19%) as colorless oils. For (*Z*)-**21**: $^1$H NMR δ 6.40 (m, 1 H, C-3 vinyl), 5.81 (d, 1 H, *J* = 11.07 Hz, C-2 vinyl), 4.54 (d, 2 H, allylic), 4.20 (q, 2 H, $OCH_2$), 1.31 (t, 3 H, $OCH_2CH_3$); UV (MeOH, $\lambda_{max}$) 226 nm; IR (neat) 1705 (C=O), 1625 (C=C) cm$^{-1}$; MS (70 eV) *m/e* 190 ($M^+$), 192 ($M^+ + 2$). Anal. Calcd for $C_6H_9O_2Br$: C, 37.33; H, 4.70. Found: C, 37.46; H, 4.75.

**Acknowledgment.** We thank D. Vincent Waterhous for conducting the NOE studies. This work was supported in part by Research Grants CA13148 and P01CA28103-08 from the National Cancer Institute.

**Registry No.** **2**, 119011-78-8; **3**, 119011-79-9; **4**, 39760-56-0; **5**, 13747-73-4; (*E*)-**6**, 51318-62-8; (*Z*)-**6**, 51371-55-2; **8**, 119011-80-2; **9**, 108-94-1; **10**, 867-13-0; **11**, 1552-92-7; **12**, 42516-28-9; **13**, 97856-56-9; **14**, 119011-81-3; (*Z*)-**14**, 119011-77-7; **15**, 583-60-8; **16**, 2209-00-9; (*Z*)-**16**, 2208-99-3; **17**, 119011-82-4; **18**, 119011-83-5; **19**, 105-36-2; **20**, 5108-87-2; (*E*)-**21**, 37746-78-4; (*Z*)-**21**, 119011-89-1; *cis*-**22**, 119011-84-6; *trans*-**22**, 119068-56-3; *cis*-**23**, 119011-85-7; *trans*-**23**, 119011-90-4; **24**, 119011-86-8; **25**, 119011-87-9; **26**, 119011-88-0; $(CH_3)_2C{=}CHCO_2Et$, 638-10-8.

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## Formation of Cis-Fused Cyclopentanoids by Michael Addition and Radical Cyclization

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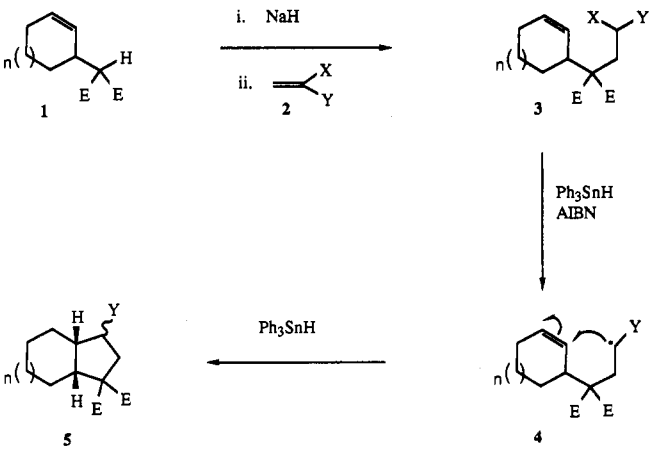
Many natural products contain cyclopentane substructures,[1] and so the development of methods for preparing five-membered carbocycles has received much attention.[2] Synthetic access to these materials using modern free radical methods[3] depends, of course, on the availability of general and straightforward ways of making the required radical precursors, and a number of studies have been published in this area.[4] We have found that the Michael reaction, when used in the manner summarized by Scheme I, and followed by radical cyclization (**3** → **4** → **5**), provides a convenient route to cis-fused cyclopentanoids. A characteristic of this strategy (Scheme I) is that the starting materials are easily prepared, not only by classical nucleophilic displacement with malonate anion, but, more importantly, by a general ene process,[5] which proceeds in suitable cases (Scheme II) with predictable stereo- and regiochemistry.

We examined a number of Michael acceptors and, of those that we tested (**2a–d**), the sulfones **2a,b** and the ester **2c** are the most useful as both reactions **1** → **3** and **3** → **5** of Scheme I generally proceed in satisfactory yield (see Table I).[6] With the exception of example **1f**, in which

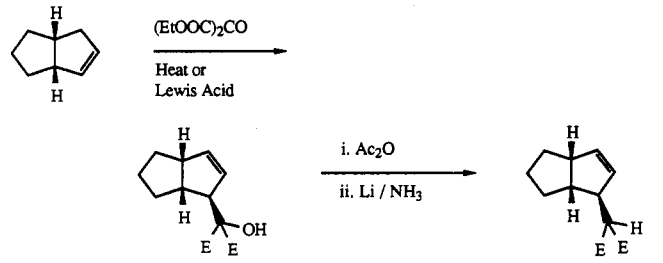
**Scheme I**[a]




2a: X = Br, Y = $SO_2Ph$; 2b: X = Br, Y = $SO_2Bu^t$
2c: X = SePh, Y = COOMe; 2d: X = Br, Y = COOMe

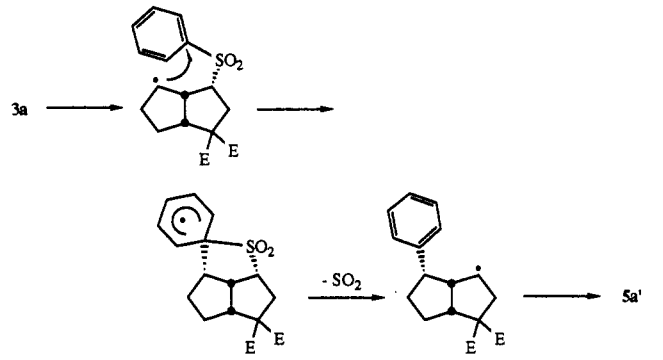
[a] E = COOEt.

**Scheme II**[a]




[a] E = COOEt.

**Scheme III**[a]




[a] E = COOEt.

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(1) See, e.g.: Paquette, L. A. *Top. Curr. Chem.* **1984**, *119*, 1 and references therein.

(2) Review: Ramaiah, M. *Synthesis* **1984**, 529.

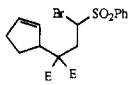
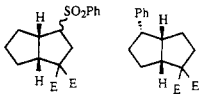
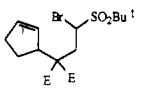
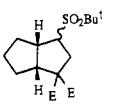
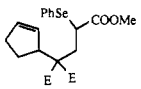
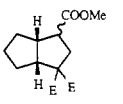
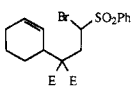
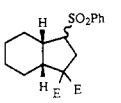
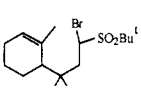
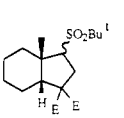
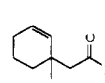
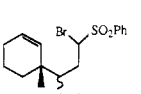
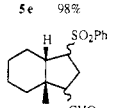
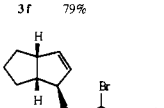
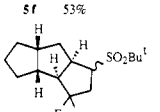
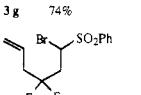
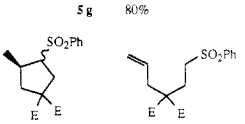
(3) Curran, D. P. *Synthesis* **1988**, 417 and 489. Hart D. J. *Science* **1984**, *223*, 883. Giese, B. *Radicals in Organic Synthesis: Formation of Carbon-Carbon Bonds*; Pergamon: Oxford, 1986. Ramaiah, M. *Tetrahedron* **1987**, *43*, 3541.

(4) (a) Bartlett, P. A.; McLaren, K. L.; Ting, P. C. *J. Am. Chem. Soc.* **1988**, *110*, 1633. (b) Barton, D. H. R.; da Silva, E.; Zard, S. Z. *J. Chem. Soc., Chem. Commun.* **1988**, 285. (c) Beckwith, A. L. J.; Roberts, D. H. *J. Am. Chem. Soc.* **1986**, *108*, 5893. (d) Boger, D. L.; Mathvink, R. J. *J. Org. Chem.* **1988**, *53*, 3377. (e) Clive, D. L. J.; Beaulieu, P. L.; Set, L. *J. Org. Chem.* **1984**, *49*, 1313. (f) Angoh, A. G.; Clive, D. L. J. *J. Chem. Soc., Chem. Commun.* **1985**, 980. (g) Set, L.; Cheshire, D. R.; Clive, D. L. J. *J. Chem. Soc., Chem. Commun.* **1985**, 1205. (h) Mohammed, A. Y.; Clive, D. L. J. *J. Chem. Soc., Chem. Commun.* **1986**, 588. (i) Clive, D. L. J.; Cheshire, D. R.; Set, L. *J. Chem. Soc., Chem. Commun.* **1987**, 353. (j) Clive, D. L. J.; Cheshire, D. R. *J. Chem. Soc., Chem. Commun.* **1987**, 1520. (k) Clive, D. L. J.; Boivin, T. L. B.; Angoh, A. G. *J. Org. Chem.* **1987**, *52*, 4943. (l) Curran, D. P.; Rakiewicz, D. M. *J. Am. Chem. Soc.* **1985**, *107*, 1448. (m) Chuang, C.-P.; Gallucci, J. C.; Hart, D. J. *J. Org. Chem.* **1988**, *53*, 3210. (n) Chuang, C.-P.; Gallucci, J. C.; Hart, D. J.; Hoffman, C. *J. Org. Chem.* **1988**, *53*, 3218. (o) Leonard, W. R.; Livinghouse, T. *Tetrahedron Lett.* **1985**, *26*, 6431. (p) Pattenden, G.; Robertson, G. M. *Tetrahedron* **1985**, *41*, 4001. (q) RajanBabu, T. V. *J. Am. Chem. Soc.* **1987**, *109*, 609. (r) Stork, G.; Baine, N. H. *J. Am. Chem. Soc.* **1982**, *104*, 2321. (s) Stork, G.; Mook, R., Jr. *J. Am. Chem. Soc.* **1983**, *105*, 3721. (t) Stork, G.; Mook, R., Jr. *J. Am. Chem. Soc.* **1987**, *109*, 2829. (u) Wilcox, C. S.; Thomasco, L. M. *J. Org. Chem.* **1985**, *50*, 546. (v) Zeigler, F. E.; Zhong-li, Zheng *Tetrahedron Lett.* **1987**, *28*, 5973. (w) Yadav, V. K.; Fallis, A. G. *Tetrahedron Lett.* **1988**, *29*, 897.

