**and 14).** To a stirred solution of **11** (113 mg, 0.228 mmol) in dry $CH_2Cl_2$ (2.3 mL) cooled at ca. −80 °C was added a 1.0 M hexane solution of $Me_2AlCl$ (0.23 mL) over 2 min. The solution was allowed to warm to −40 °C over 5.5 h and then diluted with $CH_2Cl_2$ (15 mL), and saturated aqueous $NaHCO_3$ (10 mL) was added. Phases were separated, and the aqueous phase was extracted with $CH_2Cl_2$ (10 mL × 4). The combined organic phases were washed with brine (5 mL), dried, and concentrated. The residual oil was subjected to MPLC (elution with 24:1 hexane–AcOEt, relative $t_R$ = 1.47) to give **14** (25 mg, 22%) and **13** (73 mg, 65%) in the order of elution.

**Compound 13**: colorless oil, slowly crytallized in a freezer as needles, mp 47–50 °C; $[\alpha]^{23}_D$ −92.99° (*c* 1.141, $CHCl_3$); $R_f$ 0.59 (4:1 hexane–AcOEt); IR (KBr) 1720 $cm^{-1}$; $^1H$ NMR (270 MHz) δ 0.08, 0.10 (each 3 H, s, $SiMe_2$), 0.67 (3 H, d, *J* = 6.1 Hz, Me-8), 0.94 (9 H, s, *t*-Bu), 1.01 (3 H, d, *J* = 7.1 Hz, Me-6), 1.10 (3 H, s, Me-1), 1.35–1.70 (4 H, m, H-7ax, H-7eq, H-8, and H-8a), 1.63 (3 H, d, *J* = 1.1 Hz, Me-1′), 2.08 (2 H, m, H-6 and H-4a), 2.36 (1 H, m, H-2), 3.53 (1 H, dd, *J* = 10.5, 5.1 Hz, H-5), 4.01, 4.08 (each 1 H, dd, *J* = 12.8, 6.3 Hz, H-3′), 4.49 (2 H, s, $OCH_2Ph$), 5.43 (1 H, ddd, *J* = 10.3, 4.6, 2.7 Hz, H-3), 5.53 (1 H, ddd, *J* = 6.3, 6.3, 1.1 Hz, H-2′), 6.07 (1 H, ddd, *J* = 10.3, 1.7, 1.7 Hz, H-4), 7.33 (5 H, m, Ar H), 9.45 (1 H, s, CHO); $^1H$ NMR (400 MHz) ($C_6D_6$) δ 0.07, 0.13 (each 3 H, s, $SiMe_2$), 0.59 (3 H, d, *J* = 6.7 Hz, Me-8), 0.98 (3 H, d, *J* = 7.2 Hz, Me-6), 1.02 (9 H, s, *t*-Bu), 1.14 (3 H, s, Me-1), 1.10–1.19 (1 H, m, H-7ax), 1.27 (1 H, ddd, *J* = 13.6, 2.9, 2.6 Hz, H-7eq), 1.40–1.53 (1 H, m, H-8), 1.51 (3 H, d, *J* = 0.8 Hz, Me-1′), 1.66 (1 H, dd, *J* = 10.4, 10.4 Hz, H-8a), 1.98 (1 H, m, H-6), 2.10 (1 H, ddd, *J* = 10.4, 10.4, 2.3 Hz, H-4a), 2.35 (1 H, dd, *J* = 2.3, 2.3 Hz, H-2), 3.53 (1 H, dd, *J* = 10.4, 5.2 Hz, H-5), 3.90, 3.93 (each 1 H, dd, *J* = 10.5, 6.1 Hz, H-3′), 4.37 (2 H, s, $CH_2OPh$), 5.41 (1 H, ddd, *J* = 10.2, 4.9, 2.3 Hz, H-3), 5.67 (1 H, ddd, *J* = 6.1, 6.1, 0.8 Hz, H-2′), 6.19 (1 H, ddd, *J* = 10.2, 2.3, 2.3 Hz, H-4), 7.08–7.35 (5 H, m, Ar H), 9.57 (1 H, s, CHO); MS, *m/e* 496.3327 ($M^+$, calcd 496.3370), 439, 388, 357, 331, 55 (base peak). Anal. Calcd for $C_{31}H_{48}O_3Si$: C, 74.95; H, 9.74. Found: C, 74.94; H, 9.49.

