sublimed at room temperature into the hot zone, concurrent with Cs, which was held at a temperature of ca. 100–110 °C. Argon flow was controlled by a needle valve (0.2 mmol/min). The mixture deposited onto a CsI window held at 28 K. The matrices were a transparent, deep-sea blue.

Reaction of Compound 3 with Cs in the Gas Phase: Observation of 1 by FTIR in an Argon Matrix. This reaction was carried out in essentially the same manner as with 4, the main difference being that the dibromo compound 3 was mixed with the argon in a 500:1 ratio prior to deposition.

Computations. Ab initio SCF calculations were carried out on IBM RS-6000/540 and 6000/550 computers using the GAUSSIAN 88 and GAUSSIAN 90 program.[5,18,19] Calculation of the IR frequencies were done at the restricted Hatree–Fock level on optimized geometries, using a 6-31G* basis set. The standard 0.9 multiplicative correction factor was used.

Acknowledgment. This work was supported by the National Science Foundation (DMR 8807701). The FTIR spectrometer was purchased with support from NSF grant CHE 9121643 and the computer with support from NSF grant CHE 9022151. We are grateful to Dr. V. Balaji for assistance with the calculations.

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Trimethylsilyl Trifluoromethanesulfonate Mediated Dialkylcuprate Addition to Epoxy Esters: An Unusual Intramolecular Transesterification Process

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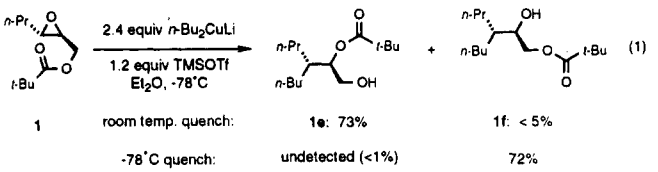
Epoxides are important starting materials and intermediates in organic synthesis because of their ready access and their high reactivity toward nucleophiles. The emergence of the Sharpless epoxidation procedure has increased the importance of these electrophiles by providing a route to 2,3-epoxy alcohols of high enantiomeric purity.[3] Development of synthetic methods allowing regioselective ring opening of 2,3-epoxy alcohols by a wide range of nucleophiles further enhances the utility of epoxides in organic synthesis.[4] While investigating the regiochemistry of Lewis acid promoted organocuprate addition to trimethylacetate-protected 2,3-epoxy alcohols,[5] we encountered an intriguing reaction providing products in which an unusual migration of the ester moiety[6] had occurred following the regiospecific addition of the cuprate to C-3 of 2,3-epoxy alcohol pivaloylates. Further investigation of this unexpected result has shown that this reaction is synthetically useful and provides a convenient protocol for the direct, regioselective preparation of an important class of monoprotected 1,2-diols that are only difficulty accessed by more traditional means.

At the outset of our investigations *trans*-3-propyloxiranemethanol trimethylacetate (1) was added to a solution of Bu_2CuLi/TMSOTf (2.4:1.2 equiv relative to 1) in Et_2O at −78 °C. After stirring for 30 min at −78 °C and then at room temperature for 30 min, the reaction was quenched with aqueous NH_4Cl/NH_4OH (10:1). Utilizing this protocol 1e was isolated as the major product, with the ester moiety residing on the secondary carbon. The transesterification was shown to be under thermodynamic control as the "unrearranged" addition product (1f) predominated when the reaction was quenched at −78 °C (eq 1).



(1)

The selectivity for acylation of the secondary alcohol in preference to the primary alcohol is reminiscent of the dibutyltin-promoted monoacylation of 1,2-diols reported previously by Roelens and co-workers.[7] However, given the uncertainty of the role that the trialkylsilyl triflates play in the present reaction,[8] a mechanistic rationale for the observations reported is difficult. It would seem reasonable that the usual intramolecular acyl migration through a dioxolanyl intermediate is operational in these transformations.[6,9] Thus, the primary alkoxide generated in this equilibrium process could be preferentially trapped by an electrophile (R_3SiOTf), shutting down the intramolecular acyl migration and leaving the carboxylate at the secondary alcohol center. However, all efforts to trap silyl ether products have failed, even in those instances where t-$BuMe_2SiOTf$ was utilized as the electrophile under conditions where these protected alcohols were stable.[10] Consequently, no evidence exists to document such a proposed mechanism.

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(10) For example, the reaction of 1 with Me_2CuLi/t-$BuMe_2SiOTf$ provides 57% of 1a and <5% of 1b. Furthermore, we have found that the *tert*-butyldimethylsilyl-protected alcohol of 1a is stable to the reaction and workup conditions for this reaction. Thus, a sample of this protected alcohol was recovered to the extent of 86% when it was present during the reaction between substrate 1 and Me_2CuLi/t-$BuMe_2SiOTf$. Products 1a and 1b were isolated in similar yields regardless of the presence (or absence) of the *tert*-butyldimethylsilyl-protected form of 1a.

