica gel, 30% THF/hexane) R_f 0.45 (single spot); IR ($CHCl_3$) 6.0 μm; ^{1}H NMR ($CDCl_3$) 8.95, (s, 1 H), 7.8–7.1 (AB, 2 H), 7.08 (s, 1 H), 6.05 (s, 2 H), 3.08 (t, 2 H), 2.75 (t, 2 H), 2.2 (m, 2 H); ^{13}C NMR ($CDCl_3$) 200.48 (s), 150.39 (s), 146.99 (s), 144.89 (s), 133.06 (d), 130.19 (d), 128.53 (s), 126.77 (s), 125.35 (d), 104.19 (d), 103.95 (d), 41.21 (t), 31.49 (t), 23.08 (t); mass spectrum (70 eV), m/e 240.077 (M^+, 240.078 calcd for $C_{15}H_{12}O_3$).

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Registry No. 5d, 66003-47-2; **5e**, 75534-18-8; **5f**, 75534-19-9; **5g**, 75548-48-0; **5h**, 75534-20-2; **8**, 75534-21-3; **9**, 75534-22-4; **11**, 75534-23-5; **12a**, 75534-24-6; **12b**, 75534-25-7; **12c**, 75534-26-8; **12d**, 75534-27-9; **13**, 75534-28-0; **14a**, 54558-75-7; **14b**, 41624-53-7; **14c**, 75534-29-1; **14d**, 75534-30-4; **15**, 75534-31-5; **16**, 75534-32-6; *tert*-butyl mercaptan, 75-66-1; 3-bromocyclohexene, 1521-51-3; 3-(*tert*-butylthio)cyclohexene, 75534-33-7; 2,3-epoxycyclohexyl *tert*-butyl sulfone, 75534-34-8; *tert*-butyldimethylchlorosilane, 18162-48-6; 3-methoxyphenylacetic acid, 1798-09-0; 2-(3-methoxyphenyl)ethanol, 5020-41-7; 2-(2-bromo-5-methoxyphenyl)ethanol, 75534-35-9; 1,2,3,4,4a,9,10,10a-octahydro-6,7-dimethoxy-10a-[(1,1-dimethylethyl)sulfonyl]-4-phenanthrenol, 75534-36-0; 2,3,4a,9,10,10a-hexahydro-6,7-dimethoxy-10a-[(1,1-dimethylethyl)sulfonyl]-4(1*H*)-phenanthrenone, 75534-37-1.

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Regio- and Stereochemistry of Dialkylcuprate Additions to Selected Alkylidene Oxiranes

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The stereochemistry of the vinyloxiranes obtained by the treatment of several alkylidene cyclohexanones with dimethylsulfonium methylide is discussed. The structure and stereochemistry of the products produced by treatment of the vinyloxiranes with lithium dibutyl- or dimethylcuprate are discussed.

The regio- and stereochemical course of the reaction of dialkylcuprates with allyl[3] and propargyl esters,[4] allyl carbamates,[5] propargyl ethers,[6] and propargyl-[7] and vinyloxiranes[8] has been well documented. In general, ad-

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