calcd for $C_{11}H_{10}S_5$ 301.9386, obsd 301.9383. Recently it has been found that trituration of a mixture of **21** and **22** with pentane and chilling at −20 °C gives pure crystalline **22**. Removal of the pentane under reduced pressure gives **21**.

Preparation of 2-Phenyl-*exo*-3,4,5-trithiatricyclo-[5.2.1.0^{2,6}]decane (24) (Table II, Line 11). Repetitive trituration with pentane and chilling at −20 °C gave a solid: mp 54–56 °C; ^{1}H NMR δ 5.30 (m, 5 H), 4.00 (d, J = 2.0 Hz, 1 H), 3.20 (s, 1 H), 2.48 (d, J = 10.8 Hz, 1 H), 2.38 (s, 1 H), 1.60 (m, 2 H), 1.40 (m, 1 H), 1.30 (d, J = 10.8 Hz, 1 H), 1.05 (m, 1 H); ^{13}C NMR 143.2 (s), 127.6, 126.8 (3C), 86.9 (s), 69.3 (d), 45.1 (d), 42.1 (d), 33.9 (t), 27.3 (t), 24.4 (t) ppm; IR (neat) 3050, 2950, 2850, 1660–1940 (weak overtones), 1590, 1480, 1460, 1440, 1300, 1160, 1025, 900, 750, 700, 640 cm^{-1}; mass spectrum, m/e calcd for $C_{13}H_{14}S_3$ 266.0257, obsd 266.0249; M_r calcd 266, obsd 264.

Preparation of 2-*p*-Anisyl-*exo*-3,4,5-trithiatricyclo-[5.2.1.0^{2,6}]decane (25) (Table II, Line 12). **26** (380 mg, 65%) was isolated as a yellow oil: ^{1}H NMR δ 7.20 (m, 2 H), 6.83 (m, 2 H), 3.95 (d, J = 2.0 Hz, 1 H), 3.80 (s, 3 H), 3.20 (s, 1 H), 2.50 (d, J = 10.8 Hz, 1 H), 2.38 (s, 1 H), 1.30–1.75 (s of m, 3 H), 1.25 (d, J = 10.8 Hz, 1 H), 1.10 (m, 1 H); ^{13}C NMR 158.43 (s), 135.49 (s), 128.36 (d), 115.24 (d), 86.92 (s), 69.46 (d), 55.20 (q), 45.32 (d), 42.19 (d), 34.09 (t), 27.37 (t), 24.40 (t) ppm; IR (neat) 3025, 2950, 1600, 1500, 1450, 1260, 1180, 1030, 900, 820, 740 cm^{-1}; MS (70 eV), M$^+$ not observed, m/e 200 (30%) was observed indicating immediate loss of sulfur followed by a loss of ethylene to give m/e 172 (100%). Anal. Calcd for $C_{14}H_{16}OS_3$: C, 56.8; H, 5.4; S, 32.4. Found: C, 56.8; H, 5.7; S, 32.7.

Preparation of 1,2,3,4,9,10-Hexahydro-9,10-*exo*-epoxy-1,4-*exo*-methano-4a,9a-*exo*-trithiaanthracene (29) (Table II, Line 13). Chromatography over silica gel with pentane/Et_2O (65:35) as eluant gave 20 mg of **29** as a viscous oil, yield 46%: ^{1}H NMR δ 7.35 (m, 2 H), 7.20 (m, 2 H), 5.60 (s, 2 H), 3.15 (d, J = 10.4 Hz, 1 H), 2.58 (m, 2 H), 1.25 (m, 2 H), 1.10 (d, J = 10.4 Hz, 1 H), 0.75 (m, 2 H); ^{13}C NMR 147.18 (s), 126.51 (d), 121.90 (d), 91.84 (s), 91.53 (d), 45.75 (t), 46.41 (d), 22.88 (t) ppm; IR (neat) 3005, 2900, 1640, 1450, 1320, 1200, 900, 720 cm^{-1}; mass spectrum, m/e calcd for $C_{15}H_{14}OS_3$ 306.0206, obsd 306.0201.

Preparation of 1,2,3,4,9,10-Hexahydro-1,4-*exo*-methano-9,10-*exo*-methano-4a,9a-*exo*-trithiaanthracene (33) and 1,2,3,4,9,10-Hexahydro-1,4-*exo*-methano-9,10-*endo*-methano-4a,9a-*exo*-trithiaanthracene (34). A mixture of **31** and **32** (200 mg, 1 mmol) (**38**/**39** = 2.0) and 150 mg (4.7 mmol) of sulfur in 8 mL of DMSO was heated at 100 °C under an atmosphere of N_2 for 8 h. The reaction mixture was poured into 20 mL of ice-cold water. This was then extracted twice with 15 mL of ether. The ethereal layer was washed with brine and dried over Na_2SO_4. The crude, obtained after removal of the ether under reduced pressure, was chromatographed over silica gel by using CCl_4/petroleum ether (4:1) as eluant, to give 20 mg of **34** and 50 mg of **33**. Total yield of **33** and **34** was 23%.

For 34 (R_f 0.39): ^{1}H NMR δ 7.00 (m, 2 H), 6.90 (m, 2 H), 3.40 (s, 2 H), 2.80 (d, J = 10.3 Hz, 1 H), 2.70 (s, 2 H), 2.50 (d, J = 11.2 Hz, 1 H), 1.90 (d, J = 11.2 Hz, 1 H), 1.70 (m, 4 H), 1.20 (d, J = 10.3 Hz, 1 H); ^{13}C NMR 147.44, 125.63, 123.70, 89.59, 52.07, 50.63, 47.69, 43.69, 24.43 ppm; IR (CCl_4) 3080, 1450, 1260, 970 cm^{-1}; mass spectrum, m/e calcd for $C_{16}H_{16}S_3$ 304.0414, obsd 304.0413.

For 33 (R_f 0.53): ^{1}H NMR δ 7.20 (m, 2 H), 7.05 (m, 2 H), 3.90 (d, J = 9.8 Hz, 1 H), 3.70 (s, 2 H), 3.25 (d, J = 10.3 Hz, 1 H), 2.70 (s, 2 H), 1.85 (d, J = 9.8 Hz, 1 H), 1.10 (d, J = 10.3 Hz, 1 H), 0.85 (m, 4 H); ^{13}C NMR 148.18, 125.70, 123.10, 93.20, 59.39, 56.63, 49.64, 45.63, 24.65 ppm; IR (neat) 3000, 1450, 1260, 900, 750 cm^{-1}; mass spectrum, calcd for $C_{16}H_{16}S_3$ 304.0414, obsd 304.0417.

Both **33** and **34** when left for extended periods of time at room temperature became glassy solids, insoluble in $CDCl_3$.

Acknowledgment. We thank the Robert A. Welch Foundation for support of this work. We are grateful to Professor Shigeru Oae for suggesting the initial experiments.

Supplementary Material Available: Tables of ^{1}H NMR chemical shifts in the trithiolanes and pentathiepanes, significant ^{1}H and ^{13}C chemical shifts for **5** and **6**, and NMR and MS data of polysulfides obtained in the sulfuration of norbornadiene (3 pages). Ordering information is given on any current masthead page.

Construction of Five-Membered Rings by Michael Addition-Radical Cyclization

Derrick L. J. Clive,* Taryn L. B. Boivin, and A. Gaëtan Angoh

Chemistry Department, University of Alberta, Edmonton, Alberta, Canada T6G 2G2

Received March 4, 1987

Enamines react with Michael acceptors **8–10** to produce ketones that, on treatment with lithium acetylides, afford hydroxy acetylenes **3**. These compounds then undergo radical cyclization when treated with triphenyltin hydride and AIBN. The products **6** are formed by 5-exo–digonal closure and furnish substituted cyclopentanones by ozonolysis.

Until recently, most procedures used in synthesis for making carbon–carbon bonds were based on ionic or concerted reactions, and the possibility of using free radicals was not widely recognized—at least outside the area of polymer chemistry.[1] This situation is now changing, and free-radical methods[2] for making carbon–carbon bonds will, undoubtedly, come to occupy an important place in organic synthesis. There already exists extensive modern literature[2,3] on *intermolecular* reactions (e.g., eq 1, A = electron-withdrawing group), and there is a rapidly growing interest[2,4,5] in the synthetic utility of intramolecular cy-

(1) For early, isolated examples of the synthetic use of radicals to make carbon–carbon bonds, see: (a) Bakuzis, P.; Campos, O. O. S.; Bakuzis, M. L. F. *J. Org. Chem.* **1976**, *41*, 3161. (b) Büchi, G.; Wüest, H. *Ibid.* **1979**, *44*, 546. See also: Julia, M. *Acc. Chem. Res.* **1971**, *4*, 386.

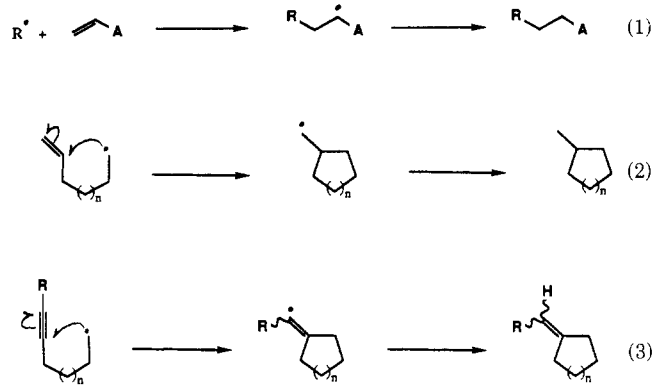
(2) Giese, B. *Radicals in Organic Synthesis*: Formation of Carbon–Carbon Bonds; Pergamon: Oxford, 1986.

(3) Giese, B. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 753.

(4) (a) Hart, D. J. *Science (Washington, D.C.)* **1984**, *223*, 883. (b) Surzur, J.-M. In *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum: New York, 1982; Chapter 3.

0022-3263/87/1952-4943$01.50/0

clizations of the types shown in eq 2 and 3.



In regard to the radical cyclization, at least three areas of research can be discerned in recent publications: (i) development of methods to render members of the common compound types easily amenable to the technique of radical cyclization.[6] (ii) study of the characteristics of the ring closure itself.[7] (iii) use of radical cyclization in the synthesis of complex molecules.[5]

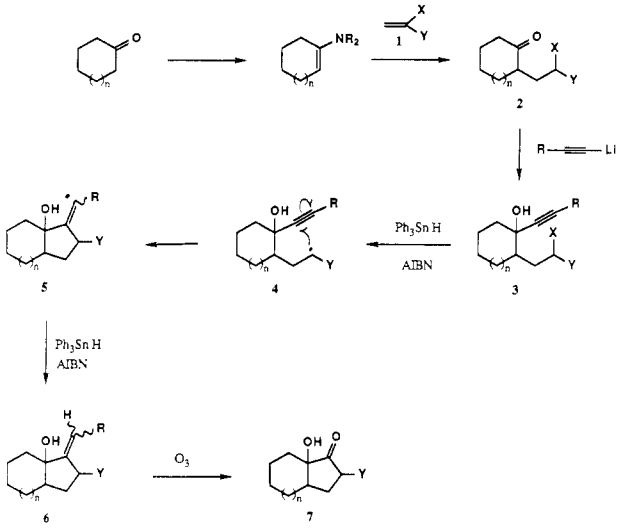
Naturally, the last of these areas depends on the status of the other two, and while considerable mechanistic information is available on radical cyclization,[7] there is an obvious need for the development of simple methods that allow the process to be applied to those classes of compounds such as olefins,[8] ketones,[5d,9] acids,[10] and allylic alcohols[6] that are encountered most frequently in synthesis.

In this context, we report full details of our work[9a] on the Michael addition–radical cyclization sequence (Scheme I). In the first step a ketone is converted into its enamine, which is then allowed to react with a Michael acceptor **1** carrying groups X and Y that are chosen on the basis of criteria described below. The adduct **2** is treated with a lithium acetylide (**2** → **3**) to produce an acetylene in which the triple bond is suitably located to capture the radical (see **4**) produced by treatment with a stannane (**3** → **4**). Ring closure (**4** → **5** → **6**) then affords material that can be cleaved (**6** → **7**) by ozonolysis to a cyclopentanone.

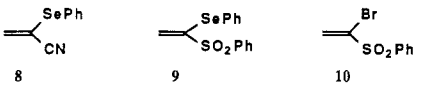
Results and Discussion

The requirements of the Michael acceptor **1** are that it should react in the desired sense with enamines,[11] it should contain a group X of such a nature that the bond C–X undergoes homolysis on treatment with a stannyl radical $R_3Sn^{\bullet}$, and it should contain a substituent Y that can be

Scheme I



used as a starting point for further manipulation. We have used the values X = Br and SePh,[12] and we examined the three Michael acceptors **8**,[13] **9**,[14] and **10**.[15] These are



readily prepared in two steps, as follows: Reaction of benzeneselenenyl chloride with an excess[16] of acrylonitrile and base-induced elimination of hydrogen chloride from the product gives **8**. Compound **9** is similarly prepared from phenyl vinyl sulfone and benzeneselenenyl bromide. Likewise, compound **10** is available by the successive action of bromine and base on the sulfone.

Each of these substances undergoes the classic[17] Michael reaction with enamines to afford ketones after mild aqueous hydrolysis. The ketones we prepared were made from pyrrolidine enamines and are shown in Table I. As expected, each ketone was obtained as a mixture of diastereomers, four in the case of **20a**[18] and two in each of the other examples.

Each Michael adduct was treated with lithium phenylacetylide, and some (see Table I) were also treated with the lithium salts of the acetylenes **25** and **26**. In no case

were any problems experienced due to deprotonation α to the carbonyl or at the other acidic center. The acetylenic unit should be properly constituted to facilitate the ring closure (see Scheme I, **4** → **5**), and, since disubstituted acetylenes undergo radical cyclization appreciably faster

(5) Recent examples: (a) Stork, G.; Sofia, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 6826. (b) Hart, D. J.; Huang, H.-C. *Tetrahedron Lett.* **1985**, *26*, 3749. (c) Curran, D. P.; Rakiewicz, D. M. *Tetrahedron* **1985**, *41*, 3943. (d) Hanessian, S.; Beaulieu, P.; Dubé, D. *Tetrahedron Lett.* **1986**, *27*, 5071. (e) Wilcox, C. S.; Gaudino, J. J. *J. Am. Chem. Soc.* **1986**, *108*, 3102. (f) Clive, D. L. J.; Angoh, A. G.; Bennett, S. M. *J. Org. Chem.* **1987**, *52*, 1339.