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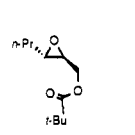
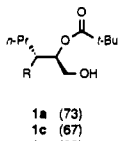
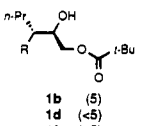
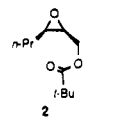
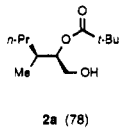
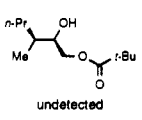
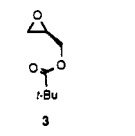
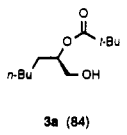
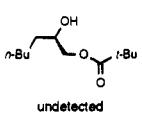
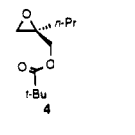
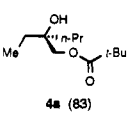
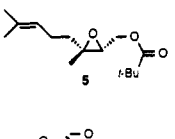
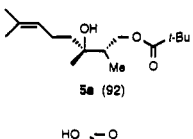
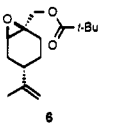
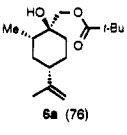
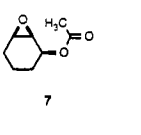
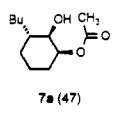
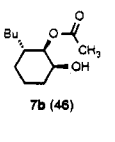
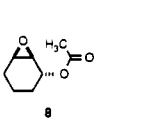
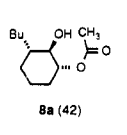
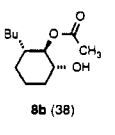
Lewis acid additives Et_3SiOTf or t-$BuMe_2SiOTf$ provide lower yields than Me_3SiOTf and similar regioselectivities to the latter in examples tested (substrate 1 reacting with Ph_2CuLi or Me_2CuLi), and pivaloyl esters appear to provide optimal results in terms of overall yields and product selectivities. Thus the pivaloyl ester provides higher regioselectivity for the secondary carboxylate than acetate, benzoate, and other (even hindered) aryl carboxylate esters. Finally, one other class of cuprate reagent ($Ph_2CuCNLi$) has been utilized in conjunction with substrate 1 and TMSOTf, and this reagent provides no difference in terms of diastereoselectivity or yield of the final product as compared to that achieved using Ph_2CuLi.

The synthetic utility of the cuprate substitution/acyl migration protocol was investigated by using a variety of dialkylcuprates in conjunction with epoxy pivaloylates possessing different substitution patterns about the epoxide. The results of these experiments are outlined in Table I. The ester migration product was readily formed from 1 and 2 with a variety of dialkylcuprates, although diphenylcuprate provided a mixture of isomers.[11] While it is apparent that acyl migration from a primary alcohol to a secondary alcohol is virtually complete (substrates 1–3), primary to tertiary alcohol acyl migration is not observed (substrates 4 and 6). One point of note is that the nerol epoxide trimethylacetate (5) reacts at the C-2 position with lithium dimethylcuprate. Apparently, nucleophilic attack at the quaternary carbon is sterically prohibited. Finally, as might be expected, secondary alcohol to secondary alcohol acyl migration provides virtually a 1:1 mixture of isomers (substrates 7 and 8).

In summary, the procedure reported herein provides an efficient route to specific classes of selectively protected diols which are cumbersome to access by more conventional means. The ability to utilize Sharpless asymmetric epoxidation technology as an entry to the requisite substrates further enhances the utility of this method, and makes it an attractive route to enantiomerically enriched 1,2-diol derivatives.

Table I. Reaction of Epoxy Esters with R_2CuLi/TMSOTf

substrate	R_2CuLi	products (% isolated yield)	
 1	R = CH_3 R = s-Bu R = n-Bu R = Ph	 1a (73) 1c (67) 1e (62) 1g (48)	 1b (5) 1d (<5) 1f (<5) 1h (44)
 2	R = CH_3	 2a (78)	 undetected
 3	R = n-Bu	 3a (84)	 undetected
 4	R = CH_3	 4a (83)	
 5	R = CH_3	 5a (92)	
 6	R = CH_3	 6a (76)	
 7	R = Bu	 7a (47)	 7b (46)
 8	R = Bu	 8a (42)	 8b (38)

Experimental Section

Reagents. Diethyl ether was distilled immediately prior to use from benzophenone ketyl under Ar. Copper bromide–methyl sulfide complex was purchased from Aldrich Chemical Co. and handled under an inert atmosphere. Standard benchtop techniques were employed for handling air-sensitive reagents, and all reactions were performed under an Ar atmosphere. The epoxy esters used as starting materials in this study were synthesized from the corresponding alcohols using trimethylacetyl chloride and pyridine in dichloromethane, unless otherwise specified. All of the necessary epoxy alcohols were either commercially available or were prepared by epoxidation of the appropriate allylic alcohol.[3,12]

