of the complex and facilitate O-alkylation and polymerization.

In conclusion, it would appear that for α-formyl esters under the conditions employed, this procedure only represents a synthetically useful method for the relatively selective C-alkylation of less extensively enolized α-formyl esters such as **2** and **5** with small, reactive, alkylating agents. With bulkier and less reactive electrophiles and/or more extensively enolized α-formyl esters, we have been unable to achieve a selective C-alkylation. However, for these more labile substrates, this procedure may be more useful than indirect procedures when the intact dicarbonyl is desired.

Experimental Section

All melting points, determined with a Thomas-Hoover apparatus, and boiling points are uncorrected. ^{1}H NMR spectra were recorded on a Varian Associates T-60 spectrometer in $CDCl_3$ with Me_4Si as an internal standard. IR spectra were determined with a Perkin-Elmer 237B grating infrared spectrometer as liquid films. UV spectra were recorded in MeOH on a Cary 118 recording spectrophotometer. TLC was performed on silica gel 60 F_{254} from EM Reagents. All solvents were appropriately dried prior to use.

General Procedure. To a magnetically stirred solution of the α-formyl ester (10 mmol) in 50 mL of dry hexane, in a one-necked round-bottom flask equipped with a reflux condenser and $CaSO_4$ drying tube, was added TlOEt (0.65 mL, 9 mmol) all at one. The salt which immediately precipitated was stirred for 15 min and the hexane decanted. The alkyl halide (160 mmol or 40 mmol plus 50 mL of solvent) was added to the residue and the suspension stirred at reflux on a water bath during which time (when an alkyl iodide was employed) it proceeded through gradual color changes from yellow to dark orange and then rapidly to bright yellow as Tl(I)[16] plated out. The Tl(I) halide was removed by suction filtration with ether rinsing. The ethereal filtrate was dried through $MgSO_4$, concentrated to a crude oil, and distilled under reduced pressure to afford the product mixture as a clear oil. **Caution**: Tl(I) salts are known to be extremely toxic. All procedures were conducted in the fume cupboard and the collected Tl(I) halide was immediately oxidized with concentrated HNO_3.

Characterization of Diethyl α-Formyl-α-methylsuccinate (1) and Diethyl α-(Methoxymethylene)succinate (3). In order to characterize the aldehyde and enol ether products of these alkylations, the clear oil resulting from the alkylation of **2** with MeI was eluted on a silica gel column with $CHCl_3$–MeOH (9:1). The earlier fractions which showed R_f 0.58 on TLC ($CHCl_3$–MeOH 95:5) were combined and evaporated to give **1**: NMR δ 1.07–1.38 (m, 6, CH_2CH_3), 1.37 (s, 3, CCH_3), 2.87 (s, 2, CH_2C), 3.87–4.43 (m, 4, CH_2CH_3), 9.13 (s, 1, CHO); IR 2980, 1715, 1630 cm^{-1}; UV λ_{max} 237 nm (ε 6000). The orange 2,4-DNP derivative was prepared according to standard procedures, mp 103–104 °C (EtOH).

The enol ether **3** was obtained in approximately 97% purity as the distilled product mixture after methylation of **2** in hexane; bp 81–105 °C (0.1 mm) [lit.[2] bp 103–104 °C (1 mm)]. TLC ($CHCl_3$–MeOH 95:5) showed the major product **3** at R_f 0.48 and a minor amount of material with R_f 0.58 corresponding to **1**: NMR δ 1.13–1.38 (m, 6, CH_2CH_3), 3.23 (s, 2, CH_2C), 3.85 (s, 3, OCH_3), 3.97–4.37 (m, 4, CH_2CH_3), 7.40 (s, 1, vinyl); IR 2960, 1783, 1715, 1640 cm^{-1}; UV λ_{max} 238 nm (ε 6320).