**Compound 14**: colorless oil; $[\alpha]^{23}_D$ −122.76° (c 1.671, $CHCl_3$); $R_f$ 0.59 (4:1 hexane–AcOEt); IR (neat) 1720 $cm^{-1}$; $^1H$ NMR (270 MHz) δ 0.06, 0.08 (each 3 H, s, $SiMe_2$), 0.70 (3 H, d, *J* = 6.6 Hz, Me-8), 0.90 (9 H, s, *t*-Bu), 0.99 (3 H, d, *J* = 7.3 Hz, Me-6), 1.09 (3 H, s, Me-1), 1.25 (1 H, br d, *J* = 12.5 Hz, H-7eq), 1.46–1.68 (1 H, m, H-8), 1.68 (3 H, s, Me-1′), 1.79 (1 H, ddd, *J* = 12.5, 12.5, 5.1 Hz, H-7ax), 1.88 (1 H, m, H-6), 2.12 (1 H, ddd, *J* = 10.5, 2.6, 2.0 Hz, H-4a), 2.32 (1 H, dd, *J* = 10.5, 10.5 Hz, H-8a), 2.42 (1 H, m, H-2), 3.74 (1 H, m, H-5), 3.97, 4.01 (each 1 H, dd, *J* = 12.3, 6.5 Hz, H-3′), 4.46 (2 H, s, $OCH_2Ph$), 5.43 (1 H, ddd, *J* = 10.0, 4.4, 2.7 Hz, H-3), 5.53 (1 H, br d, *J* = 10.0 Hz, H-4), 5.58 (1 H, dd, *J* = 6.5, 6.5 Hz, H-2′), 7.32 (5 H, m, Ar H), 9.47 (1 H, s, CHO); MS, *m/e* 496.3403 ($M^+$, calcd 496.3372), 439, 411, 331, 18 (base peak).

**(1*S*,2*S*,4a*S*,5*S*,6*S*,8*S*,8a*R*)- and (1*R*,2*R*,4a*R*,5*S*,6*S*,8*S*,8a*S*)-2-[3-(Benzyloxy)-1-methyl-1(*E*)-propenyl]-5-(methoxymethoxy)-1,6,8-trimethyl-1,2,4a,5,6,7,8,8a-octahydronaphthalene-1-carboxaldehyde (15 and 16).** To a stirred solution of **12** (83 mg, 0.194 mmol) in dry $CH_2Cl_2$ (1.9 mL) cooled at ca. −90 °C was added a 1.0 M hexane solution of $Me_2AlCl$ (0.194 mL) over 1 min. The solution was allowed to warm to −40 °C over 20 min and then stirred for 8 h at −50 to −40 °C. The mixture was diluted with $CH_2Cl_2$ (10 mL), and saturated $NaHCO_3$ (10 mL) was added. Phases were separated, and the aqueous phase was extracted with $CH_2Cl_2$ (10 mL × 4). The combined organic phases were washed with brine (5 mL), dried, and concentrated. The residual oil was subjected to MPLC (elution with 9:1 hexane–AcOEt, relative $t_R$ (**15**/**16**) = 1.34) to give **16** (1 mg, 1%), **15** (33 mg, 40%), and recovered **12** (5 mg, 6%) in the order of elution.

**Compound 15**: colorless oil; $[\alpha]^{23}_D$ −117.72° (*c* 3.799, $CHCl_3$); $R_f$ 0.29 (hexane–AcOEt, 7:1); IR (neat) 1720 $cm^{-1}$; $^1H$ NMR (270 MHz) δ 0.70 (3 H, d, *J* = 6.1 Hz, Me-8), 1.03 (3 H, d, *J* = 7.1 Hz, Me-6), 1.11 (3 H, s, Me-2), 1.35–1.73 (4 H, m, H-7ax, H-7eq, H-8, and H-8a), 1.64 (3 H, d, *J* = 1.0 Hz, Me-1′), 2.15 (1 H, tm, *J* = 10.1 Hz, H-4a), 2.32 (1 H, m, H-6), 2.43 (1 H, m, H-2), 3.43 (3 H, s, $OCH_3$), 3.47 (1 H, dd, *J* = 10.1, 5.1 Hz, H-5), 4.02, 4.06 (each 1 H, br dd, *J* = 12.5, 6.4 Hz, H-3′), 4.49 (2 H, s, $OCH_2Ph$), 4.68, 4.79 (each 1 H, d, *J* = 6.9 Hz, $OCH_2O$), 5.48 (1 H, ddd, *J* = 10.2, 4.6, 2.7 Hz, H-3), 5.53 (1 H, dt, *J* = 6.4, 1.0 Hz, H-2′), 6.03 (1 H, ddd, *J* = 10.2, 1.7, 1.7 Hz, H-4), 7.34 (5 H, m, Ar H), 9.45 (1 H, s, CHO); MS, *m/e* 426.2749 ($M^+$, calcd 426.2769), 410, 256, 135, 91 (base peak).

