Alkylative Epoxide Rearrangement. A Stereospecific Approach to Chiral Epoxide Pheromones

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The alkylative rearrangement of 1,2-epoxy-3-alkanol tosylates is applied to the synthesis of chiral epoxide pheromones. Attack at the terminal carbon atom of epoxy tosylates by lithioacetylenes and cyclization of the intermediate tosyloxy alcohols produces internal epoxides in high yield. The method is stereospecific: *threo*-epoxy tosylates give *cis*-epoxides, and *erythro*-epoxy tosylates yield *trans*-epoxides. Several diastereomerically pure epoxides were prepared in high optical purity from chiral pool intermediates derived from sugars. Pheromone components prepared include (±)-*cis*-epoxyalkene **20** and both enantiomers of *cis*-epoxy diene **16**, a female sex pheromone component of a number of lepidopteran species. These results demonstrate that alkylative rearrangement of 1,2-epoxy-3-alkanol tosylates complements existing methods for stereoselective synthesis of epoxides, including the Payne rearrangement and Sharpless epoxidation.

Introduction

The preparation of chiral compounds in high enantiomeric purity is one of the principal challenges of contemporary synthetic organic chemistry. The need for methods that directly afford enantiomerically enriched compounds is particularly apparent in the fields of pharmaceutical[1] and pheromone[2] research, since chemoreception by living organisms can be highly enantioselective. A number of biologically active, naturally occurring molecules contain unsymmetrically disubstituted epoxide rings. Figure 1 outlines the most common enantioselective synthetic approaches to chiral epoxides, including arachidonic acid metabolites[3] and female lepidopteran sex pheromones,[4] such as disparlure[5] and several other long-chain epoxides.[6]

Most reported syntheses of chiral epoxides employ optically active natural product (chiral pool) starting materials, such as α-amino acids and carbohydrates, to prepare key intermediates consisting of 2,3-epoxy-1-alkanols (Figure 1, pathway B),[5j,6b,c] 1,2-epoxy-3-alkanols (Figure 1, pathway C),[5h,k] or monoprotected diols (Figure 1, pathways D and E).[5a,b,d,f,g] While these approaches often lead to enantiomerically pure products, the syntheses are usually encumbered by protection–deprotection sequences required to form the correct epoxide precursor from a monotosylated or monomesylated diol. A more direct approach involves Sharpless epoxidation[7] of 2-alken-1-ols (Figure 1, pathway A),[5c,e,i,6a,d–f] followed by functionalization at C-1. Unfortunately, whereas *E* allylic alcohols afford the corresponding *trans*-2,3-epoxy-1-alkanols in high enantiomeric excess (94–>98%), *Z* allylic alcohols give *cis*-2,3-epoxy-1-alkanols of much lower enantiomeric purity (80–85% ee).[5e,6f,8] This poor enantioselectivity presents a problem when studying biological responses to synthetic compounds since the presence of <1% of the unwanted enantiomer may interfere with bioassays.[9] To overcome this limitation of the Sharpless epoxidation, *cis*-2,3-epoxy-1-alkanols can be enantiomerically enriched by

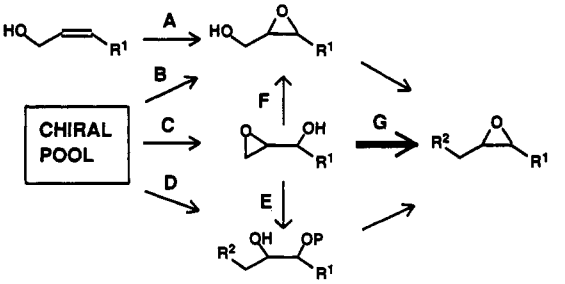

Figure 1. Key enantioselective synthetic approaches to chiral epoxides.