(6) E.g.: (a) Mohammed, A. Y.; Clive, D. L. J. *J. Chem. Soc., Chem. Commun.* **1986**, 588. (b) Stork, G.; Mook, R., Jr.; Biller, S. A.; Rychnovsky, S. D. *J. Am. Chem. Soc.* **1983**, *105*, 3741.

(7) Beckwith, A. L. J. *Tetrahedron* **1981**, *37*, 3073.

(8) (a) Clive, D. L. J.; Beaulieu, P. L. *J. Chem. Soc., Chem. Commun.* **1983**, 307. (b) Clive, D. L. J.; Beaulieu, P. L.; Set, L. *J. Org. Chem.* **1984**, *49*, 1313. (c) Angoh, A. G.; Clive, D. L. J. *J. Chem. Soc., Chem. Commun.* **1985**, 980.

(9) (a) Angoh, A. G.; Clive, D. L. J. *J. Chem. Soc., Chem. Commun.* **1985**, 941. (b) Set, L.; Cheshire, D. R.; Clive, D. L. J. *Ibid.* **1985**, 1205.

(10) Bennett, S. M.; Clive, D. L. J. *J. Chem. Soc., Chem. Commun.* **1986**, 878.

(11) Cf.: (a) Madsen, J. O.; Lawesson, S.-O. *Bull. Soc. Chim. Belg.* **1976**, *85*, 805. (b) Cook, A. G. *Enamines: Synthesis, Structure and Reactions*; Marcel Dekker: New York, 1969; p 16.

(12) Clive, D. L. J.; Chittattu, G. J.; Farina, V.; Kiel, W. A.; Menchen, S. M.; Russell, C. G.; Singh, A.; Wong, C. K.; Curtis, N. J. *J. Am. Chem. Soc.* **1980**, *102*, 4438.

(13) Janousek, Z.; Piettre, S.; Gorissen-Hervens, F.; Viehe, H. G. *J. Organomet. Chem.* **1983**, *250*, 197.

(14) Piettre, S.; Janousek, Z.; Merenyi, R.; Viehe, H. G. *Tetrahedron* **1985**, *41*, 2527.

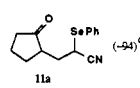
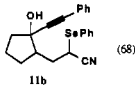
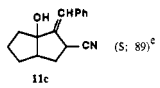
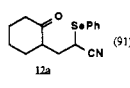
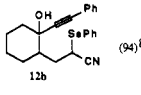
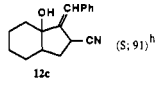
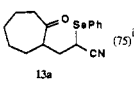
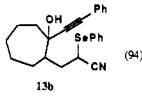
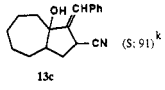
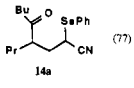
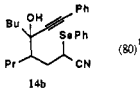
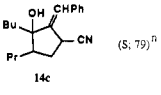
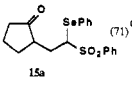
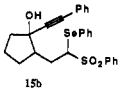
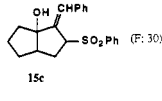
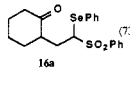
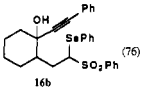
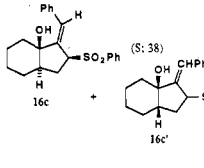
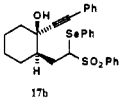
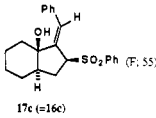
(15) Carlier, P.; Gelas-Mialhe, Y.; Vessiere, R. *Can. J. Chem.* **1977**, *55*, 3190.

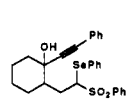
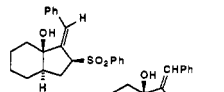
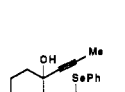
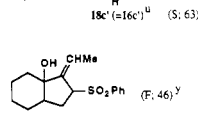
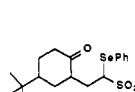
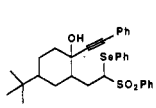
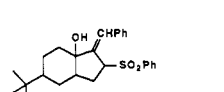
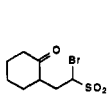
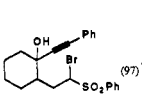
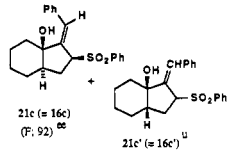
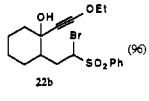
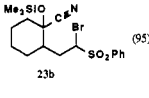
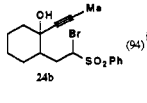
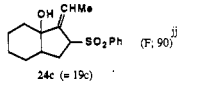
(16) It is essential to use a large (10-fold) excess of acrylonitrile in acetonitrile at 65 °C.

(17) Stork, G.; Brizzolara, A.; Landesman, H.; Szmuszkovicz, J.; Terrell, R. *J. Am. Chem. Soc.* **1963**, *85*, 207. Barieux, J.-J.; Gore, J. *Bull. Soc. Chim. Fr.* **1971**, 1649.

(18) For a discussion of the stereoselectivity of enamine reactions, see: Hickmott, P. W. *Tetrahedron* **1982**, *38*, 1975. Hickmott, P. W. *Ibid.* **1982**, *38*, 3363.

Table I[a]

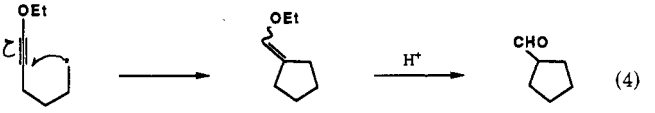
Ketone[b] (% Yield)	Cyclization Precursor (% Yield)	Cyclization Product [Slow (S) or Fast (F) Addition; % Yield]
 11a (~94)[c]	 11b (68)[d]	 11c (S; 89)[e]
 12a (91)[f]	 12b (94)[g]	 12c (S; 91)[h]
 13a (75)[i]	 13b (94)[j]	 13c (S; 91)[k]
 14a (77)[l]	 14b (80)[m]	 14c (S; 79)[n]
 15a (71)[o]	 15b (79)[p] (100)[q]	 15c (F; 30)[r]
 16a (73)[s]	 16b (76)[t]	 16c (S; 38) + 16c' (S; 31)[u]
 17a (=16a) 17b (24)[v]		 17c (=16c) (F; 55) (90)[q]

Ketone[b] (% Yield)	Cyclization Precursor (% Yield)	Cyclization Product [Slow (S) or Fast (F) Addition; % Yield]
18a (= 16a)	 18b (51)[w]	 18c (= 16c) (S; 12) + 18c' (=16c')[u] (S; 63)
19a (= 16a)	 19b (89)[x]	 19c (F; 46)[y]
 20a (98)[z]	 20b (79)[aa]	 20c (F; 65)[bb]
 21a (80)[cc]	 21b (97)[dd]	 21c (= 16c) (F; 92)[ee] + 21c' (= 16c')[u]
22a (= 21a)	 22b (96)[ff]	—[gg]
23a (= 21a)	 23b (95)[hh]	0[gg]
24a (= 21a)	 24b (94)[ii]	 24c (= 19c) (F; 90)[jj]

[a] Except where indicated, yields refer to isolated products. [b] Ketones were prepared from the corresponding pyrrolidine enamines. [c] Slight impurities. Two isomers (1:1.1). [d] 68% from enamine. Two isomers (~1:1). [e] At least three isomers. [f] Two isomers (1:1). [g] Four isomers (~2.2:1.9:1.6:1). [h] At least six isomers. [i] Two isomers (~1:1.4). [j] Two main isomers (~1:1.1); less than 7.5% of two other isomers. [k] At least three isomers. [l] Two isomers (~1:2). [m] Two isomers (1:1); trace of other isomers. [n] At least six isomers. [o] Two isomers (1:1) separated into two fractions: higher R_f (21% yield) corresponding to one isomer; lower R_f (50% yield) corresponding to a mixture of both isomers. [p] Four isomers (1:2.3:3.7:4.3). [q] Corrected for recovered starting material. [r] Mainly one isomer; yield *before* correction for recovered starting material, 25%. [s] Two isomers (1:1). [t] Four isomers (2.5:2.75:2.5:1). [u] One isomer. [v] One crystalline isomer obtained in 32% yield from **16b** (24% from **16a**). [w] Three isomers (3.8:1.8:1) obtained in 67% yield by evaporation of mother liquors from crystallization of **16b** (51% from **16a**). [x] Three isomers; the two major components being in a ratio of 1:1.4. [y] Obtained as two fractions: higher R_f (13% yield) was a mixture of two isomers (1:1); lower R_f (23% yield) was a mixture of two other isomers (1:1.6). [z] Four isomers (6.3:4.9:2.1:1). [aa] Four isomers (2.7:1.3:2:1). [bb] Three isomers (3:2:1). [cc] Two isomers (1:1). [dd] Four isomers (3:2:2.3:1). [ee] Combined yield of **21c** and **21c'**. Ratio of **21c** to **21c'** 2.3:1. [ff] Four isomers (4.8:3.9:4.7:1). [gg] See the text. [hh] Three main isomers (4.3:2.5:1); trace of a fourth isomer. [ii] Three isomers (2:1:1.3). Material that was largely one isomer was obtained by crystallization. [jj] Four isomers (1:1.6:2.2:4.2) identical with **19c**.

than terminal acetylenes,[19] we did not examine the use of acetylene itself (for production of compounds of type **3**, R = H).

After radical cyclization, the carbon originally carrying the substituent R (see **3**, Scheme I) has changed from sp to sp^2 hybridization. The nature of the substituent should allow cleavage of the double bond to a ketone[20] and, preferably, should allow other reactions as well. To this end we examined acetylene **26**, the specific aim being to develop an aldehyde synthesis along the lines of eq 4.



(4)

There exists close analogy in the literature[21] for the radical closure, but with the example we studied (compound **22b**, see Table I), our attempts to carry out the cyclization were unpromising and gave complex mixtures.

Table I lists the hydroxy acetylenes that we prepared as well as one example of a hydroxy nitrile (compound **23b**) that was also anticipated[8b] to be suitable for our purposes. (In the event, however, **23b** did not undergo cyclization.[22])

(19) For example, the cyclization shown in (i) is 39 times as fast as that shown in (ii): Crandall, J. K.; Michaely, W. J. *J. Org. Chem.* **1984**, *49*, 4244.

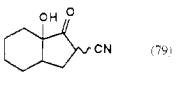
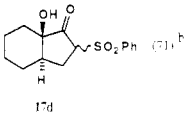
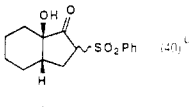
i ii

(20) R = SiR'_3 is not ideal: Büchi, G.; Wüest, H. *J. Am. Chem. Soc.* **1978**, *100*, 294.

(21) Ohnuki, T.; Yoshida, M.; Simamura, O. *Chem. Lett.* **1972**, 797.

(22) 5-Exo closure of a radical onto a nitrile triple bond is slower than onto a terminal acetylene: Griller, D.; Schmid, P.; Ingold, K. U. *Can. J. Chem.* **1979**, *57*, 831.

Table II

Cyclization Product	Ozonolysis Product (% Yield)[a]
12c	 (79)
	12d
17c	 (71)[b]
	17d
16c + 16c'	16d (≡17d) (27)[b] +  (40)[c]
	16d'

[a] Yields refer to isolated material. [b] Two isomers (1:1.1). [c] Two isomers.

In all cases these hydroxy compounds were obtained as isomer mixtures in the ratios given in the table. Except for one case (**17b**, see below), we did not establish the relative stereochemistry of the two pendant groups now attached to the original ketone skeleton. Some stereoselectivity was observed, as shown by the isomer ratios, but the stereochemistry of the major isomers could not be predicted with confidence from information available[23] on the geometric course of nucleophilic addition of acetylides to α-substituted cycloalkanones.

In **11b** the pendant chains are probably cis, the reason for this tentative assignment being that the yield for the cyclization **11b** → **11c** is high (89%) and material with trans-disposed pendants would not be expected[24] to undergo the radical closure effectively.

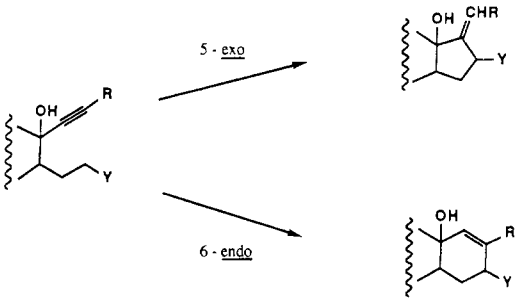
When the hydroxy acetylenes **16b** were dissolved in a mixture of dichloromethane and hexane, one isomer, **17b**, with the partial stereostructure shown (Table I), was obtained crystalline in an amount corresponding to 32% of the original mixture **16b**. The structure of **17b** followed from an X-ray crystallographic analysis of its radical cyclization product **17c** (Table I). The mother liquors from the crystallization of **16b** contained three isomers (**18b**) in a ratio of 3.8:1.8:1. The majority of the species present in this material had cis stereochemistry. This was deduced by radical cyclization to **18c'** (≡**16c'**) (63%) and **18c** (≡**16c**) (12%) followed by ozonolysis of the major product **18c'**. Two isomeric ketones (see Table II, **16d'**) were obtained that were different from the two produced by ozonolysis of compound **17c**, for which an X-ray crystal structure had been obtained.

With the acetylenes in hand, we next examined the radical cyclization (**3** → **4** → **5** → **6**, Scheme I). Two experimental procedures were adopted. In the first of these (slow addition) separate dilute benzene solutions of triphenyltin hydride and of AIBN were injected simultaneously over about 8 h into a refluxing solution of the selenide or bromide in the same solvent. The second method (fast addition), which was tried only with the sulfones, involved adding all of the stannane and AIBN in one portion at the beginning of the experiment. Our results are shown in Table I (**11c–24c**).

The selection of triphenyl- as opposed to tributyltin hydride was made on the following basis: When the stannane reduction of selenides was developed here,[12] most of the examples were such that the reaction products were devoid of aromatic hydrogens. Consequently, use of triphenyltin hydride offered a convenient spectroscopic method for proving the absence of organotin compounds in the reduction products—the low-field region of the ^{1}H NMR spectrum was devoid of signals if the material was pure. We continued to use triphenyltin hydride because it proved satisfactory in that earlier work. The aromatic stannane is less volatile than its aliphatic analogue; this can be an advantage, though a minor one.