(5) (a) Salomon, M. F.; Pardo, S. N.; Salomon, R. G. *J. Org. Chem.* **1984**, *49*, 2446. (b) Salomon, M. F.; Pardo, S. N.; Salomon, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 3797. (c) Pardo, S. N.; Ghosh, S.; Salomon, R. G. *Tetrahedron Lett.* **1981**, *22*, 1885. In the deoxygenation step of Scheme II of this reference, $Li/NH_3$ should be used; in out hands the procedure reported in Table I of ref 5c did not work.

0022-3263/89/1954-1997$01.50/0 © 1989 American Chemical Society

**Table I**[a]

| entry | starting material | Michael acceptor | Michael adduct | products of radical closure |
|---|---|---|---|---|
| 1 |  1a | **2a** |  **3a** 72% |  **5a** 61% **5a'** 18%[b] |
| 2 |  1b (= 1a) | **2b** |  **3b** 73% |  **5b** 74% |
| 3 |  1c (= 1a) | **2c** |  **3c** 77% |  **5c** 80% |
| 4 |  1d | **2a** |  **3d** 67% |  **5d** 93% |
| 5 |  1e[c] | **2b** |  **3e** 46%[d] |  **5e** 98% |
| 6 |  1f[e] | **2a** |  **3f** 79% |  **5f** 53% |
| 7 |  1g[f] | **2b** |  **3g** 74% |  **5g** 80% |
| 8 |  1h | **2a** |  **3h** 75% |  **5h** 35%[g] **5h'** 21%[g] |

[a] Yields refer to isolated materials; E = COOEt. [b] Endo assignment to phenyl group is made on the basis of the intramolecular mechanism for phenyl migration. [c] Prepared by the method of ref 7. [d] 100% yield after correction for recovered starting material. [e] Prepared by method of ref 8. [f] Prepared by method of ref 5c. Reduction of the intermediate acetate (see Scheme II) was done by using $Li/NH_3$ (90% yield) and not as stated in ref 5c. [g] Yield after correction for recovered starting material.

enamine chemistry was used (see Table I, **1f** → **3f**), all of the Michael additions were performed by the same general method: The substituted malonate was deprotonated with sodium hydride in THF and then treated with the Michael acceptor.

For the radical cyclization normal syringe pump techniques were used, dilute solutions of the stannane and initiator, each in benzene, being added over several hours to a refluxing benzene solution of the substrate. In some cases the free-radical step is complicated by formation of a rearrangement product [e.g., **5a'** (see Table I)]. This must be formed by an intramolecular mechanism[9] (see Scheme III) as no crossover products were detected (400-MHz $^1H$ NMR) in an experiment using a mixture of a phenyl sulfone and a mesityl sulfone,[10] although the individual sulfones each gave rise to some rearranged material. The stereochemistry at the phenyl-bearing carbon in **5a'** was assigned on the basis of this intramolecular mechanism.

The rearrangement can be avoided by using an aliphatic Michael acceptor (**2b**); however, the *tert*-butylsulfonyl group is not ideal as it is inert to sodium amalgam, a reagent that smoothly removes[11] an arylsulfonyl unit. We were led, therefore, to examine esters such as **2c** and **2d**. The former behaves very well in both stages of Scheme I, but the bromo ester **2d** is unsuitable as its use in the Michael addition leads to oligomeric products[12]—at least

(6) The following potential Michael acceptors were not satisfactory in the radical closure step: 1-[(1-bromoethenyl)sulfonyl]-2,4,6-trimethylbenzene, 1-[(1-bromoethenyl)sulfonyl]-3,5-bis(1,1-dimethylethyl)benzene, and (*Z*)-1-nitro-1-(phenylseleno)-1-propene. 1-Bromo-1-(methylsulfonyl)ethene gave a low yield in the Michael addition because the adduct was very susceptible to Ramberg–Bäcklund elimination of sulfur dioxide.

(7) Vig, O. P.; Salota, J. P.; Sharma, M. P.; Sharma, S. D. *Indian J. Chem.* **1968**, *6*, 188.

(8) Vig, O. P.; Vig, A. K.; Handa, V. K.; Sharma, S. D. *Indian J. Chem.* **1974**, *12*, 1158.

(9) Cf. Kohler, H. J.; Speckamp, W. N. *J. Chem. Soc., Chem. Commun.* **1980**, 142.

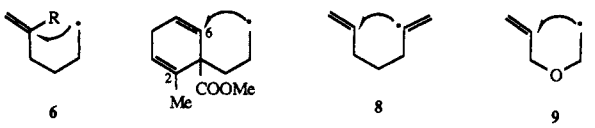
(10) An equimolar mixture of the *phenyl* sulfone corresponding to **3g** (phenyl instead of *tert*-butyl) and the *mesityl* sulfone corresponding to **3a** (2,4,6-trimethylbenzene instead of phenyl) was used.

(11) Trost, B. M.; Arndt, H. C.; Strege, P. E.; Verhoeven, T. R. *Tetrahedron Lett.* **1976**, *39*, 3477.

under our general conditions.

Table I lists our results with specific examples of the present annulation method. In most cases we used malonates because they are readily accessible, but the general technique of sequential Michael addition and radical cyclization is not limited to this compound class (see Table I, entry 6). In accordance with rules for ring fusion stereochemistry[4i] we assign cis-fusion geometry to compounds **5a–g**.

Some physical organic chemical studies[13] have been made on α-sulfonyl radicals, but their synthetic chemistry has not been well explored.[14] It is evident, however, that such species do have useful properties, and some comment is needed on the very efficient conversion of **3e** to **5e** (see Table I, entry 5). This involves closure of a sulfone-bearing radical onto the disubstituted terminus of an isolated double bond. The corresponding classical process, such as **6** (R = Me), which involves a primary radical, is slow compared with the simple case **6** (R = H), the latter being about 40 times as fast (at 25 °C).[4c,15] Another model, with which comparison can be made, is radical **7**.[4c] Here there is an intramolecular competion between the two differently substituted double bonds, and, at 70 °C, attack at C-6 is about 30 times as fast[4c] as at C-2. However, cyclization of **3e** proceeds smoothly, and there are, evidently, no problems from competing hydrogen abstraction (from stannane) before closure. We have found in this work only one example of an α-sulfonyl radical (**3h**) where such hydrogen abstraction is serious: **3h** gives the cyclized product **5h** in 35% yield only; **5h′** is formed as well (21%). Carbocyclization onto the fully substituted terminus of a nonconjugated double bond has been observed in the case of vinyl radicals,[4r-t] and also in those situations in which a tetrahydrofuran[16] or pyrrolidine[17] is generated by a 5-exo pathway. Closure of vinyl radicals (as in **8**)[18] and formation of tetrahydrofurans (as in **9**)[15] have been examined kinetically: both processes have specific rate constants that are appreciably larger than that which is characteristic of the classical hexenyl radical (**6**, R = H).[15] The vinyl




radical is very reactive,[15] and a number of other factors[15] also probably contribute to the enhanced rate of vinyl cyclizations. Formation of simple heterocycles (as in **9**) is also inherently easy, and this characteristic has been attributed to favorable C–O bond lengths and C–O–C bond angles.[15] It is evident that the cyclization of α-sulfonyl radicals is a further example of facile closure onto an isolated double bond that is substituted at its proximal terminus.[19]

## Experimental Section

The same general experimental techniques were used as reported previously,[4k] except that TLC plates were usually developed with phosphomolybdic acid[20] or an acidic solution of anisaldehyde in 95% ethanol.[21]

[(1-Bromoethenyl)sulfonyl]benzene (**2a**) was prepared as reported previously.[4k] Methyl α-bromoacrylate (**2d**)[22] was made by the literature procedure.

**1-Bromo-1-[(1,1-dimethylethyl)sulfonyl]ethene (2b). (a) 2-[(1,1-Dimethylethyl)thio]ethanol.** 2-Methyl-2-propanethiol (22.5 mL, 0.20 mol) was added slowly from a dropping funnel to a magnetically stirred solution of sodium (4.6 g, 0.20 mol) in absolute ethanol (300 mL). Stirring was continued, and, after an additional 15 min, 2-chloroethanol (13.4 mL, 0.20 mol) was added slowly. The mixture was then refluxed for 1 h, and, at that stage, the solvent was removed slowly by distillation at atmospheric pressure. The pot residue was cooled, and solid NaBr was filtered off to yield the desired alcohol as a light yellow oil (26.3 g, 98%). The crude material was suitable for the next stage: IR (neat) 3390, 1465, 1370, 1170, 1055 $cm^{-1}$; $^1H$ NMR (80 MHz, $CDCl_3$) δ 1.40 (s, 9 H), 2.55 (t, $J$ = 6.6 Hz, 2 H), 2.80 (s, 1 H), 3.80 (t, $J$ = 6.6 Hz, 2 H).