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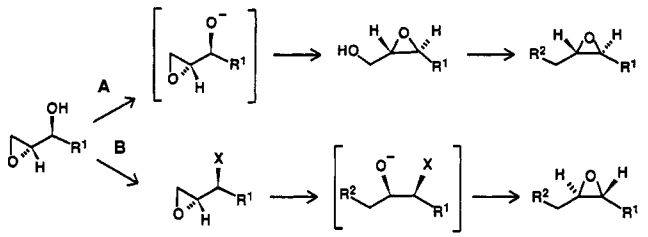


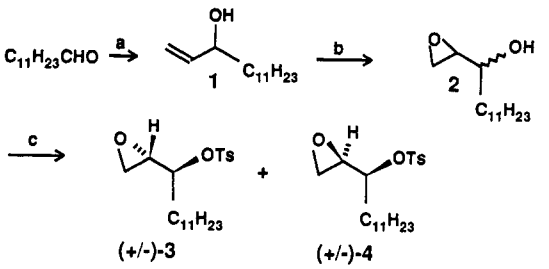
Figure 2. Payne (A) and alkylative rearrangements (B): enantiodivergent approaches to trans epoxides.

crystallization of derivatives, such as 3,5-dinitrobenzoates.[5e,6f] An alternative approach to *trans*-2,3-epoxy-1-alkanols is through the Payne rearrangement[10] of *erythro*-1,2-epoxy-3-alkanols (Figure 1, pathway F).[3] Under the conditions of the rearrangement, *threo*-1,2-epoxy-3-alkanols produce a mixture of *cis*-2,3-epoxy-1-alkanol and the starting epoxide, making this an impractical route to cis epoxides.[10c]

Because *threo*-[5h,j,k,11] and *erythro*-1,2-epoxy-3-alkanols[3,7,8,11,12] are readily available either from "chiral pool" compounds or from 1-alken-3-ols via Sharpless epoxidation, we have investigated an alternative approach to internal epoxides from 1,2-epoxy-3-alkanols by "alkylative rearrangement" of the corresponding *p*-toluenesulfonates (Figure 1, pathway G).[13] This new method is a more direct approach to internal epoxides than the three-step Payne rearrangement/alkylation sequence, it avoids protection–deprotection sequences, and it can be used to synthesize cis or trans epoxides (Figure 2).

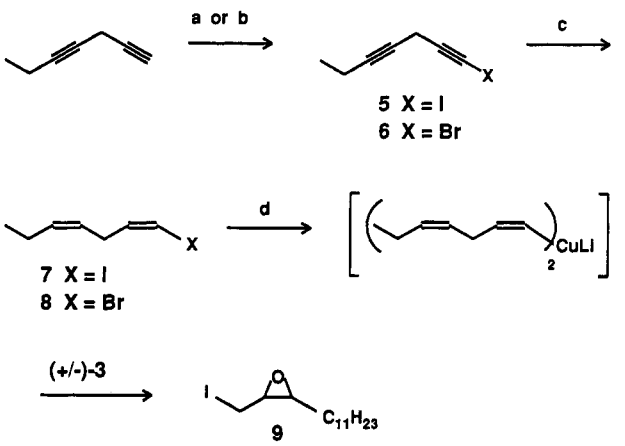
In the Payne rearrangement, the C-3 alkoxy group intramolecularly attacks the epoxide ring at C-2, leading to inversion of configuration at this center. Our method utilizes the proclivity of terminal epoxides toward nucleophilic attack at C-1, which is also the basis of a stereoselective approach to vicinal diols by regioselective nucleophilic ring opening of 1,2-epoxy-3-alkanols.[14] In our approach, the hydroxyl at C-3 is converted to a leaving group (e.g., X = tosylate) prior to nucleophilic attack at C-1. The ring-opened intermediate can be isolated or recyclized *in situ* to directly afford the desired product. This alkylative rearrangement differs from the Payne rearrangement in the configurations at C-2 and C-3. Thus, the same optically active 1,2-epoxy-3-alkanol can lead to opposite enantiomers of trans disubstituted epoxides.[15] Herein we report full details of our initial findings as well as the synthesis of both enantiomers of (*Z*,*Z*)-*cis*-2-(2,5-octadienyl)-3-undecyloxirane (**16**),[2b,16] the principal sex pheromone component of at least five arctiid moths.

Scheme I[a]



[a] Key: (a) $H_2C{=}CHMgBr$, Et_2O; (b) *m*-CPBA, CH_2Cl_2 (threo/erythro, 3:2); (c) tosyl chloride, pyridine.

