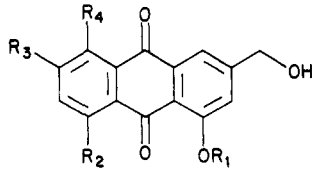
**Table I. Some Naturally Occurring 1-Hydroxy-3-(hydroxymethyl)anthraquinones**



| $R_1$ | $R_2$ | $R_3$ | $R_4$ | compounds |
|---|---|---|---|---|
| H | OH | H | H | aloe-emodin (4) |
| H | OMe | OH | H | ω-hydroxyquestin |
| H | OH | OH | H | citreorosein |
| H | OH | OMe | H | fallacinol (5) |
| H | H | H | H | ω-hydroxypachybasin (3)[3] |
| Me | OH | H | H | carviolin |

and acidified with HOAc (5 mL). Following workup as described, the crude product was crystallized from EtOH to afford pure **11** as yellow crystals (4.2 g, 79%): mp 138–139 °C; $^1$H NMR ($CDCl_3$) δ 3.50 (s, 3 H), 4.54 (s, 2 H), 7.33 (s, 1 H), 7.76 (m, 3 H), 8.32 (m, 2 H), 12.65 (s, 1 H). Anal. Calcd for $C_{16}H_{12}O_4$: C, 71.63; H, 4.51. Found: C, 71.53; H, 4.53.

**3-(Bromomethyl)-1-hydroxyanthraquinone (12).** A suspension of **11** (1.0 g, 3.7 mmol) in 30% HBr in HOAc (13 mL) was refluxed for 45 min. After cooling, the yellow crystals were filtered off and washed with cold water to give **12** (1.0 g, 85%): mp 202–203.5 °C; $^1$H NMR ($CDCl_3$) δ 4.50 (s, 2 H), 7.33 (s, 1 H), 7.75 (m, 3 H), 8.35 (m, 2 H), 12.55 (s, 1 H). Anal. Calcd for $C_{15}H_9BrO_3$: C, 56.81; H, 2.86. Found: C, 57.01; H, 3.00.

**3-(Acetoxymethyl)-1-hydroxyanthraquinone (13).** The bromide **12** (0.88 g, 2.7 mmol) was refluxed with NaOAc (1.14 g, 13.8 mmol) in HOAc (8.8 mL) for 30 min under $N_2$. After cooling, the solid mass was poured onto ice and the yellow crystals were filtered off and washed with water to give the acetate **13** (0.81 g, 2.7 mmol): mp 143–145 °C; $^1$H NMR ($CDCl_3$) δ 2.17 (s, 3 H), 5.20 (s, 2 H), 7.33 (s, 1 H), 7.78 (m, 3 H), 8.66 (m, 2 H), 12.98 (s, 1 H); high-resolution mass spectrum, *m/e* 296.0675 (calcd for $C_{17}H_{12}O_5$ 296.0685).

**ω-Hydroxypachybasin (3).** A solution of the acetate **13** (0.8 g, 2.7 mmol) was refluxed under $N_2$ with 2% KOH in EtOH for 10 min. The cooled solution was then poured into 1 N HCl (25 mL). Extraction followed by evaporation of the solvent gave **3** as yellow needles (0.65 g, 100%): mp 208–209 °C (lit.[3] mp 211–212 °C); $^1$H NMR ($CDCl_3$) δ 4.78 (s, 2 H), 7.34 (s, 1 H), 7.80 (m, 3 H), 8.34 (m, 2 H), 12.60 (s, 1 H).

**3-Bromo-5-hydroxy-7-methoxynaphthoquinone (18):** Prepared by the general method of Brassard[7a] from 2,6-dibromobenzoquinone and 1,3-dimethoxy-1-(trimethylsiloxy)-1,3-butadiene in 67% yield: mp 176–177 °C; $^1$H NMR ($CDCl_3$) δ 3.94 (s, 3 H), 6.68 (d, 1 H, *J* = 3 Hz), 7.20 (d, 1 H, *J* = 3 Hz), 7.46 (s, 1 H), 9.28 (s, 1 H). Anal. Calcd for $C_{11}H_7BrO_4$: C, 46.67; H, 2.49. Found: C, 46.47; H, 2.64.