***trans*-3-Propyloxiranemethanol Trimethylacetate (1).** ^1H NMR (300 MHz, $CDCl_3$): δ 0.86 (t, J = 7.5 Hz, 3 H), 1.19 (s, 9 H), 1.35–1.47 (m, 4 H), 2.75 (m, 1 H), 2.86 (m, 1 H), 3.84 (dd, J = 12.2, 6.2 Hz, 1 H), 4.23 (dd, J = 12.2, 3.4 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.71 (CH_3), 19.10 (CH_2), 27.05 (CH_3), 33.46 (CH_2), 38.71 (q), 55.30 (CH), 55.24 (CH), 64.53 (CH_2), 178.27 (q). IR (neat): 2963, 2936, 2875, 1732, 1481, 1462, 1398, 1366, 1283, 1155 cm^{-1}. LRMS (EI): m/e 200 (m^+, 0), 145 (75), 103 (67), 85 (57), 73 (18), 57 (100).

***cis*-3-Propyloxiranemethanol Trimethylacetate (2).** ^1H NMR (300 MHz, $CDCl_3$): δ 0.96 (t, J = 6.9 Hz, 3 H), 1.20 (s, 9 H), 1.47–1.52 (m, 4 H), 2.97–3.02 (m, 1 H), 3.15 (dt, J = 6.9, 4.5 Hz, 1 H), 4.02 (dd, J = 12.0, 6.9 Hz, 1 H), 4.27 (dd, J = 12.3, 4.5 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.84 (CH_3), 19.83 (CH_2), 26.47 (CH_2), 27.13 (CH_3), 29.90 (CH_2), 38.77 (q), 53.72 (CH), 56.22 (CH), 62.75 (CH_2), 178.48 (q).

Oxiranemethanol Trimethylacetate (3). ^1H NMR (300 MHz, $CDCl_3$): δ 1.16 (s, 9 H), 2.58 (dd, J = 4.8, 2.7 Hz, 1 H), 2.77 (dd, J = 4.5, 4.5 Hz, 1 H), 3.12 (m, 1 H), 3.86 (dd, J = 12.5, 6.3 Hz, 1 H), 4.34 (dd, J = 12.3, 3.0 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 27.00 (CH_3), 36.68 (q), 44.32 (CH_2), 49.31 (CH), 64.52 (CH_2), 178.17 (q).

2-Propyloxiranemethanol Trimethylacetate (4). The necessary allylic alcohol (2-methylene-1-pentanol) was prepared by a published procedure[13] and the epoxide prepared by standard procedure.[12] ^1H NMR (300 MHz, $CDCl_3$): δ 0.88 (t, J = 7.2 Hz, 3 H), 1.16 (s, 9 H), 1.34–1.37 (m, 2 H), 1.49–1.54 (m, 2 H), 3.47 (d, J = 11.1 Hz, 1 H), 3.51 (d, J = 11.4 Hz, 1 H), 4.01 (d, J = 11.7

(11) The stereochemistry of this transesterification process was established by $LiAlH_4$ reduction of the ester moiety of 1a. The ^1H NMR data of the resulting diol was consistent with published data for (2R*,3R*)-3-methyl-1,2-hexanediol. [Previously unreported spectral data: ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.24 (CH_3), 15.07 (CH_3), 19.99 (CH_2), 34.61 (CH_2), 35.85 (CH), 64.58 (CH_2), 76.29 (CH).] Additional evidence was obtained by comparison of the ^1H NMR of the known primary tosylate with the tosylate made from the diol described above. [Previously unreported spectral data for (2R*,3R*)-3-methyl-1-(tosyloxy)-2-hexanol: ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.11 (CH_3), 15.02 (CH_3), 19.88 (CH_2), 21.57 (CH_3), 34.08 (CH_2), 35.45 (CH), 72.65 (CH_2), 73.36 (CH), 127.94 (CH), 129.95 (CH), 132.71 (q), 145.04 (q).] Nakagawa, N.; Mori, K. *Agric. Biol. Chem.* **1984**, *48*, 2505.

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Hz, 1 H), 4.05 (d, J = 11.1 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.32 (CH_3), 15.86 (CH_2), 29.96 (CH_3), 37.18 (CH_2), 38.73 (q), 48.74 (CH_2), 66.34 (CH_2), 73.16 (CH_2), 178.27 (q).