Scheme II[a]



[a] Key: (a) (i) EtMgBr, (ii) I_2; (b) NBS, $AgNO_3$, acetone; (c) (i) $(Sia)_2BH$, (ii) AcOH; (d) (i) t-BuLi, (ii) CuI·SMe_2.

Results and Discussion

Alkylative Rearrangement of Racemic 1,2-Epoxy-3-alkanol Tosylates. Our initial studies employed (±)-*threo*- and (±)-*erythro*-1,2-epoxy-3-(tosyloxy)undecane (**3** and **4**, respectively), which were prepared as shown in Scheme I. Dodecanal was treated with vinylmagnesium bromide in anhydrous THF to afford 1-tetradecen-3-ol (**1**). Epoxidation of **1** with *m*-CPBA in CH_2Cl_2 gave a 3:2 ratio of *threo*- to *erythro*-1,2-epoxy-3-alkanols (**2**). The diastereomers could be separated by large-scale HPLC at this stage or converted to racemic tosylates **3** and **4** and separated by flash chromatography[17] on silica gel.

With both epoxy tosylate diastereomers in hand, we examined their reactivities toward a number of organometallic reagents known to alkylate epoxides. In our initial attempts we treated (±)-**3** with lithium bis((*Z*,*Z*)-1,4-heptadienyl)copper[18] in the hope of obtaining epoxy diene **16** in one step. The homocuprate was prepared *in situ* by reaction of (*Z*,*Z*)-1-iodo-1,4-heptadiene (**7**) or (*Z*,*Z*)-1-bromo-1,4-heptadiene (**8**) with 2 equiv of *t*-BuLi at low temperature followed by CuI·SMe_2. The halodienes **7** and **8** were prepared as shown in Scheme II. Treatment of 1,4-heptadiyne[19] with ethylmagnesium bromide in diethyl ether followed by I_2 afforded 1-iodo-1,4-heptadiyne (**5**) in

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(15) The fundamental reactivity of the epoxide ring is different in each case. In Payne rearrangement, the epoxide functions solely as an electrophile, whereas in alkylative epoxide rearrangement it possesses latent nucleophilic character that is revealed upon nucleophilic attack at C-1.

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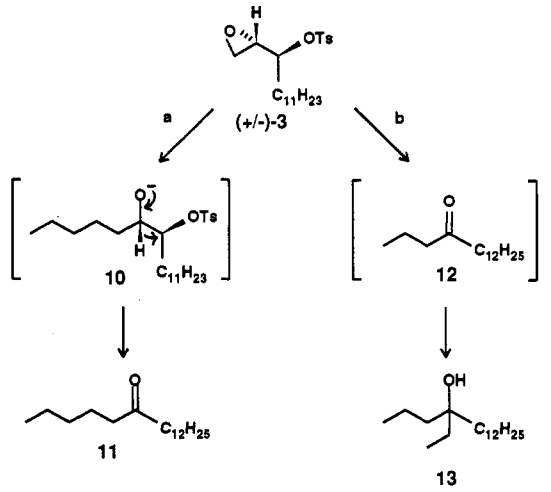
Scheme III[a]



[a] Key: (a) n-Bu_2CuLi, Et_2O; (b) Et_3Al, CH_2Cl_2.

approximately 50% yield after flash silica chromatography. Alternatively, treatment of 1,4-heptadiyne with NBS in the presence of a catalytic amount of $AgNO_3$ in acetone afforded 1-bromo-1,4-heptadiyne (**6**) in 97% yield (97% pure by GC analysis).[20] Hydroboration of either 1-halo-1,4-diyne with disiamylborane ($(Sia)_2BH$) followed by protonolysis with glacial acetic acid gave **7** or **8**.[21] Unfortunately, the reaction between (±)-**3** and the homocuprate gave a complex mixture of products from which 2-(iodomethyl)-3-undecyloxirane (**9**) was isolated. This product was apparently formed by epoxide rearrangement after nucleophilic attack by iodide rather than by the carbon nucleophile.[22]