**Compound 16**: colorless oil, $[\alpha]^{23}_D$ −127.02° (*c* 0.151, $CHCl_3$); $R_f$ 0.29 (hexane–AcOEt, 7:1); IR (neat) 1720 $cm^{-1}$; $^1H$ NMR (270 MHz) δ 0.70 (3 H, d, *J* = 6.4 Hz, Me-8), 1.02 (3 H, d, *J* = 7.3 Hz, Me-6), 1.10 (3 H, s, Me-1), 1.31 (1 H, br d, *J* = 12.9 Hz, H-7eq), 1.51–1.67 (1 H, m, H-8), 1.67 (3 H, s, Me-1′), 1.75 (1 H, ddd, *J* = 12.9, 12.9, 5.1 Hz, H-7ax), 2.07 (1 H, m, H-6), 2.18 (1 H, ddd, *J* = 10.5, 2.4, 2.4 Hz, H-4a), 2.38 (1 H, dd, *J* = 10.5, 10.5 Hz, H-8a), 2.41 (1 H, m, H-2), 3.37 (3 H, s, $OCH_3$), 3.66 (1 H, br s, H-5), 4.02, 4.08 (each 1 H, dd, *J* = 12.7, 6.2 Hz, H-3′), 4.49 (2 H, s, $OCH_2Ph$), 4.60, 4.72 (each 1 H, d, *J* = 7.1 Hz, $OCH_2O$), 5.49 (1 H, ddd, *J* = 10.0, 4.6, 2.4 Hz, H-3), 5.60 (1 H, br d, *J* = 10.0 Hz, H-4), 5.69 (1 H, br t, *J* = 6.2 Hz, H-2′), 7.33 (5 H, m, Ar H), 9.49 (1 H, s, CHO); MS, *m/e* 426.2789 ($M^+$, calcd 426.2769), 381, 364, 335, 319, 303, 91, 45 (base peak).

**Registry No.** 1, 78798-07-9; 4, 112572-86-8; 5, 79646-66-5; 6, 110715-33-8; 7, 101376-74-3; 8, 112505-65-4; 9, 112505-66-5; 9 (lactol), 112505-67-6; 10, 112505-68-7; 10 ($R^2$ = TBS), 112505-69-8; 10 ($R^2$ = MOM), 112505-72-3; 11, 112505-71-2; 11 (alcohol), 112505-70-1; 12, 112505-73-4; 13, 112505-75-6; 14, 112505-74-5; 15, 112505-77-8; 16, 112505-76-7; $(EtO)_2P(O)CH_2COMe$, 1067-74-9; (*E*,*E*)-$BnOCH_2CH{=}C(CH_3)CH{=}CHCOMe$, 112505-62-1; (*E*,*E*)-$BnOCH_2CH{=}C(CH_3)CH{=}CHCH_2OH$, 112505-63-2; (*E*,*E*)-$BnOCH_2CH{=}C(CH_3)CH{=}CHCH_2Br$, 112505-64-3; $Ph_3P{=}C(Me)CoOEt$, 5717-37-3; tetronolide, 76705-48-1.

## Preparation of (*S*)-(−)-4-Methyl-2-cyclohexen-1-one: A Useful Chiral Building Block

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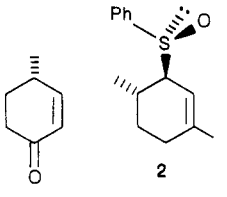
*Received August 3, 1987*

In the course of studies involving the enantioselective synthesis of trichothecenes[1] via chiral sulfinylallyl anions,[2] optically pure (*S*)-(−)-4-methyl-2-cyclohexen-1-one (**1**) was required as the starting material for the preparation of the chiral allylic sulfoxide **2**.[3] Barieux and Gore prepared




2




1

optically pure (*R*)-**1** from (*R*)-**3**-methylcyclohexanone by a sequence of reactions.[4] However, (*S*)-3-methylcyclohexanone, the starting material for (*S*)-**1**, is not commer-

(1) For a review of trichothecene, see: (a) Doyle, T. W.; Bradner, W. T. *Anticancer Agents Based on Natural Product Models*; Cassady, J. M., Douros, J. D., Eds.; Academic: New York, 1980; p 43–72. For reviews of recent syntheses, see: (b) Roberts, J. S.; Bryson, I. *Nat. Prod. Rep.* **1984**, *1*, 105. (c) McDougal, P. G.; Schmuff, N. R. *Prog. Chem. Org. Nat. Prod.* **1985**, *47*, 153.

