Stereochemistry in the Reaction of Optically Active Allylsilanes with *m*-Chloroperoxybenzoic Acid[1]

Tamio Hayashi,* Yasuo Okamoto, Keiji Kabeta, Toshiya Hagihara, and Makoto Kumada

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan

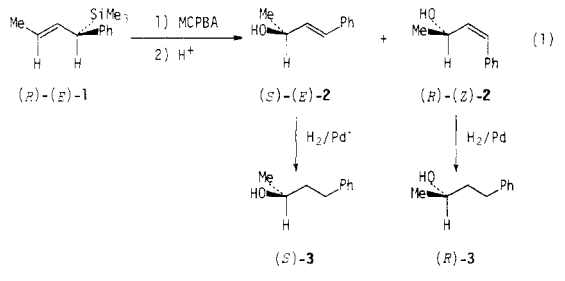
Received March 20, 1984

An optically active allylsilane (*R*)-(*E*)-1-phenyl-1-(trimethylsilyl)-2-butene (**1**) (81% ee) was allowed to react with *m*-chloroperoxybenzoic acid (MCPBA) in dichloromethane to give, after acidic methanolysis, (*S*)-(*E*)-4-phenyl-3-buten-2-ol (**2**) (71–73% ee) and (*R*)-(*Z*)-**2** (72% ee) in 98% yield, the ratio of (*E*)-**2** to (*Z*)-**2** being 81 to 19. Reaction of (*R*)-(*Z*)-**1** (24% ee) with MCPBA gave (*R*)-(*E*)-**2** (19% ee) as a single oxidation product. These results indicate that MCPBA attacked the double bond anti with respect to the silyl group. A mechanism is proposed to account for the stereochemical pathway.

Allylsilanes are known to undergo substitution of the silyl group by a wide variety of electrophiles with 1,3-transposition of the allylic group (S_E' reaction).[2] We have previously reported the S_E' reaction of optically active allylsilanes with trifluoroacetic acid-*d*[3] and carbon electrophiles such as aldehydes, *tert*-butyl chloride, acetyl chloride, and ethylene oxide activated by a Lewis acid,[4] which proceeded selectively with anti stereochemistry to afford optically active products. Use of a peroxy acid as electrophile has been reported to produce allyl alcohols via β,γ-epoxy silanes,[5,6] though allylsilanes successfully used for the oxidation have been limited to those bearing β-substituents or certain cyclic structures. Here we describe our results obtained for the *m*-chloroperoxybenzoic acid (MCPBA) oxidation of optically active allylsilanes, where MCPBA entered the double bond anti with respect to the silyl group giving optically active allyl alcohols.[7]

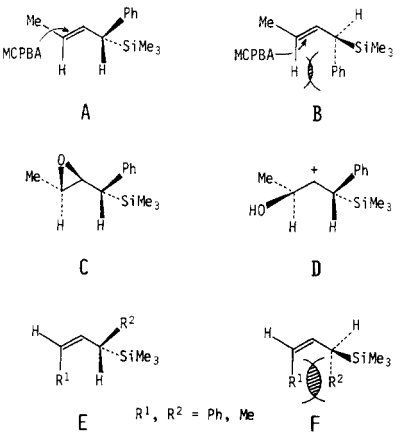
Results and Discussion

An optically active allylsilane (*R*)-(*E*)-1-phenyl-1-(trimethylsilyl)-2-butene (**1**) (81% ee)[4a] was allowed to react with MCPBA (1.1 equiv) and sodium bicarbonate (1.0 equiv) in dichloromethane at 0 °C for 1 h. Treatment of the reaction mixture with acetic acid in methanol gave 98% yield of 4-phenyl-3-buten-2-ol (**2**) consisting of *E* and *Z* isomers in a ratio of 81:19 (eq 1).[8] The *E* and *Z* isomers



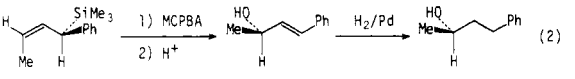
(1)