***cis*-3-Methyl-3-(4-methyl-3-pentenyl)oxiranemethanol Trimethylacetate (2,3-Epoxynerol Trimethylacetate, 5).** ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.17 (s, 9 H), 1.29 (s, 3 H), 1.38–1.49 (m, 1 H), 1.56 (s, 3 H), 1.64 (s, 3 H), 2.07 (m, 1 H), 2.92 (dd, J = 6.8, 4.2 Hz, 1 H), 3.96 (dd, J = 12.3, 7.2 Hz, 1 H), 4.27 (dd, J = 12.2, 4.2 Hz, 1 H), 5.04 (t, J = 7.5 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 17.51, 21.85, 24.00, 25.55, 27.06, 33.15, 38.67, 60.53, 60.96, 63.11, 123.12, 132.39, 178.41.

(1*R*,2*R*,4*S*)-1,2-Epoxy-1-(hydroxymethyl)-4-(2-propenyl)cyclohexane Trimethylacetate (6). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.18 (s, 9 H), 1.52–1.60 (m, 2 H), 1.64–1.70 (m, 1 H), 1.66 (s, 3 H), 1.81–1.92 (m, 2 H), 2.05–2.16 (m, 2 H), 3.18 (s, 1 H), 3.87 (d, J = 11.7 Hz, 1 H), 4.18 (d, J = 11.7 Hz, 1 H), 4.64 (s, 1 H), 4.70 (s, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.95 (CH_3), 24.39 (CH_2), 25.46 (CH_2), 27.08 (CH_3), 30.09 (CH_2), 36.36 (CH), 38.82 (q), 57.45 (q), 57.61 (CH), 67.61 (CH_2), 109.33 (CH_2), 148.53 (q), 178.19 (q). $[\alpha]^{27}_{589}$ = −30.7°, c = 0.5 ($CHCl_3$).

General Procedure for the Dialkylcuprate/TMSOTf-Mediated Ring Opening of Epoxy Esters. To an Ar-purged, oven-dried 25-mL round-bottom flask containing a magnetic stir bar and spectum inlet was placed 0.50 g of $CuBr{\cdot}SMe_2$ (2.4 mmol) and 10 mL of Et_2O. This stirred solution was cooled to −78 °C with an external dry ice/2-propanol bath, and the temperature was allowed to stabilize during a 15-min period. To this stirred solution was added 3.0 mL of a 1.6 M solution of *n*-BuLi (4.8 mmol). This solution was stirred for 15 min, and 0.23 mL of TMSOTf (1.2 mmol) was added via syringe. After the mixture was stirred for 5 min, 0.20 g of epoxy ester 1 (1.0 mmol) was added via syringe, and the stirred reaction mixture was maintained at −78 °C for 30 min. The cooling bath was removed to allow the reaction mixture to reach room temperature, and 10 mL of an aqueous NH_4OH/NH_4Cl (1:10) solution was added slowly. The biphasic mixture was transferred to a separatory funnel with the aid of 50 mL of Et_2O, and the organic layer was washed twice with 10 mL of aqueous NH_4OH/NH_4Cl and brine (10 mL) and then dried over $MgSO_4$. The organic layer was filtered, and the volatiles were removed in vacuo. The resulting yellow oil was purified by flash chromatography to yield 188 mg (73%) of **1a**.

(2*R,3*R**)-3-Methyl-2-(trimethylacetoxy)hexan-1-ol (1a).** ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.86–0.90 (m, 6 H), 1.20 (s, 9 H), 1.26–1.41 (m, 1 H), 1.78–1.86 (m, 1 H), 2.00 (bs, 1 H), 3.64 (dd, J = 12.1, 6.6 Hz, 1 H), 3.72 (dd, J = 12.2, 3.3 Hz, 1 H), 4.72 (dt, J = 9.3, 3.3 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.15 (CH_3), 15.36 (CH_3), 19.89 (CH_2), 27.15 (CH_3), 33.88 (CH), 34.16 (CH_2), 39.00 (CMe_3), 63.36 (CH_2), 79.48 (CH), 179.36 (q). LRMS (EI): m/e 216 (m^+, 0), 185 (4), 145 (7), 116 (9), 101 (23), 85 (42), 72.11, 71 (14), 57 (100), 55 (15), 43 (12), 41 (23). IR (neat): 3446, 2960, 2935, 2875, 1729, 1711, 1481, 1285, 1165 cm^{-1}. Anal. Calcd for $C_{12}H_{24}O_3$: C, 66.61; H, 11.19. Found: C, 66.15; H, 11.23. HRMS: calcd for $C_{12}H_{24}O_3$ (m, + 1) 217.1804, found 217.1794.