**(b) [(1,1-Dimethylethyl)thio]ethene.** The literature procedure for a similar compound was followed[23] but with some alterations. A 100-mL round-bottomed flask containing a magnetic stirring bar and solid potassium hydroxide (4.00 g, 71.3 mmol) was equipped with a 8-in. Vigreaux column that was well lagged with cottonwool and aluminum foil. The column carried a thermometer and a condenser set for distillation. The flask was lowered into an oil bath set at 250 °C, and the above sulfide (26.3 g, 195 mmol) was added quickly by pipette through the thermometer inlet. After a few moments distillation started and was allowed to continue until the pot residue was dry. The water that codistilled was separated, and the vinyl sulfide was obtained, after drying over anhydrous potassium carbonate, as a colorless, extremely lacrimatory oil (20.4 g, 89%). The material, which was used directly in the next step, had the following characteristics: $^1H$ NMR ($CDCl_3$, 400 MHz) δ 1.34 (s, 9 H), 5.28 (d, $J$ = 9.0 Hz, 1 H), 5.36 (d, $J$ = 16.0 Hz, 1 H), 6.52 (dd, $J$ = 9.0, 16.0 Hz, 1 H).

**(c) [(1,1-Dimethylethyl)sulfonyl]ethene.** The literature procedure for oxidation of phenyl vinyl sulfide was followed.[24] Hydrogen peroxide (68 mL, 30% solution, 0.60 mmol) was added dropwise to a magnetically stirred solution of the above sulfide (20.4 g, 0.176 mol) dissolved in glacial acetic acid (80 mL). The mixture was then refluxed for 20 min, cooled, and extracted with dichloromethane (3 × 75 mL). The organic extract was dried ($MgSO_4$) and evaporated under water pump vacuum. Residual acetic acid was removed by azeotropic distillation with toluene (30 mL). This process was repeated three times to afford a yellow solid. Recrystallization from hexane–dichloromethane gave the sulfone (14.3 g, 55%) as long, white needles, which were used directly in the next step: IR ($CCl_4$ solution) 1315, 1135 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 400 MHz) δ 1.40 (s, 9 H), 6.28 (d, $J$ = 10.0 Hz, 1 H), 6.48 (d, $J$ = 17.0 Hz, 1 H), 6.68 (dd, $J$ = 10.0, 17.0 Hz, 1 H).

**1-Bromo-1-[(1,1-dimethylethyl)sulfonyl]ethene (2b).** Bromine (3.30 mL, 64.1 mmol) in dry carbon tetrachloride (6.7 mL) was added dropwise to a solution of the above sulfone (1.90 g, 12.8 mmol) in carbon tetrachloride (35 mL). The mixture was stirred for 8 h, and then additional bromine (3.30 mL, 64.1 mmol) in carbon tetrachloride (6.7 mL) was added dropwise. After a further 24 h the solvent was evaporated. Flash chromatography of the resulting dark red material over silica gel (4 × 15 cm) with 15% ethyl acetate–hexane afforded 1,2-dibromoethyl 1,1-dimethylethyl sulfone (2.85 g, 9.26 mmol, 72%) as a white solid.

(12) Cf. Fouchet, B.; Joucla, M.; Messager, J. C.; Toupet, L. *J. Chem. Soc., Chem. Commun.* **1982**, 858.

(13) Block, E. *Reactions of Organosulfur Compounds*; Academic: New York, 1978. Vacher, B.; Samat, A.; Chanon, M. *Tetrahedron Lett.* **1985**, *26*, 5129.

(14) Ueno, Y.; Khare, R. K.; Okawara, M. *J. Chem. Soc., Perkin Trans. 1* **1983**, 2637 and references therein.

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(20) Phosphomolybdic acid (15 g) and ceric ammonium sulfate (2.5 g) dissolved in a mixture of water (485 mL) and concentrated sulfuric acid (15 mL).

(21) Anisaldehyde (15 drops) in a mixture of 95% ethanol (94 mL) and concentrated sulfuric acid (6 mL).

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This was dissolved immediately in dry dichloromethane (30 mL), and triethylamine (1.5 mL, 10.8 mmol) in dry dichloromethane (2 mL) was added dropwise, with stirring, over 5 min. Stirring was continued at room temperature for 18 h, and the mixture was then cooled to 0 °C and diluted with ether (20 mL). The resultant precipitate was filtered off. Concentration of the filtrate gave **2b** as a solid. Three recrystallizations from hexane–dichloromethane afforded material (2.05 g, 94%) as off-white needles suitable for the Michael reaction. An analytical sample was prepared by sublimation (120 °C, 0.20 mm): mp 64 °C; FT-IR ($CCl_4$ cast) 1300, 1131, 1070, 765, 640, 580 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 200 MHz) $\delta$ 1.48 (s, 9 H), 6.51 (d, $J$ = 2.5 Hz, 1 H), 6.92 (d, $J$ = 2.5 Hz, 1 H); $^{13}C$ NMR ($CDCl_3$, 75.5 MHz) $\delta$ 24.33 (q), 61.72 (s), 125.03 (t), 134.44 (s); MS $m/z$ 227 ($M^+$). Anal. Calcd for $C_6H_{11}BrO_2S$: C, 31.73; H, 4.88; Br, 35.18; S, 14.12. Found: C, 31.82; H, 4.87; Br, 35.29; S, 14.09.

**Methyl 2-(Phenylseleno)propenoate.** The literature procedure[25] was followed (but with some modification) with use of methyl acrylate (1.80 mL, 20.0 mmol) and phenylselenenyl chloride (3.83 g, 20.0 mmol) in dichloromethane (20 mL) and triethylamine (2.46 g, 24.3 mmol) in benzene (50 mL). After the addition of triethylamine, the mixture was stirred for 3 h and then evaporated. Flash chromatography[26] of the residue over silica gel (5 × 15 cm) using 5% ethyl acetate–hexane afforded **2c** (3.05 g, 63%) as a light yellow oil, which decomposed slowly at −5 °C: $^1H$ NMR (80.0 MHz, $CDCl_3$) $\delta$ 3.72 (s, 3 H), 5.48 (s, 1 H), 6.70 (s, 1 H), 7.15–7.75 (m, 5 H).

**Diethyl 2-(2-Cyclopenten-1-yl)-2-[2-bromo-2-(phenylsulfonyl)ethyl]propane-1,3-dioate (3a).** Diethyl 2-(cyclopenten-1-yl)propane-1,3-dioate[27] (835 mg, 3.69 mmol) in dry THF (4 mL + 1-mL rinse) was injected dropwise into a stirred suspension of sodium hydride (182 mg, 50% dispersion in oil, 3.78 mmol) in THF (35 mL) at 50 °C. When evolution of hydrogen had ceased (ca. 30 min), the mixture was cooled to 0 °C, and **2a** (736 mg, 2.98 mmol) in THF (3 mL + 1-mL rinse) was injected over 20 min. The mixture was stirred for 3 h at 0 °C, quenched with saturated aqueous ammonium chloride (5 mL), and extracted with ether (3 × 15 mL). The combined extracts were washed with brine (10 mL), dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (3 × 15 cm) using 20% ethyl acetate–hexane afforded **3a** (1.02 g, 72%) as a white solid, which was a chromatographically (TLC) inseparable mixture of two isomers in a 1.4:1 ratio ($^{13}C$ NMR): mp 63–66 °C; FT-IR ($CHCl_3$ cast) 1726, 1445, 1329, 1246, 1207, 1158, 1085 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 300 MHz) $\delta$ 1.25 (m, 6 H), 1.53–1.72 (m, 1 H), 1.92–2.15 (m, 1 H), 2.39 (m, 2 H), 2.46 (dd, $J$ = 10.0, 16.0 Hz, 0.57 H), 2.47 (dd, $J$ = 9.3, 16.0 Hz, 0.43 H), 3.18 (dd, $J$ = 1.8, 3.2 Hz, 0.55 H), 3.24 (dd, $J$ = 1.8, 3.2 Hz, 0.45 H), 3.46 (m, 1 H), 4.04–4.28 (m, 4 H), 5.11 (dd, $J$ = 1.8, 10.0 Hz, 0.57 H), 5.14 (dd, $J$ = 1.8, 9.3 Hz, 0.43 H), 5.66 (m, 0.4 H), 5.80 (m, 1.6 H), 7.60 (m, 2 H), 7.72 (m, 1 H), 7.98 (m, 2 H). Irradiation at $\delta$ 5.14 resulted in collapse of the signals at $\delta$ 3.24 and 3.18 to a pair of doublets and simplification of the signals at $\delta$ 2.46 and 2.47: $^{13}C$ NMR ($CDCl_3$, 75.5 MHz) $\delta$ 13.92, 25.10, 25.30, 31.79, 31.90, 34.78, 34.85, 49.88, 50.04, 58.93, 59.02, 60.66, 60.89, 61.56, 61.77, 61.88, 129.10, 130.11, 130.14, 130.26, 130.45, 133.36, 133.47, 134.56, 135.15, 169.78, 169.86, 170.08; exact mass, $m/z$ calcd for $C_{20}H_{25}{}^{81}BrO_6S$ 474.0535, found 474.0539. Anal. Calcd for $C_{20}H_{25}BrO_6S$: C, 50.75; H, 5.32; O, 20.28; S, 6.77. Found: C, 50.77; H, 5.22; O, 20.13; S, 6.71.