Chart I

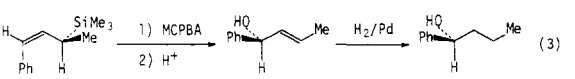


were converted into their trimethylsilyl ethers and isolated by preparative GLC. The alcohol (*E*)-**2** ($[\alpha]^{20}_D$ −11.8° (*c* 2.4, benzene))[9] was hydrogenated in the presence of Pd/C catalyst to give 4-phenylbutan-2-ol (**3**), which had the rotation of $[\alpha]^{20}_D$ +13.5° (*c* 2.1, chloroform) indicating that **3** is an *S* isomer of 78% ee.[10] The ^{1}H NMR spectra of (*E*)-**2** and **3** in the presence of a chiral shift reagent Eu(dcm)$_3$[11] showed that they were 71–73% ee. On the other hand, *Z* alcohol **2** proved to be an *R* isomer of ~72% ee by the NMR studies of **3** obtained by the hydrogenation of (*Z*)-**2**. It follows that the MCPBA oxidation of (*R*)-(*E*)-**1** produced the allyl alcohols (*S*)-(*E*)-**2** and (*R*)-(*Z*)-**2** with high stereoselectivity.

Oxidation of *Z* allylsilane, (*R*)-(*Z*)-**1** (24% ee),[4a] with MCPBA in a similar manner gave the *E* alcohol **2** with over 98% selectivity, the hydrogenation of which afforded (*R*)-**3** of 19% ee ($[\alpha]^{20}_D$ −3.4° (*c* 2.4, chloroform))[10] (eq 2).



(2)



(3)

(1) Optically Active Allylsilanes. 8. For part 7, see ref 4c.

(2) Reviews: (a) Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761. (b) Sakurai, H. *Pure Appl. Chem.* **1982**, *54*, 1. (c) Colvin, E. W. "Silicon in Organic Synthesis"; Butterworth: London, 1981; pp 97–124. (d) Weber, W. P. "Silicon Reagents for Organic Synthesis"; Springer-Verlag: New York, 1983; pp 173–205.

(3) Hayashi, T.; Ito H.; Kumada, M. *Tetrahedron Lett.* **1982**, *23*, 4605.

(4) (a) Hayashi, T.; Konishi, M.; Ito, H.; Kumada, M. *J. Am. Chem. Soc.* **1982**, *104*, 4962. (b) Hayashi, T.; Konishi, M.; Kumada, M. *J. Am. Chem. Soc.* **1982**, *104*, 4963. (c) Hayashi, T.; Kabeta, K.; Yamamoto, T.; Tamao, K.; Kumada, M. *Tetrahedron Lett.* **1983**, *24*, 5661.

(5) (a) Carter, M. J.; Fleming, I. *J. Chem. Soc., Chem. Commun.* **1976**, 679. (b) Au-Yeung, B.-W.; Fleming, I. *J. Chem. Soc., Chem. Commun.* **1977**, 79. (c) Fleming, I.; Au-Yeung, B.-W. *Tetrahedron Suppl.* **1981**, *37*, 13.

(6) Nishiyama, H.; Yokoyama, H.; Narimatsu, S.; Itoh, K. *Tetrahedron Lett.* **1982**, *23*, 1267. See also, Hudrlik, P. F.; Withers, G. P. *Tetrahedron Lett.* **1976**, 29.

(7) Recently, anti stereochemistry of the MCPBA oxidation has been reported in an exocyclic system: Fleming, I.; Terrett, N. K. *Tetrahedron Lett.* **1983**, *24*, 4153.

(8) Attempts to isolate a presumed β,γ-epoxy silane[5,6] were unsuccessful. Workup before the acidic methanolysis gave a mixture of the alcohol **2** and its trimethylsilyl ether.

(9) Kenyon, J.; Partridge, S. M.; Phillips, H. *J. Chem. Soc.* **1936**, 85. See also: Sato, T.; Gotoh, Y.; Wakabayashi, Y.; Fujisawa, T. *Tetrahedron Lett.* **1983**, *24*, 4123. Kawasaki, M.; Suzuki, Y.; Terashima, S. *Chem. Lett.* **1984**, 239.

(10) (a) Pickard, R. H.; Kenyon, J. *J. Chem. Soc.* **1914**, *105*, 1115. (b) Jacques, J.; Gros, C.; Bourcier, S. In "Stereochemistry, Fundamentals and Methods"; Kagan, H. B. Ed.; Georg Thieme: Stuttgart, 1977; Vol. 4, p 226.