**Aloe-emodin ω-Methyl Ether (15).** A solution of **9** (0.13 g, 0.60 mmol) and 3-bromojuglone[12] (**14**) (0.10 g, 0.40 mmol) in $CH_2Cl_2$ (4 mL) containing $K_2CO_3$ (0.16 g, 1.2 mmol) was stirred and heated in a sealed tube under $N_2$ at 75 °C for 1 h. NaOAc (0.1 g, 1.2 mmol) was then added and heating was continued for an additional 0.5 h. Standard workup gave orange crystals of **15** (0.10 g, 63%): mp 147.5–148 °C; $^1$H NMR ($CDCl_3$) δ 3.50 (s, 3 H), 4.55 (s, 2 H), 7.32 (m, 2 H), 7.80 (m, 3 H), 12.10 (s, 1 H), 12.16 (s, 1 H); high-resolution mass spectrum *m/e* 284.0689 (calcd for $C_{16}H_{12}O_5$ 284.0685).

**Aloe-emodin ω-Acetate (17).** The ether **15** was converted into aloe-emodin ω-acetate in 93% yield by using the same procedure as for the synthesis of **13** from **11** without isolation of the bromide: mp 194.5–195.5 °C. Anal. Calcd for $C_{17}H_{12}O_6$: C, 65.39; H, 4.33. Found: C, 65.15; H, 4.11.

**Aloe-emodin (4).** The acetate **17** was hydrolyzed under the same conditions used for **13** to give aloe-emodin (**4**) in 100% yield: mp 222–223 °C (lit.[10] mp 223–224 °C).

**Fallacinol ω-Methyl Ether (19).** A solution of the diene **9** (0.61 g, 2.8 mmol) in $CH_2Cl_2$ (5 mL) was added to a rapidly stirred solution of **18** (0.36 g, 1.3 mmol) in $CH_2Cl_2$ (10 mL) at −25 °C over 10 min. After 2 h at this temperature, $K_2CO_3$ (anhydrous) (0.53 g, 3.8 mmol) was added and the reaction stirred at room temperature for 10 h. The filtered solution was chromatographed, the solvent evaporated, and the residue treated with EtOH to afford **19** as yellow crystals (1.88 g, 83%): mp 174.5–175.5 °C; $^1$H NMR ($CDCl_3$) δ 3.50 (s, 3 H), 4.00 (s, 3 H), 4.60 (s, 2 H), 6.63 (d, 1 H, *J* = 2 Hz), 7.26 (d, 1 H, *J* = 2 Hz), 7.36 (d, 1 H, *J* = 2 Hz), 7.74 (d, 1 H, *J* = 2 Hz), 12.14 (s, 1 H), 12.26 (s, 1 H); high-resolution mass spectrum, *m/e* 314.0782 (calcd for $C_{17}H_{14}O_6$ 314.0790).

**Fallacinol ω-Acetate (21).** Ether **19** was converted into fallacinol ω-acetate in93% yield by using the same procedure as for the synthesis of **3** from **11** without isolation of the bromide: mp 19–191 °C; $^1$H NMR ($CDCl_3$) δ 1.12 (s, 3 H), 3.98 (s, 3 H), 5.23 (s, 2 H), 7.23 (d, 1 H, *J* = 2 Hz), 7.30 (d, 1 H, *J* = 2 Hz), 7.38 (d, 1 H, *J* = 2 Hz), 7.83 (d, 1 H, *J* = 2 Hz), 12.21 (s, 1 H), 12.30 (s, 1 H); high-resolution mass spectrum, *e/e* 342.0736 (clacd for $C_{18}H_{14}O_7$ 342.0739).