The fact that the experimentally convenient technique of fast addition is successful shows that α-sulfonyl carbon radicals cyclize onto the substituted triple bond faster than they abstract hydrogen from the stannane—at least at the prevailing initial concentration (ca. 0.2 M) of the stannane.

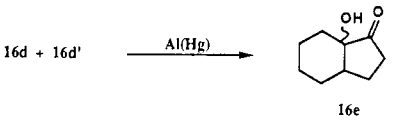
In the early stages of this work we were concerned about the regiochemistry of the cyclization, as both 5-exo (which was observed) and 6-endo closures are allowed (eq 5).[25]



(5)

Compound **17c** (Table I) was obtained crystalline; its structure was determined by X-ray diffraction analysis.

Compounds **12c**, **17c**, and a mixture of **16c** and **16c'** were ozonized on an appropriate scale to warrant isolation of the products (Table II), which were easily identified as cyclopentanones by IR measurements. In these cases (Table II), the major cyclization pathway, if not all of it, must have been of the 5-exo type. The ozonolysis experiments serve to show that the radical cyclization products are synthetically equivalent to ketones. The sulfone unit is available for further manipulation, or it can be removed.[26] For example, a mixture of isomers corresponding to **16c** and **16c'** was ozonized, and the resulting ketones were treated with aluminum amalgam. Cis and trans ring-fused ketones **16e** were produced (eq 6).



(6)

16e

Compounds **19b** and **24b** closed only in the desired fashion as the vinyl signals of the products had coupling constants (ca. 7 Hz) that defined the presence of ethylidene groups, as required by 5-exo closure. The chemical shifts of the vinylic signals of **11c**, **13c**, **14c**, **15c**, and **20c** were all similar to those of the compounds for which structures were determined by ozonolysis or X-ray analysis, and the structural assignments shown were based on this fact.[27]

(23) Ashby, E. C.; Laemmle, J. T. *Chem. Rev.* **1975**, *75*, 521.
(24) Beckwith, A. L. J.; Roberts, D. H.; Schiesser, C. H.; Wallner, A. *Tetrahedron Lett.* **1985**, *26*, 3349.
(25) Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 734.
(26) Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1965**, *87*, 1344.
(27) The chemical shift of the vinylic proton in 1-phenylcyclohexene is δ 6.0 ($CDCl_3$): Yamamoto, H.; Miura, M.; Nojima, M.; Kusabayashi, S. *J. Chem. Soc., Perkin Trans. 1* **1986**, 173. In benzylidenecyclopentane it is δ 6.34 ($CDCl_3$): Moore, W. M.; Salajegheh, A.; Peters, D. G. *J. Am. Chem. Soc.* **1975**, *97*, 4954.

Conclusion

The Michael addition–radical cyclization sequence summarized in Scheme I, especially with R = Ph, is a simple method for construction of five-membered rings, which, on ozonolysis, give cyclopentanones bearing substituents that can be used in further reactions.

Experimental Section

Unless otherwise stated the following particulars apply. Experiments were carried out under argon that was purified by passage through a column (3.5 × 42 cm) of R-311 catalyst[28] and then through a similar column of Drierite.

Glassware was dried in an oven for at least 3 h (130 °C), cooled in a desiccator, quickly assembled, and sealed with rubber septa (when applicable). Inlet and exit needles for argon were passed through a septum on the apparatus, and argon was purged through the system. The exit needle was removed, and the apparatus was kept under a slight static pressure of argon. Stirring was effected by using a dry, Teflon-coated magnetic stirring bar.

Solvents were distilled before use for chromatography or extractions. Where required, solvents and reagents were dried with suitable drying agents and distilled under argon. Dry tetrahydrofuran and benzene were distilled from sodium–benzophenone ketyl; triethylamine was distilled from calcium hydride. Commercial solutions (Aldrich) of *n*-butyllithium in hexanes were titrated before use by the diphenylacetic acid method.[29] Azobis(isobutyronitrile) (AIBN) from Eastman was used without further purification and stored at 5 °C.

Products were isolated from solution by concentration under water pump vacuum at 30 °C using a rotary evaporator. Where compounds were isolated by simple evaporation of their solutions, the residues were kept under vacuum (<0.1 mmHg) until of constant weight. Melting points were measured with a Kofler block melting point apparatus. Boiling points quoted for products distilled in a Kugelrohr apparatus refer to the oven temperature.

Commercial silica (Merck 60F-254) thin-layer chromatography (TLC) plates were used. Silica gel for flash column chromatography was Merck type 60 (230–400 mesh). TLC plates were examined under UV radiation (254 nm), treated with iodine vapor, and charred on a hot plate after being sprayed with sulfuric acid (6 N in methanol).

Combustion elemental analyses were performed in the microanalytical laboratories of the University of Alberta or by Butterworth Laboratories Ltd. in England. Infrared spectra were recorded on a Perkin-Elmer 297 spectrophotometer or a Nicolet 7000 FT-IR model. Liquids were run as neat films on potassium chloride plates, and solids were run as solutions in the specified solvent in 0.5-mm potassium chloride cells. Proton NMR spectra were recorded on a Bruker WH-200 (at 200 MHz), Bruker AM300 (at 300 MHz), or Bruker WH-400 (at 400 MHz) spectrometer in the specified deuteriated solvent with tetramethylsilane (TMS) as an internal standard. ^{13}C NMR spectra were recorded on a Bruker HFX-90 (at 22.6 MHz), Bruker WH-200 (at 50.3 MHz), Bruker AM300 (at 75.5 MHz), or Bruker WH-400 (at 100.6 MHz) spectrometer in deuteriated chloroform with TMS as an internal standard. The following abbreviations are used in the text: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Mass spectra were recorded on an A.E.I. MS50 mass spectrometer at an ionizing voltage of 70 EV.

2-(Phenylseleno)-2-propenenitrile (8).[13] Acrylonitrile (3.62 g, 68.4 mmol) was added to a solution of phenylselenenyl chloride (1.31 g, 6.84 mmol) in dry acetonitrile (15 mL), and the mixture was heated at 65 °C for 15 h and cooled to room temperature. Triethylamine (1.43 mL, 10.2 mmol) in benzene (25 mL) was added, and the resulting mixture was stirred for a further 10 h. The suspension was filtered with hexane. Evaporation of the solvent and flash chromatography of the residue over silica gel (3 × 15 cm) first with 1% ethyl acetate–hexane (to elute diphenyl diselenide) and then with 5% ethyl acetate–hexane gave **8** as a pale yellow oil: 1.24 g (88%); IR (neat) 2220, 1690, 740, 690 cm^{-1}; ^1H NMR ($CDCl_3$, 80 MHz) δ 6.10 (s, 1 H), 6.55 (s, 1 H), 7.20–7.55 (m, 5 H). The compound was used immediately in the next stage.

[[1-(Phenylseleno)ethenyl]sulfonyl]benzene (9).[14] A solution of phenyl vinyl sulfone[30] (10.76 g, 0.064 mol) in dry carbon tetrachloride (25 mL) was added dropwise to a stirred solution (200 mL) of phenylselenenyl bromide (16.26 g, 0.064 mol) in the same solvent. The mixture was then refluxed for 18 h, cooled to room temperature, and concentrated under reduced pressure to afford [[2-bromo-1-(phenylseleno)ethyl]sulfonyl]benzene. Triethylamine (8.95 mL, 0.064 mol) in dry benzene (200 mL) was added, and the mixture was stirred at room temperature for 18 h. The resulting suspension was filtered, the solvent was evaporated, and the residue was redissolved in dichloromethane (100 mL). The organic layer was washed with water (3 × 20 mL), dried ($MgSO_4$), and evaporated. Flash chromatography of the resulting dark red solid in three portions, each over silica gel (5 × 15 cm), using 20% ethyl acetate–hexane, followed by crystallization from ether afforded **9** (15.3 g, 74%) as a white solid: mp 68–69 °C (lit.[14] mp 68–69 °C); IR (CCl_4) 3070, 1475, 1448, 1440, 1328, 1165, 1080, 692, 612 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 5.86 (d, J = 2 Hz, 1 H), 6.98 (d, J = 2 Hz, 1 H), 7.22 (m, 5 H), 7.50 (m, 3 H), 7.80 (m, 2 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz), δ 121.3, 128.8, 129.0, 129.7, 130.7, 133.7, 134.5. Anal. Calcd for $C_{14}H_{12}O_2SSe$: C, 52.02; H, 3.74. Found: C, 52.08, H, 3.69.

A small amount of the intermediate bromide did not react with the triethylamine and was isolated: ^1H NMR ($CDCl_3$, 80 MHz) δ 3.55 (t, J = 10 Hz, 1 H), 4.25 (m, 2 H), 7.05–8.15 (m, 10 H).

[(1-Bromoethenyl)sulfonyl]benzene (10).[15] A solution of bromine (5 mL, 20% w/v in carbon tetrachloride, 19.4 mmol) was added dropwise to a carbon tetrachloride solution (10 mL) of phenyl vinyl sulfone[30] (2.56 g, 15.2 mmol) at room temperature. The mixture was stirred for 8 h, and then additional bromine (2.5 mL of the stock solution) was added in one portion and, after a further 15 h, the solvent was evaporated. The residue was crystallized twice from dichloromethane–ether to give the corresponding dibromide (3.65 g, 73%) as a white solid: mp 74–75 °C (lit.[15] mp 73–75 °C); IR (CCl_4) 1450, 1347, 1343, 1195, 633 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.60, (dd, J = 11.5, 10.0 Hz, 1 H), 4.28 (dd, J = 11.5, 3.0 Hz, 1 H), 4.96 (dd, J = 10.0, 3.0 Hz, 1 H), 7.63 (m, 2 H), 7.76 (m, 1 H), 7.99 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 29.3, 65.1, 129.3, 129.4, 130.1, 135.1; MS (chemical ionization, NH_3), m/z 344, 346 (M + 18).

Triethylamine (0.54 mL, 3.87 mmol) was added dropwise over 5 min to a stirred solution of the dibromide (1.06 g, 3.23 mmol) in dry dichloromethane (20 mL), and stirring was continued at room temperature for 18 h. The solution was then washed with water (3 × 5 mL), dried ($MgSO_4$), and evaporated. Flash chromatography of the dark brown residue over silica gel (4 × 15 cm) using 15% ethyl acetate–hexane afforded **10** (706.2 mg, 88%) as a white solid: mp 36–37 °C (lit.[15] mp 42–44 °C); IR (CCl_4) 1448, 1353, 1337, 1165, 1076, 936, 680, 610, 560 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.30 (d, J = 3 Hz, 1 H), 7.14 (d, J = 3 Hz, 1 H), 7.60 (m, 2 H), 7.72 (m, 1 H), 7.98 (m, 2 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 129.1, 129.2, 129.7, 134.3, 136.4; exact mass, m/z calcd for $C_8H_7{}^{81}BrO_2S$ 247.9329, found 247.9329. Satisfactory combustion analytical values could not be obtained.

3-(2-Oxocyclopentyl)-2-(phenylseleno)propanenitrile (11a). 2-(Phenylseleno)-2-propenenitrile (8; 325 mg, 1.56 mmol) in dry THF (2 mL + 1 mL rinse) was injected dropwise at room temperature into a stirred solution of freshly distilled 1-(1-cyclopenten-1-yl)pyrrolidine[17] (178 mg, 1.30 mmol) in THF (8 mL). The mixture was stirred for 3 h, water (10 mL) was added, and stirring was continued for an additional 30 min. The mixture was extracted with ether (3 × 25 mL), dried ($MgSO_4$), and evaporated. Flash chromatography of the crude product over silica gel (2 × 15 cm) using 20% ethyl acetate–hexane gave **11a** (360 mg, 94%) as a mixture of isomers in a 1:1.1 ratio (^1H NMR). The sample contained trace impurities as judged by ^1H and ^{13}C NMR: IR (CCl_4) 2220, 1735, 1575, 740, 690 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.4–1.6 (m, 1 H), 1.8 (m, 2 H), 2.0–2.50 (m, 6 H), 3.93 (dd, J = 8, 8.5 Hz, 0.4 H), 4.03 (dd, J = 9.6, 6.3 Hz, 0.6 H), 7.43 (m, 3 H), 7.72 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 20.2, 20.3, 23.5, 23.7, 23.8, 29.1, 29.5, 32.6, 33.3, 37.4, 46.5, 46.6, 47.2, 53.7, 119.7, 125.3, 129.2, 129.3, 129.4, 129.5, 136.1, 136.2, 135.6, 218.4, 218.7; exact mass, m/z calcd for $C_{14}H_{15}NOSe$ 293.0319, found 293.0319.

(28) Supplied by Chemical Dynamics Corp., South Plainfield, NJ.
(29) Kofron, W. G.; Baclawski, L. M. *J. Org. Chem.* **1976**, *41*, 1879.
(30) Kende, A.; Paquette, L. A.; Carr, R. V. C. *Org. Synth.* **1985**, *64*, 157.

Satisfactory combustion analytical values could not be obtained.

3-(2-Oxocyclohexyl)-2-(phenylseleno)propanenitrile (12a). The procedure employed for **11a** was followed using 2-(phenylseleno)-2-propenenitrile (**8**; 275 mg, 1.31 mmol) in THF (2 mL + 1 mL rinse) and freshly distilled 1-(1-cyclohexen-1-yl)-pyrrolidine[17] (180 mg, 1.19 mmol) in THF (6 mL). The reaction mixture was stirred at room temperature for 3 h and then worked up. Flash chromatography of the crude product over silica gel (2 × 15 cm) using 20% ethyl acetate–hexane gave **12a** (335 mg, 91%) as a chromatographically resolvable (TLC, silica, 20% ethyl acetate–hexane) mixture of two isomers in a 1:1 ratio (^{1}H NMR): IR (neat) 2217, 1705, 745, 695 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.2–2.15 (m, 7 H), 2.2–2.45 (m, 3 H), 2.45–2.75 (m, 1 H), 3.8 (dd, J = 8.8, 7.6 Hz, 0.5 H), 3.98 (dd, J = 12, 6 Hz, 0.5 H), 7.31–7.50 (m, 3 H), 7.65–7.8 (m, 2 H); exact mass, m/z calcd for $C_{15}H_{17}NOSe$ 307.0475, found 307.0463. Satisfactory combustion analytical values could not be obtained.