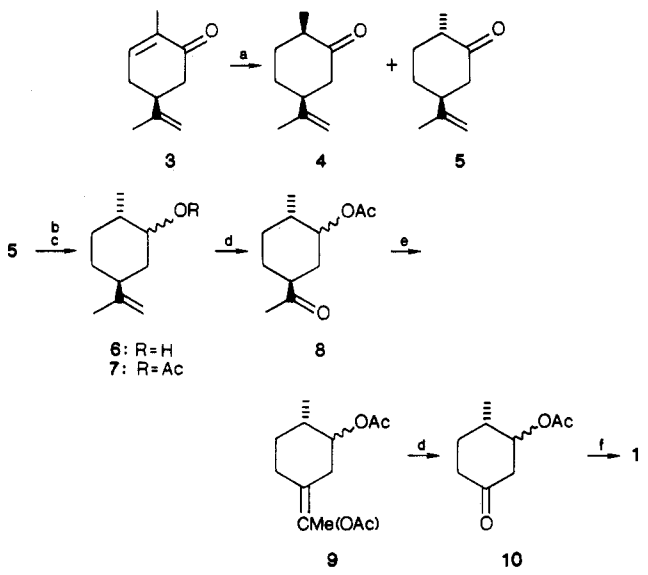
(2) (a) Hua, D. H.; Venkataraman, S.; Coulter, M. J.; Sinai, G.-Z. *J. Org. Chem.* **1987**, *52*, 719. (b) Hua, D. H. *J. Am. Chem. Soc.* **1986**, *108*, 3835. (c) Hua, D. H.; Sinai, G.-Z.; Venkataraman, S. *J. Am. Chem. Soc.* **1985**, *107*, 4088.

(3) Hua, D. H.; Venkataraman, S.; Chan, Y.-K.-R.; Paukstelis, J. K. *J. Am. Chem. Soc.*, submitted for publication.

(4) Barieux, J.-J.; Gore, J. *Bull. Soc. Chim. Fr.* **1971**, 3978. (*R*)-**1** was prepared in five steps.

0022-3263/88/1953-1095$01.50/0 

**Scheme I**[a]




[a] (a) Li, $NH_3$ (liquid); (b) Dibal-H; (c) $Ac_2O$, pyr; (d) $O_3$; $CH_2Cl_2$; (e) $Ac_2O$, *p*-TsOH; (f) $Et_3N$, toluene.

cially available.[5] Recently, Hiroi and Sato reported the asymmetric synthesis of (*S*)-1 from 4-methylcyclohexanone in poor optical yield (26% ee).[6] Herein, we describe a convenient and high-yielding preparation of (*S*)-1[7] from readily available (*S*)-(+)-carvone (3) (Scheme I).

Reduction of 3 with lithium in liquid ammonia provided 85% yield of a mixture of cis and trans ketones (4 and 5; 14:86), which were readily separated by column chromatography ($\Delta R_f$ 0.10; hexane–ether, 6:1). More trans ketone 5 was obtained by the equilibrium of cis ketone 4 to a 14:86 cis–trans mixture (98% yield) by exposure to 1 equiv of potassium hydroxide in methanol at 25 °C. Trans ketone 5 was converted to acetates 7 by reduction with diisobutylaluminum hydride (Dibal-H) in toluene at −78 °C (92% yield) followed by acetylation of the resulting alcohols (6) with acetic anhydride in pyridine (89% yield). Ozonolysis of acetates 7 with ozone in $CH_2Cl_2$–$CH_3OH$ at −78 °C afforded ketones 8 in 95% yield. Treatment of ketones 8 with acetic anhydride and *p*-toluenesulfonic acid (*p*-TsOH) at 90 °C for 6 h resulted in 35% recovery of ketones 8 and 60% conversion into enol acetate 9. Ozonolysis of 9 with ozone at −78 °C (85% yield) followed by elimination of the resulting β-acetoxy ketones (10) with triethylamine in toluene at 25 °C completed the synthesis of pure (*S*)-1, $[\alpha]^{22}_D$ −119° (*c* 0.37 in ethanol) (lit.[4] $[\alpha]^{22}_D$ +112° for *R* configuration).

Allylic isomerization of 6 or 7 to 3-isopropylidene-6-methylcyclohexanol or its acetate, respectively, was attempted with acids (e.g., HCl or *p*-TsOH) or $RhCl_3 \cdot 3H_2O$ in EtOH,[8] but only the substrate olefins were recovered along with a mixture of byproducts.

The ease with which both (*S*)-(−)- and (*R*)-(+)-4-methyl-2-cyclohexen-1-one may be prepared from commercially inexpensive (*S*)- and (*R*)-carvone should make them useful chiral building blocks for the preparation of optically active compounds of synthetic and medicinal interest.[3,7] The synthetic scheme is straightforward and readily amenable to larger scale preparations (e.g., 0.1 mol).