**Fallacinol (5).** The acetate **21** was hydrolyzed under the same conditions used for **11** to give fallacinol (**5**) in 100% yield: mp 239–240 °C (lit.[10] mp 238–239 °C); high-resolution mass spectrum, *m/e* 300.0630 (calcd for $C_{16}H_{12}O_6$ 300.0630).

**Acknowledgment.** This work was supported by a grant from the National Institutes of Health, CA 30377.

**Registry No.** **2**, 2549-78-2; **3**, 51995-90-5; **4**, 481-72-1; **5**, 569-05-1; **6**, 2065-37-4; **7**, 73311-51-0; **9**, 93564-92-2; (*E*)-**10**, 88806-83-1; (*Z*)-**10**, 88806-84-2; **11**, 93564-93-3; **12**, 93564-94-4; **13**, 93564-95-5; **14**, 52431-65-9; **15**, 93564-96-6; **17**, 65615-58-9; **18**, 93564-97-7; **19**, 93564-98-8; **21**, 20194-61-0; methyl *cis*-ω-bromosenecioate, 27652-13-7; methyl *trans*-ω-bromosenecioate, 19041-17-9; 2,6-dibromobenzoquinone, 19643-45-9; 1,3-dimethoxy-1-(trimethylsiloxy)-1,3-butadiene, 74272-66-5.

## Sulfur-Directed Diels–Alder Reactions. Synthesis of 1,5-Disubstituted Cyclohexene Derivatives

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We recently required a 1,5-disubstituted cyclohexene derivative of general structure **1**. Preparation of **1** using the Diels–Alder reaction appeared attractive (Scheme I); however, this substitution pattern is opposite that obtained from thermal or Lewis acid catalyzed Diels–Alder reactions of isoprene and typical electron-poor dienophiles.[1] Others have approached closely related problems by the temporary introduction of a powerful directly group in either the dienophile (nitro,[2] phenylsulfonyl[3]) or the diene. The latter solution was more appropriate to the case at hand, and consequently the powerfully directing phenylthio group was chosen. To our surprise, inspection of the literature turned up no examples of the Diels–Alder reaction of simple dienes like **2a** with unsymmetrical dienophiles.[4] The parent diene **2b** has been studied by Cohen, who found that the sulfur serves admirably as a regiocontrol element.[5] Should this be the case with **2a**, the resulting Diels–Alder adduct **3** would be expected to undergo desulfurization to provide the desired 1,5-disubstituted cyclohexene **1**. We now describe an operationally simple and inexpensive synthesis of diene **2a** and report that it does indeed serve as a synthetic equivalent of isoprene, having

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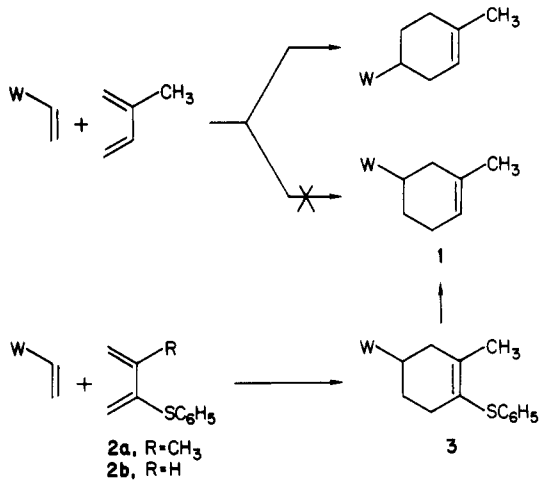
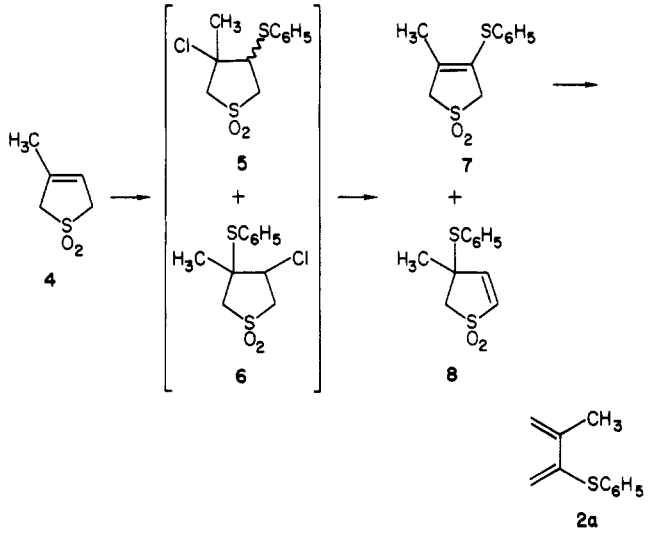
0022-3263/85/1950-0141$01.50/0 