3-(2-Oxocycloheptyl)-2-(phenylseleno)propanenitrile (13a). The procedure employed for **11a** was followed using 2-(phenylseleno)-2-propenenitrile (**8**; 278 mg, 1.33 mmol) in THF (2 mL + 1 mL rinse) and freshly distilled 1-(1-cyclohepten-1-yl)pyrrolidine[17] (200 mg, 1.21 mmol) in THF (8 mL). The reaction mixture was stirred at room temperature for 3 h and then worked up. Flash chromatography of the crude product over silica gel (2 × 15 cm) using 15% ethyl acetate–hexane gave **13a** (291 mg, 75%) as a mixture of two isomers in a 1:1.4 ratio (^{13}C NMR): IR (neat) 2230, 1698, 748, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.1–2.02 (m, 9 H), 2.20–2.70 (m, 3 H), 2.80–3.10 (m, 1 H), 3.67–3.87 (m, 1 H), 7.31–7.50 (m, 3 H), 7.65–7.82 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 15.2, 23.3, 23.4, 23.6, 24.2, 28.6, 28.7, 28.8, 31.1, 32.1, 34.2, 35.4, 43.2, 43.3, 48.9, 49.9, 65.7, 119.7, 119.8, 125.6, 125.7, 129.4, 129.5, 129.6, 136.2, 213.7, 213.8; exact mass, m/z calcd for $C_{16}H_{19}NOSe$ 321.0632, found 321.0638. Satisfactory combustion analytical values could not be obtained.

5-Oxo-2-(phenylseleno)-4-propylnonanenitrile (14a). The procedure employed for **11a** was followed using 2-(phenylseleno)-2-propenenitrile (**8**; 325 mg, 1.56 mmol) in THF (2 mL + 1 mL rinse) and freshly distilled 4-(1-butyl-1(*E*)-pentenyl)-morpholine[31] (274 mg, 1.3 mmol) in THF (8 mL). The reaction mixture was stirred at room temperature for 3 h and then worked up. Flash chromatography of the crude product over silica gel (2 × 15 cm) using 6% ethyl acetate–hexane gave **14a** (352 mg, 77%) as a mixture of two isomers in a 1:2 ratio (^{13}C NMR): IR (CCl_4) 2225, 1709, 1579, 742, 691 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.9 (m, 6 H), 1.15–1.80 (m, 9 H), 2.18–2.31 (m, 1 H), 2.33–2.54 (m, 2 H), 2.75–2.90 (m, 1 H), 3.55–3.65 (m, 1 H), 7.35–7.47 (m, 3 H), 7.68–7.74 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 13.7, 13.9, 19.9, 22.2, 23.5, 24.2, 25.5, 32.8, 33.4, 34.1, 42.1, 42.2, 49.1, 49.9, 119.5, 119.7, 125.5, 125.8, 129.4, 129.4, 129.5, 129.6, 136.1, 212.1, 212.4; exact mass, m/z calcd for $C_{18}H_{23}NOSe$ 351.1101, found 351.1109.

2-[2-(Phenylseleno)-2-(phenylsulfonyl)ethyl]cyclopentanone (15a). The procedure employed for **11a** was followed using **9** (1.00 g, 3.09 mmol) in THF (15 mL) and freshly distilled 1-(1-cyclopenten-1-yl)pyrrolidine[17] (346 mg, 2.54 mmol) in THF (60 mL). The reaction mixture was stirred at room temperature for 3 h and then worked up. Flash chromatography of the crude product over silica gel (4 × 15 cm) using 25% ethyl acetate–hexane afforded two fractions. The material of higher R_f (222 mg, 21%) was a single isomer (^{1}H NMR): FT-IR ($CHCl_3$ cast) 1722, 1306, 1146, 1080, 743, 685 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.42–2.05 (m, 4 H), 2.08–2.40 (m, 4 H), 2.55–2.75 (m, 1 H), 5.00 (dd, J = 3.2, 11.4 Hz, 1 H), 7.24 (m, 3 H), 7.51 (m, 5 H), 7.90 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 20.6, 29.1, 30.4, 38.1, 45.3, 64.9, 127.4, 128.5, 128.8, 129.1, 129.3, 133.6 134.8, 137.3, 220.3; MS (chemical ionization, NH_3), m/z 426 (M + 18). Anal. Calcd for $C_{19}H_{20}O_3SSe$: C, 56.02; H, 4.95; S, 7.87; Se, 19.38. Found: C, 56.31; H, 5.04; S, 7.91; Se, 19.6.

The fraction of lower R_f (520 mg, 50%) contained (^{1}H NMR) two components, the above faster running compound and a second isomer: FT-IR ($CHCl_3$ cast) 1736, 1309, 1146, 1080, 740, 685 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.20–2.46 (m, 8 H), 2.66 (m, 1 H), 4.17 (dd, J = 4.0, 11.4 Hz, 0.7 H), 5.02 (dd, J = 3.1, 11.4 Hz, 0.3 H, higher R_f isomer), 7.28 (m, 3 H), 7.56 (m, 5 H), 7.93 (m, 2 H); MS (chemical ionization, NH_3), m/z 426 (M + 18). Before separation the ratio of the isomers in the total reaction product was 1:1 (^{1}H NMR).

2-[2-(Phenylseleno)-2-(phenylsulfonyl)ethyl]cyclohexanone (16a). the procedure employed for **11a** was followed using **9** (789 mg, 2.43 mmol) in dry THF (5 mL + 2 mL rinse) and freshly distilled 1-(1-cyclohexen-1-yl)pyrrolidine (352 mg, 2.33 mmol) in THF (20 mL). The reaction mixture was stirred at room temperature for 3 h and then worked up. Flash chromatography of the crude product over silica gel (3 × 15 cm) with 20% ethyl acetate–hexane gave **16a** (715.1 mg, 73%) as a thick syrup, which was a chromatographically (TLC) inseparable mixture of two isomers in a 1:1 ratio (^{1}H NMR). An analytical sample was prepared by crystallization from dichloromethane–ether; mp 72–73 °C. The material from the flash chromatography showed the following: IR (CCl_4) 1715, 1480, 1450, 1440, 1330, 1310, 1155, 1135, 1090, 695 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.10–2.50 (m, 10 H), 2.93 (m, 1 H), 4.30 (dd, J = 6.0, 8.5 Hz, 0.5 H), 4.58 (dd, J = 3.0, 12.0 Hz, 0.5 H), 7.27 (m, 2 H), 7.56 (m, 5 H), 7.94 (m, 3 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 24.9, 25.2, 27.7, 27.8, 29.6, 30.4, 33.6, 34.9, 42.0, 48.0, 48.5, 65.1, 66.1, 128.7, 128.8, 128.8, 129.2, 129.4, 133.6, 134.9, 135.1, 211.4, 212.0; exact mass, m/z calcd for $C_{20}H_{22}O_3SSe$ 422.0455, found 422.0452. Anal. Calcd for $C_{20}H_{22}O_3SSe$: C, 57.00; H, 5.26; O, 11.39; S, 7.61. Found: C, 57.29; H, 5.24; O, 10.61; S, 7.73.

4-(1,1-Dimethylethyl)-2-[2-(phenylseleno)-2-(phenylsulfonyl)ethyl]cyclohexanone (20a). The procedure employed for **11a** was followed using **9** (584.8 mg, 1.80 mmol) in THF (5 mL + 2 mL rinse) and freshly distilled 1-[4-(1,1-dimethylethyl)-1-cyclohexen-1-yl]pyrrolidine[17] (372.0 mg, 1.80 mmol) in THF (25 mL). The reaction mixture was stirred at room temperature for 3 h and then worked up. Flash chromatography of the crude product over silica gel (4 × 15 cm) using 25% ethyl acetate–hexane gave **20a** (845.2 mg, 98%) as a colorless oil, which was a chromatographically (TLC) inseparable mixture of four isomers in a 6.3:4.9:2.1:1 ratio (^{1}H NMR): IR (neat) 1712, 1478, 1448, 1322, 1312, 1155 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.85 (m, 9 H), 0.94–2.68 (m, 9 H), 2.92 (m, 1 H), 4.15 (dd, J = 4.5, 10.0 Hz, 0.07 H), 4.22 (dd, J = 2.5, 12.0 Hz, 0.15 H), 4.32 (dd, J = 6.0, 9.0 Hz, 0.34 H), 4.61 (dd, J = 3.0, 12.5 Hz, 0.44 H), 7.24 (m, 3 H), 7.49–7.68 (m, 5 H), 7.91 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ (carbonyl signals only) 206.9, 212.0, 212.4, 214.5; exact mass, m/z calcd for $C_{24}H_{30}O_3SSe$ 478.1081, found 478.1075. Satisfactory combustion analytical values could not be obtained.

2-[2-Bromo-2-(phenylsulfonyl)ethyl]cyclohexanone (21a). The procedure employed for **11a** was followed using **10** (564.4 mg, 2.29 mmol) in THF (5 mL + 1 mL rinse) and freshly distilled 1-(1-cyclohexen-1-yl)pyrrolidine[17] (293.4 mg, 1.94 mmol) in THF (20 mL). The reaction mixture was stirred at room temperature for 3 h and then worked up. Flash chromatography of the crude product over silica gel (3 × 15 cm) using 25% ethyl acetate–hexane gave **21a** (537.3 mg, 80%) as a colorless oil, which was a chromatographically (TLC) inseparable mixture of two isomers in a 1:1 ratio (^{1}H NMR). White, crystalline material, enriched in one isomer, was obtained from ether–dichloromethane; mp 73–104 °C. The material obtained directly from the flash chromatography had the following: IR (CCl_4) 1715, 1455, 1335, 1325, 1160, 1140, 1095, 920, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.30–2.82 (m, 11 H), 4.92 (dd, J = 5.5, 9.5 Hz, 0.5 H), 5.26 (dd, J = 2.5, 11.5 Hz, 0.5 H), 7.60 (m, 2 H), 7.72 (m, 1 H), 7.98 (m, 2 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 24.9, 25.2, 27.6, 27.8, 32.0, 32.6, 33.1, 34.9, 42.0, 42.1, 47.7, 48.2, 62.7, 64.7, 129.7, 123.0, 134.4, 134.5, 210.7, 211.6; exact mass, m/z calcd for $C_{14}H_{17}{}^{81}BrO_3S$ 346.0061, found 346.0057. Anal. Calcd for $C_{14}H_{17}BrO_3S$: C, 48.70; H, 4.96; Br, 23.14; S, 9.29. Found: C, 48.50; H, 5.04; Br, 23.08; S, 9.20.

3-[2-Hydroxy-2-(phenylethynyl)cyclopentyl]-2-(phenylseleno)propanenitrile (11b). *n*-Butyllithium (1.6 M in hexanes, 1.53 mL, 2.46 mmol) was injected dropwise into a stirred solution of phenylacetylene (376 mg, 3.69 mmol) in dry THF (8 mL) at −78 °C. The mixture was stirred for 15 min, and ketones **11a** (360 mg, 1.23 mmol) in THF (3 mL + 1 mL rinse) were added dropwise over 5 min. Stirring was continued for 2 h at −78 °C, saturated aqueous ammonium chloride (10 mL) was added, and the mixture was extracted with ether (3 × 25 mL). The combined organic extracts were washed with brine (1 × 20 mL), dried ($MgSO_4$), and

(31) White, W. A.; Weingarten, H. *J. Org. Chem.* **1967**, *32*, 213.

evaporated. Flash chromatography of the crude product over silica gel (2 × 15 cm) using 20% ethyl acetate–hexane gave alcohols **11b** as a mixture of two isomers (350 mg, 68% total overall yield from the enamine) in a 1:1 ratio (^{13}C NMR): IR (neat) 3440, 2235, 1600, 1575, 760, 740, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.30–2.45 (m, 10 H), 3.80–4.05 (m, 1 H), 7.25–7.48 (m, 8 H), 7.68–7.80 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ (nonaromatic signals only) 20.7, 24.5, 28.9, 29.3, 34.8, 35.5, 42.1, 42.3, 48.7, 49.4, 78.1, 86.9, 87.0, 89.4, 120.1, 120.4; exact mass, *m/z* calcd for $C_{22}H_{21}NOSe$ 395.0788, found 395.0792. Anal. Calcd for $C_{22}H_{21}NOSe$: C, 66.98; H, 5.39; N, 3.55. Found: C, 65.65; H, 5.49; N, 3.59. Satisfactory C analysis could not be obtained.

3-[2-Hydroxy-2-(phenylethynyl)cyclohexyl]-2-(phenylseleno)propanenitrile (12b). The procedure employed for **11b** was followed using *n*-butyllithium (1.6 M in hexanes, 0.86 mL, 1.39 mmol), phenylacetylene (163 mg, 1.6 mmol) in dry THF (5 mL), and ketones **12a** (330 mg, 1.07 mmol) in THF (3 mL + 1 mL rinse). Flash chromatography of the crude product over silica gel (2 × 15 cm) using 20% ethyl acetate–hexane gave **12b** (414 mg, 94.7%) as a mixture of four isomers in a 2.2:1.9:1.6:1 ratio (^{13}C NMR): IR (neat) 3450, 2240, 1590, 1575, 760, 745, 695 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.2–2.15 (m, 11 H), 2.2–2.6 (m, 1 H), 3.75–4.15 (m, 1 H), 7.15–7.49 (m, 8 H), 7.62–7.80 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ (aromatic, acetylene, nitrile, and carbinol signals) 69.0, 69.4, 73.0, 73.4, 84.2, 84.4, 86.9, 87.0, 89.2, 89.3, 92.5, 93.0, 119.8, 120.1, 120.4, 120.7, 122.2, 122.3, 125.9, 126.1, 126.1, 128.1, 128.2, 128.2, 128.4, 129.3, 129.3, 129.4, 131.5, 131.6, 136.0, 136.2, 136.2, 136.4; exact mass, *m/z* calcd for $C_{23}H_{23}NOSe$ 409.0948, found 409.0952. Anal. Calcd for $C_{23}H_{23}NOSe$: C, 67.46; H, 5.66; N, 3.42. Found: C, 64.95; H, 5.41; N, 3.37. Satisfactory C analysis could not be obtained.