**Diethyl 2-(2-Cyclopenten-1-yl)-2-[2-bromo-2-[(1,1-dimethylethyl)sulfonyl]ethyl]propane-1,3-dioate (3b).** The procedure employed for **3a** was followed with diethyl 2-(cyclopenten-1-yl)propane-1,3-dioate[27] (254 mg, 1.12 mmol) in THF (1 mL + 1-mL rinse), sodium hydride (44 mg, 60% dispersion in oil, 1.10 mmol) in dry THF (10 mL), and **2b** (228 mg, 1.00 mmol) in THF (2 mL + 1-mL rinse). Flash chromatography of the crude product over silica gel (2 × 15 cm) using 15% ethyl acetate–hexane gave **3b** (330 mg, 73%) as a thick syrup, which was a chromatographically (TLC) inseparable mixture of two isomers in a 1.4:1 ratio ($^1H$ NMR): FT-IR ($CCl_4$ cast) 2972, 1728, 1311, 1246, 1119 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 300 MHz) $\delta$ 1.24 (m, 6 H), 1.54 (s) and 1.56 (s) [both signals together correspond to 9 H], 1.60–1.80 (m, 1 H), 1.93–2.18 (m, 1 H), 2.30 (m, 2 H), 2.41–2.60 (m, 1 H), 3.27 (dd, $J$ = 1.5, 3.0 Hz, 0.58 H), 3.34 (dd, $J$ = 2.0, 3.0 Hz, 0.42 H), 3.46 (m, 1 H), 4.04–4.30 (m, 4 H), 5.32 (dd, $J$ = 1.5, 8.5 Hz) and 5.34 (dd, $J$ = 2.0, 8.5 Hz) [both signals together correspond to 1 H]; $^{13}C$ NMR ($CDCl_3$, 75.5 MHz) $\delta$ 13.89, 25.09, 25.32, 25.34, 31.81, 31.90, 35.30, 50.43, 50.46, 54.33, 54.73, 59.16, 59.27, 61.51, 61.70, 61.77, 63.33, 63.37, 130.19, 130.40, 133.27, 133.69, 170.01, 170.20, 170.42; exact mass, $m/z$ calcd for $C_{18}H_{29}{}^{81}BrO_6S$ 454.0848, found 454.0845. Anal. Calcd for $C_{18}H_{29}BrO_6S$: C, 47.68; H, 6.45; Br, 17.62; S, 7.07. Found: C, 47.73; H, 6.26; Br, 17.84; S, 7.05.

**Diethyl 2-(2-Cyclopenten-1-yl)-2-[2-(methoxycarbonyl)-2-(phenylseleno)ethyl]propane-1,3-dioate (3c).** The procedure employed for **3a** was followed with use of diethyl 2-(cyclopenten-1-yl)propane-1,3-dioate[27] (226 mg, 1.00 mmol) in dry THF (1 mL + 1-mL rinse), sodium hydride (40 mg, 60% dispersion in oil, 1.00 mmol) in THF (20 mL), and **2c** (527 mg, 2.19 mmol) in THF (4 mL + 1-mL rinse), but, in this case, the Michael acceptor was injected into the cold solution over a period of 4 h. The mixture was then quenched and worked up in the usual way. Flash chromatography of the crude product over silica gel (2 × 15 cm) using 5% ethyl acetate–hexane afforded **3c** (360 mg, 77%) as a thick syrup, which was a chromatographically inseparable mixture (TLC) of two isomers in a 1:1 ratio ($^1H$ NMR): FT-IR ($CCl_4$ cast) 1731, 1415, 1230, 1190, 740 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 300 MHz) $\delta$ 1.21 (m, 6 H), 1.65 (m, 1 H), 1.96 (m, 1 H), 2.14–2.41 (m, 3 H), 2.55 (m, 1 H), 3.48 (m, 1 H), 3.53 (s, 1.5 H), 3.55 (s, 1.5 H), 3.85–4.23 (m, 5 H), 5.57–5.80 (m, 2 H), 7.31 (m, 3 H), 7.60 (m, 2 H); $^{13}C$ NMR ($CDCl_3$, 75.5 MHz) $\delta$ 13.85, 13.99, 25.17, 25.39, 31.85, 31.94, 34.61, 34.73, 36.85, 50.30, 50.51, 51.66, 60.55, 60.67, 61.12, 61.29, 127.71, 128.79, 128.95, 130.60, 130.85, 132.81, 132.93, 136.15, 136.19, 137.94, 170.32, 170.41, 170.55, 173.05, 173.22; exact mass, $m/z$ calcd for $C_{22}H_{28}O_6Se$ 468.1051, found 468.1065. Anal. Calcd for $C_{22}H_{28}O_6Se$: C, 56.53; H, 6.04; O, 20.54. Found: C, 56.33; H, 5.86; O, 20.14.

**Diethyl 2-(2-Cyclohexen-1-yl)-2-[2-bromo-2-(phenylsulfonyl)ethyl]propane-1,3-dioate (3d).** The procedure employed for **3a** was followed with use of diethyl 2-(cyclohexen-1-yl)propane-1,3-dioate[28] (222 mg, 0.925 mmol) in dry THF (1 mL + 1-mL rinse), sodium hydride (60 mg, 50% dispersion in oil, 1.25 mmol) in THF (10 mL), and **2a** (186 mg, 0.752 mmol) in THF (1 mL + 1-mL rinse). Flash chromatography of the crude product over silica gel (2 × 15 cm) using 20% ethyl acetate–hexane afforded **3d** (246 mg, 67%) as a white solid, which was a chromatographically (TLC) inseparable mixture of two isomers in a 1.3:1 ratio ($^1H$ NMR): mp 77–82 °C; FT-IR ($CHCl_3$ cast) 1730, 1445, 1325, 1310, 1242, 1215, 1195, 1155, 1080 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 300 MHz) $\delta$ 1.30 (m, 6 H), 1.40–2.05 (m, 6 H), 2.46 (dd, $J$ = 9.5, 16.0 Hz, 0.52 H), 2.54 (dd, $J$ = 9.5, 16.0 Hz, 0.48 H), 2.91 (m, 0.56 H), 3.00 (m, 0.44 H), 3.28 (dd, $J$ = 1.5, 16.0 Hz, 0.54 H), 3.33 (dd, $J$ = 1.5, 16.0 Hz, 0.46 H), 4.40–4.35 (m, 4 H), 5.12 (dd, $J$ = 1.5, 9.5 Hz, 0.56 H), 5.28 (dd, $J$ = 1.5, 9.5 Hz, 0.44 H), 5.76 (m, 2 H), 7.60 (m, 2 H), 7.72 (m, 1 H), 7.98 (m, 2 H). Irradiation at $\delta$ 5.28 resulted in collapse of the signal at $\delta$ 2.54 to a doublet and simplification of the signals at $\delta$ 3.28 and 3.33. Irradiation at $\delta$ 5.12 resulted in collapse of the signal at $\delta$ 2.46 to a doublet and simplification of the signals at $\delta$ 3.28 and 3.33. Irradiation at $\delta$ 3.28 resulted in collapse of the two signals at $\delta$ 5.2, and 5.12 to two doublets and simplification of the signals at $\delta$ 2.46 and 2.54: $^{13}C$ NMR ($CDCl_3$, 75.5 MHz) $\delta$ 13.90, 22.20, 22.32, 24.24, 24.48, 24.91, 34.09, 34.19, 39.97, 40.23, 58.75, 59.29, 60.86, 61.13, 61.51, 61.59, 61.74, 61.93, 65.83, 126.83, 127.47, 129.09, 129.34, 129.97, 130.07, 130.13, 134.51, 135.29, 169.41, 169.71; exact mass, $m/z$ calcd for $C_{21}H_{27}{}^{81}BrO_6S$ 488.0691, found 488.0688. Anal. Calcd for $C_{21}H_{27}BrO_6S$: C, 51.75; H, 5.58; O, 19.70; S, 6.58. Found: C, 51.79; H, 5.43; O, 19.66; S, 6.39.

**Diethyl 2-(2-Methyl-2-cyclohexen-1-yl)-2-[2-bromo-2-[(1,1-dimethylethyl)sulfonyl]ethyl]propane-1,3-dioate (3e).** The procedure employed for **3a** was followed with use of diethyl 2-(2-methyl-2-cyclohexen-1-yl)propane-1,3-dioate (**1e**)[7] (170 mg,

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(26) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923. The compound should not be purified by distillation as it is thermally unstable.

(27) Moffett, R. B. *Organic Syntheses*; Wiley: New York, 1963; Collect. Vol. IV, p 291.

(28) Moffett, R. B.; Hart, C. A.; Hoehn, W. M. *J. Am. Chem. Soc.* **1947**, *69*, 1854.

0.670 mmol) in dry THF (1 mL + 1-mL rinse), sodium hydride (27 mg, 60% dispersion in oil, 0.670 mmol) in THF (15 mL), and **2b** (140 mg, 0.617 mmol) in THF (2 mL + 1-mL rinse). In this case the crude product was distilled (Kugelrohr; 155 °C, 0.2 mm) after workup to afford **3e** (138 mg, 46%; 100% based on conversion) as a thick syrup, which was a chromatographically inseparable (TLC) mixture of two isomers in a 2.1:1 ratio ($^1$H NMR). Unreacted diester (112 mg, 65%) was also recovered during the distillation (Kugelrohr; 110 °C, 0.2 mm). Compound **3e**: FT-IR ($CCl_4$ cast) 2968, 2920, 1735, 1309, 1240, 1119 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 200 MHz) δ 1.33–1.49 (m, 6 H), 1.49–2.17 (m, 18 H), 2.56 (dd, $J$ = 8.5, 15.5 Hz, 0.69 H), 2.71 (dd, $J$ = 9.0, 16.0 Hz, 0.312 H), 3.19 (m, 1 H), 3.59 (dd, $J$ = 1.8, 16.0 Hz, 0.33 H), 3.64 (dd, $J$ = 1.8, 16.0 Hz, 0.67 H), 4.19–4.43 (m, 4 H), 5.51 (dd, $J$ = 1.8, 9.0 Hz, 0.3 H), 5.61 (dd, $J$ = 1.8, 8.5 Hz, 1.2 H), 5.65–5.76 (m, 0.5 H); $^{13}$C NMR ($CDCl_3$, 75.5 MHz) δ 14.20, 14.32, 14.37, 21.81, 22.41, 23.33, 24.98, 25.41, 25.69, 25.84, 26.50, 26.60, 29.30, 36.20, 36.46, 36.67, 43.19, 43.96, 44.57, 55.47, 55.45, 55.82, 56.02, 59.83, 59.96, 62.01, 62.20, 62.43, 63.95, 128.00, 129.44, 133.26, 134.52, 170.15, 170.46, 171.13, 171.22; exact mass, $m/z$ calcd for $C_{22}H_{33}{}^{81}BrO_6S$ 482.1161, found 482.1162. Anal. Calcd for $C_{22}H_{33}BrO_6S$: C, 49.89; H, 6.91; Br, 16.59; S, 6.66. Found: C, 50.08; H, 6.98; Br, 16.88; S, 6.58.