**Scheme I**



**Scheme II**



a reversed Diels–Alder regiochemical preference.

A two-step preparation of diene **2a**[6] is outlined in Scheme II. Isoprene cyclic sulfone **4**[7] undergoes chlorosulfenylation[8] to afford a mixture of adducts **5** and **6**. The **5/6** mixture is not isolated but is directly dehydrochlorinated[8] in situ with excess triethylamine to yield **7** and **8** in a ratio of 3.2:1, respectively. Pure **7** is easily isolated by direct crystallization in 52% overall yield.[9] Bulb-to-bulb distillation of **7** (oven temperature 170 °C, ca. 20 mm) results in sulfur dioxide extrusion,[8-10] providing **2a** in 75–85% yield on a multigram scale. The **2a** obtained in this manner was used in subsequent Diels–Alder reactions without further purification. Despite attempts to slow its decomposition by storage at −20 °C in the presence of free radical inhibitors, **2a** has proven unstable to prolonged storage and its use within a few days of preparation is recommended.

A variety of conditions for the Diels–Alder reaction of **2a** was explored. Although early attempts under thermal conditions were moderately successful, this approach was quickly abandoned in favor of the significantly cleaner Lewis acid catalyzed reactions. A survey of catalysts ($AlCl_3$, $BF_3{\cdot}Et_2O$, $SnCl_4$, $ZnCl_2$) in both ether and methylene chloride established that in the case of **2a** and methyl vinyl ketone, zinc chloride in ether was the combination of choice.[11] The utility of **2a** as an isoprene equivalent with regioreversed Diels–Alder specificity under these conditions is illustrated in Scheme III. Cycloaddition with

**Scheme III**

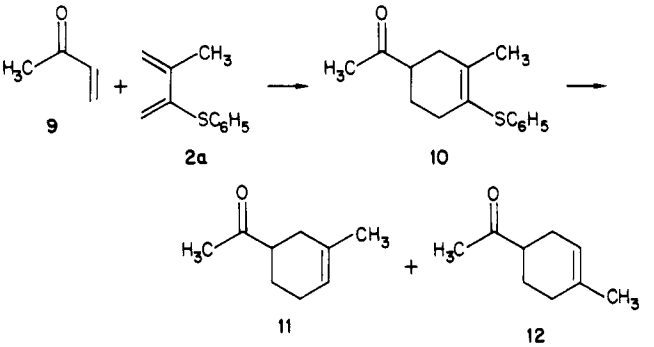
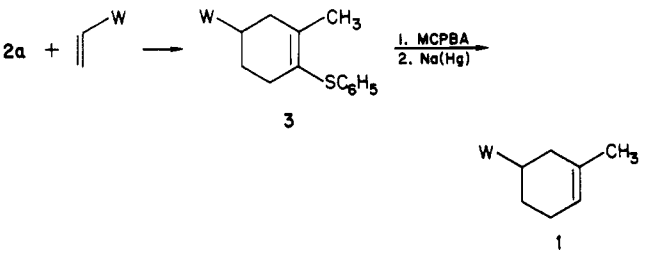