3-[2-Hydroxy-2-(phenylethynyl)cycloheptyl]-2-(phenylseleno)propanenitrile (13b). The procedure employed for **11b** was followed using *n*-butyllithium (1.6 M in hexanes, 1.36 mL, 2.19 mmol), phenylacetylene (298 mg, 2.92 mmol) in dry THF (10 mL), and ketones **13a** (470 mg, 1.46 mmol) in THF (3 mL + 1 mL rinse). Flash chromatography of the crude product over silica gel (2 × 15 cm) using 15% ethyl acetate–hexane gave alcohols **13b** (585 mg, 94.6%) as a mixture of isomers: IR (neat) 3450, 2232, 757, 740, 695 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.2–2.3 (m, 13 H), 2.3–2.55 (m, 1 H), 3.7–4.1 (m, 1 H), 7.14–7.50 (m, 8 H), 7.62–7.80 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 27.0, 27.4, 28.2, 28.3, 35.2, 35.4, 42.3, 42.6, 48.1, 48.7, 72.8, 73.1, 83.7, 83.9, 93.5, 94.0, 119.8, 120.4, 122.3, 126.0, 126.1, 128.0, 128.1, 128.2, 128.3, 129.2, 129.3, 129.4, 131.4, 131.6, 136.0, 136.1; exact mass, *m/z* calcd for $C_{24}H_{25}NOSe$ 423.1101, found 423.1100. Anal. Calcd for $C_{24}H_{25}NOSe$: C, 68.24; H, 5.97; N, 3.32. Found: C, 68.07; H, 6.13; N, 3.44.

5-Hydroxy-5-(phenylethynyl)-2-(phenylseleno)-4-propylnonanenitrile (14b). The procedure employed for **11b** was followed using *n*-butyllithium (1.6 M in hexanes, 1.19 mL, 1.91 mmol), phenylacetylene (293 mg, 2.86 mmol) in dry THF (8 mL), and ketones **14a** (335 mg, 0.956 mmol) in THF (3 mL + 1 mL rinse). Flash chromatography of the crude product over silica gel (2 × 15 cm) using 10% ethyl acetate–hexane gave **14b** (346 mg, 80%) as a mixture of two isomers in a 1:1 ratio (^{1}H NMR): IR (neat) 3450, 2230, 1580, 755, 740, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.82–1.02 (m, 6 H), 1.10–1.80 (m, 10 H), 1.85–1.01 (m, 2 H), 2.05 (m, 0.5 H), 2.11 (s, 0.5 H), 2.2–2.4 (m, 1 H), 3.97–4.08 (m, 0.5 H), 4.10–4.19 (m, 0.5 H), 7.30–7.50 (m, 8 H), 7.79–7.80 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 14.0, 14.2, 14.4, 21.1, 21.7, 22.8, 25.3, 26.1, 26.4, 26.5, 32.3, 32.8, 34.1, 34.5, 37.7, 38.4, 46.3, 46.9, 74.6, 85.6, 91.4, 91.7, 120.2, 120.5, 122.2, 122.3, 126.2, 126.4, 128.2, 128.3, 128.4, 128.5, 129.1, 129.2, 129.3, 129.4, 131.5, 131.6, 135.9, 136.0, 136.1, 136.2; exact mass, *m/z* calcd for $C_{26}H_{31}NOSe$ 453.1571, found 453.1581. Anal. Calcd for $C_{26}H_{31}NOSe$: C, 68.85; H, 6.89; N, 3.09. Found: C, 69.13; H, 6.90; N, 3.10.

1-(Phenylethynyl)-2-[2-(phenylseleno)-2-(phenylsulfonyl)ethyl]cyclopentan-1-ol (15b). The procedure employed for **11b** was followed using *n*-butyllithium (1.6 M in hexanes, 0.40 mL, 0.81 mmol), phenylacetylene (0.09 mL, 0.81 mmol) in dry THF (30 mL), and ketones **15a** (1:1 isomer mixture, 131.0 mg, 0.32 mmol) in THF (4 mL + 1 mL rinse). Flash chromatography of the crude product over silica gel (1 × 5 cm) using 25% ethyl acetate–hexane gave unreacted starting material (27.0 mg, 21%) and **15b** (130.3 mg, 79%; quantitative yield based on conversion). Alcohols **15b** were obtained as a thick syrup, which was a chromatographically (TLC) inseparable mixture of four isomers in a 1:2:3.7:4.3 ratio (^{1}H NMR): FT-IR ($CHCl_3$ cast) 3465, 1445, 1305, 1144, 743, 689 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.12–2.39 (m, 9 H), 2.59 (m, 1 H), 4.23 (dd, *J* = 7.0, 8.5 Hz, 0.42 H), 4.88 (dd, *J* = 2.5, 11.5 Hz, 0.35 H), 5.01 (dd, *J* = 3.5, 11.5 Hz, 0.18 H), 5.07 (dd, *J* = 2.5, 9.5 Hz, 0.05 H), 7.12–7.60 (m, 13 H), 7.84 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz), δ (nonaromatic signals only) 20.6, 28.8, 30.4, 30.8, 31.9, 42.0, 43.1, 45.3, 47.5, 48.7, 66.1, 66.2, 78.1, 78.6; exact mass, *m/z* calcd for $C_{27}H_{26}O_3SSe$ 510.0767, found 510.0774. Satisfactory combustion analytical values could not be obtained.

1-(Phenylethynyl)-2-[2-(phenylseleno)-2-(phenylsulfonyl)ethyl]cyclohexan-1-ol (16b; 18b) and (1*R,2*R**)-1-(Phenylethynyl)-2-[2-(phenylseleno)-2-(phenylsulfonyl)ethyl]cyclohexan-1-ol (17b).** The procedure employed for **11b** was followed using *n*-butyllithium (1.6 M in hexanes, 0.41 mL, 0.64 mmol), phenylacetylene (0.09 mL, 0.819 mmol) in dry THF (20 mL) at −78 °C, and ketones **16a** (135 mg, 0.321 mmol) in THF (4 mL + 1 mL rinse). Flash chromatography of the crude product over silica gel (2 × 15 cm) using 25% ethyl acetate–hexane gave **16b** (127.7 mg, 76%) as a thick syrup, which was a chromatographically (TLC) inseparable mixture of four isomers in a 2.6:2.8:2.6:1 ratio (^{1}H NMR): FT-IR ($CHCl_3$ cast) 3485, 1488, 1476, 1445, 1305, 1145, 1080, 755, 742, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.80–2.86 (m, 12 H), 4.16 (m, 0.11 H), 4.34 (dd, *J* = 4.0, 11.0 Hz, 0.29 H), 4.94 (dd, *J* = 3.6, 10.6 Hz, 0.31 H), 5.06 (dd, *J* = 3.0, 11.5 Hz, 0.29 H), 7.10–8.00 (m, 15 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ (nonaromatic signals only) 20.9, 21.0, 23.8, 23.9, 24.4, 24.7, 25.1, 25.4, 25.6, 28.8, 28.9, 31.3, 31.4, 31.5, 33.0, 39.7, 40.1, 41.5, 42.1, 43.5, 45.2, 45.7, 65.9, 67.0, 68.9, 72.8, 74.6, 84.6, 87.0, 87.2, 89.4, 89.5, 93.7; MS, *m/z* 524.5 (M^+). Anal. Calcd for $C_{28}H_{28}O_3SSe$: C, 64.24; H, 5.39; O, 9.17; S, 6.12. Found: C, 64.03; H, 5.28; O, 8.95; S, 6.17.

The syrupy mixture of isomers afforded **17b** as a single crystalline compound (32.6% of the mixture) from dichloromethane–hexane. Compound **17b** was later assigned the indicated structure on the basis of an X-ray crystallographic analysis of its radical cyclization product **17c**. Compound **17b**: FT-IR (CH_2Cl_2 cast) 3560, 1445, 1302, 1288, 1146, 1140, 1080 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.20–2.44 (m, 11 H), 2.76 (m, 1 H), 4.94 (dd, *J* = 3.6, 10.6 Hz, 1 H), 7.26 (m, 10 H), 7.31 (m, 3 H), 7.77 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 20.9, 28.9, 31.3, 40.1, 43.4, 67.0, 128.3, 128.5, 128.6, 128.7, 129.1, 129.5, 131.6, 133.4, 135.3; MS (chemical ionization, NH_3), *m/z* 542 (M + 18). Anal. Calcd for $C_{28}H_{28}O_3SSe$: C, 64.24; H, 5.39. Found: C, 63.98; H, 5.42.

The mother liquors from the crystallization that afforded **17b** were concentrated. The residue **18b** amounted to 67% of the original mixture and contained three isomers in a 1:1.8:3.8 ratio (^{1}H NMR) and a just detectable trace of the crystalline trans isomer **17b**. The material showed the following: IR (CCl_4) 3610, 3500, 1446, 1320, 1310, 1155 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.80–2.66 (m, 12 H), 4.16 (dd, *J* = 2.5, 12.5 Hz, 0.15 H), 4.34 (dd, *J* = 4.0, 11.0 Hz, 0.60 H), 5.06 (dd, *J* = 3.0, 11.5 Hz, 0.25 H), 7.12–7.66 (m, 13 H), 7.90 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ (nonaromatic signals only) 20.9, 23.7, 23.8, 25.0, 25.4, 28.7, 31.1, 31.5, 32.8, 41.4, 42.1, 43.3, 44.9, 45.5, 65.8, 66.8, 66.9, 69.8, 72.6, 74.6, 86.9, 87.0, 89.1, 89.3; MS, *m/z* 524 (M^+).

1-Propynyl-2-[2-(phenylseleno)-2-(phenylsulfonyl)ethyl]cyclohexan-1-ol (19b). Propyne (ca. 1 mL) was condensed in a test tube sealed with a septum and transferred rapidly via cannula to a stirred and cooled (−78 °C) solution of *n*-butyllithium (1.55 M in hexanes, 0.75 mL, 1.16 mmol) in THF (20 mL). The mixture was stirred for 20 min, and ketones **16a** (287 mg, 0.681 mmol) in THF (4 mL + 1 mL rinse) were added dropwise over 10 min. Stirring was continued for 4 h at −78 °C. The cooling bath was removed, and after 30 min the mixture was quenched with saturated aqueous ammonium chloride (15 mL) and extracted with ether (3 × 20 mL). The combined extracts were washed with brine (10 mL), dried ($MgSO_4$), and evaporated. Flash chromatography of the crude product over silica gel (2 × 15 cm) using 25% ethyl acetate–hexane afforded **19b** (280 mg, 89%) as a white solid, which was a chromatographically (TLC) inseparable mixture of three isomers, the two major ones being in a 1:1.4 ratio (^{1}H NMR): mp 87–112 °C; FT-IR ($CHCl_3$ cast) 3480, 2932, 1446, 1439, 1305, 1146, 1082, 744, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ

0.90–2.70 (m, 15 H), 4.28 (dd, J = 4.0, 11.0 Hz, 0.6 H), 4.98 (m, 0.4 H), 7.26 (m, 3 H), 7.55 (m, 5 H), 7.92 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 20.9, 23.8, 25.1, 28.6, 28.9, 30.6, 41.6, 45.4, 66.0, 66.9, 72.3, 128.7, 128.9, 129.1, 129.3, 129.5, 133.6, 135.2, 137.5; exact mass, m/z calcd for $C_{23}H_{26}O_3SSe$ 462.0768, found 462.0773. Satisfactory combustion analytical values could not be obtained.

4-(1,1-Dimethylethyl)-1-(phenylethynyl)-2-[2-(phenylseleno)-2-(phenylsulfonyl)ethyl]cyclohexan-1-ol (20b). The procedure employed for **11b** was followed using n-butyllithium (1.6 M in hexanes, 0.33 mL, 0.52 mmol), phenylacetylene (81.6 mg, 0.80 mmol) in dry THF (30 mL), and ketones **20a** (124.0 mg, 0.260 mmol) in THF (2 mL + 1 mL rinse). Flash chromatography of the crude product over silica gel (1 × 15 cm) using 25% ethyl acetate–hexane gave **20b** (119 mg, 79%) as a colorless oil, which was a chromatographically (TLC) inseparable mixture of four isomers in a 2.7:1.3:2:1 ratio (^{1}H NMR): IR (CCl_4) 3620, 3465, 1480, 1450, 1325, 1315, 1155 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.69–2.80 (m, 20 H), 4.20 (dd, J = 1.5, 15.0 Hz, 0.14 H), 4.38 (dd, J = 3.5, 12.0 Hz, 0.29 H), 4.76 (dd, J = 4.95, 10.5 Hz, 0.19 H), 5.05 (m, 0.38 H), 7.12–8.12 (m, 15 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ (nonaromatic signals only) 21.2, 24.8, 27.4, 27.5, 27.6, 28.7, 29.9, 29.9, 30.9, 31.4, 31.7, 32.4, 32.7, 35.6, 41.0, 41.4, 41.7, 42.2, 43.8, 44.7, 45.6, 47.0, 47.2, 47.5, 66.2, 66.6, 67.8, 72.1, 72.9, 75.0, 87.2; exact mass, m/z calcd for $C_{32}H_{36}O_3SSe$ 580.1550, found 580.1554. Satisfactory combustion analytical values could not be obtained.

2-[2-Bromo-2-(phenylsulfonyl)ethyl]-1-(phenylethynyl)-cyclohexan-1-ol (21b). The procedure employed for **11b** was followed using n-butyllithium (1.6 M in hexanes, 2.0 mL, 3.20 mmol), phenylacetylene (0.44 mL, 4.0 mmol) in dry THF (30 mL), and ketones **21a** (484.3 mg, 1.40 mmol) in THF (9 mL + 2 mL rinse). Flash chromatography of the crude product over silica gel (3 × 15 cm) using 25% ethyl acetate–hexane gave **21b** (608 mg, 97%) as a colorless oil, which was a chromatographically (TLC) inseparable mixture of four isomers in a 3:2:2.3:1 ratio (^{1}H NMR). On standing, the material solidified (mp 44–45 °C) but attempts to recrystallize it were unsuccessful: FT-IR ($CHCl_3$ cast) 3580, 1488, 1446, 1320, 1308, 1300, 1082, 755, 678 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.36–2.32 (m, 10 H), 2.34–2.70 (m, 1 H), 2.84–3.16 (m, 1 H), 4.88 (dd, J = 4.0, 10.5 Hz, 0.12 H), 5.00 (dd, J = 4.0, 10.5 Hz, 0.28 H), 5.54 (dd, J = 3.5, 10.5 Hz, 0.24 H), 5.65 (dd, J = 2.5, 11.5 Hz, 0.36 H), 7.16–7.76 (m, 8 H), 7.94 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ (nonaromatic signals only) 20.8, 23.7, 23.8, 24.5, 24.7, 25.0, 25.2, 25.3, 28.4, 28.8, 31.5, 32.9, 33.4, 34.0, 36.2, 39.7, 39.9, 41.4, 41.5, 42.1, 43.5, 43.8, 44.8, 45.6, 64.0, 64.9, 65.8, 66.4, 68.7, 72.5, 74.4, 84.5, 87.2, 87.4, 88.9, 89.3, 93.1; exact mass, m/z calcd for $C_{22}H_{23}{}^{81}BrO_3S$ 448.0532, found 448.0534. Anal. Calcd for $C_{22}H_{23}BrO_3S$: C, 59.06; H, 5.18; O, 10.73; S, 7.17. Found: C, 58.74; H, 5.07; O, 11.07; S, 6.92.