**4-Bromo-2-(1-methyl-2-cyclohexen-1-yl)-4-(phenylsulfonyl)butanal (3f).** A solution of diethyl 2-(1-methyl-2-cyclohexen-1-yl)ethanal (**1f**)[8] (330 mg, 2.49 mmol), pyrrolidine (0.20 mL, 2.42 mmol), and *p*-toluenesulfonic acid (1 mg, 0.003 mmol) in benzene (70 mL) was refluxed for 5.5 h in a Soxhlet apparatus containing a thimble packed with crushed calcium hydride. The benzene solution was then cooled and evaporated, and the crude enamine was quickly dissolved in dry THF (30 mL) and used immediately in the next step.

[(1-Bromoethenyl)sulfonyl]benzene (**2a**) (407 mg, 1.65 mmol) in THF (2 mL + 1-mL rinse) was injected dropwise into the enamine solution. The mixture was stirred for 1.5 h at room temperature and then quenched with saturated aqueous ammonium chloride (10 mL) and extracted with ether (3 × 25 mL). The combined extracts were washed with brine (10 mL), dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (3 × 15 cm) using 20% ethyl acetate–hexane gave **3f** (505 mg, 79%) as a thick syrup, which was a chromatographically (TLC) inseparable mixture of three isomers in a 4.8:1.8:1 ratio ($^1$H NMR): FT-IR ($CH_2Cl_2$ cast) 2935, 2860, 2830, 2035, 1718, 1447, 1325, 1310, 1151, 1083, 753, 729, 688 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 300 MHz) δ 1.12 (s, 0.75 H), 1.14 (s, 1.82 H), 1.16 (s, 0.43 H), 1.34–1.52 (m, 1 H), 1.55–1.72 (m, 3 H), 1.90–2.10 (m, 3 H), 2.52–2.95 (m, 2 H), 4.75 (dd, $J$ = 2.5, 11.5 Hz, 0.4 H), 5.45 (m, 0.7 H), 5.60 (m, 0.3 H), 5.78 (m, 1 H), 7.60 (m, 2 H), 7.72 (m, 1 H), 7.96 (m, 2 H), 9.70 (m, 0.24 H), 9.86 (m, 0.63 H), 9.92 (d, $J$ = 2.0 Hz, 0.13 H); $^{13}$C NMR ($CDCl_3$, 75.5 MHz) δ 15.30, 18.59, 24.63, 24.78, 25.51, 25.82, 26.13, 28.82, 34.76, 32.27, 32.49, 37.34, 37.83, 57.79, 58.79, 63.24, 64.70, 64.87, 65.86, 128.51, 128.70, 129.15, 129.85, 133.06, 133.21, 134.59, 135.59, 204.01, 204.24, 204.54; exact mass, $m/z$ calcd for $C_{17}H_{21}{}^{81}BrO_3S$ 386.0375, found 386.0376. Satisfactory combustion analytical values could not be obtained.

**Diethyl 2-(1α,3aα,4,5,6,6aα-Hexahydropentalen-1-yl)-2-[2-bromo-2-[(1,1-dimethylethyl)sulfonyl]ethyl]propane-1,3-dioate (3g).** The procedure employed for **3a** was followed with use of **1g**[5] (30 mg, 1.15 mmol) in dry THF (1 mL + 1-mL rinse), sodium hydride (46 mg, 60% dispersion in oil, 1.15 mmol) in THF (10 mL), and **2b** (228 mg, 1.01 mmol) in THF (2 mL + 1-mL rinse). Flash chromatography of the crude product over silica gel (2 × 15 cm) using 20% ethyl acetate–hexane gave **3g** (367 mg, 74%) as a thick syrup, which was a chromatographically (TLC) inseparable mixture of two isomers in a 1:1 ratio ($^1$H NMR): FT-IR ($CCl_4$ cast) 2940, 1729, 1310, 1242, 1202, 1119 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 200 MHz) δ 1.18–1.33 (m, 6 H), 1.33–1.52 (m, 4 H), 1.54 (s, 4.5 H), 1.56 (s, 4.5 H), 1.58–1.90 (m, 2 H), 2.43 (dd, $J$ = 9.5, 15.5 Hz, 1 H), 2.52 (dd, $J$ = 8.0, 15.5 Hz, 1 H), 3.09 (m, 2 H), 3.27 (dd, $J$ = 2.0, 15.5 Hz, 0.58 H), 3.29 (dd, $J$ = 2.5, 16.0 Hz, 0.42 H), 4.15 (m, 4 H), 5.39 (dd, $J$ = 2.5, 8.5 Hz, 0.5 H), 5.48 (dd, $J$ = 2.0, 9.0 Hz, 0.5 H), 5.56 (m, 2 H); $^{13}$C NMR ($CDCl_3$, 75.5 MHz) δ 13.94, 14.03, 25.02, 25.13, 25.21, 31.55, 31.64, 35.26, 35.55, 35.85, 35.98, 43.78, 44.29, 50.57, 54.73, 55.30, 59.30, 59.66, 59.86, 60.01, 61.58, 61.68, 61.82, 63.35, 128.73, 128.90, 138.51, 138.83, 170.14, 170.35, 170.57; exact mass, $m/z$ calcd for $C_{21}H_{33}{}^{81}BrO_6S$ 494.1161, found 494.1169. Anal. Calcd for $C_{21}H_{33}BrO_6S$: C, 51.12; H, 6.74; Br, 16.19; S, 6.49. Found: C, 51.25; H, 6.65; Br, 16.02; S, 6.48.

**Diethyl 2-(2-Propen-1-yl)-2-[2-bromo-2-(phenylsulfonyl)ethyl]propane-1,3-dioate (3h).** The procedure employed for **3a** was followed with use of diethyl 2-(2-propen-1-yl)propane-1,3-dioate[29] (411 mg, 2.05 mmol) in dry THF (2 mL + 1-mL rinse), sodium hydride (110 mg, 50% dispersion in oil, 2.29 mmol) in THF (25 mL), and **2a** (457 mg, 1.85 mmol) in THF (2 mL + 1-mL rinse). Flash chromatography of the crude product over silica gel (3 × 15 cm) using 15% ethyl acetate–hexane gave **3h** (625 mg, 75%) as a single crystalline isomer ($^1$H NMR): mp 76–77 °C; FT-IR ($CCl_4$ cast) 1732, 1445, 1330, 1310, 1290, 1230, 1210, 1155, 1080 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 300 MHz) δ 1.26 (dt, $J$ = 1.5, 7.5 Hz, 6 H), 2.51 (dd, $J$ = 10.0, 16.0 Hz, 1 H), 2.65 (dd, $J$ = 7.5, 14.5 Hz, 1 H), 2.76 (dd, $J$ = 7.5, 14.5 Hz, 1 H), 3.20 (dd, $J$ = 2.0, 16.0 Hz, 1 H), 4.06–4.28 (m, 4 H), 4.95 (dd, $J$ = 2.0, 10.0 Hz, 1 H), 5.12 (m, 2 H), 5.47–5.63 (m, 1 H), 7.61 (m, 2 H), 7.72 (m, 1 H), 7.98 (m, 2 H); $^{13}$C NMR ($CDCl_3$, 75.5 MHz) δ 13.90, 13.95, 34.67, 37.28, 55.72, 60.25, 61.85, 62.08, 120.43, 129.15, 130.20, 131.01, 134.63, 134.94, 169.70, 169.178; exact mass, $m/z$ calcd for $C_{18}H_{23}{}^{81}BrO_6S$ 448.0380, found 448.0387. Anal. Calcd for $C_{18}H_{23}BrO_6S$: C, 48.33; H, 5.18; O, 21.46; S, 7.17. Found: C, 48.27; H, 5.15; O, 21.49; S, 7.39.

**General Procedure for Radical Cyclization.** The substrate (0.5–1.5 mmol) was placed in a 100-mL oven-dried 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 dry benzene (25–60 mL) was injected. The flask was lowered into an oil bath that had been preheated to 80 °C, and benzene solutions of triphenyltin hydride (1.5 equiv, 0.01–0.1 M) and AIBN (0.3 equiv, 0.006 M) were injected simultaneously over 10 h with a double syringe pump. Refluxing was continued for an arbitrary period of 2 h after the end of the addition, and the mixture was then cooled and evaporated. In the case of bromides and residue was taken up in ether (ca. 20 mL) and stirred with an aqueous solution (10 mL) containing an excess of potassium fluoride. The precipitated tributyltin fluoride was removed by filtration, and the ether layer was separated, dried ($MgSO_4$), and evaporated. The residue was then processed as described for the individual examples.