**Table I**



| W | Diel–Alder condns[a] | yield of 3,[b] % | yield of 1,[b] % | Diels–Alder regioselectivity[c] |
|---|---|---|---|---|
| $COCH_3$ | 7 equiv, $Et_2O$, 2 h | 77 | 70 | 95:5 |
| $COOCH_3$ | 20 equiv, $Et_2O$, 2 days | 68 | 65 | 93:7 |
| C≡N | 30 equiv, neat, 2 days | 77 | 74 | 96:4 |

[a] Equivalents of dienophile, solvent, time. All Diels–Alder reactions conducted at 25 °C in the presence of 3 equiv of anhydrous $ZnCl_2$. [b] Isolated yield of purified material. [c] Ratio of 1 relative to its isomer derived from the opposite Diels–Alder regioisomer. Determined by GLC comparison with authentic samples prepared by thermal Diels–Alder reaction of isoprene and the appropriate dienophile.

(1) Onishchenko, A. S. "Diene Synthesis"; Daniel Davey & Co.: New York, 1964; pp 142–155.
(2) Danishefsky, S.; Hershenson, F. M. *J. Org. Chem.* **1979**, *44*, 1180.
(3) Shen, M.; Schultz, A. G. *Tetrahedron Lett.* **1981**, *22*, 3347.
(4) Numerous sulfur-substituted dienes have been prepared and used in the Diels–Alder reaction. Review: Petrzilka, M.; Grayson, J. I. *Synthesis* **1981**, 753. More recent examples: (a) Overman, L. E.; Petty, C. B.; Ban, T.; Huang, G. T. *J. Am. Chem. Soc.* **1983**, *105*, 6335. (b) Cohen, T.; Kosarych, Z. *J. Org. Chem.* **1982**, *47*, 4005. (c) Kozikowski, A. P.; Huie, E. M. *J. Am. Chem. Soc.* **1982**, *104*, 2923. (d) Bridges, A. J.; Fischer, J. W. *Tetrahedron Lett.* **1983**, *24*, 445, 447. Trost, Vladuchick, and Bridges have previously studied in detail the internal competition of sulfur and oxygen substituents as regiocontrol elements in the diene component of the Diels–Alder reaction: Trost, B. M.; Vladuchick, W. C.; Bridges, A. J. *J. Am. Chem. Soc.* **1980**, *102*, 3548, 3554. For a recent discussion of theoretical aspects of the regiochemical outcome of Diels–Alder reactions, see: Alston, P. V.; Gordon, M. D.; Ottenbrite, R. M.; Cohen, T. *J. Org. Chem.* **1983**, *48*, 5051 and references cited therein.
(5) Cohen, T.; Mura, A. J., Jr.; Shull, D. W.; Fogel, E. R.; Ruffner, R. J.; Falck, J. R. *J. Org. Chem.* **1976**, *41*, 3218.
(6) Diene **2a** has been prepared previously via **7** and its reaction with maleic anhydride has been reported: Backer, H. J.; Blass, T. A. H. *Recl. Trav. Chim. Pays.-Bas* **1942**, *61*, 785, 924. Although we have not attempted to repeat the previously described synthesis of **7**, the preparation of **7** described herein appears to be considerably more convenient.
(7) (a) Frank, R. L.; Seven, R. P. "Organic Syntheses" Wiley: New York, 1955, Collect. Vol. III, p 499. (b) Commercially available from ICN K & K Laboratories, Plainview, NY.
(8) (a) Hopkins, P. B.; Fuchs, P. L. *J. Org. Chem.* **1978**, *43*, 1208. (b) Gundermann, K. D.; Holtman, P. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 678.
(9) All of the compounds isolated and described herein have been characterized by IR, $^1H$ NMR, and low-resolution MS.
(10) "1,4-Cycloaddition Reactions": Hamer, J., Ed.; Academic Press: New York, 1967; pp 31–38.
(11) Others have made similar observations in the case of sulfur-substituted dienes: see ref 4c.

excess methyl vinyl ketone proceeded smoothly at 25 °C to provide **10** in 77% yield. Of great interest is the regioselectivity of this process, which was proven by sequential oxidation to the corresponding sulfone (MCPBA) and desulfonylation (6% Na–Hg, $CH_3OH$, $Na_2HPO_4$[12]) to provide **11** in 70% chromatographed yield from **10**. GLC comparison of **11** prepared in this fashion with an authentic mixture of **11** and **12** prepared by direct Diels–Alder reaction of isoprene with methyl vinyl ketone[13] indicated an **11**/**12** ratio of 95:5. Similar results were obtained with methyl acrylate and acrylonitrile as indicated in Table I.