2-[2-Bromo-2-(phenylsulfonyl)ethyl]-1-(ethoxyethynyl)-cyclohexan-1-ol (22b). The procedure employed for **11b** was followed using n-butyllithium (1.6 M in hexanes, 1.90 mL, 3.04 mmol), ethoxyacetylene (Aldrich) (291 mg, 4.16 mmol) in dry THF (40 mL), and ketones **21a** (469 mg, 1.36 mmol) in THF (4 mL + 1 mL rinse). Flash chromatography of the crude product over silica gel (2 × 15 cm) using 25% ethyl acetate–hexane gave **22b** (546 mg, 96%) as light yellow oil, which was a chromatographically (TLC) inseparable mixture of four isomers in a 4.8:3.9:4.7:1 ratio (^{1}H NMR): IR (CCl_4) 3605, 3500, 2246, 1444, 1322, 1150 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.10–2.02 (m, 13.5 H), 2.25–2.52 (m, 0.7 H), 2.81–3.00 (m, 0.8 H), 4.10 (dq, J = 7.0 Hz, 2 H), 4.80 (dd, J = 3.5, 12.0 Hz, 0.07 H), 4.94 (dd, J = 4.0, 10.5 Hz, 0.33 H), 5.42 (dd, J = 3.5, 10.0 Hz, 0.27 H), 5.48 (dd, J = 2.5, 11.5 Hz, 0.33 H), 7.59 (m, 2 H), 7.70 (m, 1 H), 7.99 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ (nonaromatic signals only) 14.4, 14.5, 21.2, 23.9, 24.0, 24.5, 25.1, 25.5, 28.5, 29.0, 31.6, 33.2, 34.5, 36.0, 38.1, 40.9, 42.3, 42.9, 44.0, 44.6, 45.6, 64.1, 66.1, 66.5, 72.2, 74.3, 74.7, 75.0, 96.0; exact mass, m/z calcd for $C_{18}H_{23}{}^{81}BrO_4S$ 416.0481, found 416.0478.

2-[2-Bromo-2-(phenylsulfonyl)ethyl]-1-(trimethylsiloxy)cyclohexanecarbonitrile (23b). Trimethylsilyl cyanide (0.12 mL, 0.92 mmol) was injected in one portion into a stirred solution of ketones **21a** (286 mg, 0.830 mmol) and zinc iodide (1 mg, 0.003 mmol) in dichloromethane (10 mL). Stirring was continued for 2 h, and the reaction mixture was quenched with saturated aqueous ammonium chloride (10 mL) and extracted with ether (3 × 10 mL). The combined extracts were washed with brine (5 mL), dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (2 × 15 cm) using 20% ethyl acetate–hexane afforded **23b** (350 mg, 95%) as a colorless oil, which was a chromatographically (TLC) inseparable mixture of four isomers in a 4.3:2.5:1 ratio (^{1}H NMR): FT-IR ($CHCl_3$ cast) 1423, 1327, 1311, 1255, 1153, 1138, 1118, 847 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.21 (m, 9 H), 1.15–2.46 (m, 10.5 H), 2.81 (m, 0.5 H), 4.72 (dd, J = 2.5, 12.0 Hz, 0.13 H), 4.81 (dd, J = 3.5, 11.5 Hz, 0.32 H), 5.16 (two overlapping dd, J = 3.5, 11.0 Hz, J = 3.5, 11.0 Hz, 0.55 H), 7.61 (m, 2 H), 7.72 (m, 1 H), 7.99 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 1.1, 1.1, 1.3, 1.5, 20.1, 23.2, 24.3, 24.4, 24.7, 27.5, 28.3, 30.7, 33.0, 33.2, 35.8, 38.0, 39.6, 43.3, 43.4, 45.9, 46.1, 63.6, 64.9, 65.8, 74.7, 76.9, 119.5, 129.1, 129.1, 129.2, 130.0, 130.0, 130.2, 134.5, 134.6, 134.7, 134.9; exact mass, m/z calcd for $C_{18}H_{26}{}^{81}BrNO_3SSi$ 445.0566, found 445.0571.

2-[2-Bromo-2-(phenylsulfonyl)ethyl]-1-propynylcyclohexan-1-ol (24b). The procedure employed for **19b** was followed using propyne (ca. 2 mL), n-butyllithium (1.6 M in hexanes, 0.72 mL, 1.15 mmol) in THF (25 mL), and ketones **21a** (198 mg, 0.574 mmol) in THF (4 mL + 1 mL rinse). The mixtures was stirred for 4 h at −78 °C and then worked up. Flash chromatography of the residue over silica gel (2 × 15 cm) using 25% ethyl acetate–hexane afforded **24b** (209 mg, 94%) as a thick syrup, which was a chromatographically (TLC) inseparable mixture of three isomers in a 2:1:1.3 ratio (^{1}H NMR): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.80–2.55 (m, 13.6 H), 2.79 (octet, J = 3.5, 6.5 Hz, 0.7 H), 2.93 (octet, J = 3.5, 6.5 Hz, 0.7 H), 4.90 (dd, J = 4.0, 11.5 Hz, 0.3 H), 5.40 (dd, J = 3.5, 10.5 Hz, 0.2 H), 5.55 (dd, J = 2.5, 11.5 Hz, 0.5 H), 7.58 (m, 2 H), 7.70 (m, 1 H), 8.00 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ (nonaromatic signals only) 14.2, 21.0, 21.0, 23.7, 23.9, 24.4, 25.1, 25.4, 28.3, 28.9, 31.3, 31.5, 32.8, 34.3, 36.1, 40.0, 41.8, 42.4, 43.5, 44.6, 45.5, 64.2, 66.2, 66.6, 68.5, 72.2, 74.3, 79.1, 79.4, 80.8, 83.1, 83.3, 83.6.

Analytical material enriched in one isomer was obtained by crystallization from ethyl acetate–hexane: mp 72–118 °C; FT-IR ($CHCl_3$ cast) 3490, 1447, 1320, 1310, 1149, 1083, 749, 571 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.10–2.05 (m, 15 H), 2.79 (octet, J = 3.5, 6.5 Hz, 1 H), 5.55 (dd, J = 2.5, 11.5 Hz, 1 H), 7.58 (m, 2 H), 7.70 (m, 1 H), 8.00 (m, 2 H); exact mass, m/z calcd for $C_{17}H_{21}{}^{81}BrO_3S$ 386.0374, found 386.0365. Anal. Calcd for $C_{17}H_{21}BrO_3S$: C, 52.99; H, 5.49; Br, 20.74; S, 8.32. Found: C, 53.09; H, 5.68; Br, 20.62; S, 8.53.

General Procedure for Radical Cyclization. Dry benzene and oven-dried apparatus were used. AIBN (Eastman) was used without further purification. The substrate (0.5–1.5 mmol) was placed in a 100-mL round-bottomed flask equipped with a Teflon-coated stirring bar and a reflux condenser sealed with a rubber septum. The system was flushed with argon for 5–10 min, and benzene (25–60 mL) was injected. The flask was lowered into an oil bath, preheated to 80 °C, and benzene solutions of triphenyltin hydride (1.5 equiv, 0.2 M) and AIBN (0.3 equiv, 0.006 M) were injected simultaneously over 10 h with a double syringe pump. The mixture was arbitrarily refluxed for a period of 2 h after the end of the addition, cooled, and evaporated. The residue was then processed as described for the individual examples.

Octahydro-6a-hydroxy-1-(phenylmethylene)-2-pentalenecarbonitrile (11c). The general procedure for radical cyclization was followed using selenides **11b** (164 mg, 0.42 mmol) in benzene (15 mL), triphenyltin hydride (175 mg, 0.50 mmol) in benzene (7 mL), and AIBN (20 mg, 0.11 mmol) in benzene (7 mL). Flash chromatography of the crude product over silica gel (2 × 15 cm) using 30% ethyl acetate–hexane afforded **11c** (88 mg, 89%) as a partially resolvable (TLC) mixture of isomers: IR (neat) 3450, 2240, 1600, 760, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.0–2.8 (m, 10 H), 3.5–4.95 (m, including br t, J = 8 Hz, 1 H), 6.7–6.93 (br s, 1 H), 7.10–7.80 (m, 5 H); exact mass, m/z calcd for $C_{16}H_{17}NO$ 239.1310, found 239.1311. Anal. Calcd for $C_{16}H_{17}NO$: C, 80.28; H, 7.16; N, 5.85. Found: C, 80.25; H, 7.31; N, 5.87.

Octahydro-7a-hydroxy-1-(phenylmethylene)-1*H*-indene-2-carbonitrile (12c). The general procedure for radical cyclization was followed using selenides **12b** (180 mg, 0.44 mmol) in benzene (15 mL), triphenyltin hydride (175 mg, 0.50 mmol) in benzene (7 mL), and AIBN (20 mg, 0.11 mmol) in benzene (7 mL). Flash chromatography of the crude product over silica gel (2 × 15 cm) using 20% ethyl acetate–hexane gave **12c** (101 mg, 91%)

as a partially resolvable (TLC, silica, 20% ethyl acetate–hexane) mixture of isomers: IR (cast from CCl_4) 3450, 2235, 1595, 1550, 752, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 0.9–2.55 (m, 12 H), 3.45–3.85 (m, 1 H), 6.5–7.0 (8 br s, 1 H), 7.2–7.5 (m, 5 H); exact mass, m/z calcd for $C_{17}H_{19}NO$ 253.1466, found 253.1473. Anal. Calcd for $C_{17}H_{19}NO$: C, 80.60; H, 7.56; N, 5.53. Found: C, 80.62; H, 7.45; N, 5.51.

Decahydro-8a-hydroxy-1-(phenylmethylene)-2-azulenecarbonitrile (13c). The general procedure for radical cyclization was followed using selenides **13b** (230 mg, 0.54 mmol) in benzene (20 mL), triphenyltin hydride (219 mg, 0.62 mmol) in benzene (7 mL), and AIBN (20 mg, 0.11 mmol) in benzene (7 mL). Flash chromatography of the crude product over silica gel (2 × 15 cm) using 20% ethyl acetate–hexane gave **13c** (152 mg, 91.7%) as a partially resolvable (TLC, silica, 25% ethyl acetate–hexane) mixture of isomers: IR (cast from CCl_4) 3460, 2235, 742, 698 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 1.1–2.6 (m, 14 H), 3.40–3.85 (m, 1 H), 6.7–6.95 (3 br s, 1 H), 7.2–7.7 (m, 5 H); exact mass, m/z calcd for $C_{18}H_{21}NO$ 267.1623, found 267.1628. Anal. Calcd for $C_{18}H_{21}NO$: C, 80.84; H, 7.92; N, 5.24. Found: C, 80.44; H, 7.95; N, 5.23.

3-Butyl-3-hydroxy-2-(phenylmethylene)-4-propylcyclopentanecarbonitrile (14c). The general procedure for radical cyclization was followed using selenides **14b** (145 mg, 0.32 mmol) in benzene (10 mL), triphenyltin hydride (134 mg, 0.38 mmol) in benzene (6 mL), and AIBN (16 mg, 0.97 mmol) in benzene (6 mL). Flash chromatography of the crude product over silica gel (2 × 15 cm) using 20% ethyl acetate–hexane gave **14c** (75 mg, 79%) as a mixture of isomers: IR (neat) 3460, 2240, 1690, 1595, 755, 698 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 0.59–2.6 (m, 20 H), 3.6–3.9 (m, 1 H), 6.6–7.02 (d, J = 6 Hz, 1 H), 7.15–7.55 (m, 5 H); exact mass, m/z calcd for $C_{20}H_{27}NO$ 297.2093, found 297.2095. Anal. Calcd for $C_{20}H_{27}NO$: C, 80.76; H, 9.15; N, 4.71. Found: C, 80.59; H, 9.02; N, 4.66.

Octahydro-6a-hydroxy-1-(phenylmethylene)-2-(phenylsulfonyl)pentalene (15c). The general procedure was not followed in this experiment. Triphenyltin hydride (288.7 mg, 0.823 mmol) in benzene (5 mL) and AIBN (10 mg, 0.06 mmol) in benzene (5 mL) were added in one portion to a refluxing solution of selenides **15b** (271.7 mg, 0.533 mmol) in benzene (50 mL). The mixture was stirred under reflux for 15 h, cooled, and evaporated as usual. Flash chromatography of the crude product over silica gel (2 × 15 cm) gave **15c** (46.6 mg, 25%; 30% based on conversion) as a thick syrup, which was mostly one isomer with a trace of a second (^1H NMR), together with unreacted starting material (50.3 mg, 19%). **15c**: FT-IR (CCl_4 cast) 3500, 1440, 1302, 1280, 1139, 1080, 730 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.19–2.09 (m, 7 H), 2.71 (m, 1 H), 2.91 (m, 1 H), 3.88 (s, 1 H), 4.01 (d, 1 H), 6.03 (s, 0.94 H), 6.39 (d, J = 0.5 Hz, 0.06 H), 7.11–7.41 (m, 4 H), 7.58–7.70 (m, 4 H), 7.90 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 23.4, 24.9, 26.1, 27.2, 30.9, 31.4, 31.8, 37.8, 54.9, 74.5, 76.5, 89.0, 127.8, 128.0, 128.1, 128.4, 128.6, 128.8, 129.1, 129.2, 130.3, 131.9, 133.9, 134.3, 135.2, 136.3, 140.2; exact mass, m/z calcd for $C_{20}H_{22}SO_3$ 354.1256, found 354.1295.