**Diethyl (3aα,6aα)-Octahydro-3-(phenylsulfonyl)pentalene-1,1-dicarboxylate (5a) and Diethyl (3aα,4β,6aα)-Octahydro-4-phenylpentalene-1,1-dicarboxylate (5a′).** The general procedure for radical cyclization was followed with use of bromides **3a** (362 mg, 0.764 mmol) in benzene (60 mL), triphenyltin hydride (410 mg, 1.17 mmol) in benzene (10 mL), and AIBN (10 mg, 0.06 mmol) in benzene (10 mL). Flash chromatography of the crude product over silica gel (2 × 15 cm) using first 10% ethyl acetate–hexane and then gradually a more polar mixture (up to 90% ethyl acetate) afforded two compounds. That of higher $R_f$ (57 mg, 18%) was a solid, which was recrystallized from hexane and identified ($^1$H NMR) as the rearranged product **5a′**: mp 48–49 °C; FT-IR ($CHCl_3$ cast) 3040, 1729, 1240, 1170, 1090, 695 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 300 MHz) δ 1.18–1.50 (m, 9 H), 1.70–2.00 (m, 4 H), 2.16 (m, 1 H), 3.10 (m, 1 H), 3.30 (m, 2 H), 4.08–4.30 (m, 4 H), 7.12–7.32 (m, 5 H); $^{13}$C NMR ($CDCl_3$, 75.5 MHz) δ 13.08, 13.19, 24.14, 26.75, 27.82, 32.74, 47.44, 47.68, 47.78, 60.04, 60.23, 65.28, 124.79, 126.93, 127.10, 127.54, 135.53, 141.63, 169.98, 171.39; exact mass, $m/z$ calcd for $C_{20}H_{26}O_4$ 330.1843, found 330.1837. Anal. Calcd for $C_{20}H_{26}O_4$: C, 72.70; H, 7.93. Found: C, 72.55; H, 7.90.

The thick syrupy material of lower $R_f$ (226 mg, 61%) was a chromatographically (TLC) inseparable mixture of two isomers, corresponding to the cis ring-fused compounds **5a** in a 1.9:1 ratio ($^{13}$C NMR): FT-IR ($CHCl_3$ cast) 3040, 1725, 1442, 1360, 1295, 1260, 1240, 1180, 1144, 1080, 1170, 720, 700 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 300 MHz) δ 0.92–1.15 (t, $J$ = 8.5 Hz, 2.6 H), 1.17–1.40 (m, 5.4 H), 1.47–1.75 (m, 1.2 H), 1.75–1.90 (m, 1.4 H), 1.90–2.10 (m, 1.4 H), 2.18 (dd, $J$ = 5.5, 13.0 Hz, 0.7 H), 2.50 (dd, $J$ = 8.5, 14.5 Hz, 0.3 H), 2.62–2.87 (m, 1.7 H), 3.07 (m, 0.3 H), 3.22 (q, $J$ = 8.5 Hz, 0.7 H), 3.36 (m, 1.0 H), 3.48 (q, $J$ = 8.5 Hz, 0.3 H), 4.02–4.30 (m, 4 H), 7.42–7.72 (m, 3 H), 7.90 (m, 2 H); $^{13}$C NMR ($CDCl_3$, 75.5 MHz) δ 13.84, 14.01, 14.06, 14.10, 14.20, 26.68, 27.49, 28.40, 28.67, 30.46,

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32.07, 32.39, 36.09, 43.50, 45.39, 48.13, 50.56, 61.49, 61.57, 61.80, 62.39, 62.52, 63.98, 69.78, 127.98, 128.52, 129.21, 129.27, 133.59, 133.71, 138.79, 140.28, 169.15, 170.49, 170.66, 171.51; exact mass, $m/z$ calcd for $C_{20}H_{26}O_6S$ 394.1450, found 394.1446. Anal. Calcd for $C_{20}H_{26}O_6S$: C, 60.89; H, 6.64; S, 8.13. Found: C, 60.82; H, 6.60; S, 7.98.

**Diethyl (3aα,6aα)-Octahydro-3-[(1,1-dimethylethyl)-sulfonyl]pentalene-1,1-dicarboxylate (5b).** The general procedure for radical cyclization was followed with use of bromides **3b** (303 mg, 0.668 mmol) in benzene (60 mL), triphenyltin hydride (355 mg, 1.01 mmol) in benzene (10 mL), and AIBN (10 mg, 0.06 mmol) in benzene (10 mL). Flash chromatography of the crude product over silica gel (2 × 15 cm) using 25% ethyl acetate–hexane gave **5b** (185 mg, 74%) as a thick syrup, which was a chromatographically (TLC) inseparable mixture of two isomers in a 8:1 ratio ($^{13}C$ NMR): FT-IR ($CCl_4$ cast) 2968, 1730, 1460, 1288, 1264, 1182, 1115 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 300 MHz) δ 0.98–1.13 (m, 1 H), 1.26 (m, 7 H), 1.39 (s) and 1.42 (s) [both signals together correspond to 9 H], 1.72–1.82 (m, 1.5 H), 1.82–1.94 (m, 1.5 H), 2.04–2.16 (m, 1 H), 2.40 (dd, $J$ = 5.5, 13.5 Hz, 1 H), 2.74 (t, $J$ = 13.5 Hz, 1 H), 2.88 (quintet, $J$ = 8.0 Hz, 1 H), 3.23 (q, $J$ = 9.0 Hz, 1 H), 3.44 (ddd, $J$ = 5.5, 8.0, 13.5 Hz, 1 H), 4.12–4.28 (m, 4 H); $^{13}C$ NMR ($CDCl_3$, 75.5 MHz) δ 13.98, 14.09, 14.12, 23.82, 23.89, 24.03, 26.83, 27.32, 28.97, 29.36, 30.60, 32.80, 33.73, 38.61, 44.68, 45.42, 46.68, 48.91, 55.44, 60.68, 61.46, 61.54, 61.70, 61.76, 61.93, 62.17, 62.75, 169.07, 170.0, 171.03, 171.06; exact mass, $m/z$ [$(M - SO_2C_4H_9)^+$] calcd for $C_{14}H_{21}O_4$ 253.1439, found 253.1429. Anal. Calcd for $C_{18}H_{30}O_6S$: C, 57.73; H, 8.07; S, 8.56. Found: C, 57.51; H, 7.78; S, 8.29.

**(3aα,6aα)-Octahydropentalene-1,1,3-tricarboxylic Acid, 1,1-Diethyl 3-Methyl Ester (5c).** The general procedure for radical cyclization was followed with use of selenides **3c** (100 mg, 0.214 mmol) in benzene (30 mL), triphenyltin hydride (130 mg, 0.371 mmol) in benzene (10 mL), and AIBN (10 mg, 0.06 mmol) in benzene (10 mL). Flash chromatography of the crude product over silica gel (1 × 15 cm) using 5% ethyl acetate–hexane gave **5c** (53.4 mg, 80%) as a thick syrup, which was a chromatographically (TLC) inseparable mixture of two isomers in a 4:1 ratio ($^1H$ NMR): FT-IR ($CCl_4$ cast) 1731, 1260, 1250, 1230 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 300.0 MHz) δ 1.07 (m, 2 H), 1.24, 1.25 (two superimposed triplets, $J$ = 7.5 Hz, 6 H), 1.30–1.60 (m, 1 H), 1.65–1.85 (m, 3 H), 2.17 (dd, $J$ = 3.0, 12.5 Hz, 1 H), 2.49–2.71 (m, 1 H), 2.72–2.97 (m, 2 H), 3.20 (m, 1 H), 3.66 (s, 0.6 H), 3.68 (s, 2.4 H), 4.17 (m, 4 H); $^{13}C$ NMR ($CDCl_3$, 75.5 MHz) δ (signals due to major isomer only) 14.05, 14.15, 27.09, 30.24, 30.43, 32.76, 44.23, 44.69, 47.55, 51.46, 61.12, 61.43, 62.95, 169.91, 172.03, 173.46; exact mass, $m/z$ calcd for $C_{16}H_{24}O_6$ 312.1572, found 312.1575. Anal. Calcd for $C_{16}H_{24}O_6$: C, 61.52; H, 7.74. Found: C, 61.21; H, 7.71.

**Diethyl (3aα,7aα)-Octahydro-3-(phenylsulfonyl)-1*H*-indene-1,1-dicarboxylate (5d).** The general procedure for radical cyclization was followed with use of bromides **3d** (246 mg, 0.505 mmol) in benzene (60 mL), triphenyltin hydride (275 mg, 0.782 mmol) in benzene (10 mL), and AIBN (10.0 mg, 0.06 mmol) in benzene (10 mL). Flash column chromatography of the crude product over silica gel (2 × 15 cm) using 20% ethyl acetate–hexane gave **5d** (191 mg, 93%) as a thick syrup, which was a chromatographically inseparable mixture of two isomers in a 1.5:1 ratio ($^1H$ NMR): FT-IR ($CCl_4$ cast) 1728, 1445, 1305, 1265, 1245, 1147, 1085 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 300 MHz) δ 0.72–1.83 (m, 12 H), 1.88–2.02 (m, 2 H), 2.08 (m, 0.4 H), 2.22 (m, 0.1 H), 2.43–2.55 (m, 0.8 H), 2.60 (d, $J$ = 4.5 Hz, 0.2 H), 2.75 (m, 0.3 H), 2.86–3.00 (m, 1.2 H), 3.22–3.60 (m, 2 H), 3.96–4.33 (m, 4 H), 7.42–7.70 (m, 3 H), 7.90 (m, 2 H); $^{13}C$ NMR ($CDCl_3$, 75.5 MHz) δ 13.69, 13.98, 14.04, 20.59, 21.14, 22.66, 23.57, 24.29, 24.50, 25.09, 25.71, 32.53, 33.69, 39.26, 40.41, 42.14, 43.60, 44.95, 60.31, 61.67, 61.79, 61.86, 62.04, 62.77, 63.35, 65.63, 128.11, 128.75, 129.15, 129.28, 130.43, 133.57, 133.72, 136.23, 169.17, 170.52, 170.73, 172.04; exact mass, $m/z$ calcd for $C_{21}H_{28}O_6S$ 408.1610, found 408.1604. Anal. Calcd for $C_{21}H_{28}O_6S$: C, 61.74; H, 6.91; S, 7.85. Found: C, 61.66; H, 6.65; S, 7.91.