## Experimental Section

**General Methods.** Nuclear magnetic resonance spectra were obtained in deuteriochloroform on a Bruker WM-400 (400 MHz in $^1H$ and 100 MHz in $^{13}C$) spectrometer and are reported in ppm (δ units) downfield of internal tetramethylsilane. Infrared spectra were recorded on a Perkin-Elmer 1330 spectrophotometer and are reported in wavenumbers ($cm^{-1}$ units). Mass spectra were determined on a Finnigan 4000 automated gas chromatograph/EI–CI mass spectrometer. Microanalyses were carried out by the MicAnal Organic Microanalysis, Tucson, AZ. Satisfactory elemental analyses were obtained for all compounds. Optical rotations were measured on a Perkin-Elmer 241 polarimeter. Davisil silica gel, grade 643 (200–425 mesh), was used for the flash chromatographic separation.

**(3*S*,6*R*)-3-Isopropenyl-6-methylcyclohexanone (4) and (3*S*,6*S*)-3-Isopropenyl-6-methylcyclohexanone (5).**[9] To a cold (−35 °C) solution of 15 g (0.1 mol) of (*S*)-(+)-carvone (3), 150 mL of THF, and 45 mL of *t*-BuOH in 400 mL of liquid $NH_3$ under argon was added 1.4 g (0.2 mol) of lithium wire. The mixture was stirred vigorously and refluxed (−35 °C) for 15 min, and 50 mL of aqueous $NH_4Cl$ solution was added carefully. The $NH_3$ was allowed to evaporate at 25 °C (about 2 h), and the reaction mixture was diluted with $H_2O$ (300 mL) and extracted with ether (200 mL) three times. The combined extracts were washed with $H_2O$ (100 mL) and brine (50 mL), dried ($MgSO_4$), concentrated, and column chromatographed on silica gel, with use of hexane–ether as eluent to give 11.11 g (73.1% yield) of the less polar trans ketone 5 and 1.81 g (11.9% yield) of the more polar cis ketone 4. Small amounts of the alcohols (i.e., 6 and its C-6 epimers), from the overreduction of ketones 4 and 5, were also obtained.

5: $[\alpha]^{23}_D$ −10.4° (*c* 0.5, EtOH) (lit.[10] $[\alpha]^{23}_D$ −16.79°, neat); IR (neat) 1640, 1450, 1370; $^1H$ NMR δ 4.76 (d, *J* = 2 Hz, 1 H, =CH), 4.73 (d, *J* = 2 Hz, 1 H, =CH), 2.5–1.3 (m, 8 H), 1.74 (s, 3 H, $=CCH_3$), 1.03 (d, *J* = 6.5 Hz, 3 H, $CH_3$); $^{13}C$ NMR δ 212.4 (s), 147.6 (s), 109.6 (t), 47.0 (d), 46.9 (t), 44.8 (d), 34.9 (d), 30.8 (d), 20.5 (q), 14.3 (q); MS, *m/z* 152 ($M^+$).

4: $[\alpha]^{23}_D$ −31.3° (*c* 1.4, $CHCl_3$); IR (neat) 1641, 1450, 1372; $^1H$ NMR δ 4.83 (s, 1 H, =CH), 4.70 (s, 1 H, =CH), 2.6–1.6 (m, 8 H), 1.73 (s, 3 H, $=CCH_3$), 1.11 (d, *J* = 6.5 Hz, 3 H, $CH_3$); $^{13}C$ NMR δ 213.94, 146.75, 111.42, 44.49, 44.03, 43.83, 30.51, 26.26, 21.47, 15.49; MS, *m/z* 152 ($M^+$).

**(1*S*,3*S*,6*S*)- and (1*R*,3*S*,6*S*)-3-Isopropenyl-6-methylcyclohexanol (6).** To a solution of 13.4 g (88 mmol) of ketone 5 in 360 mL of toluene at −78 °C under argon was added 70 mL (0.1 mol) of Dibal-H (1.5 M in toluene), and the solution was stirred at −78 °C for 2 h. To the solution was added 10 mL of methanol, and the solution was poured into a mixture of 600 mL of ether and 200 mL of $H_2O$ and filtered through Celite. The organic layer was separated, and the aqueous layer was extracted twice with ether (200 mL). The combined organic layer was washed with brine (100 mL), dried ($MgSO_4$), concentrated, and column chromatographed to give 12.49 g (92% yield) of 6, a mixture of two isomeric alcohols: IR (neat) 3400, 1640, 1450, 1360; $^1H$ NMR δ 4.69 (s, 2 H, $=CH_2$), 3.89 (s, 0.5 H, CHO), 3.19 (m,

(5) Syntheses of (*S*)-(−)-3-methylcyclohexanone, in various degree of purity, by a sequence of reactions have been reported. See: (a) Nakazaki, M.; Naemura, K.; Nakahara, S. *J. Org. Chem.* **1979**, *44*, 2438. (b) Goering, H. L.; Silversmith, E. F. *J. Am. Chem. Soc.* **1955**, *77*, 5172. (c) Macbeth, A. K.; Mills, J. A. *J. Chem. Soc.* **1947**, 205. (d) Rupe, H. *Justus Liebigs Ann. Chem.* **1927**, *459*, 206.