(*E*)-(7a*R,2*S**,3a*R**)-Octahydro-7a-hydroxy-1-(phenylmethylene)-2-(phenylsulfonyl)-1*H*-indene (16c) and (7a*R**,3a*S**)-Octahydro-7a-hydroxy-1-(phenylmethylene)-2-(phenylsulfonyl)-1*H*-indene (16c′).** The general procedure for radical cyclization was followed using selenides **16b** (346 mg, 0.661 mmol) in benzene (20 mL), triphenyltin hydride (284 mg, 0.808 mmol) in benzene (10 mL), and AIBN (5 mg, 0.03 mmol) in benzene (10 mL). Evaporation of the solvent and flash chromatography of the residue over silica gel (2 × 15 cm) using ethyl acetate–hexane afforded two solids, which were each recrystallized from dichloromethane–hexane. The compound of lower R_f (75.5 mg, 31% yield) was identified as the cis ring-fused compound **16c′**: mp 147–160 °C; FT-IR ($CHCl_3$ cast) 3490, 1447, 1301, 1142, 1083, 751 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.78–2.04 (m, 10 H), 2.48 (m, 1 H), 3.26 (s, 1 H), 4.25 (t, J = 8.5 Hz, 1 H), 6.81 (d, J = 1.5 Hz, 1 H), 7.32 (m, 5 H), 7.59 (m, 3 H), 7.93 (m, 2 H); exact mass, m/z [(M − $SO_2C_6H_5$)$^+$] calcd for $C_{16}H_{19}O$ 227.1436, found 227.1435. Anal. Calcd for $C_{22}H_{24}O_3S$: C, 71.71; H, 6.57; S, 8.70. Found: C, 71.82; H, 6.80; S, 9.04.

The compound of higher R_f (91.6 mg, 38% yield) was identified as the trans ring-fused material **16c**: mp 157–162 °C; FT-IR ($CHCl_3$ cast) 3492, 1448, 1494, 1276, 1140, 1082, 742 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 0.68–2.02 (m, 11 H), 3.10 (d, J = 1.5 Hz, 1 H), 4.17 (dt, J = 1.5, 8.5 Hz, 1 H), 6.59 (d, J = 1.5 Hz, 1 H), 7.28 (m, 5 H), 7.60 (m, 3 H), 7.94 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 21.3, 25.1, 25.4, 28.9, 34.5, 48.9, 68.7, 76.6, 127.7, 127.7, 129.2, 129.2, 129.4, 133.4, 133.9, 135.9, 137.5, 140.0; exact mass, m/z calcd for $C_{22}H_{24}O_3S$ 368.1446, found 368.1419.

(*E*)-(7a*R,2*S**,3a*R**)-Octahydro-7a-hydroxy-1-(phenylmethylene)-2-(phenylsulfonyl)-1*H*-indene (17c).** The special procedcure employed for **15c** was followed using selenide **17b** (72.3 mg, 0.138 mmol) in benzene (20 mL), triphenyltin hydride (67.3 mg, 0.192 mmol) in benzene (5 mL), and AIBN (5 mg, 0.03 mmol) in benzene (5 mL). The mixture was stirred under reflux for 15 h, cooled, and evaporated. Flash chromatography of the residue over silica gel (1 × 15 cm) afforded unreacted starting material (28.0 mg, 39%) and **17c** (28.1 mg, 55%; 90% based on conversion) as a white solid. **17c**: mp 165–166 °C; FT-IR ($CHCl_3$ cast) 3485, 1442, 1303, 1142, 1078, 742 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 0.68–2.04 (m, 11 H), 3.10 (d, J = 1.5 Hz, 1 H), 4.17 (dt, J = 1.5, 8.5 Hz, 1 H), 6.59 (d, J = 1.5 Hz, 1 H), 7.29 (m, 5 H), 7.60 (m, 3 H), 7.93 (m, 2 H); ^{13}C NMR ($CDCl_3$, 50.3, MHz) δ 21.3, 25.1, 25.5, 28.9, 34.5, 48.9, 68.7, 76.6, 127.7, 129.2, 129.4, 133.4, 133.9, 136.0, 139.0; exact mass, m/z [(M − $SO_2C_6H_5$)$^+$] calcd for $C_{16}H_{19}S$ 227.1435, found 227.1433.

In a subsequent experiment **17c** was recrystallized from ethyl acetate–hexane (mp 164–165 °C), and the structure of the compound was determined by single-crystal X-ray analysis.

Crystal data for 17c: empirical formula $C_{22}H_{24}O_3S$; molecular weight 368.50; a = 9.771 (2), b = 6.804 (2), c = 28.593 (7) Å; β = 94.23 (2)°; V = 1896 Å^3; monoclinic space group $P2_1/n$; Z = 4; D_{calcd} = 1.291 g cm^{-3}; μ (Mo Kα) = 1.80 cm^{-1}. Data were collected with an Enraf-Nonius CAD4 automated diffractometer, ω–2θ scan, type $\omega = 2\theta$, using Mo Kα radiation (λ = 0.710 73 Å) up to a maximum of 2θ of 50.00°, graphite crystal, incident beam monochromator. Of 3637 unique reflections, 1639 having $I > \sigma(I)$ were used in the structure solution and refinement. Data were corrected for Lorentz and polarization effects, but not for absorption, with the Enraf-Nonius Structure Determination Package Plus.[32] The structure was solved by the direct-methods program MULTAN.[33] Refinement of atomatic parameters, with non-hydrogen atoms assigned anisotropic thermal parameters, was carried out by using full-matrix least-squares techniques on F_o minimizing $\sum w(|F_o| - |F_c|)^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes, respectively, and the weighting factor w is given by $w = 4F_o^2/\sigma^2(F_o)^2$.

During the latter stages of refinement the contributions from all H atoms were included in the calculations. The H atoms attached to C were included at their calculated positions (C–H 0.95 Å, appropriate sp^2 and sp^3 geometry) with thermal parameters 1.2 times those of the attached C atom and constrained to "ride" on these same C atoms. The H atom on O3 was located in a difference Fourier and also constrained to ride on this atom.

The final agreement factors were $R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.070$, $R_2 = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2) = 0.065$.

In the final cycle the largest shift in any parameter was 0.04 times its estimated standard deviation and the error in an observation of unit weight was 1.59 e. An analysis of R_2 in terms of F_o, $\lambda^{-1}\sin\theta$, and various combinations of Miller indices showed no unusual trends. The highest peak in the final difference Fourier was 0.28 (7) e Å^{-3}; it is not located near any other atom and is without chemical significance.

(*E*)-(7a*R,2*S**,3a*R**)-Octahydro-7a-hydroxy-1-(phenylmethylene)-2-(phenylsulfonyl)-1*H*-indene (18c) and (7a*R**,3a*S**)-Octahydro-7a-hydroxy-1-(phenylmethylene)-2-(phenylsulfonyl)-1*H*-indene (18c′).** After crystallization of **17b** (see above), the mother liquor was concentrated to afford solid material. A portion (645.3 mg, 1.23 mmol) was cyclized by the general procedure with benzene (60 mL), triphenyltin hydride

(32) The computer programs used in this analysis include several locally written or modified programs and the Enraf-Nonius Structure Determination Package: Frenz, B. A. *Computing in Crystallography*; Delft University: Delft, Holland, 1978; pp 64–71.

(33) Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. M. *Multan 11/12. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data*; Universities of York and Louvain: York, England, and Louvain, Belgium, 1982.

(685.8 mg, 1.96 mmol) in benzene (10 mL), and AIBN (9.2 mg, 0.06 mmol) in benzene (10 mL). Evaporation of the solvent and flash chromatography of the residue using 25% ethyl acetate–hexane gave a solid (286 mg) containing mainly (>90%) one compound (^{1}H NMR), which was identified as the cis ring-fused material **18c′**: mp 147–148 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.74–2.17 (m, 10 H), 2.48 (m, 1 H), 3.30 (s, 1 H), 4.26 (m, 1 H), 6.81 (d, J = 1.5 Hz, 1 H), 7.32 (m, 5 H), 7.58 (m, 3 H), 7.94 (m, 2 H).

The trans ring-fused compound **18c** (44.3 mg, 12%) was also isolated from the flash chromatography: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.67–2.06 (m, 11 H), 3.10 (d, J = 1.5 Hz, 1 H), 4.17 (dt, J = 1.5, 8.5 Hz, 1 H), 6.60 (dd, J = 1.5 Hz, 1 H), 7.26 (m, 5 H), 7.58 (m, 3 H), 7.94 (m, 2 H).

Octahydro-1-ethylidene-7a-hydroxy-2-(phenylsulfonyl)-1*H*-indene (19c). The procedure employed for **15c** was followed using triphenyltin hydride (336.7 mg, 0.96 mmol), AIBN (5 mg, 0.03 mmol), and selenides **19b** (274.1 mg, 0.59 mmol) in dry benzene (30 mL). Flash chromatography of the residue over silica gel (2 × 15 cm) using 25% ethyl acetate–hexane gave two compounds as thick syrups, which were each a chromatographically (TLC) inseparable mixture of two different isomers (^{1}H NMR) together with unreacted starting material (126.0 mg, 46%). The compound of higher R_f (24.3 mg, 13% yield; 25% based on conversion) was composed of two isomers in a 1:1 ratio (^{1}H NMR): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.02–2.01 (m, 13 H), 2.08 (br d, J = 11.5 Hz, 0.48 H), 2.46 (br d, J = 11.5 Hz, 0.52 H), 2.96 (d, J = 1.5 Hz, 0.54 H), 3.37 (d, J = 1.5 Hz, 0.46 H), 3.99 (br t, J = 9.0 Hz, 0.45 H), 4.33 (br t, J = 8.0 Hz, 0.55 H), 5.62 (dq, J = 1.5, 7.5 Hz, 0.51 H), 5.92 (dq, J = 1.5, 7.0 Hz, 0.49 H), 7.48–7.75 (m, 3 H), 7.92 (m, 2 H).

The compound of lower R_f (41.2 mg, 23% yield; 42% based on conversion) was composed of two isomers in a 1:1.6 ratio (^{1}H NMR): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.59–2.56 (m, 14.5 H), 3.86 (s, 0.38 H), 3.99 (m, 0.60 H), 4.10 (m, 0.23 H), 4.40 (br t, J = 9.0 Hz, 0.32 H), 5.81 (dq, J = 1.5, 7.5 Hz, 0.62 H), 5.99 (dq, J = 1.5, 7.0 Hz, 0.38 H), 7.42–7.75 (m, 3 H), 7.94 (m, 2 H).

Octahydro-7a-hydroxy-5-(1,1-dimethylethyl)-1-(phenylmethylene)-2-(phenylsulfonyl)-1*H*-indene (20c). The procedure employed for **15c** was followed using selenides **20b** (47.9 mg, 0.083 mmol) in benzene (40 mL), triphenyltin hydride (44.5 mg, 0.127 mmol) in benzene (5 mL), and AIBN (2 mg, 0.01 mmol) in benzene (5 mL). The mixture was stirred under reflux for 15 h and then worked up. Flash chromatography of the crude product over silica gel (1 × 15 cm) using 25% ethyl acetate–hexane gave **20c** (22.9 mg, 65%) as an oily mixture of three isomers in a 5:4:1 ratio (^{1}H NMR), which was resolvable into two spots by TLC (silica, 25% ethyl acetate–hexane). Total material: FT-IR ($CHCl_3$ cast) 3480, 1440, 1295, 1285, 1141, 1078, 749 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.42–2.06 (m, 18.5 H), 2.54 (m, 0.5 H), 3.12 (d, J = 1.5 Hz, 0.33 H), 3.19 (d, J = 1.5 Hz, 0.17 H), 3.60 (s, 0.50 H), 4.12 (m, 0.10 H), 4.19 (dt, J = 1.5, 8.5 Hz, 0.50 H), 4.30 (dt, J = 1.5, 8.5 Hz, 0.40 H), 6.56 (d, J = 1.5 Hz, 0.17 H), 6.59 (d, J = 1.5 Hz, 0.33 H), 6.82 (d, J = 1.5 Hz, 0.50 H), 7.29 (m, 5 H), 7.60 (m, 3 H), 7.92 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ (nonaromatic signals only) 14.2, 21.4, 22.3, 23.4, 23.5, 25.7, 25.8, 27.3, 27.4, 27.5, 27.7, 28.9, 29.6, 30.0, 31.0, 32.0, 32.1, 32.4, 32.8, 34.3, 34.3, 40.9, 43.7, 46.3, 47.7, 49.4, 49.5, 69.0, 69.5, 69.8, 76.2, 78.0, 80.5; exact mass, m/z [(M − $SO_2C_6H_5$)$^+$] calcd for $C_{20}H_{27}O$ 283.2062, found 283.2063.

(*E*)-(7a*R,2*S**,3a*R**)-Octahydro-7a-hydroxy-1-(phenylmethylene)-2-(phenylsulfonyl)-1*H*-indene (21c) and (7a*R**,3a*S**)-Octahydro-7a-hydroxy-1-(phenylmethylene)-2-(phenylsulfonyl)-1*H*-indene (21c′) from Bromide 21b.** The procedure employed for **15c** was followed using bromides **21b** (639.1 mg, 1.43 mmol) in benzene (60 mL), triphenyltin hydride (745.2 mg, 2.12 mmol) in benzene (10 mL), and AIBN (10 mg, 0.06 mmol) in benzene (10 mL). After evaporation of the solvent, the crude product mixture was taken up in either (ca. 25 mL) and was stirred with an aqueous solution (ca. 20 mL) containing an excess of potassium fluoride.[34] The precipitated tri-*n*-butyltin fluoride was removed by filtration, and the ether layer was separated, dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (3 × 15 cm) using 25% ethyl acetate–hexane gave an oily mixture of two compounds **21c** and **21c′** (489 mg, 92%) in a 2.3:1 ratio: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.70–1.68 (m, 4 H), 1.80–2.04 (m, 6 H), 2.48 (m, 1 H), 3.10 (d, J = 1.5 Hz, 0.3 H), 3.30 (s, 0.7 H), 4.17 (dt, J = 1.5, 8.5 Hz, 0.3 H), 4.25 (t, J = 8.5 Hz, 0.7 H), 6.59 (d, J = 1.5 Hz, 0.3 H), 6.80 (d, J = 1.5 Hz, 0.7 H), 7.30 (m, 5 H), 7.59 (m, 3 H), 7.94 (m, 2 H).