**Diethyl (3aα,7aα)-Octahydro-3a-methyl-3-[(1,1-dimethylethyl)sulfonyl]-3*H*-indene-1,1-dicarboxylate (5e).** The general procedure for radical cyclization was followed with use of bromides **3e** (251 mg, 0.522 mmol) in benzene (55 mL), triphenyltin hydride (278 mg, 0.792 mmol) in benzene (10 mL), and AIBN (10.0 mg, 0.06 mmol) in benzene (10 mL). Flash column chromatography of the crude product over silica gel (2 × 15 cm) using 25% ethyl acetate–hexane afforded two fractions. The thick syrupy material of higher $R_f$ (23.2 mg, 11%) was a single isomer ($^1H$ NMR) of **5e**: FT-IR ($CCl_4$ cast) 2976, 2936, 1732, 1207, 1287, 1271, 1243, 1179, 1116 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 200 MHz) δ 1.02–1.80 (m, 25 H), 2.38 (m, 1 H), 2.65 (dd, $J$ = 5.0, 13.0 Hz, 1 H), 2.84 (dd, $J$ = 10.5, 15.0 Hz, 1 H), 3.08 (dd, $J$ = 8.5, 15.0 Hz, 1 H), 3.75 (dd, $J$ = 10.5, 8.5 Hz, 1 H), 4.02–4.35 (m, 4 H); $^{13}C$ NMR ($CDCl_3$, 75.5 MHz) δ 13.98, 14.06, 20.94, 23.47, 23.70, 24.49, 24.99, 25.18, 33.84, 34.71, 47.49, 51.02, 56.19, 61.18, 61.86, 61.91, 62.28, 170.61, 171.28; exact mass, $m/z$ [$(M - OCH_2CH_3)^+$] calcd for $C_{18}H_{29}O_5S$ 357.1736, found 357.1749.

The fraction of lower $R_f$ (183 mg, 87%) was a thick syrup, which was a different isomer ($^1H$ NMR) of **5e**: FT-IR ($CCl_4$ cast) 2940, 1726, 1270, 1247, 1115 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 200 MHz) δ 0.81–1.79 (m, 24 H), 1.97 (m, 2 H), 2.28 (dd, $J$ = 7.5, 14.5 Hz, 1 H), 2.63 (m, 1 H), 3.11 (dd, $J$ = 7.5, 13.0 Hz, 1 H), 3.58 (dd, $J$ = 13.0, 14.5 Hz, 1 H), 4.08–4.35 (m, 4 H); $^{13}C$ NMR ($CDCl_3$, 75.5 MHz) δ 13.72, 13.78, 19.92, 20.20, 21.34, 23.47, 24.28, 26.42, 35.84, 46.18, 48.76, 69.16, 60.75, 61.68, 61.79, 63.19, 170.64, 172.65; exact mass, $m/z$ calcd for $C_{20}H_{34}O_6S$ 402.2077, found 402.2075. Anal. Calcd for $C_{20}H_{34}O_6S$: C, 59.67; H, 8.51; S, 7.97. Found: C, 59.81; H, 8.46; S, 8.23.

**(3aα,7aα)-Octahydro-7a-methyl-3-(phenylsulfonyl)-7a*H*-indene-1-carbaldehyde (5f).** The general procedure for radical cyclization was not followed in this experiment. Triphenyltin hydride (283.5 mg, 0.809 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 bromides **3f** (186 mg, 0.482 mmol) in benzene (70 mL). The mixture was stirred under reflux for 15 h, cooled, and evaporated. Flash chromatography of the residue over silica gel (2 × 15 cm) using 24% ethyl acetate–hexane afforded two fractions. The thick syrupy material of slightly higher $R_f$ (51.3 mg, 34%) was amixture of four isomers of **5f** in a 2.4:3.3:1:1 ratio ($^1H$ NMR): FT-IR ($CH_2Cl_2$ cast) 2931, 2860, 2720, 1718, 1447, 1303, 1288, 1147, 1086, 725, 690, 600 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 300 MHz) δ 0.82–2.26 (m, 12 H), 2.30–2.46 (m, 1.5 H), 2.66 (m, 0.5 H), 2.86–3.32 (m, 1 H), 3.5–3.76 (m, 1 H), 7.52–7.71 (m, 3 H), 7.92 (m, 2 H), 9.65 (m, 0.31 H), 9.73 (d, $J$ = 1.0 Hz, 0.43 H), 9.76 (d, $J$ = 2.0 Hz, 0.13 H), 9.85 (d, $J$ = 2.0 Hz, 0.13 H); $^{13}C$ NMR ($CDCl_3$, 75.5 MHz) δ 14.25, 16.91, 17.56, 20.41, 20.82, 21.03, 21.15, 21.48, 21.56, 22.58, 23.44, 23.95, 24.25, 24.47, 24.67, 24.85, 25.45, 25.64, 29.53, 34.96, 45.21, 45.60, 46.42, 50.64, 52.03, 59.51, 61.86, 62.86, 65.38, 127.94, 128.00, 128.09, 128.56, 128.65, 129.39, 133.61, 133.79, 138.79, 202.32, 203.18, 204.75; exact mass, $m/z$ calcd for $C_{17}H_{22}O_3S$ 306.1290, found 306.1287. Satisfactory combustion analytical values could not be obtained for this compound.

The fraction of lower $R_f$ (27.8 mg, 19%) was a thick syrup, which was also a mixture of the same four isomers of **5f** but in a ratio of 1.9:1.9:1.0:7.8 ($^1H$ NMR): FT-IR ($CCl_4$ cast) 2925, 2850, 2720, 1715, 1442, 1300, 1280, 1140, 1082, 750, 685, 580 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 300 MHz) δ 0.73–2.24 (m, 13 H), 2.30–2.45 (m, 1 H), 2.84–3.00 (m, 1 H), 3.60–3.79 (m, 1 H), 7.50–7.72 (m, 3 H), 7.92 (m, 2 H), 9.65 (m, 0.15 H), 9.73 (t, $J$ = 1.5, 8.0 Hz, 0.15 H), 9.76 (d, $J$ = 2.0 Hz, 0.08 H), 9.85 (d, $J$ = 2.0 Hz, 0.62 H); $^{13}C$ NMR ($CDCl_3$, 75.5 MHz) δ 20.72, 20.93, 21.38, 22.69, 23.31, 23.71, 24.14, 24.37, 24.57, 25.33, 32.28, 32.57, 33.13, 34.85, 45.56, 46.67, 48.59, 50.52, 51.91, 59.40, 61.76, 65.27, 65.59, 124.33, 127.83, 127.98, 128.45, 128.54, 129.22, 133.48, 133.76, 140.62, 202.73, 202.85, 202.12; exact mass, $m/z$ calcd for $C_{17}H_{22}O_3S$ 306.1290, found 306.1275. Satisfactory combustion analytical values could not be obtained for this compound.

**Diethyl (3aα,4aβ,7aβ,7bα)-Decahydro-3-[(1,1-dimethylethyl)sulfonyl]-1*H*-cyclopenta[*b*]pentalene-1,1-dicarboxylate (5g).** The general procedure for radical cyclization was followed with use of bromides **3g** (276 mg, 0.559 mmol) in benzene (60 mL), triphenyltin hydride (296 mg, 0.843 mmol) in benzene (10 mL), and AIBN (10.0 mg, 0.06 mmol) in benzene (10 mL). Flash chromatography of the crude product over silica gel (2 × 15 cm) using 25% ethyl acetate–hexane gave **5g** (186 mg, 80%) as a thick syrup, which was a chromatographically (TLC) inseparable mixture of two isomers in a 4.8:1 ratio ($^{13}C$ NMR): FT-IR ($CCl_4$ cast) 2952, 1729, 1289, 1265, 1250, 1160 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 300 MHz) δ 1.20–1.31 (m, 6 H), 1.38 (s) and 1.40 (s) [both signals together correspond to 9 H], 1.41–1.81 (m, 6 H), 1.86 (ddd, $J$ = 2.5, 8.5, 10.5 Hz, 1 H), 2.05 (m, 1 H), 2.25 (dddd,

$J$ = 7.5, 13.5, 1 H), 2.41 (dd, $J$ = 13.0 Hz, 1 H), 2.99 (dd, $J$ = 5.0, 8.0 Hz, 1 H), 3.12 (quintet, $J$ = 8.0 Hz, 1 H), 3.44 (ddd, $J$ = 5.5, 7.5, 13.0 Hz, 1 H), 4.08–4.31 (m, 4 H); $^{13}$C NMR ($CDCl_3$, 75.5 MHz) δ 14.00, 14.08, 23.44, 23.90, 24.15, 25.54, 25.93, 31.89, 33.19, 33.59, 33.71, 34.16, 34.67, 36.84, 38.43, 43.25, 45.22, 45.96, 46.01, 48.11, 48.36, 48.60, 55.44, 55.79, 57.33, 59.69, 59.73, 60.64, 61.53, 61.63, 61.73, 61.94, 63.26, 63.77, 169.44, 170.42, 170.83, 172.07; exact mass calcd for $C_{21}H_{34}O_6S$ 414.2076, found 414.2122. Anal. Calcd for $C_{21}H_{34}O_6S$: C, 60.84; H, 8.27; S, 7.73. Found: C, 60.90; H, 8.23; S, 7.58.