(6) Hiroi, K.; Sato, S. *Synthesis* **1985**, 635.

(7) Recent uses of (±)-1 in organic synthesis, stereoselective 1,4-addition: (a) Lucchetti, J.; Krief, A. *Tetrahedron Lett.* **1981**, *22*, 1623. (b) Thomas, J. A.; Heathcock, C. H. *Tetrahedron Lett.* **1980**, *21*, 3235. (c) Ouannes, C.; Dressaire, G.; Langlois, Y. *Tetrahedron Lett.* **1977**, 815. 1,2-Addition (synthesis of verrucarins): (d) Trost, B. M.; Ribgy, J. H. *J. Org. Chem.* **1978**, *43*, 2938. Diels–Alder reaction: (e) Geribaldi, S.; Torri, G.; Azzaro, M. *Bull. Soc. Chim. Fr.* **1973**, 2521. Stereoselective [2 + 2] cycloaddition: (f) Ficini, J.; Eman, A.; Touzin, A. M. *Tetrahedron Lett.* **1976**, 679.

(8) (a) Torii, S.; Uneyama, K.; Okamato, K. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 3590. (b) Harrod, J. F.; Chalk, A. J. *J. Am. Chem. Soc.* **1964**, *86*, 1776.

(9) 1,4-Reduction of carvone with $Bu_3SnH$–$Pd(PPh_3)_4$ in 95% yield has been reported: (a) Xian, Y. T.; Four, P.; Guibe, F.; Balavoine, G. *Nouv. J. Chim.* **1984**, *8*, 611. (b) Four, P.; Guibe, F. *Tetrahedron Lett.* **1982**, *23*, 1825. The stereochemistry of the products from the above method was not mentioned. Furthermore, lithium/liquid $NH_3$ reduction method is more economical.

(10) Merkel, D. *Die Ätherischen Öle*; Gildemeister, E., Hoffmann F. Eds., Akademie Verlag: Berlin, 1963; Vol. IIIc, p 244.

0.5 H, CHO), 2.4–0.9 (m, 8 H), 1.72 (s, 3 H, =$CCH_3$), 1.03 (d, $J$ = 6.4 Hz, 3 H, $CH_3$), 0.97 (d, $J$ = 6.4 Hz, 3 H, $CH_3$); $^{13}C$ NMR δ 150.1, 149.2, 108.5, 108.2, 76.2, 70.8, 44.1, 40.5, 39.9, 38.6, 37.7, 36.0, 33.2, 31.3, 31.0, 29.6, 28.1, 20.8, 20.7, 18.3, 18.2; MS, $m/z$ 154 ($M^+$).

**(1*R*,3*S*,6*S*)- and (1*S*,3*S*,6*S*)-3-Isopropenyl-6-methylcyclohexyl Acetate (7).** A mixture of 9.2 g (59.7 mmol) of alcohols **6** and 11.2 mL (0.118 mol) of acetic anhydride in 160 mL of pyridine was stirred at 85 °C for 3 h. The solution was cooled, poured into $H_2O$ (400 mL), and extracted three times with ether (200 mL each). The combined extract was washed with 1 N HCl (100 mL), saturated $NaHCO_3$ (100 mL), and brine (50 mL), dried ($MgSO_4$), concentrated, and filtered through a small silica gel column to give 10.42 g (89% yield) of the two isomeric acetates **7**: IR (neat) 1725, 1640, 1450, 1370, 1240; $^1H$ NMR δ 5.05 (br s, 0.5 H, CHO), 4.7 (m, 2 H, =$CH_2$), 4.47 (br t, $J$ = 10 Hz, 0.5 H, CHO), 2.2–1.1 (m, 8 H), 2.08 (s, 1.5 H, $CH_3$), 2.06 (s, 1.5 H, $CH_3$), 1.7 (s, 3 H, =$CCH_3$), 0.91 (d, $J$ = 6.4 Hz, 1.5 H, $CH_3$), 0.88 (d, $J$ = 6.8 Hz, 1.5 H, $CH_3$); $^{13}C$ NMR δ 170.7 (2 C), 149.6, 148.8, 108.8, 108.6, 78.1, 73.4, 43.6, 38.5, 37.0, 36.8, 35.5, 34.8, 33.0, 31.1, 30.8, 29.6, 29.0, 21.2, 21.1, 20.84, 20.77, 18.1, 18.0; MS, $m/z$ 196 ($M^+$).