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Registry No. 1, 73587-50-5; 1 2,4-DNP derivative, 73587-51-6; **2**, 5472-38-8; **2** Tl(I) salt, 73587-43-6; **3**, 73587-52-7; **5** Tl(I) salt, 73587-44-7; **6** Tl(I) salt, 73597-06-5; diethyl α-ethyl-α-formylsuccinate, 73587-53-8; diethyl α-(ethoxymethylene)succinate, 70145-31-2; diethyl α-formyl-α-isopropylsuccinate, 73587-54-9; diethyl α-(isopropoxymethylene)succinate, 73587-55-0; ethyl α-formyl-α-methylcaproate, 73587-56-1; ethyl α-(methoxymethylene)-caproate, 73587-57-2; ethyl α-ethyl-α-formylcaproate, 73587-58-3; ethyl α-(ethoxymethylene)caproate, 73587-59-4; ethyl α-formyl-α-isopropylcaproate, 73587-60-7; ethyl α-(isopropoxymethylene)-caproate, 73587-61-8; ethyl α-(methoxymethylene)phenylacetate, 15937-30-1; ethyl α-(ethoxymethylene)phenylacetate, 15937-27-6.

(16) When employing alkyl bromides as the alkylating agent, the precipitation of the light yellow TlBr is more difficult to visualize. However, the end point of the reaction can be determined to be when the suspension separates into a light yellow (TlBr) precipitate and a light orange supernatant.

Preparation of Allylic Alcohols from Epoxides Using Iodotrimethylsilane

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The transformation of epoxides into allylic alcohols by use of iodotrimethylsilane and 1,5-diazabicyclo-[5.4.0]undec-5-ene is described. The scope and limitations of this reaction are examined. This method is complementary to the method of Sharpless in the case of trisubstituted epoxides and proceeds under milder reaction conditions than the method employing lithium dialkylamides.

Synthetic studies required the regioselective conversion of an epoxide into an allylic alcohol. Although this transformation might be accomplished by the use of lithium dialkylamides,[1] the basic reaction conditions that must be employed can promote undesired side reactions. A recent improvement on this reaction by Yamamoto[2] involves the use of dialkylaluminum amides. Sodium phenyl selenide has been used for the opening of epoxides under mildly basic reaction conditions.[3] Subsequent oxidative elimination affords allylic alcohols. With trisubstituted epoxides this method is regioselective and produces the more hindered allylic alcohol. While this work was in progress, Noyori and co-workers[4] reported the use of trimethylsilyl trifluoromethanesulfonate and 1,5-diazabicyclo[5.4.0]undec-5-ene (DBN) to effect the epoxide to allylic alcohol transformation. Although this reaction proceeds

(1) Crandall, J. K.; Crawley, L. C. *Org. Synth.* **1974**, *53*, 17.
(2) Yasuda, A.; Tanaka, S.; Oshima, K.; Yamamoto, H.; Nozaki, H. *J. Am. Chem. Soc.* **1974**, *96*, 6513.
(3) Sharpless, K. B.; Lauer, R. F. *J. Am. Chem. Soc.* **1973**, *95*, 2697.
(4) Murata, S.; Suzuki, M.; Noyori, R. *J. Am. Chem. Soc.* **1979**, *101*, 2738.

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under mild conditions, the silyl sulfonate is highly sensitive to moisture and is not commercially available. In this paper, we report a study of the conversion of epoxides into allylic alcohols with iodotrimethylsilane and DBN. While isolated examples of the reaction of epoxides with halosilanes have been communicated, the products of these reactions are reported to be either halohydrins or halosilyl ethers.[5] The related cleavage of five- and six-membered-ring cyclic ethers has been studied by Olah,[6] Jung,[7] and Voronkov.[8]