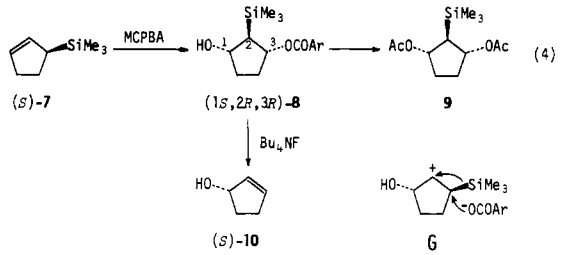
(11) McCreary, M. D.; Lewis, D. W.; Wernick, D. L.; Whitesides, G. M. *J. Am. Chem. Soc.* **1974**, *96*, 1038.

0022-3263/84/1949-4224$01.50/0 © 1984 American Chemical Society

Similar stereochemistry was observed in the oxidation of (*Z*)-1-phenyl-3-(trimethylsilyl)1-butene (**4**) (eq 3). Treatment of (*S*)-(*Z*)-**4** (44% ee)[12] with MCPBA gave (*S*)-(*E*)-1-phenyl-2-buten-1-ol (**5**) of 35% ee ($[\alpha]^{20}_D$ +12.5° (*c* 2.1, chloroform)) whose stereochemical assignment was carried out by reduction into known (*S*)-1-phenylbutan-1-ol (**6**).[13]

The stereochemical results obtained above can be illustrated by the mechanism shown in Chart I. Allylsilanes have been reported to exist in the conformation where the carbon–silicon bond is coplanar with the π lobes of the carbon–carbon double bond due to the σ–π conjugative interaction.[14] The possible conformations for the allylsilane (*R*)-(*E*)-**1** are A and B. Anti attack of MCPBA on conformation A will produce (*S*)-(*E*)-**2** via β,γ-epoxy silane[5,6] C or cationic intermediate D stabilized by the σ–π conjugation,[15] and the attack on B will produce (*R*)-(*Z*)-**2**. The conformation B is less favorable than A because of the disadvantageous steric repulsion between the olefin moiety and the phenyl group on the α-carbon, which may cause the preferential formation of (*S*)-(*E*)-**2** over (*R*)-(*Z*)-**2**. In case of the *Z* allylsilanes (*R*)-(*Z*)-**1** and (*S*)-(*Z*)-**4**, the conformation E is much more favorable than F which suffers strong steric repulsion between the phenyl and methyl groups. Thus, the alcohol (*R*)-(*E*)-**2** or (*S*)-(*E*)-**5** resulting from *E* was produced exclusively.

The oxidation of 3-(trimethylsilyl)cyclopentene (**7**) proceeded in a different way. Reaction of (*S*)-**7** ($[\alpha]^{20}_D$ −49.1° (*c* 0.5, benzene), 22–25% ee)[4c] with MCPBA in dichloromethane gave, regardless of the presence or absence of sodium bicarbonate, a high yield of *trans,trans*-1-hydroxy-2-(trimethylsilyl)-3-[(*m*-chlorobenzoyl)oxy]-cyclopentane (**8**) ($[\alpha]^{20}_D$ −6.6° (*c* 1.1, CCl_4)) which was shown to be ~30% ee by the ^1H NMR using Eu(dcm)$_3$[11] (eq 4). The structure of **8** was confirmed by ^1H NMR



spectra of diacetate **9** obtained by alkaline hydrolysis followed by acetylation. Treatment of **8** with tetrabutylammonium fluoride[16] in THF gave (*S*)-2-cyclopentenol[17] (**10**) of ~19% ee. Thus the configuration of **8** proved to be 1*S*,2*R*,3*R*, indicating that the electrophilic attack of MCPBA in the cyclic system is also anti. The MCPBA adduct **8** may be formed by nucleophilic attack of the benzoate on the cationic intermediate G with the silyl group migrating to the vicinal cationic carbon.