(2*R,3*S**)-4-Methyl-3-propyl-2-(trimethylacetoxy)hexan-1-ol (Mixture of Stereoisomers at C-4, 1c).** ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.76–0.91 (m, 9 H), 1.18 (s, 4 H), 1.19 (s, 5 H), 1.26–1.62 (m, 6 H), 1.97 (bs, 1 H), 3.61–3.67 (m, 2 H), 4.94–5.00 (m, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 11.97, 12.15, 14.42, 14.51 (15.67), 15.97, 21.72, 22.31, 26.83, 27.03, 27.11, 27.13, 28.75, 29.37, 35.63, 35.66, 39.00, 42.74, 43.03, 64.81, 65.33, 75.51, 77.26, 179.54. IR (neat): 3456 (bs), 2960 (s), 2930, 2872, 1728, 1708, 1462, 1284, 1163 cm^{-1}. LRMS (EI): m/e 258 (m^+, 0), 227 (12), 145 (13), 143 (10), 125 (8), 116 (8), 101 (16), 85 (60), 83 (14), 71 (9), 69 (16), 57 (100), 55 (9), 43 (10), 41 (20). Anal. Calcd for $C_{15}H_{30}O_3$: C, 69.70; H, 11.71. Found: C, 69.34; H, 11.65.

(2*R,3*S**)-3-Propyl-2-(trimethylacetoxy)heptan-1-ol (1e).** ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.86 (m, 6 H), 1.20 (s, 9 H), 1.24 (m, 10 H), 1.63 (m, 1 H), 2.16 (bs, 1 H, OH), 3.68 (m, 2 H), 4.87 (dt, J = 5.7, 4.5 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.90 (CH_3), 14.31 (CH_3), 20.14 (CH_2), 22.84 (CH_2), 27.12 (CH_3), 29.23 (CH_2), 29.68 (CH_2), 31.76 (CH_2), 38.94 (CH), 38.99 (CMe_3), 63.74 (CH_2), 77.72 (CH), 179.53 (q). IR (neat): 2959, 2873, 1732, 1481, 1462, 1283, 1155 cm^{-1}. LRMS (EI): m/e 258 (m^+, 0), 227 (37), 145 (33), 143 (38), 116 (19), 113 (10), 101 (42), 85 (85), 83 (18), 71 (13), 69 (19), 57 (100), 55 (16), 43 (10), 41 (25). Anal. Calcd for $C_{15}H_{30}O_3$: C, 69.70; H, 11.71. Found: C, 69.47; H, 11.58.

(2*R,3*S**)-3-Phenyl-2-(trimethylacetoxy)hexan-1-ol (1g).** ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.82 (t, 1 H), 1.02–1.22 (m, 1 H), 1.60–1.74 (m, 3 H), 2.94 (dt, J = 9.9, 4.2 Hz, 1 H), 3.37 (dd, J = 12.2, 6.0 Hz, 1 H), 3.56 (dd, J = 12.2, 2.7, 1 H), 5.07 (ddd, J = 9.3, 6.2, 3.0 Hz, 1 H), 7.18–7.33 (m, 5 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.92, 20.17, 27.21, 33.72, 39.04, 46.32, 63.61, 78.38, 126.92, 128.37, 128.66, 140.96, 178.99. IR (neat): 3444, 2935, 2870, 1726, 1710, 1480, 1457, 1283, 1162, 1032 cm^{-1}. LRMS (EI): m/e 278 (m^+, 0), 260 (3), 176 (9), 145 (39), 134 (23), 133 (18), 117 (7), 104 (9), 91 (71), 85 (69), 57 (100). HRMS: calcd for $C_{17}H_{26}O_3$ (m + 1) 279.1960, found 279.1863.

(2*R,3*S**)-3-Phenyl-1-(trimethylacetoxy)hexan-2-ol (1h).** ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.82 (t, 3 H), 1.05–1.15 (m, 2 H), 1.18 (s, 9 H), 1.55–1.68 (m, 1 H), 1.93–2.04 (m, 1 H), 2.60–2.68 (m, 1 H), 3.72–3.79 (m, 1 H), 3.87–3.98 (m, 2 H), 7.12–7.30 (m, 5 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.95, 20.39, 27.13, 33.56, 38.80, 49.17, 67.34, 74.04, 126.77, 128.19, 128.61, 141.47, 178.89. IR (neat): 3477, 2958, 2933, 2872, 1728, 1713, 1480, 1454, 1285, 1163, 701 cm^{-1}. LRMS (EI): m/e 278 (m^+, 0), 260 (7), 145 (82), 134 (49), 133 (10), 104 (12), 92 (23), 91 (91), 85 (84), 57 (100), 41 (10). HRMS: calcd for $C_{17}H_{26}O_3$ (m + 1) 279.1960. Found: 279.1976.