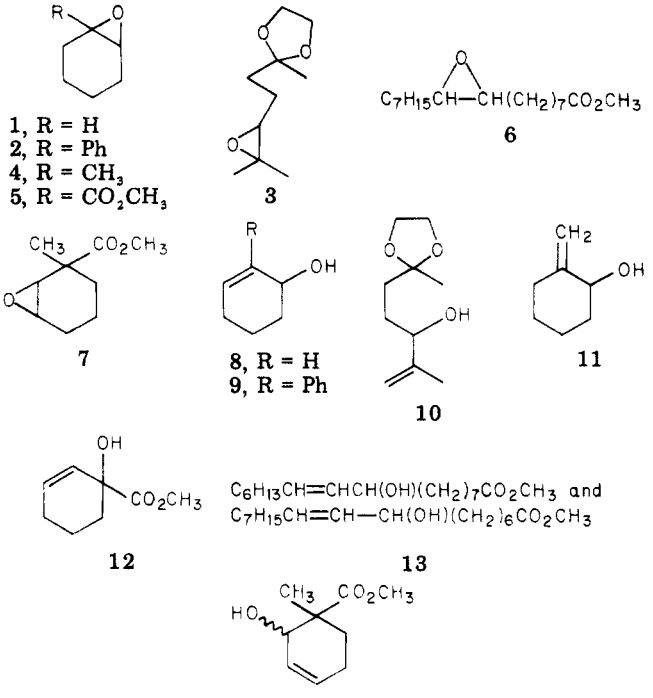
Results and Discussion

Reaction parameters to be defined included the base, solvent, reaction temperature, and order of addition of reagents. DBN proved to be a more effective dehydrohalogenation agent than triethylamine or diisopropylethylamine. The initial epoxide opening proceeded rapidly at ambient temperature, as evidenced by TLC. However, the dehydrohalogenation step was not complete until the reaction temperature was raised to reflux. In agreement with the results of previous workers, the epoxide opening could be conducted in a variety of aprotic solvents. The dehydrohalogenation, however, afforded best yields in acetonitrile. The results of changing the order of addition of reagents indicated that, except in the case of **2**, method A was the superior procedure. In that case the yield of allylic alcohol was lowered by the competing side reaction which produced a 30% yield of 2-phenylcyclohexanone. Presumably, this side reaction involved a hydride shift. The improved yield of allylic alcohol with method B may only reflect the minimization of this side reaction. Less than 5% of the crude reaction product was 2-phenylcyclohexanone.

Several representative epoxides were prepared[9] and examined to determine the scope and limitations of the reaction. The results are shown in Table I. With the exception of **5**, all trisubstituted epoxides afforded secondary alcohols in good yield. The alcohols **9** and **14** were oxidized to α,β-unsaturated ketones and compared with authentic samples. Compounds **8**,[10] **11**,[11] and **12**[12] had previously been synthesized by independent routes. The spectral properties reported were identical with ours. Hydroxy ketal **10** exhibited IR, ^{1}H NMR, ^{13}C NMR, and mass spectral data completely in accord with the assigned structure.

As demonstrated in Table I, the reaction conditions are compatible with the presence of esters and cyclic ketals. Since Jung has shown that these groups react with iodotrimethylsilane, the selectivity is notable. The mild conditions and operational simplicity of this method offer distinct advantages over the use of dialkylamide bases. Our method is complementary to the organoselenium method of Sharpless in that trisubstituted epoxides afford secondary allylic alcohols. Although the Noyori procedure affords slightly higher yields, the ready availability of iodotrimethylsilane clearly makes this method a competitive alternative.

Table I. Conversion of Epoxides into Allylic Alcohols



epoxide	% yield of product[a]	allylic alcohol
1	79	8
2	68	9
3	50	10
4	69	11
5	21	12
6	75	13
7	70	14

[a] Yields of chromatographed products.

Experimental Section

General. Diethyl ether and THF were distilled from lithium aluminum hydride. All organic extracts were dried over Na_2SO_4. Melting points were determined on a Fisher-Johns melting-point apparatus and are uncorrected. Infrared spectra were determined on a Beckman IR-4250 spectrometer. Nuclear magnetic resonance spectra were determined on a Varian A60 instrument in $CDCl_3$ with absorptions recorded in parts per million downfield from internal Me_4Si. High-resolution mass spectra were recorded on an AEI MS-902 high-resolution mass spectrometer. ^{13}C NMR spectra were determined on a JEOLCO FX-90Q spectrometer. Iodotrimethylsilane was purchased from Aldrich.