In another experiment, the two compounds obtained as above were separated. The minor compound, which was of higher R_f was identified as trans ring-fused material **21c**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.72–2.06 (m, 11 H), 3.10 (d, J = 1.5 Hz, 1 H), 4.16 (dt, J = 1.5, 9.0 Hz, 1 H), 6.62 (d, J = 1.5 Hz, 1 H), 7.32 (m, 5 H), 7.68 (m, 3 H), 7.96 (m, 2 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 21.4, 25.2, 25.5, 29.0, 33.0, 34.6, 49.0, 68.8, 76.6, 127.8, 129.1, 129.2, 129.3, 129.5, 133.4, 133.9, 136.1, 136.3, 139.2.

The major component, which was of lower R_f and was identified as cis ring-fused material **21c′**, was contaminated by some of the above isomer: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.70–2.08 (m, 10 H), 2.48 (m, 1 H), 3.10 (d, J = 1.5 Hz, 0.1 H), 3.30 (s, 0.9 H), 4.17 (m, 0.1 H), 4.25 (t, J = 8.5 Hz, 0.9 H), 6.59 (d, J = 1.5 Hz, 0.1 H), 6.79 (d, J = 1.5 Hz, 0.9 H), 7.31 (m, 5 H), 7.58 (m, 3 H), 7.92 (m, 2 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 22.5, 23.9, 29.3, 29.5, 31.4, 48.3, 69.6, 80.2, 127.8, 127.8, 129.1, 129.2, 129.4, 133.9, 135.2, 135.7, 136.3, 137.5.

Octahydro-1-ethylidene-7a-hydroxy-2-(phenylsulfonyl)-1*H*-indene (24c) from Bromides 24b. The special procedure employed for **15c** was followed using triphenyltin hydride (268.0 mg, 0.76 mmol), AIBN (10 mg, 0.06 mmol), and bromides **24b** (193.4 mg, 0.50 mmol) in dry benzene (65 mL). Reflux was continued for 15 h, and then the product mixture was processed as for **21c** and **21c′**. Flash chromatography of the residue over silica gel (2 × 15 cm) using 25% ethyl acetate–hexane gave **24c** (138.0 mg, 90%) as a thick syrup, which was a mixture of four isomers in a 1:1.6:2.2:4 ratio (^{1}H NMR). The material was identical (^{1}H NMR) with that generated from **19b**: FT-IR ($CHCl_3$ cast) 3480, 1438, 1292, 1136 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.59–2.56 (m, 14.5 H), 2.96 (d, J = 1.5 Hz, 0.18 H), 3.37 (d, J = 1.5 Hz, 0.11 H), 3.86 (s, 0.24 H), 3.99 (m, 0.47 H), 4.10 (m, 0.18 H), 4.33 (br t, J = 8.0 Hz, 0.09 H), 4.40 (br t, J = 9.0 Hz, 0.20 H), 5.61 (dq, J = 1.5, 7.5 Hz, 0.19 H), 5.81 (dq, J = 1.5, 7.5 Hz, 0.36 H), 5.91 (dq, J = 1.5, 7.0 Hz, 0.19 H), 5.99 (dq, J = 1.5, 7.0 Hz, 0.25 H), 7.42–7.76 (m, 3 H), 7.92 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 13.7, 14.0, 15.7, 21.2, 21.5, 22.2, 22.3, 23.4, 24.8, 25.0, 25.1, 25.4, 25.8, 26.5, 28.9, 29.2, 30.1, 30.5, 30.6, 32.2, 33.2, 34.4, 36.1, 46.4, 46.8, 47.3, 48.3, 58.8, 64.6, 65.0, 67.7, 67.8, 79.6, 126.9, 128.9, 129.0, 129.1, 129.3, 130.4, 133.7, 133.8, 137.0; exact mass m/z calcd for $C_{17}H_{22}O_3S$ 306.1290, found 306.1283.

Octahydro-7a-hydroxy-1-oxo-1*H*-indene-2-carbonitrile (12d). An ozone–oxygen stream was bubbled through a solution of ketones **12c** (120 mg, 0.474 mmol) in dry methanol (5 mL) at −78 °C until the starting had just disappeared (5 min; TLC, silica, 25% ethyl acetate–hexane). Argon was passed through the solution for 5 min to remove the excess of ozone, and trimethyl phosphite (0.08 mL, 6.60 mmol) was injected. The cold bath was removed, and the solution was stirred for 12 h. Evaporation of the solvent and flash chromatography of the crude product over silica gel (1 × 15 cm) with 25% ethyl acetate–hexane gave **12d** (67 mg, 79%) as a mixture of isomers that was homogeneous by TLC (silica, 24% ethyl acetate–hexane): IR (neat) 3440, 2245, 1750 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.00–2.65 (m, 11 H), 3.10–3.95 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 20.2, 24.1, 24.4, 25.2, 25.3, 29.8, 30.0, 30.4, 34.7, 35.5, 43.8, 75.0, 75.2, 116.9, 117.5, 203.5, 203.9; exact mass, m/z calcd for $C_{10}H_{13}NO_2$ 179.0942, found 179.0944. Anal. Calcd for $C_{10}H_{13}NO_2$: C, 67.00; H, 7.31; N, 7.81. Found: C, 67.67; H, 7.29; N, 7.46.

(7a*R,3a*R**)-Octahydro-7a-hydroxy-1-oxo-2-(phenylsulfonyl)-1*H*-indene (17d).** A gentle stream of ozone was passed through a cold (−78 °C) solution of alkene **17c** (56.5 mg, 0.153 mmol) in 4:1 dichloromethane–methanol (5 mL) until a blue color developed (ca. 3 min). The excess of ozone was removed by a stream of argon, and dimethyl sulfide (0.5 mL) was added dropwise. The mixture was allowed to warm to room temperature over ca. 15 min and stirred for 15 h. Evaporation of the solvent and flash chromatography of the residue over silica gel (1 × 15 cm) using 25% ethyl acetate–hexane gave a white solid **17d** (32.0 mg, 71%) as a chromatographically (TLC) inseparable mixture

(34) Liebner, J. E.; Jacobus, J. *J. Org. Chem.* **1979**, *44*, 449.

of two isomers in a 1:1.1 ratio (^{1}H NMR). The material was recrystallized from ether–dichloromethane: mp 141–142 °C; FT-IR (Nujol) 3509, 3487, 1744, 1447, 1377, 1318, 1302, 1292, 1180, 1146, 1084, 1073, 738, 727, 585, 565 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.10–1.96 (m, 9.5 H), 2.30 (m, 2.0 H), 2.62 (qd, J = 1.5, 6.5, 13.5 Hz, 0.5 H), 3.84 (dd, J = 8.5, 9.5 Hz, 0.51 H), 4.12 (dd, J = 1.5, 9.7 Hz, 0.46 H), 7.59 (m, 2 H), 7.69 (m, 1 H), 7.90 (m, 2 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 20.3, 24.2, 24.3, 25.2, 25.4, 26.8, 27.0, 30.3, 30.4, 42.6, 43.6, 66.9, 68.8, 75.7, 76.5, 129.0, 129.1, 129.2, 134.0, 134.1, 134.2, 137.8, 138.6, 202.3, 203.5; exact mass, m/z [(M – CO)$^+$] calcd for $C_{14}H_{18}O_3S$ 266.0977, found 266.0975. Anal. Calcd for $C_{15}H_{18}O_4S$: C, 61.20; H, 6.16. Found: C, 61.08; H, 6.15.

(7a*R,3a*R**)-Octahydro-7a-hydroxy-1-oxo-2-(phenylsulfonyl)-1-*H*-indene (16d) and (7a*R**,3a*S**)-Octahydro-7a-hydroxy-1-oxo-2-(phenylsulfonyl)-1-*H*-indene (16d').** The procedure for **17d** was followed using alkenes **16c** and **16c'** (237.0 mg, 643.2 mmol) in 5:1 dichloromethane–methanol (25 mL). Flash chromatography of the crude product over silica gel (2 × 15 cm) using 25% ethyl acetate–hexane afforded two solids, which were each a chromatography (TLC) inseparable mixture of two isomers (^{1}H NMR), together with cis ring-fused unreacted starting material (49.9 mg, 21%). The material of higher R_f 51.1 mg, 27% yield; 34% based on conversion) was recrystallized from ether–dichloromethane and identified as the trans ring-fused ketones **16d** in a 1:1.1 ratio that had *not* been altered (^{1}H NMR) by crystallization: mp 140–145 °C; FT-IR (MeOH) 1752, 1307, 1147, 1084 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.09–1.95 (m, 9.5 H), 2.30 (m, 2 H), 2.62 (qd, J = 1.5, 6.5, 13.5 Hz, 0.5 H), 3.82 (dd, J = 8.5, 9.5 Hz, 0.55 H), 4.12 (dd, J = 1.5, 9.7 Hz, 0.45 H), 7.59 (m, 2 H), 7.69 (m, 1 H), 7.90 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 20.4, 20.4, 24.3, 24.4, 25.3, 25.4, 26.8, 27.1, 30.3, 30.4, 42.7, 43.6, 67.0, 68.9, 75.8, 129.1, 129.1, 129.1, 129.2, 134.1, 134.3; exact mass, m/z [(M – CO)$^+$] calcd for $C_{14}H_{18}O_3S$ 266.0976, found 266.0975.

The compound of lower R_f (75.6 mg, 40% yield; 50% based on conversion) was identified as the cis ring-fused materials **16d'**: mp 120–150 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.16–2.46 (m, 11.65 H), 2.74 (m, 0.35 H), 3.99 (m, 1 H), 7.60 (m, 2 H), 7.70 (m, 1 H), 7.90 (m, 2 H); exact mass, m/z [(M – CO)$^+$ calcd for $C_{14}H_{18}O_3S$ 266.0976, found 266.0975.

Octahydro-7a-hydroxy-1-oxo-1-*H*-indene (16e). The general literature procedure[26] was followed. Three strips of aluminum foil (1 × 5 cm) were dipped into a 2% w/v aqueous solution of mercurous chloride for 15 s, then into 95% ethanol, and finally into ether. The strips were immediately cut into 0.5-cm square pieces and dropped into a stirred solution of sulfones **16d** and **16d'** (30.8 mg, 0.105 mmol) in 10% aqueous THF (10 mL). Stirring was continued for 6 h, and the mixture was then refluxed for 3 h, cooled, filtered, and evaporated. The resulting oil was dissolved in dichloromethane, and the solution was dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (1 × 15 cm) using 25% ethyl acetate–hexane afforded unreacted starting material (8.0 mg, 25%) and **16e** (12.0 mg, 74%; 98% based on conversion). Compound **16e**: FT-IR (CCl_4 cast) 3420, 1742, 1710, 1442 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.78–2.58 (series of multiplets); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 20.7, 24.2, 24.7, 24.9, 25.1, 25.8, 28.1, 30.5, 31.4, 34.2, 35.1, 42.2, 45.9, 49.7, 75.1, 216.6; exact mass, m/z calcd for $C_9H_4O_2$ 154.0994, found 154.1000.

Supplementary material available: Crystal structure data (23 pages) for **17c** available from the authors.

Acknowledgment of financial support is made to the Natural Sciences and Engineering Research Council of Canada. We thank Dr. R. Ball of this department for the X-ray structure determination.

Structural and Solvent/Electrolyte Effects on the Selectivity and Efficiency of the Anodic Oxidation of Para-Substituted Aromatic Ethers. An Efficient Route to Quinol Ether Ketals and Quinol Ethers

Michael P. Capparelli, Richard E. DeSchepper, and John S. Swenton*

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

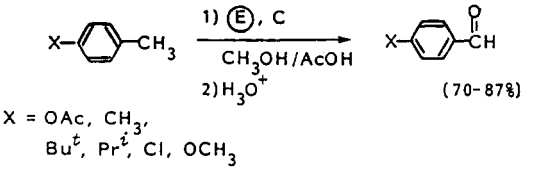
Received July 8, 1987

The anodic oxidations of the methyl ethers of *p*-arylphenols [*p*-aryl = C_6H_5, *o*-$CH_3C_6H_4$, *p*-$CH_3OC_6H_4$, *o*-[$(CH_3)_2$-*t*-BuSiOCH_2]C_6H_4, *o*-[$(H_3CO)_2HC$]C_6H_4, *o*-$HO_2CC_6H_4$], the 2-hydroxyethyl ethers of *p*-arylphenols [*p*-aryl = C_6H_5, *o*-$CH_3C_6H_4$, *p*-$CH_3OC_6H_4$, 3,4-$(CH_3O)_2C_6H_3$, 2-thiopheneyl], and the 2-hydroxyethyl ethers of *p*-alkylphenols [*p*-R = CH_3, C_2H_5, *i*-C_3H_7, *t*-C_4H_9] and 4-methyl-1-naphthol were studied. The *p*-aryl aromatic ethers underwent anodic oxidation in good yield to give the corresponding *p*-quinol ether ketals. The ratio of nuclear to side-chain products from anodic oxidation of *p*-alkylanisole derivatives is dependent upon the electrolysis conditions. The 2-hydroxyethyl ether derivatives of *p*-alkylphenols markedly favor the formation of nuclear oxidation products—providing a useful route to the corresponding *p*-quinol ether ketals. In addition, methanolic potassium fluoride improves the efficiency of these anodic oxidation processes by about 400% relative to methanolic potassium hydroxide. These reactions were performed at a constant current (1.0–2.0 A) in a single cell and serve as preparative routes to *p*-quinol ether ketals and quinol ethers via acid hydrolysis.

Introduction

The anodic oxidation of aromatic compounds in methanol often serves as a general route for the preparation of quinone bisketals.[1,2] Although 1,4-dimethoxy aromatic compounds are most often used for the oxidation, benzene,[3] monomethoxylated aromatic compounds,[4,5] and heterocyclic ring systems[5] have also been successfully em-

Scheme I. Side-Chain Oxidation of Para-Substituted Toluenes



(1) Swenton, J. S. *Acc. Chem. Res.* **1983**, *16*, 74 and references cited therein.

(2) (a) Weinberg, N. L.; Belleau, B. *J. Am. Chem. Soc.* **1963**, *85*, 2525. (b) Henton, D. R.; McCreery, R. L.; Swenton, J. S. *J. Org. Chem.* **1980**, *45*, 369. (c) Henton, D. R.; Anderson, D. K.; Manning, M. J.; Swenton, J. S. *J. Org. Chem.* **1980**, *45*, 3422.

0022-3263/87/1952-4953$01.50/0