**Diethyl 4-Methyl-3-(phenylsulfonyl)-1,1-cyclopentanedicarboxylate (5h) and Diethyl 2-(2-Propen-1-yl)-2-[2-(phenylsulfonyl)ethyl]propane-1,3-dioate (5h′).** The general procedure for radical cyclization was followed with use of bromides **3h** (331 mg, 0.740 mmol) in benzene (60 mL), triphenyltin hydride (410 mg, 1.17 mmol) in benzene (10 mL), and AIBN (10.0 mg, 0.06 mmol) in benzene (10 mL). Flash chromatography of the crude product over silica (2 × 15 cm) using 25% ethyl acetate–hexane gave two fractions. The thick syrupy material of lower $R_f$ was a mixture of **5h** (83 mg,[30] 30% yield; 35% based on conversion) together with **5h′** (51 mg,[30] 19% yield; 21% based on conversion). The fraction of higher $R_f$ (44.9 mg, 13%) was unreacted starting material. The mixture of products **5h** and **5h′** had the following characteristics: FT-IR ($CCl_4$ cast) 1730, 1440, 1305, 1253, 1181, 1149, 1080 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 300 MHz) δ (signals assigned to reduction product **5h′**) 1.21 (t, $J$ = 7.5 Hz, 6 H), 2.20 (two superimposed dd, $J$ = 4.0, 13.0 Hz and $J$ = 8.0, 9.0 Hz, 2 H), 2.58 (d, $J$ = 7.5 Hz, 2 H), 3.14 (two superimposed dd, $J$ = 4.0, 13.0 Hz, and $J$ = 8.0, 9.0 Hz, 2 H), 4.14 (q, $J$ = 7.5 Hz) and 4.15 (q, $J$ = 7.5 Hz) [both signals together correspond to 4 H], 5.05 (m, 2 H), 5.51 (m, 1 H), 7.54–7.72 (m, 3 H), 7.70 (m, 2 H); (signals assigned to cyclization product **5h**) 0.98–1.49 (m, 9 H), 1.80 (m, 0.30 H), 2.38 (m, 2.3 H), 2.62–2.80 (m, 2.4 H), 3.25 (m, 0.4 H), 3.53 (m, 0.6 H), 4.05–4.32 (m, 4 H), 7.41–8.02 (m, 5 H); $^{13}$C NMR ($CDCl_3$, 75.5 MHz) δ 13.5, 15.3, 19.2, 25.4, 34.0, 34.6, 35.2, 35.9, 37.3, 41.0, 41.7, 51.3, 55.4, 57.9, 58.0, 61.2, 61.4, 65.2, 69.0, 119.4, 127.7, 128.1, 128.4, 128.7, 128.8, 130.8, 133.1, 133.3, 135.7, 139.5, 169.5, 170.2, 171.4; exact mass, $m/z$ [$(M - SO_2C_6H_5)^+$] calcd for $C_{12}H_{19}O_4$ 227.1283, found 227.1283.

An authentic sample of **5h′** was prepared by the procedure employed for **3a** with diethyl 2-(2-propen-1-yl)propane-1,3-dioate[29] (248 mg, 1.24 mmol) in dry THF (1 mL + 1-mL rinse), sodium hydride (66.4 mg, 50% dispersion in oil, 1.38 mmol) in THF (15 mL), and phenyl vinyl sulfone[24] (176 mg, 1.05 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 **5h′** (172 mg, 44%) as a colorless oil: $^1$H NMR ($CDCl_3$, 300 MHz) δ 1.21 (t, $J$ = 7.5 Hz, 6 H), 2.20 (two superimposed dd, $J$ = 4.0, 13.0 Hz and $J$ = 8.0, 9.0 Hz, 2 H), 2.58 (d, $J$ = 7.5 Hz, 2 H), 3.14 (two superimposed dd, $J$ = 4.0, 13.0 Hz, and $J$ = 8.0, 9.0 Hz, 2 H), 4.14 (q, $J$ = 7.5 Hz), and 4.15 (q, $J$ = 7.5 Hz) [both signals together correspond to 4 H], 5.05 (m, 2 H), 5.51 (m, 1 H), 7.54–7.72 (m, 3 H), 7.70 (m, 2 H); $^{13}$C NMR ($CDCl_3$, 75.5 MHz) δ 14.01, 25.91, 37.80, 51.85, 55.96, 61.72, 119.88, 128.12, 129.32, 131.30, 133.80, 138.70, 169.97; exact mass, $m/z$ calcd for $C_{18}H_{24}O_6S$ 368.1294, found 368.1290.

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**Registry No.** **1a**, 53608-93-8; **1d**, 6305-63-1; **1e**, 118893-25-7; **1f**, 60415-75-0; **1g**, 118920-25-5; **1h**, 2049-80-1; **2a**, 17101-78-9; **2b**, 118893-26-8; **2c**, 75804-36-3; **2d**, 4519-46-4; **3a** (isomer 1), 118893-27-9; **3a** (isomer 2), 118893-46-2; **3b** (isomer 1), 118893-28-0; **3b** (isomer 2), 118893-47-3; **3c** (isomer 1), 118893-29-1; **3c** (isomer 2), 118893-48-4; **3d** (isomer 1), 118893-30-4; **3d** (isomer 2), 118893-49-5; **3e** (isomer 1), 118893-31-5; **3e** (isomer 2), 118893-50-8; **3f**, 118893-32-6; **3g** (isomer 1), 118893-33-7; **3g** (isomer 2), 118893-51-9; **3h**, 118893-34-8; **5a** (isomer 1), 118893-35-9; **5a** (isomer 2), 118893-52-0; **5a′**, 118893-36-0; **5b** (isomer 1), 118893-37-1; **5b** (isomer 2), 118893-53-1; **5c** (isomer 1), 118893-38-2; **5c** (isomer 2), 118893-54-2; **5d** (isomer 1), 118893-39-3; **5d** (isomer 2), 118893-55-3; **5e** (isomer 1), 118893-40-6; **5e** (isomer 2), 118893-56-4; **5f** (isomer 1), 118893-41-7; **5f** (isomer 2), 119007-00-0; **5f** (isomer 3), 119007-01-1; **5f** (isomer 4), 119007-02-2; **5g** (isomer 1), 118893-42-8; **5g** (isomer 2), 119007-03-3; **5h**, 118893-43-9; **5h′**, 118893-44-0; 2-[(1,1-dimethylethyl)thio]ethanol, 5396-50-9; 2-methyl-2-propanethiol, 75-66-1; 2-chloroethanol, 107-07-3; [(1,1-dimethylethyl)thio]ethene, 14094-13-4; [(1,1-dimethylethyl)-sulfonyl]ethene, 18288-23-8; 1,2-dibromoethyl 1,1-dimethylethyl sulfone, 118893-45-1; methyl acrylate, 96-33-3; phenylselenenyl chloride, 5707-04-0; phenyl vinyl sulfone, 5535-48-8.

(30) This weight is calculated from the weight of the mixture and from its composition as determined by $^1$H NMR spectroscopy.

## Reactions of Norbornyl Aldehydes with Diiron Nonacarbonyl: A Stereoselective Pathway to "Geminal-Faced" Esters and Alcohols

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Metal complexes are useful reagents for the synthesis of many organic compounds. The stereoselectivity that often accompanies these reactions[1-3] is of paramount interest, and a focus of this report is on the stereocontrol mediated by iron carbonyl in its reactions with norbornyl aldehydes.

The reported reactions of aldehydes with iron carbonyl reagents have been limited to α,β-unsaturated systems in which stable π-complexes are formed. For example, acrolein coordinates with diiron nonacarbonyl to provide (acrolein)iron tetracarbonyl[4] and cinnamaldehyde gives rise to a heterodieneiron tricarbonyl in which the iron fragment is coordinated to the C=C—C=O linkage.[5] The norbornyl aldehydes chosen for this study were not expected to form stable complexes. Therefore, it was hoped that their carbonyl functions would become reactive sites in the presence of diiron nonacarbonyl, and these expectations were indeed realized.

In the presence of diiron nonacarbonyl in refluxing hexane or tetrahydrofuran (THF), norbornane-2-carboxaldehyde (**1**) was converted to the endo,endo congener (90% isomeric purity) of norbornan-2-ylmethyl norbornane-2-carboxylate (**2**) in 54% and 71% yields, respectively, after 48 h (Scheme I). In addition, a minor amount (4–6%) of the reduction product, *endo*-2-(hydroxymethyl)norbornane (**3**), was generated as well, which possessed an isomeric purity of 85% (Table I).

Under the same reaction conditions, in hexane or THF, 3-methylnorbornane-2-carboxaldehyde (**4**) was converted to (3-methylnorbornan-2-yl)methyl 3-methylnorbornane-2-carboxylate (**5**) in 51% and 77% yields, respectively, after 48 h. The synthesis of **5** occurred without the stereoselectivity associated with **2**, but this lack of stereocontrol possibly resulted from the variation displayed by the 3-methyl functions of the "geminal-faced" ester. An alcohol was not isolated from this reaction, but its presence was suggested by TLC.

Although yield enrichments were observed for esters **2** and **5** with a change of solvent, alcohol formation remained approximately the same. Nevertheless, these results emphasized the importance of solvent characteristics as a parameter for ester synthesis. Indeed, it is well known[6,7] that THF stabilizes iron carbonyl through complexation,

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