General Procedures for the Conversion of Epoxides into Allylic Alcohols. Method A. To a stirred solution of the epoxide (2.5 mmol) in acetonitrile (5 mL) at 0 °C was added DBN (5 mmol), followed by dropwise addition of iodotrimethylsilane (2.75 mmol). After 15 min, the dark solution was heated to reflux for 12–48 h. The cooled solution was then concentrated in vacuo, diluted with brine, and extracted three times with ether. At this stage, the silyl ether was hydrolyzed by shaking the organic layer with aqueous acid in a separatory funnel. The organic layer was dried and concentrated, and the residue was chromatographed on silica gel to afford pure allylic alcohol.

Method B. To a stirred solution of the epoxide (2.5 mmol) in benzene (5 mL) at 10 °C was added dropwise iodotrimethyl-

(5) Lavigne, A. A.; Tancrede, J.; Pike, R. M.; Tabit, C. T. *J. Organomet. Chem.* **1968**, *15*, 57. Malinovsky, M. S.; Romantsevich, M. K. *Z. Obshch. Khim.* **1957**, *27*, 1873. Patnode, W. I.; Saner, R. D. U.S. Patent 2 381 137.

(6) Olah, G. A.; Narang, S. C.; Gupta, B. G. B.; Malhotra, R. *J. Org. Chem.* **1979**, *44*, 1247.

(7) Jung, M. E.; Lyster, M. A. *J. Org. Chem.* **1977**, *42*, 3761.

(8) Voronkov, M. G.; Dubinskaya, E. I.; Pavlov, S. F.; Gorokova, V. G. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1976**, 2355.

(9) Epoxide **1** is available from Aldrich. **2**: Levy, J.; Sfiras, J. *Bull. Soc. Chim. Fr.* **1931**, *49*, 1830. **3**: Anderson, W. K.; Veysoglu, T. *J. Org. Chem.* **1973**, *38*, 2267. **4**: Bartlett, P. D.; Rosenwald, R. H. *J. Am. Chem. Soc.* **1934**, *56*, 1990. **5**: Hollands, R.; Becher, D.; Gaudemer, A.; Polonsky, J. *Tetrahedron* **1968**, *24*, 1633. **6**: Witnauer, L. P.; Swern, D. *J. Am. Chem. Soc.* **1950**, *72*, 3364. **7**: Epoxidation carried out as for **2**. The olefinic acid has been prepared by Julia, M.; Salard, J. M.; Chottard, J. C. *Bull. Soc. Chim. Fr.* **1973**, 2478. The product was approximately a 50/50 mixture of stereoisomeric epoxides.

(10) Alcohol **8** is sold by Aldrich. References to spectra are in their catalogue.

(11) Crandall, J. K.; Lin, L.-H., C. *J. Org. Chem.* **1968**, *33*, 2375.

(12) Hollands, R.; Becher, D.; Gaudemer, A.; Polonsky, J. *Tetrahedron* **1968**, *24*, 1633.

silane (2.75 mmol). After 30 min the solution was concentrated in vacuo and acetonitrile (5 mL) and DBN (5 mmol) were then added. The solution was heated to reflux for 12–48 h. The cooled reaction was then worked up as in method A.

2-Cyclohexen-1-ol (8): NMR 5.75–5.50 (m, 2 H), 4.30–3.95 (m, 2 H), 2.18–1.40 (m, 6 H); IR 3400, 1070 cm^{-1}.

2-Phenyl-2-cyclohexen-1-ol (9): NMR 7.60–6.90 (m, 5 H), 6.15–5.90 (m, 1 H), 4.63 (br s, 1 H), 3.50–3.28 (m, 1 H), 2.60–1.40 (m, 6 H); IR 3450, 1060 cm^{-1}.