(2*R,3*S**)-3-Methyl-2-(trimethylacetoxy)hexan-1-ol (2a).** ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.85–0.89 (m, 6 H), 1.12–1.36 (m, 4 H), 1.19 (s, 9 H), 1.73–1.81 (m, 1 H), 2.26 (bs, 1 H), 3.64–3.66 (m, 2 H), 4.78 (dt, J = 6.0, 4.5 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.06 (CH_3), 14.40 (CH_3), 20.00 (CH_2), 27.14 (CH_3), 33.93 (CH), 35.34 (CH_2), 39.06 (q), 63.94 (CH_2), 78.69 (CH), 179.53 (q). LRMS (EI): m/e 216 (m^+, 0), 185 (8), 145 (12), 116 (14), 101 (46), 85 (64), 72 (9), 71 (12), 57 (100), 55 (22), 43 (19), 41 (24). IR (neat): 3451, 2961, 2934, 2875, 1729, 1705, 1481, 1461, 1285, 1165 cm^{-1}. Anal. Calcd for $C_{12}H_{24}O_3$: C, 66.61; H, 11.19. Found: C, 66.23; H, 11.34. HRMS: calcd for $C_{12}H_{24}O_3$ (m + 1) 217.1804, found 217.1814.

2-(Trimethylacetoxy)heptan-1-ol (3a). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.85 (t, 3 H), 1.19 (s, 9 H), 1.26–1.28 (m, 4 H), 1.54 (m, 2 H), 1.90 (s, 1 H), 3.58 (dd, J = 12.0, 6.3 Hz, 1 H), 3.67 (dd, J = 12.0, 3.3 Hz, 1 H), 4.82–4.89 (m, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.87 (CH_3), 22.39 (CH_2), 24.81 (CH_2), 27.13 (CH_3), 30.42 (CH_2), 31.48 (CH_2), 38.90 (q), 65.17 (CH_2), 75.46 (CH), 179.20 (q). LRMS (EI): m/e 216 (m^+, 0.1), 185 (17), 145 (17), 131 (8), 116 (43), 101 (68), 85 (84), 57 (100), 41 (20). IR (neat): 3504, 2961, 2932, 1730, 1711, 1460, 1286, 1153 cm^{-1}. Anal. Calcd for $C_{12}H_{24}O_3$: C, 66.61; H, 11.19. Found: C, 66.74; H, 10.86.

2-Ethyl-1,2-pentanediol 1-Trimethylacetate (4a). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.84 (t, J = 7.8 Hz, 3 H), 0.87 (t, J = 7.5 Hz, 3 H), 1.17 (s, 9 H), 1.26–1.52 (m, 6 H), 1.92 (s, 1 H), 3.92 (s, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 7.49 (CH_3), 14.55 (CH_3), 16.39 (CH_2), 27.08 (CH_3), 29.15 (CH_2), 38.47 (CH_2), 38.82 (q), 68.90 (CH_2), 73.66 (q), 178.51 (q). LRMS (EI): m/e 187 (8), 173 (13), 103 (8), 102 (9), 101 (100), 85 (29), 59 (13), 57 (49), 55 (8), 41 (11). IR (neat): 3504, 2961, 2932, 2874, 1731, 1712, 1460, 1284, 1157 cm^{-1}. HRMS: calcd for $C_{12}H_{24}O_3$ (m + H) 217.1804, found 217.1773.

(2*R,3*R**)-2,3,7-Trimethyl-6-octene-1,3-diol 1-Trimethylacetate (5a).** ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.96 (d, J = 6.9 Hz, 1 H), 1.15 (s, 3 H), 1.16 (s, 9 H), 1.43–1.50 (m, 2 H), 1.58 (s, 3 H), 1.64 (s, 3 H), 1.86–1.89 (m, 2 H), 2.00–2.05 (m, 2 H), 3.90 (dd, J = 11.1, 7.5 Hz, 1 H), 4.19 (dd, J = 11.0, 5.1 Hz, 1 H), 5.08 (t, J = 7.2 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.10 (CH_3), 17.57 (CH_3), 22.16 (CH_2), 24.55 (CH_3), 25.61 (CH_3), 27.10 (CH_3), 38.69 (q), 39.17 (CH_2), 41.76 (CH), 66.49 (CH_2), 73.80 (q), 124.27 (CH), 131.91 (q), 178.53 (q). LRMS (EI): m/e 270 (m^+, 0), 252 (2), 150 (20), 135 (100), 121 (13), 109 (64), 103 (21), 95 (10), 93 (13), 85 (37), 82 (10), 71 (15), 69 (49), 67 (14), 57 (59), 43 (21), 41 (25). IR (neat): 3511, 2971, 2929, 2878, 1729, 1712, 1481, 1462, 1399, 1377, 1288, 1165 cm^{-1}. Anal. Calcd for $C_{16}H_{30}O_3$: C, 71.05; H, 11.19. Found: C, 70.66; H, 11.14.