The results described herein clearly indicate that the phenylthio group controls the Diels–Alder regioselectivity of diene **2a** and demonstrate that 1,5-disubstituted cyclohexene derivatives which are unavailable by direct Diels–Alder reaction of monosubstituted dienophiles and 2-alkyl-1,3-butadienes may be obtained by the temporary introduction of a phenylthio substituent.

## Experimental Section[14]

**3-Methyl-4-(phenylthio)-2,5-dihydrothiophene 1,1-Dioxide (7).** A freshly prepared solution of benzenesulfenyl chloride (generated in situ by the method of Fuchs[8a]) (154 mmol, 1.0 M) in methylene chloride at 25 °C under argon was treated with 19.6 g (148 mmol) of isoprene cyclic sulfone,[7] and the deep orange mixture was stirred for 4 days at 25 °C followed by 1 day at reflux. The resulting yellow-brown mixture was cooled to 0 °C, and 22.6 mL (16.4 g, 162 mmol) of triethylamine was added dropwise over 15 min. The mixture was allowed to warm to 25 °C and stirred for 2 days. The resulting solution was diluted with ca. 500 mL of ether and washed sequentially with 150 mL of water, two 50-mL portions of 3% aqueous hydrochloric acid, 100 mL of saturated aqueous sodium bicarbonate, and 100 mL of saturated brine. The combined bicarbonate and brine washes were back-extracted with a small portion of ether, and the combined organic extracts were treated with decolorizing charcoal and magnesium sulfate and filtered through a bed of Celite. Concentration in vacuo afforded a yellow-orange oil which deposited crystals on cooling to 8 °C overnight. Cold (0 °C) 65% ether in hexanes (200 mL) was added, and the cold suspension was stirred vigorously for 4 min and vacuum filtered. The solid was resuspended in 75 mL of fresh, precooled (0 °C) 65% ether in hexanes, stirred for 1 min at 0 °C, filtered, and dried in vacuo to provide 18.5 g (52%) of **7** as pale yellow crystals, mp 67–68 °C. Since the solubility of **7** is appreciable in 65% ether in hexanes, it is imperative that the crystal washing process (which removes **8** from **7**) be carried out quickly at 0 °C. **7**: $^1H$ NMR (80 MHz) $\delta$ 2.07 (3 H, m, $CH_3$), 3.7 (2 H, m), 3.9 (2 H, m), 7.3 (5 H, s, $C_6H_5$); IR ($CH_2Cl_2$) 1330 and 1150 ($SO_2$) $cm^{-1}$; MS *m/e*, (EI) (relative intensity) 240 (28, $M^+$), 176 (61, $M^+ - SO_2$), 161 (80, $M^+ - SO_2 - CH_3$), 143 (44), 135 (46), 110 (79), 109 (47, $C_6H_5S^+$), 85 (100), 65 (99), 51 (41). Anal. Calcd for $C_{11}H_{12}O_2S_2$: C, 54.97; H, 5.03; S, 26.68. Found: C, 55.02; H, 5.03; S, 26.40. A small quantity of **8** was isolated by column chromatography. **8**: $^1H$ NMR (80 MHz) $\delta$ 1.65 (3 H, s, $CH_3$), 3.20 (1 H, d, $J$ = 15 Hz, C*H*H), 3.43 (1 H, d, $J$ = 15 Hz, CH*H*), 6.40 (1 H, d, $J$ = 7 Hz, C*H*=CH), 6.60 (1 H, d, $J$ = 7 Hz, CH=C*H*), 7.4 (5 H, s, $C_6H_5$).