Experimental Section

Optical rotations were measured with a Perkin-Elmer 241 polarimeter. ^1H NMR spectra were obtained on a JEOL MH-100 spectrometer. Optically active allylsilanes (*E*)-**1** and (*Z*)-**1** were prepared by palladium-catalyzed asymmetric cross-coupling of [α-(trimethylsilyl)benzyl]magnesium bromide with (*E*)- and (*Z*)-1-bromopropene, respectively.[4a] Optically active 3-(trimethylsilyl)cyclopentene (**7**) was prepared by hydrosilylation of cyclopentadiene in the presence of a chiral palladium catalyst.[4c]

Reaction of (*R*)-(*E*)-1-Phenyl-1-(trimethylsilyl)-2-butene (1) with MCPBA. To a mixture of 0.622 g (3.04 mmol) of (*R*)-(*E*)-**1** (81% ee) and 0.252 g (2.99 mmol) of sodium bicarbonate in 10 mL of dichloromethane was added at −78 °C a solution of 0.720 g (3.34 mmol) of 80% MCPBA in 15 mL of dichloromethane. The mixture was stirred at 0 °C for 1 h, and the solvent was removed under reduced pressure. To the residue were added 12 mL of methanol and 2 mL of acetic acid, and the mixture was stirred at room temperature for 10 min. Ether (50 mL) was added and the solution was washed with 20% sodium hydroxide (4 × 50 mL) and water, dried over anhydrous magnesium sulfate, and concentrated under reduced pressure. Purification of the residue by preparative TLC on silica gel utilizing chloroform as eluent gave 0.441 g (98% yield) of 4-phenyl-3-buten-2-ol (**2**) whose ^1H NMR showed that **2** consisted of *E* and *Z* isomers in a ratio of 81:19.

To a solutin of *E* and *Z* alcohols **2** obtained above in 3 mL of THF were added successively 0.58 mL (4.5 mmol) of pyridine and 0.48 mL (5.9 mmol) of trimethylchlorosilane at 0 °C. The mixture was stirred at room temperature for 3.5 h, hydrolyzed with water, and extracted four times with hexane. The hexane extracts were washed with 5% cupric sulfate and water, dried over anhydrous magnesium sulfate, and evaporated. The residue was passed through a short silica gel column to give 0.546 g (82% yield) of (*E*)- and (*Z*)-1-phenyl-3-[(trimethylsilyl)oxy]-1-butene. The *E* and *Z* silyl ethers were isolated by preparative GLC (Silicone DC550). ^1H NMR (CCl_4) for the *E* isomer: δ 0.11 (s, 9 H), 1.28 (d, J = 6 Hz, 3 H), 4.38 (quint, 1 H), 6.05 (dd, J = 6, 16 Hz, 1 H), 6.38 (d, J = 16 Hz, 1 H), 6.96–7.41 (m, 5 H). ^1H NMR (CCl_4) for the *Z* isomer: δ −0.04 (s, 9 H), 1.31 (d, J = 6 Hz, 3 H), 4. 68 (dq, J = 9, 6 Hz, 1 H), 5.60 (dd, J = 9, 12 Hz, 1 H), 6.32 (d, J = 12 Hz, 1 H), 7.01–7.41 (m, 5 H).

The silyl ethers were desilylated to the corresponding alcohols (*E*)- and (*Z*)-**2** by a standard method (AcOH/MeOH).[18] (*E*)-**2**: $[\alpha]^{20}_D$ −11.8° (*c* 2.4, benzene) (lit.[9] $[\alpha]_D$ 18.2°); ^1H NMR (CCl_4) δ 1.31 (d, J = 6 Hz, 3 H), 1.35 (s, 1 H), 4.38 (quint, J = 6 Hz, 1 H), 6.12 (dd, J = 6, 16 Hz, 1 H), 6.48 (d, J = 16 Hz, 1 H), 7.00–7.40 (m, 5 H). (*Z*)-**2**: ^1H NMR (CCl_4) δ 1.30 (d, J = 6 Hz, 3 H), 1.39 (s, 1 H), 4.63 (dq, J = 9, 6 Hz, 1 H), 5.58 (dd, J = 9, 12 Hz, 1 H), 6.38 (d, J = 12 Hz, 1 H), 6.95–7.35 (m, 5 H). Enantiomeric purity of (*E*)-**2** determined by NMR analysis in the presence of Eu(dcm)$_3$[11] was 71%. The methine signal of the major enantiomer appeared at higher field than that of the minor enantiomer.