(1*S*,2*S*,4*S*)-1-(Hydroxymethyl)-4-(2-propenyl)-2-methylcyclohexanol Trimethylacetate (6a). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.97 (d, 3 H), 1.21 (s, 9 H), 1.24–1.42 (m, 2 H), 1.67–1.72 (m, 2 H), 1.70 (s, 3 H), 1.94–2.04 (m, 2 H), 4.10 (d, J = 11.7 Hz, 1 H), 4.22 (d, J = 11.7 Hz, 1 H), 4.66–4.67 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.00 (CH_3), 20.97 (CH_3), 27.19 (CH_3), 28.58 (CH_2), 36.17 (CH_2), 36.97 (CH_2), 38.99 (q), 41.02 (CH), 44.76 (CH), 65.11 (CH_2), 73.42 (q), 108.72 (CH_2), 149.30 (q), 179.06 (q). LRMS

(EI): *m/e* 268 (m^+, 0), 250 (2), 156 (37), 139 (34), 135 (29), 57 (100), 43 (28), 41 (38). HRMS: calcd for $C_{16}H_{28}O_3$ (m + H) 269.2117, found 269.2047. $[\alpha]^{27}_{589} = -22.2°$, $c = 0.5$ ($CHCl_3$).

(1*R,2*S**,3*S**)-1-Acetoxy-2,3-epoxycyclohexane (7).** ^1H NMR (300 MHz, $CDCl_3$): δ 1.20–1.38 (m, 1 H), 1.78–1.82 (m, 2 H), 2.07 (s, 3 H), 3.26 (s, 2 H), 5.07–5.12 (m, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.82, 70.80, 54.14, 52.73, 24.32, 22.43, 21.05, 19.26.

(1*R,2*R**,3*R**)-1-Acetoxy-2,3-epoxycyclohexane (8).** ^1H NMR (300 MHz, $CDCl_3$): δ 1.23–1.29 (m, 2 H), 1.41 (m, 1 H), 1.77–1.83 (m, 2 H), 1.95–2.00 (m, 1 H), 2.06 (s, 3 H), 3.03 (d, J = 3.9 Hz, 1 H), 3.19 (s, 1 H), 5.01 (t, J = 6.6 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.42, 21.05, 23.61, 25.72, 52.52, 53.30, 68.02, 170.18.

(1*R,2*S**,6*R**)-2-Acetoxy-6-butylcyclohexanol (7a).** ^1H NMR (300 MHz, $CDCl_3$): δ 0.83–0.89 (m, 6 H), 1.20–1.36 (m, 6 H), 1.44–1.47 (m, 3 H), 1.60–1.70 (m, 2 H), 2.07 (s, 3 H), 3.36 (dd, J = 8.9, 2.7 Hz, 1 H), 5.06 (t, J = 2.7 Hz, 1 H). ^{13}C NMR (74 MHz, $CDCl_3$): δ 14.03, 19.61, 22.58, 22.98, 28.43, 28.85, 31.26, 31.52, 39.29, 73.45, 74.28, 171.30. IR (neat): 3460, 2933, 2859, 1738, 1721, 1247 cm^{-1}. LRMS (EI): *m/e* 214 (m^+, 0), 154 (10), 11 (20), 137 (41), 136 (100), 43 (48).

(1*R,2*S**,3*R**)-2-Acetoxy-3-butylcyclohexanol (7b).** ^1H NMR (300 MHz, $CDCl_3$): δ 0.84 (t, J = 6.6 Hz, 3 H), 0.99–1.04 (m, 2 H), 1.17–1.32 (m, 7 H), 1.39–1.58 (m, 2 H), 1.78–1.86 (m, 3 H), 2.07 (s, 3 H), 3.98 (s, 1 H), 4.61 (dd, J = 10.1, 2.7 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.94, 18.85, 21.11, 22.81, 28.61, 30.78, 31.21, 31.51, 35.45, 68.00, 78.53, 170.65. IR (neat): 3460, 2934, 2860, 1729, 1721, 1244 cm^{-1}. LRMS (EI): *m/e* 214 (m^+, 0), 154 (14), 111 (27), 98 (60), 97 (100), 43 (46).

(1*R,2*R**,6*S**)-2-Acetoxy-6-butylcyclohexanol (8a).** ^1H NMR (300 MHz, $CDCl_3$): δ 0.83–0.89 (m, 3 H), 1.13–1.90 (m, 2 H), 1.23–1.26 (m, 6 H), 1.29–1.36 (m, 2 H), 1.66–1.81 (m, 3 H), 2.05 (s, 3 H), 2.08–2.09 (m, 1 H), 3.17 (dt, J = 9.3, 2.7 Hz, 1 H), 4.52–4.61 (m, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.03, 22.59, 22.98, 28.69, 29.52, 30.21, 31.48, 31.53, 43.06, 76.75, 78.38, 171.46. IR (neat): 3418, 2934, 2861, 1736, 1721, 1458, 1244 cm^{-1}. LRMS (EI): *m/e* 214 (m^+, 0), 154 (6), 111 (13), 97 (100), 70 (18), 43 (35).