Ethylene Ketal of 5-Hydroxy-6-methyl-6-hexen-2-one (10): ^1H NMR 4.93 (m, 1 H), 4.8 (m, 1 H), 4.1 (br s, 1 H), 3.92 (s, 4 H), 2.85 (m, 1 H), 1.5–1.9 (m, 7 H), 1.32 (s, 3 H); IR 3460, 1655, 1070 cm^{-1}; ^{13}C NMR 147.324, 110.539, 109.781, 75.218, 64.383, 34.751, 29.115, 23.590, 17.468.

2-Methylenecyclohexanol (11): NMR 4.85 (br s, 1 H), 4.74 (br s, 1 H), 3.97 (m, 2 H), 2.4–1.2 (m, 8 H); IR 3400, 1640, 905 cm^{-1}.

Methyl 1-Hydroxy-2-cyclohexenoate (12): NMR 6.15–5.50 (m, 2 H), 3.79 (s, 3 H), 3.30 (br s, 1 H), 2.25–1.50 (m, 6 H); IR 3480, 1730, 1640, 1240 sm^{-1}; ^{13}C NMR 176.741, 132.372, 126.792, 71.588, 52.735, 33.884, 24.511, 18.281.

Mixture of Methyl 9-Hydroxy-10-heptadecenoate and Methyl 8-Hydroxy-9-heptadecenoate (13): NMR 5.63–5.4 (m, 2 H), 4.10–3.90 (m, 2 H), 3.65 (s, 3 H), 2.50–0.70 (m, 27 H); IR 3400, 1735, 1165 cm^{-1}.

Methyl 2-Hydroxy-1-Methyl-3-cyclohexenoate (14): NMR (one diastereomer) 5.76 (br s, 1 H), 5.65 (br s, 1 H), 4.85 (br s, 1 H), 4.55 (m, 1 H), 3.73 (s, 3 H), 2.25–1.40 (m, 4 H), 1.20 (s, 3 H); (other diastereomer) 5.76 (br s, 1 H), 5.65 (br s, 1 H), 4.85 (m, 1 H), 4.05 (m, 1 H), 3.73 (s, 3 H), 2.25–1.40 (m, 4 H), 1.26 (s, 3 H); IR 3430, 1735, 1115 cm^{-1}.

Oxidation of 9. Alcohol **9** was oxidized by the method of Jones to afford 2-phenylcyclohexenone in 88% yield, mp 91–93 °C (lit.[13] mp 95 °C).

Oxidation of 14. Alcohol **14** was oxidized by the method of Corey[14] to afford methyl 1-methyl-2-oxo-3-cyclohexenoate in 78% yield: NMR 7.08–6.73 (m, 1 H), 6.11–5.85 (m, 1 H, 3.70 (s, 3 H), 2.70–1.60 (m, 4 H), 1.39 (s, 3 H); IR 1735, 1685, 1260, 1115 cm^{-1}; ^{13}C NMR 196.568, 173.003, 149.274, 120.796, 53.331, 52.248, 33.288, 23.536, 20.231.

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Registry No. 1, 286-20-4; 2, 4829-01-0; 3, 39810-29-2; 4, 1713-33-3; 5, 17550-59-3; 6, 73611-70-8; 7, 73611-71-9; 8, 822-67-3; 9, 32363-86-3; 10, 24108-30-3; 11, 4065-80-9; 12, 58547-47-0; 14, isomer 1, 73611-72-0; 14, isomer 2, 73611-73-1; methyl 9-hydroxy-10-heptadecenoate, 73611-74-2; methyl 8-hydroxy-9-heptadecenoate, 73611-75-3; 2-phenylcyclohexenone, 4556-09-6; methyl 1-methyl-2-oxo-3-cyclohexenoate, 73611-76-4.