A solution of 90 mg (0.61 mmol) of (*E*)-**2** and 10 mg of 10% Pd-C in 2 mL of benzene was placed in a stainless micro autoclave and magnetically stirred with hydrogen at 50 atm for 24 h. The reaction mixture was passed through a short silica gel column and evaporated to give 4-phenylbutan-2-ol (**3**) in a quantitative yield, which showed $[\alpha]^{20}_D$ +13.5° (*c* 2.1, chloroform) (lit.[10] for (*S*)-**3** $[\alpha]_D$ +17.2° (chloroform)). ^1H NMR in the presence of Eu(dcm)$_3$[11] showed that **3** thus obtained was 73% ee, the methyl doublet of the *S* isomer appearing at lower field than that of the *R* isomer.

Hydrogenation of (*Z*)-**2** in a similar manner to that above gave (*R*)-**3** of 72% ee, which was determined by ^1H NMR analysis using Eu(dcm)$_3$.[11]

Reaction of (*R*)-(*Z*)-1-Phenyl-1-(trimethylsilyl)-2-butene (1) with MCPBA. This reaction was carried out starting with (*R*)-(*Z*)-**1** of 24% ee as described for (*R*)-(*E*)-**1**. Preparative TLC on silica gel (chloroform) gave 68% yield of (*E*)-4-phenyl-3-buten-2-ol (**2**) with $[\alpha]^{20}_D$ +2.94° (*c* 2.7, benzene). NMR analysis showed that no *Z* isomer was present.

The alcohol **3** obtained by the hydrogenation of (*E*)-**2** was *R* isomer of 19% ee ($[\alpha]^{20}_D$ −3.4° (*c* 2.4, chloroform)), which was

(12) Hayashi, T.; Okamoto, Y.; Kumada, M., to be published.
(13) Mislow, K.; Hamermesh, C. L. *J. Am. Chem. Soc.* **1955**, *77*, 1590.
(14) (a) Weidner, U.; Schweig, A. *Angew. Chem.* **1972**, *84*, 167. (b) Weidner, U.; Schweig, A. *J. Organomet. Chem.* **1972**, *39*, 261. See also, ref 4a.
(15) (a) Traylor, T. G.; Hanstein, W.; Berwin, H. J.; Clinton, V. A.; Brown, R. S. *J. Am. Chem. Soc.* **1971**, *93*, 5715. (b) Eaborn, C. *J. Chem. Soc., Chem. Commun.* **1972**, 1255.
(16) Fluoride ion mediated elimination of β-silylalkyl esters has been reported to proceed with anti stereochemistry, which may support that **8** has trimethylsilyl and (*m*-chlorobenzoyl)oxy groups in trans positions: (a) Fleming, I.; Terrett, N. K. *Tetrahedron Lett.* **1983**, *24*, 4151. (b) Luo, F.-T.; Negishi, E. *J. Org. Chem.* **1983**, *48*, 5144. We thank Prof. Negishi for sending us the preprint.
(17) Hill, R. K.; Edwards, A. G. *Tetrahedron Lett.* **1964**, 3239.
(18) Bundy, G. L.; Peterson, D. C. *Tetrahedron Lett.* **1978**, 41.

confirmed by ^1H NMR in the presence of Eu(dcm)$_3$.[11] The methyl signal of the major enantiomer appeared at higher field than that of minor enantiomer.