(1*R,2*R**,3*S**)-2-Acetoxy-3-butylcyclohexanol (8b).** ^1H NMR (300 MHz, $CDCl_3$): δ 0.82–0.86 (m, 3 H), 1.19–1.44 (m, 11 H), 1.64–1.90 (m, 3 H), 2.09 (s, 3 H), 3.41–3.49 (m, 1 H), 4.46 (dd, J = 9.8, 9.6 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.92, 21.08, 22.78, 23.06, 28.61, 29.71, 31.33, 33.85, 40.89, 73.78, 81.49, 172.33. IR (neat): 3459, 2933, 2859, 1738, 1721, 1376, 1246 cm^{-1}. LRMS (EI): *m/e* 214 (m^+, 0), 170 (15), 127 (25), 96 (100), 81 (35), 43 (50).

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Supplementary Material Available: ^1H and ^{13}C NMR spectra to indicate the purity of new compounds (32 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Selection of a Sommelet–Hauser or a Stevens Rearrangement Pathway of *N*,*N*-Dimethyl(substituted benzyl)ammonium *N*-Alkylides

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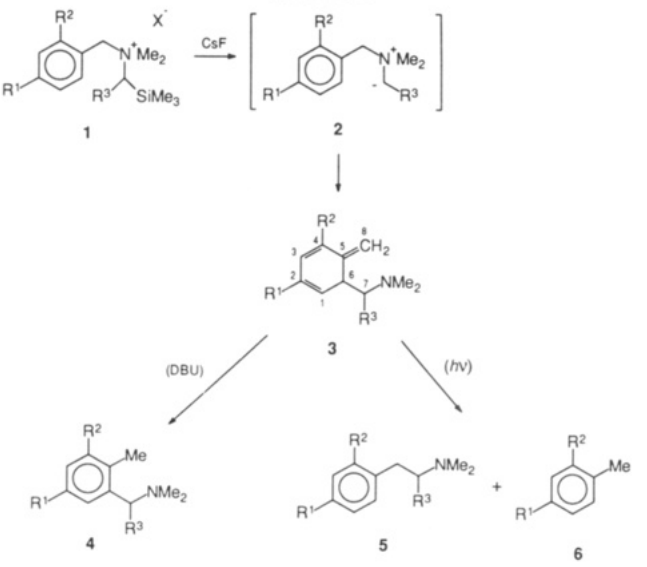
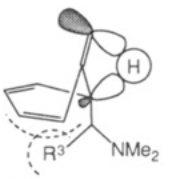
Benzylammonium *N*-ylides isomerize to a Sommelet–Hauser or a Stevens rearrangement product. The Sommelet–Hauser product is produced as a result of a [2,3] sigmatropic rearrangement of the ylide followed by proton migration to restore aromaticity, and the Stevens product has been regarded as a result of a [1,2] shift of the ylide through a caged radical pair intermediate.[1]

Scheme I



We revealed previously, in studies of fluoride ion induced desilylation reaction of *N*,*N*-dimethyl-*N*-[1-(trimethylsilyl)alkyl](substituted benzyl)ammonium halides (**1**), that the Sommelet–Hauser rearrangement products **4** are formed predominantly from the *N*-methylides (**2**, R^3 = H) with an electron-donating or a weak electron-releasing substituent (Hammett para-substituent constant, $\sigma_p < 0.23$), but the Stevens products **5** become predominant with increase of the Hammett σ_p constants ($\sigma_p > 0.6$).[2-4] The *N*-alkylides (**2**, R^3 = alkyl) were converted into **5** and toluenes (**6**), and both compounds were produced via radical-forming and -destroying pathways from 6-(1-aminoalkyl)-5-methylene-1,3-cyclohexadienes (**3**), which were initially formed by a [2,3] sigmatropic rearrangement of **2**.[5]

The conversion of **3** to **4** requires a [1,3] antarafacial migration of a hydrogen at the 6-position of **3** to the *exo*-methylene carbon (C-8) under thermal condition.



When R^3 of **3** is an alkyl group, its steric bulk interferes with the torsion of the molecule, thus allowing the [1,3] proton migration. Therefore, the carbon–carbon bond between C-6 and C-7 may be cleaved homolytically to a radical pair, radical recombination gives **5**, and hydrogen atom abstraction produces **6**.[5] Addition of a strongly basic amine to the reaction could aid the conversion of **3** to **4** by a proton-dissociation and -recombination pathway. Irradiation by UV light could assist the isomerization from **3** to **5** via the radical pathway or a suprafacial [1,3] migration of the aminoalkyl group to the C-8 carbon.[6]

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