The failure of a lithium dienyl cuprate to effect the desired epoxide migration prompted us to investigate the reaction of epoxy tosylates with simple dialkyl cuprates, and the results are shown in Scheme III. Unexpectedly, when either (±)-**3** or (±)-**4** was treated with lithium di-*n*-butylcopper in diethyl ether the only detectable product was 6-octadecanone (**11**), which was identified by comparison with an authentic sample. The formation of this ketone apparently arises from displacement of tosylate by a 1,2-hydride shift in the desired ring-opened intermediate **10**. This type of hydride migration is well established in halohydrin chemistry.[23] Analogous rearrangement occurred when (±)-**3** reacted with triethylaluminum in CH_2Cl_2 to give 4-ethyl-4-hexadecanol (**13**). The rearrangement product, 4-hexadecanone (**12**), apparently reacted with a second equivalent of triethylaluminum, as shown in Scheme III. In an attempted synthesis of disparlure by alkylative epoxide rearrangement, (2*R*,3*R*)-1,2-epoxy-3-(tosyloxy)tridecane was treated with lithium bis(4-methylpentyl)copper, but the reaction failed to produce the desired epoxide.[5j] Interestingly, higher order cuprates have been used to perform the desired alkylative epoxide rearrangement of racemic epoxy mesylates,[24] and Li_2CuCl_4-catalyzed reaction of (S)-glycidyl tosylate with Grignard reagents has been reported to yield optically active hydroxy tosylates.[22]

A method for the preparation of homopropargylic alcohols by alkylation of epoxides with 1-lithioalkynes in the presence of BF_3-Et_2O has found extensive use since its initial report.[25] Under these conditions, epichlorohydrin is cleanly converted to 5-chloro-1-phenyl-1-pentyn-4-ol.[25] Apparently, the alkoxide generated by epoxide cleavage is coordinated to boron, preventing further reaction. Although application of this method to alkylative epoxide rearrangement would afford an alcohol intermediate, it appeared to be an excellent way to introduce an acetylenic nucleophile. The new epoxide ring could be formed *in situ* upon treatment with base, and partial catalytic hydrogenation would then afford the target epoxyalkene.

As expected, treatment of (±)-**3** with 2.75 equiv each of 1-lithio-1,4-heptadiyne and BF_3:Et_2O in anhydrous THF at −78 °C gave (±)-*threo*-10-(tosyloxy)-3,6-heneicosadiyn-9-ol (**14**). This intermediate could be isolated or recyclized *in situ* by treatment with potassium carbonate in anhydrous methanol, affording (±)-*cis*-2-(2-octadiynyl)-3-undecyloxirane (**15**) in 56% yield from (±)-**3**. Catalytic hydrogenation of **15** gave (±)-*cis*-epoxy diene **16**, which was spectroscopically and chromatographically identical to the natural epoxide isolated from the female sex glands of *Creatonotos gangis*.[2b] In a similar manner, (±)-*trans*-epoxy diene **18** was prepared from (±)-**4**, and (±)-*cis*-epoxyalkene **20**, a sex pheromone component of the ruby tiger moth *P. fuliginosa*,[6b] was prepared from (±)-**3** (Scheme IV).

We found the alkylative rearrangement to be *diastereospecific*; threo epoxy tosylates gave pure cis epoxides and erythro epoxy tosylates gave pure trans epoxides. In order to rigorously establish the relative configurations of the epoxides, we hydrogenated (±)-**16** to (±)-*cis*-2-octyl-3-undecyloxirane and (±)-**18** to (±)-*trans*-2-octyl-3-undecyloxirane. These samples were found to be spectroscopically and chromatographically identical to authentic samples prepared by known methods.[16a] In addition, the relative configurations of the epoxides could be assigned by the ^1H NMR chemical shifts of the ring protons; resonances of the cis epoxide protons (2.91–2.95 ppm) consistently occurred at lower field than those of the trans epoxide protons (2.65–2.83 ppm).

Enantioselective Synthesis of Epoxides by Alkylative Rearrangement. The synthesis of optically active epoxides by alkylative rearrangement requires optically active threo and erythro epoxy tosylate intermediates. As there are a number of efficient methods for the preparation of optically pure 1,2-epoxy-3-alkanols from carbohydrates,[11] we chose to synthesize *threo*-(2*R*,3*R*)-1,2-epoxy-3-(tosyloxy)tetradecane (**31**), *threo*-(2*S*,3*S*)-1,2-epoxy-3-(tosyloxy)tetradecane (**38**), and *erythro*-(2*R*,3*S*)-1,2-epoxy-3-(tosyloxy)tetradecane (**26**) from common chiral templates. Whereas the overall yields for the multistep syntheses of these intermediates were not high, inexpensive reagents were employed and reactions could be performed on sufficient scale to afford each epoxy tosylate in quantities of 0.2–1 g.