Reaction of (*S*)-(*Z*)-1-Phenyl-3-(trimethylsilyl)-1-butene (4) with MCPBA. In a similar manner to that described for (*R*)-(*E*)-1, 2.80 g (13.7 mmol) of (*S*)-(*Z*)-**4** ([α]$^{20}_D$ +65.5° (*c* 1.5, benzene), 44% ee)[12] was treated with 3.25 g (15.1 mmol) of 80% MCPBA and 1.26 g (15.0 mmol) of sodium bicarbonate in 100 mL of dichloromethane at 0 °C for 1.5 h. To the residue obtained by removal of the solvent under reduced pressure were added 60 mL of acetic acid and 20 mL of water, and the mixture was stirred at room temperature for 1.5 h. Ether was added and the solution was washed with 20% sodium hydroxide (4 × 50 mL) and aqueous sodium thiosulfate, dried over anhydrous magnesium sulfate, and evaporated under reduced pressure to give 1.82 g of crude (*E*)-1-phenyl-2-buten-1-ol (**5**), which was contaminated with 30–40% of (*E*)-4-phenyl-3-buten-2-ol (**2**). The alcohol (*E*)-**5** was purified by silica gel medium-pressure liquid chromatography (MPLC) (ethyl acetate/hexane = 1/1). It was observed that (*E*)-**5** was isomerized slowly into (*E*)-**2** during the chromatographic separation. (*E*)-**5**: [α]$^{20}_D$ +12.5° (*c* 2.1, chloroform); ^1H NMR (CCl_4) δ 1.72 (d, J = 5 Hz, 3 H), 1.56–1.92 (broad s, 1 H), 4.97–5.16 (m, 1 H), 5.40–5.80 (m, 2 H), 7.04–7.46 (m, 5 H). ^1H NMR in the presence of Eu(dcm)$_3$[11] indicated that the enantiomeric purity of (*E*)-**5** was 35%, the ortho phenyl proton of the major enantiomer appearing at higher field than that of the minor one.

Hydrogenation (50 atm) of (*E*)-**5** in the presence of 10% Pd-C in benzene for 13 h gave quantitatively (*S*)-1-phenylbutan-1-ol (**6**) with [α]$^{27}_D$ −14.3° (*c* 4.52, benzene) (lit.[13] [α]$^{27}_D$ −45.93° (*c* 6.1, benzene) for (*S*)-**6**).

Reaction of (*S*)-3-(Trimethylsilyl)cyclopentene (7) with MCPBA. To a mixture of 1.02 g (7.30 mmol) of (*S*)-**7** (22–25% ee) and 0.646 g (7.69 mmol) of sodim bicarbonate in 10 mL of dichloromethane was added at 0 °C a solution of 1.66 g (7.67 mmol) of 80% MCPBA in 25 mL of dichloromethane. The mixture was stirred at room temperature for 14 h, and the solvent was evaporated. Ether (40 mL) was added and the solution was washed with 20% sodium hydroxide (2 × 30 mL) and dried over anhydrous sodium sulfate. Removal of the solvent under reduced pressure gave 1.79 g (78% yield) of 1-hydroxy-2-(trimethylsilyl)-3-[(*m*-chlorobenzoyl)oxy]cyclopentane (**8**). An analytically pure sample was obtained by preparative TLC on silica gel (chloroform): [α]$^{20}_D$ −6.6° (*c* 1.1, CCl_4); ^1H NMR ($CDCl_3$) δ 0.07 (s, 9 H), 1.32 (t, J = 3 Hz, 1 H, d upon spin-decoupling at 4.08 or 5.15), 1.65–2.10 (broad m, 4 H), 4.08 (q, J = 3 Hz, 1 H, t upon spin-decoupling at 1.32), 5.15 (q, J = 3 Hz, 1 H, t upon spin-decoupling at 1.32), 7.10–7.47, 7.64–7.92 (m, 4 H). ^1H NMR in the presence of Eu(dcm)$_3$ showed that the enantiomeric purity of **8** was around 30%. Anal. Calcd for $C_{15}H_{21}O_3ClSi$: C, 57.56; H, 6.76. Found: C, 57.42; H, 6.79.

To a solution of 0.818 g (2.61 mmol) of **8** in 10 mL of methanol was added 0.7 mL of 30% aqueous potassium hydroxide, and the mixture was allowed to reflux for 6 h. Methanol was evaporated and 10 mL of water was added. The mixture was extracted with ether (4 × 10 mL), and the combined ether extracts were washed with 20% sodium hydroxide and dried over anhydrous sodium sulfate. Removal of the solvent under reduced pressure afforded 0.447 g (98% yield) of 1,3-dihydroxy-2-(trimethylsilyl)cyclopentane. An analytical sample was obtained as colorless needles, mp 83.0–83.5 °C, by recrystallization from hexane: ^1H NMR ($CDCl_3$) δ 0.04 (s, 9 H), 1.28 (broad s, 1 H), 1.75–1.90 (broad d, 4 H), 2.75 (broad s, 2 H), 4.17 (broad s, 2 H). Anal. Calcd for $C_8H_{18}O_2Si$: C, 55.12; H, 10.41. Found: C, 55,36; H, 10.67.