**2-Methyl-3-(phenylthio)-1,3-butadiene (2a).** A bulb-to-bulb distillation apparatus was charged with 3.5 g (14.6 mmol) of **7** and heated at an oven temperature of 170 °C (water aspirator, ca. 20 mm). The distillate was collected at −78 °C, yielding 2.05 g (80%) of **2a** as a yellow oil: $^1H$ NMR (80 MHz) $\delta$ 1.95 (3 H, m, $CH_3$), 5.05 (1 H, m), 5.2 (1 H, m), 5.5 (2 H, m), 7.1–7.4 (5 H, m, $C_6H_5$); $^1H$ NMR (60 MHz, $C_6D_6$) $\delta$ 1.75 (3 H, m, $CH_3$), 4.95 (1 H, m), 5.25 (1 H, m), 5.37 (1 H, m), 5.72 (1 H, m), 6.9–7.6 (5 H, m, $C_6H_5$); IR ($CH_2Cl_2$) 1585, 915 (C=$CH_2$) $cm^{-1}$; MS, *m/e* (EI) (relative intensity) 176 (42, $M^+$), 161 (60, $M^+ - CH_3$), 135 (37), 110 (90), 109 (41), 86 (49), 85 (94), 84 (82), 77 (42), 69 (46), 65 (100), 51 (77).

**4-Acetyl-2-methyl-1-(phenylthio)cyclohexene (10).** To 2.05 g (11.6 mmol) of **2a** in 10 mL of ether at 25 °C were added 6.5 mL (5.6 g, 80.1 mmol) of methyl vinyl ketone and 4.7 g (34.6 mmol) of anhydrous zinc chloride. The mixture was stirred for 2 h, diluted with 150 mL of ether, and washed with two 100-mL portions of water. The organic layer was dried over magnesium sulfate, filtered, and concentrated in vacuo to provide an orange oil. Flash chromatography ($SiO_2$, 15% ethyl acetate/hexanes) afforded 2.2 g (77%) of **10** as a yellow oil: $^1H$ NMR (80 MHz) $\delta$ 1.97 (3 H, m, $CH_3C$=C), 2.17 (3 H, m, $CH_3CO$), 1.3–2.8 (7 H, m), 7.15 (5 H, s, $C_6H_5$); IR ($CH_2Cl_2$) 1720 (C=O), 1595 $cm^{-1}$; MS, *m/e* (EI) (relative intensity) 246 (18, $M^+$), 231 (2, $M^+ - CH_3$), 203 (3, $M^+ - COCH_3$), 137 (28, $M^+ - C_6H_5S$), 109 (20, $C_6H_5S^+$), 93 (100), 91 (36), 77 (46), 65 (28).

**4-Acetyl-2-methyl-1-(phenylsulfonyl)cyclohexene.** Oxidation of **10** (2.2 g) with 4 equiv of MCPBA in methylene chloride at 0 °C for 6 h essentially as described elsewhere[8a] provided the corresponding crude vinyl sulfone as a viscous oil in near quantitative yield. This material was used without purification in the following step. Vinyl sulfone: $^1H$ NMR $\delta$ 1.2–2.8 (7 H, m), 2.15 (6 H, s, $CH_3CO$, $CH_3C$=C), 7.3–8.05 (5 H, m, $C_6H_5$); IR ($CH_2Cl_2$) 1720 (C=O), 1310 and 1160 ($SO_2$) $cm^{-1}$; MS, *m/e* (EI) (relative intensity) 278 (1, $M^+$), 235 (33, $M^+ - CH_3CO$), 137 (25, $M^+ - SO_2C_6H_5$), 93 (56), 91 (47), 77 (88), 58 (100).