**(1*R*,3*S*,6*S*)- and (1*S*,3*S*,6*S*)-3-Acetyl-6-methylcyclohexyl Acetate (8).** Into a cold (−78 °C) solution of 7.2 g (36.7 mmol) of acetates **7** in 100 mL of MeOH and 500 mL of $CH_2Cl_2$ under argon was bubbled ozone until the solution became light blue (about 1 h). The ozone addition was stopped, and the solution was stirred under argon at −78 °C for 15 min and at 25 °C for 30 min. To the solution were added 45 g of zinc dust and 100 mL of acetic acid, and the resulting mixture was stirred at 25 °C for 30 min and filtered through Celite. The filtrate was neutralized with 5 N NaOH solution (340 mL), the organic layer was separated, and the aqueous layer was extracted twice with ether (400 mL). The organic layer and ether extracts were combined, washed with water (100 mL) and brine (100 mL), dried ($MgSO_4$), and concentrated to give 6.93 g (95% yield) of ketones **8**: IR (neat) 1725, 1700, 1440, 1360, 1240; $^1H$ NMR δ 5.07 (br s, 0.5 H, CHO), 4.44 (td, $J$ = 10 Hz, 4 Hz, 0.5 H, CHO), 2.7–1.1 (m, 8 H), 2.15 (s, 1.5 H, $CH_3$), 2.14 (s, 1.5 H, $CH_3$), 2.09 (s, 1.5 H, $CH_3$), 2.06 (s, 1.5 H, $CH_3$), 0.92 (d, $J$ = 6.5 Hz, 1.5 H, $CH_3$), 0.88 (d, $J$ = 6.5 Hz, 1.5 H, $CH_3$); $^{13}C$ NMR δ 211.0, 209.5, 170.6, 170.4, 77.2, 72.3, 49.7, 45.2, 36.6, 34.5, 33.1, 32.4, 32.1, 28.1, 27.8, 27.5, 24.1, 20.9, 17.9, 17.7; MS, $m/z$ 198 ($M^+$).

**(1*R*,6*S*)- and (1*S*,6*S*)-3-(α-Acetoxyethylidene)-6-methylcyclohexyl Acetate (9).** A solution of 6 g (30.3 mmol) of ketones **8** and 5.82 g (30.6 mmol) of *p*-TsOH in 225 mL of acetic anhydride was heated at 90 °C for 6 h under argon. About 30 mL of acetic anhydride (containing generated acetic acid) was distilled from the mixture under reduced pressure (30 mmHg) at the end of each hour. The mixture was then cooled to room temperature, diluted with ether (400 mL), washed with $H_2O$ (100 mL), saturated $NaHCO_3$ (50 mL), and brine (50 mL), and dried ($MgSO_4$). The solvent was evaporated, and the residue was column chromatographed to give 4.36 g (60% yield) of enol acetates **9** as four isomers and 2.1 g (35% recovery) of ketones **8** and their C-3 epimers.

**9**: IR (neat) 1725, 1425, 1360, 1225; $^1H$ NMR δ 4.91 (m, 0.25 H, CHO), 4.80 (m, 0.25 H, CHO), 4.42 (td, $J$ = 10.3 Hz, 4.6 Hz, 0.25 H, CHO), 4.33 (td, $J$ = 10.1 Hz, 4.6 Hz, 0.25 H, CHO), 2.9–1.0 (m, 7 H), 2.14 (s, $CH_3$), 2.13 (s, $CH_3$), 2.09 (s, $CH_3$), 2.06 (s, $CH_3$), 2.05 (s, $CH_3$), 2.03 (s, $CH_3$), 1.88 (s, 0.75 H, =$CCH_3$), 1.87 (s, 0.75 H, =$CCH_3$), 1.86 (s, 0.75 H, =$CCH_3$), 1.80 (s, 0.75 H, =$CCH_3$), 0.920 (d, $J$ = 6.4 Hz, 0.75 H, $CH_3$), 0.917 (d, $J$ = 6.4 Hz, 0.75 H, $CH_3$), 0.912 (d, $J$ = 6.8 Hz, 0.75 H, $CH_3$), 0.911 (d, $J$ = 6.8 Hz, 0.75 H, $CH_3$); $^{13}C$ NMR δ 171.1, 170.9, 170.5, 170.4, 169.3, 169.2, 169.0, 168.97, 139.2, 138.8, 138.7, 122.3, 122.0, 121.0, 120.7, 77.07, 76.7, 74.1, 73.8, 62.7, 37.0, 36.8, 36.7, 34.6, 34.4, 33.9, 32.5, 32.4, 32.2, 32.0, 30.8, 29.5, 29.3, 27.5, 27.4, 26.0, 21.1, 20.9, 20.7, 20.6, 18.0, 17.7, 17.0, 16.7, 15.8, 15.7, 15.5; MS $m/z$ 240 ($M^+$).