The 1,2,5,6-diacetonide of D-mannitol was prepared according to the method of Kirstead *et al.*[26] Oxidative cleavage of the diacetonide with lead tetraacetate afforded (*R*)-glyceraldehyde acetonide (**21**) in 73% yield after distillation.[27] Undecylmagnesium bromide in diethyl ether at 0 °C added preferentially to the *Si* face of the aldehyde

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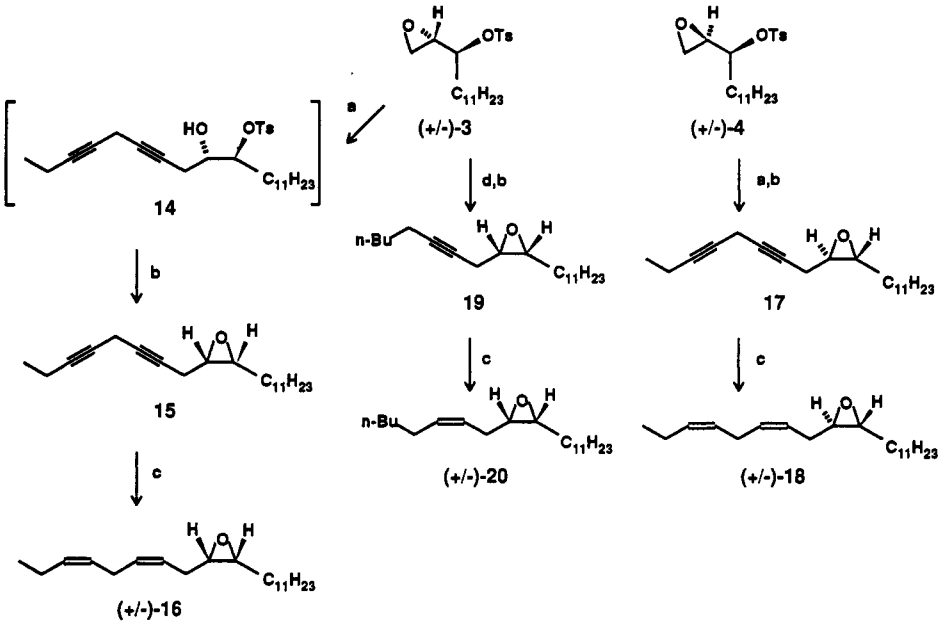
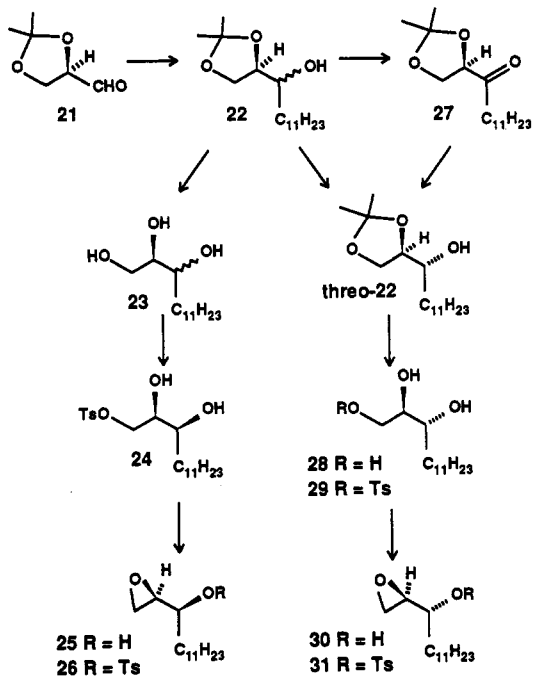
Scheme IV[a]



[a] Key: (a) $CH_3CH_2C{\equiv}CCH_2C{\equiv}CLi$, $BF_3{\cdot}OEt_2$, THF; (b) K_2CO_3, MeOH; (c) H_2, Pd–$BaSO_4$, quinoline, pentane; (d) $C_5H_{11}C{\equiv}CLi$, $BF_3{\cdot}OEt_2$, THF.