**1-Methyl-5-acetylcyclohexene (11).** The crude vinyl sulfone from the previous step was desulfonylated in methanol (90 mL) containing disodium phosphate (5.05 g) with 6% sodium amalgam (13.4 g) at 0 °C to 25 °C.[12] After 1 day, a fresh portion of amalgam (2.3 g) was added, and the resulting suspension was stirred an additional day at 25 °C. The mixture was diluted with ether and washed sequentially with two portions of water, five 3-mL portions of Jones reagent,[15] 30 mL of water, 50 mL of saturated aqueous sodium bicarbonate, and 100 mL of brine. Drying over magnesium sulfate and concentration in vacuo yielded a pale yellow oil which was chromatographed ($SiO_2$, 15% ethyl acetate/hexanes) followed by bulb-to-bulb distillation (90 °C, 1.2 mm) to afford 0.87 g (70%) of **11** as a colorless liquid: $^1H$ NMR $\delta$ 1.1–2.2 (6 H, m), 1.65 (3 H, m, $CH_3C$=C), 2.16 (3 H, s, $CH_3CO$), 2.3–2.8 (1 H, m), 5.2–5.45 (1 H, m, CH=C); IR ($CH_2Cl_2$) 1725 (C=O) $cm^{-1}$; MS, *m/e* (EI) (relative intensity) 138 (20, $M^+$), 123 (9, $M^+ - CH_3$), 95 (100, $M^+ - CH_3CO$), 93 (26), 91 (30), 79 (38), 77 (38), 67 (52), 55 (43).

**Acknowledgment.** We thank the Dreyfus Foundation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Research Corporation for generous financial support of our programs. The 500-MHz NMR spectrometer was purchased and supported by instrumentation grants from the Murdoch Foundation, NSF, and NIH.

**Registry No.** 1 (W = $COCH_3$), 41723-53-9; 1 (W = $COOCH_3$), 6493-78-3; 1 (W = C≡N), 24054-27-1; **2a**, 91891-84-8; **3** (W = $COCH_3$), 93604-49-0; **3** (W = $COOCH_3$), 93604-50-3; **3** (W = CN), 93604-51-4; **4**, 1193-10-8; **5**, 93604-52-5; **6**, 93604-53-6; **7**, 93604-54-7; **8**, 93604-55-8; **9**, 78-94-4; **12**, 6090-09-1; $ZnCl_2$, 7646-85-7; methyl 4-methylcyclohex-3-enecarboxylate, 6493-79-4; 4-methylcyclohex-3-enecarbonitrile, 6824-60-8; 4-acetyl-2-methyl-1-(phenylsulfonyl)cyclohexene, 93604-56-9; methyl propenoate, 96-33-3; 2-propenenitrile, 107-13-1; benzenesulfenyl chloride, 931-59-9.

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

(13) Methyl vinyl ketone and isoprene are known[1] to produce a ca. 1:3 mixture of **11** and **12**, respectively, at 120 °C.

(14) Proton nuclear magnetic resonance ($^1H$ NMR) spectra were determined on a Varian CFT 20 (80 MHz) or EM360 (60 MHz) spectrometer in chloroform-$d_1$ unless otherwise specified and are reported in parts per million ($\delta$) downfield from internal tetramethylsilane (0.00 : $\delta$). Infrared spectra (IR) were recorded on a Beckman AccuLab 4 infrared spectrophotometer. Mass spectra (MS) were measured on a Hewlett-Packard Model 5985 mass spectrometer. Gas–liquid chromatography was performed on a Hewlett-Packard 5790A gas chromatograph. Methylene chloride was distilled from calcium hydride; ether was distilled from benzophenone ketyl. Zinc chloride was fused and stored under hexanes. All other commerical chemicals were used as received. Chromatography was performed on Merck silica gel 60, (230–400 mesh).

(15) Treatment with Jones reagent (Meinwald, J.; Crandall, J.; Hymans, W. E. "Organic Syntheses" Wiley: New York, 1973; Collect. Vol. V, p 866) effects reoxidation of the small quantity of alcohol produced by carbonyl reduction during this reaction.