A mixture of 91 mg (0.52 mmol) of the diol, 0.11 mL (1.2 mmol) of acetic anhydride, 0.18 mL (4.3 mmol) of triethylamine, and 2 mg of 4-(*N*,*N*-dimethylamino)pyridine in 0.5 mL of THF was stirred at room temperature for 14 h. Ether was added and the solution was washed with water, dried over anhydrous magnesium sulfate, and evaporated under reduced pressure. The residue was passed through a short silica gel column to give 121 mg (90% yield) of 1,3-diacetoxy-2-(trimethylsilyl)cyclopentane (**9**): ^1H NMR ($CDCl_3$) δ 0.15 (s, 9 H), 1.53 (t, J = 3 Hz, 1 H, s upon spin-decoupling at 5.10), 1.80–1.98 (m, 4 H), 2.09 (s, 6 H), 5.10 (q, J = 3 Hz, 2 H, t upon spin-decoupling at 1.53).

A solution of 1 M tetrabutylammonium fluoride in THF (4 mL, 4.0 mmol) was added to 1.05 g (3.34 mmol) of **8**. After stirring at room temperature for 26 h, 20 mL of ether was added. The solution was washed successively with water and 20% sodium hydroxide, dried over anhydrous sodium sulfate, and evaporated. Distillation (~100 °C (17 mm), bath temperature) followed by preparative GLC (Silicone DC550) gave 0.11 g (36% yield) of (*S*)-2-cyclopentenol[17] (**10**): [α]$^{21}_D$ −13.2° (*c* 1.6, CCl_4). ^1H NMR in the presence of Eu(dcm)$_3$[11] showed that the enantiomeric purity of (*S*)-**10** was ~19%, the methine proton of the *S* isomer appearing at higher field than that of the *R* isomer.

Registry No. (*R*)-(*E*)-**1**, 82570-93-2; (*R*)-(*Z*)-**1**, 82570-94-3; (*S*)-(*E*)-**2**, 81176-43-4; (*R*)-(*Z*)-**2**, 92075-80-4; (*S*)-**3**, 22148-86-3; (*R*)-**3**, 39516-03-5; (*S*)-(*Z*)-**4**, 88133-09-9; (*S*)-(*E*)-**5**, 92075-81-5; (*S*)-**6**, 22135-49-5; (*S*)-**7**, 89576-21-6; (1*S*,2*R*,3*R*)-**8**, 91948-47-9; **9**, 91948-49-1; (*S*)-**10**, 6426-28-4; MCPBA, 937-14-4; (*E*)-1-phenyl-3-[(trimethylsilyl)oxy]-1-butene, 92075-82-6; (*Z*)-1-phenyl-3-[(trimethylsilyl)oxy]-1-butene, 92075-83-7; 1,3-dihydroxy-2-(trimethylsilyl)cyclopentane, 91948-48-0.

Synthesis of Biological Markers in Fossil Fuels. 2. Synthesis and ^{13}C NMR Studies of Substituted Indans and Tetralins

Maciej Adamczyk* and David S. Watt

Department of Chemistry, University of Wyoming, Laramie, Wyoming 82071

Daniel A. Netzel*

Wyoming Research Institute, University Station, Laramie, Wyoming 82071

Received February 3, 1984

Unambiguous syntheses of all possible methyl, ethyl, *n*-propyl, and *n*-butyl derivatives of indan and tetralin were developed using the Kumada coupling procedure involving the reaction of aryl or vinyl halides with Grignard reagents in the presence of [1,3-bis(diphenylphosphino)propyl]nickel(II) chloride. An analysis of the ^{13}C NMR spectra of these compounds was also completed.

Partially aromatized steranes[1] such as 5,17-dimethyl-18,19-dinorcholesta-8,11,13-triene[2] (**1**) represent an unusual but interesting family of biomarkers.[3] These "molecular fossils" are potentially useful probes for addressing prob-

0022-3263/84/1949-4226$01.50/0 © 1984 American Chemical Society