Scheme V



carbonyl, affording a 3:1 mixture of erythro and threo alcohols (**22**, Scheme V). Acid-catalyzed deketalization[28] and recrystallization from ethyl acetate gave a 4:1 mixture of *erythro*-(2*R*,3*S*)-1,2,3-tetradecanetriol and *threo*-(2*R*,3*R*)-1,2,3-tetradecanetriol (**23**). Selective monotosylation[29] of the primary hydroxyl group by reaction with 1 equiv of TsCl in pyridine followed by flash chromatography afforded *erythro*-(2*R*,3*S*)-1-(tosyloxy)-2,3-tetradecanediol (**24**). Subsequent treatment with anhydrous potassium carbonate yielded *erythro*-(2*R*,3*S*)-1,2-epoxy-3-tetradecanol (**25**), which then gave *erythro*-(2*R*,3*S*)-1-epoxy-3-(tosyloxy)tetradecane (**26**) upon treatment with TsCl in pyridine (Scheme V). By taking advantage of the diastereofacial bias of lithium tri-*sec*-butylborohydride (L-Selectride),[30] we also prepared threo epoxy tosylate **31** (Scheme V). DMSO-based oxidation[31] of **22** afforded ketone **27**, which was reduced by L-Selectride to give a 10:1 mixture of *threo*-**22** and *erythro*-**22**. Through the same series of reactions which led to **26**, we prepared *threo*-(2*R*,3*R*)-1,2,3-tetradecanetriol (**28**), *threo*-(2*R*,3*R*)-1-(tosyloxy)-2,3-tetradecanediol (**29**), *threo*-(2*R*,3*R*)-1,2-epoxy-3-tetradecanol (**30**), and *threo*-(2*R*,3*R*)-1,2-epoxy-3-(tosyloxy)tetradecane (**31**).

L-(+)-Diethyl tartrate was employed as a chiral template in the synthesis of (2*S*,3*S*)-epoxy tosylate (**38**) (Scheme VI). Diol **32**[32] was monosilylated before conversion to aldehyde **34**[33] by Swern oxidation.[31a] Wittig coupling with the ylide derived from *n*-decyltriphenylphosphonium bromide[34] gave predominantly the (*Z*)-alkene (**35**). Fluorodesilylation of the *E*/*Z* mixture followed by catalytic hydrogenation gave alcohol **36**. At this point, the synthesis of epoxy alcohol **37** followed two alternative paths: (a) tosylation, followed by acid-catalyzed deketalization and treatment with potassium carbonate, or the reverse, (b) acid-catalyzed deketalization, monotosylation of the primary hydroxyl, and treatment with base. Tosylation of **37** afforded *threo*-(2*S*,3*S*)-1,2-epoxy-3-(tosyloxy)tetradecane (**38**) as a white, crystalline solid after purification by flash silica chromatography. An alternative route to alcohol **36** of comparable efficiency started with monobenzylated diol **39**.[11a] By the same series of reactions as

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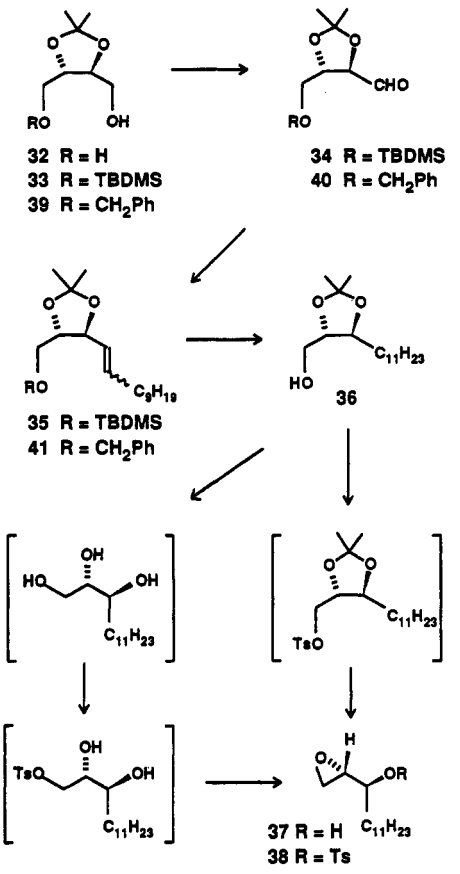
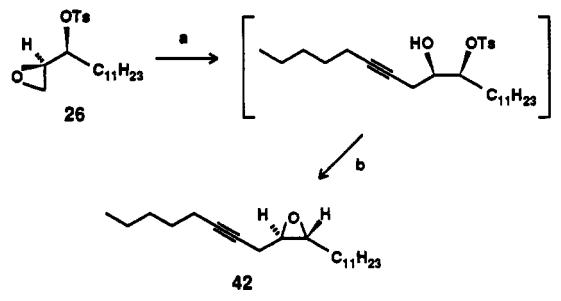
Scheme VI