(13) Bachmann, W. E.; Wick, L. B. *J. Am. Chem. Soc.* **1950**, *72*, 3388.
(14) Corey, E. J.; Suggs, J. W. *Tetrahedron Lett.* **1975**, 2647.

Stereochemical Course of the Haworth-Type Synthesis of Optically Active 2-(1-Methylpropyl)naphthalene[1]

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The preparation of (*S*)-2-(1-methylpropyl)naphthalene has been accomplished by starting from (*S*)-(1-methylpropyl)benzene with detectable racemization. The partially unstereospecific steps have been distinguished by evaluating the optical purity of key intermediates through chemical correlations with known optically active compounds.

As an extension of our studies on the synthetic and stereochemical aspects connected with obtaining optically active aromatic hydrocarbons,[1,2] we were interested in evaluating the limits and the applicability of the Haworth-type synthesis[3] in the preparation of optically active polysubstituted naphthalene derivatives as well as of more complex chiral polynuclear substrates.

To test the stereochemical course of this type of sequence we chose to synthesize (*S*)-2-(1-methylpropyl)-naphthalene (**1**) by starting from (*S*)-(1-methylpropyl)-benzene (**2**), since the maximum rotatory powers of **1** and **2** were known.[2c,h]

Our preliminary results[3e] showed that in the sequence **2** → **1** (Scheme I) a rather high degree of racemization had occurred. In the present work we report the results of our investigation where special effort was made to follow the relationship between the optical purity of the starting material and of the final product.

Results and Discussion

Since it is known that optically active **2** racemizes even at 0 °C in the presence of aluminum chloride,[4] the conversion of samples of optically active **2** into the methyl 3-[4-(1-methylpropyl)benzoyl]propionate (**3**) was accomplished in 75–82% yields by following the Perrier modi-

(1) Optically Active α- and β-Naphthalene Derivatives. 5. For part 4, see O. Piccolo, R. Menicagli, and L. Lardicci, *Tetrahedron*, **35**, 1751 (1979).
(2) (a) L. Lardicci, R. Menicagli, and P. Salvadori, *Gazz. Chim. Ital.*, **98**, 738 (1968); (b) L. Lardicci and R. Menicagli, *Chim. Ind. (Milan)*, **51**, 1387 (1969); (c) L. Lardicci and R. Menicagli, *Atti Soc. Toscana Sci. Nat. Pisa, Mem. P. V., Ser. A*, **77**, 25 (1970); (d) R. Menicagli and L. Lardicci, *Chem. Ind. (London)*, 1490 (1971); (e) L. Lardicci, P. Salvadori, A. M. Caporusso, R. Menicagli, and E. Belgodere, *Gazz. Chim. Ital.*, **102**, 64 (1974); (f) L. Lardicci and R. Menicagli, *J. Org. Chem.*, **37**, 1060 (1972); (g) R. Menicagli, L. Lardicci, and C. Botteghi, *Chem. Ind. (London)*, 920 (1974); (h) R. Menicagli, O. Piccolo, L. Lardicci, and M. L. Wis, *Tetrahedron*, **35**, 1301 (1979).
(3) (a) E. deBerry Barnett and F. G. Sanders, *J. Chem. Soc.*, 434 (1933); (b) E. Berliner, *Org. React.*, **5**, 229 (1949); (c) E. J. Eisenbraun, C. W. Hinman, J. M. Springer, J. W. Burnham, T. S. Cho, P. W. Flanagan, and M. C. Hamming, *J. Org. Chem.*, **36**, 2480 (1971); (d) I. Agranat and Y. S. Shih, *Synthesis*, 865 (1974); (e) R. Menicagli, O. Piccolo, and L. Lardicci, *Chim. Ind. (Milan)*, **57**, 499 (1975).
(4) E. L. Eliel, P. M. Wilken, and F. T. Fang, *J. Org. Chem.*, **22**, 231 (1957).

0022-3263/80/1945-2581$01.00/0