**(3*R*,4*S*)- and (3*S*,4*S*)-3-Acetoxy-4-methylcyclohexanone (10).** The mixture of enol acetates **9** was subjected to the same conditions as described above for the reaction of **7** with ozone. The titled compounds (85% yield; ratio of 1:1) were separated by column chromatography.

(3*R*,4*S*)-*cis*-3-Acetoxy-4-methylcyclohexanone: more polar isomer, $[\alpha]^{23}_D$ + 47.3° (*c* 0.127, $CHCl_3$); IR (neat) 1725, 1460, 1420, 1375, 1240; $^1H$ NMR δ 5.27 (m, 8 Hz wide, 1 H, CHO, equatorial H), 2.6–1.8 (m, 7 H), 2.05 (s, 3 H, $CH_3CO$), 1.01 (d, $J$ = 6.8 Hz, 3 H, $CH_3$); $^{13}C$ NMR δ 208.2, 169.9, 74.5, 45.2, 39.8, 33.4, 28.1, 20.5, 16.3; MS, $m/z$ 170 ($M^+$).

(3*S*,4*S*)-*trans*-3-Acetoxy-4-methylcyclohexanone: less polar isomer, $[\alpha]^{23}_D$ +18.5° (*c* 0.13, $CHCl_3$); IR (neat) 1725, 1700, 1458, 1250; $^1H$ NMR δ 4.80 (td, $J$ = 10 Hz, 4.8 Hz, 1 H, CHO, axial H), 2.8–1.4 (m, 7 H), 2.06 (s, 3 H, $CH_3$), 1.07 (d, $J$ = 6.5 Hz, 3 H, $CH_3$); $^{13}C$ NMR δ 207.4 (s), 169.7 (s), 75.4 (d), 45.3 (t), 39.2 (t), 34.6 (q), 28.3 (d), 20.7 (t), 16.5 (q); MS, $m/z$ 170 ($M^+$).

**(*S*)-(−)-4-Methyl-2-cyclohexen-1-one (1).** A mixture of 2.80 g (16.5 mmol) of a mixture of 3(*R*),4(*S*)- and 3(*S*),4(*S*)-3-acetoxy-4-methylcyclohexanone and 4.6 mL (33 mmol) of triethylamine in 65 mL of toluene was stirred under argon at 25 °C for 3 h. The mixture was poured into $H_2O$ (100 mL) and extracted three times with ether (100 mL each). The combined extracts were washed with $H_2O$ (50 mL) and brine (50 mL), dried ($MgSO_4$), concentrated, and column chromatographed to give 1.71 g (94% yield) of enone **1**: $[\alpha]^{22}_D$ −119° (*c* 0.37, EtOH) (lit.[4] $[\alpha]^{22}_D$ +112°, in EtOH; for *R* configuration); IR (neat) 3020, 2960, 1670; $^1H$ NMR δ 6.81 (d, $J$ = 10.1 Hz, 1 H, =CH), 5.95 (d, $J$ = 10.1 Hz, 1 H, =CH), 2.6–1.6 (m, 5 H), 1.76 (d, $J$ = 7.1 Hz, $CH_3$); $^{13}C$ NMR[11] δ 199.16 (s), 155.94 (d), 128.12 (d), 36.43 (d), 30.66 (t), 30.45 (t), 19.77 (q); MS, $m/z$ 110 ($M^+$).

**Acknowledgment.** We gratefully acknowledge the financial support from the National Science Foundation (Grant CHE-8419265) and the National Institute of General Medical Sciences (Grant GM 36336). Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for generous financial support. We also thank the NSF for a grant for the purchase of the Perkin-Elmer 241 polarimeter.

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## Electron Transfer Induced Desilylation of Trimethylsilyl Enol Ethers

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*Received September 9, 1987*

The trimethylsilyl moiety is now widely used as a protecting group for alcohols through the formation of trimethylsilyl ethers and for aldehydes and ketones through the formation of trimethylsilyl enol ethers. The trimethylsilyl protecting group has routinely been removed with fluoride ion,[1] acid,[2] or base.[3] Unfortunately, these reagents offer little in the way of selectively between trimethylsilyl enol ethers and trimethylsilyl ethers. We now report a selective method for the deprotection of trimethylsilyl enol ethers in the presence of trimethylsilyl ethers. This method is based on the photoinduced single-electron transfer[4,5] from the easily oxidized tri-

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