Scheme VII[a]



[a] Key: (a) $C_5H_{11}C{\equiv}CLi$, $BF_3{\cdot}OEt_2$, THF; (b) K_2CO_3, CH_3OH.

described above, aldehyde **40** and alkene **41** were prepared and converted to alcohol **36** by hydrogenation/hydrogenolysis.

In order to establish the degree of enantioselectivity afforded by alkylative epoxide rearrangement, we employed erythro epoxy tosylate **26** as a test reactant (Scheme VII). We prepared an optically active trans epoxyalkyne and compared its specific rotation with that of a sample of known enantiomeric excess.[13] When **26** was treated with 1-lithio-1-heptyne and $BF_3{\cdot}Et_2O$ followed by anhydrous potassium carbonate in methanol, (2*R*,3*R*)-2-(2-octynyl)-3-undecyloxirane (**42**, $[\alpha]^{23}_D = -4.2 \pm 0.2°$) was obtained in 52% yield. This glyceraldehyde-derived trans epoxyalkyne had a larger rotation than a sample of its optical antipode ($[\alpha]^{23}_D = +2.5 \pm 0.1°$; 66% ee).[35] The high optical purity of the product illustrates that the alkylative rearrangement step is stereoselective, as expected. Using the same series of reactions which led to the racemate (Scheme IV), we also prepared (*Z*,*Z*)-(2*S*,3*R*)-*cis* epoxy diene **16** from threo epoxy tosylate **38** and (*Z*,*Z*)-(2*R*,3*S*)-*cis* epoxy diene **16** from threo epoxy tosylate **31**. Both antipodes had optical rotations of nearly equal absolute value, which were slightly larger than those previously reported for synthetic samples of **16**.[5e,6a] In addition, we prepared (*Z*,*Z*)-(2*R*,3*R*)-*trans*-epoxy diene **18** from erythro epoxy tosylate **26**.[13]

Conclusion

Alkylative rearrangement constitutes a new route to unsaturated, chiral epoxides from 1,2-epoxy-3-alkanols. Using this approach, we have prepared several diastereomerically pure epoxides in high optical purity, including both enantiomers of epoxide **16**, the principal female sex pheromone component of a number of lepidopteran species. Two routes leading to enantiomerically enriched samples of **16** have been reported previously, one involving asymmetric epoxidation/alkylation,[5e] the other based on structural elaboration of D-xylose.[6c] Not surprisingly, the route involving asymmetric epoxidation of *cis*-2-alken-1-ols afforded 2,3-epoxy-1-alkanols in low % ee; derivatization and enrichment by crystallization was necessary in order to obtain epoxy alcohols of higher enantiomeric purity. Although the synthesis of **16** from D-xylose presumably afforded enantiomerically pure product, the (*Z*,*Z*)-epoxy diene was only present in 40% excess over the (*E*,*Z*)-isomer, requiring an additional separation step. Moreover, the optical rotation of the epoxy diene derived from D-xylose was presumably that of a mixture of geometric isomers.

Either enantiomer of a trans propargylic or allylic internal epoxide could be prepared by Sharpless epoxidation of a 1-alken-3-ol, followed by optical enrichment of the resulting *erythro*-1,2-epoxy-3-alkanols, tosylation, and alkyllative rearrangement. The corresponding cis epoxides could be obtained easily by inverting the configurations of the *erythro*-1,2-epoxy-3-alkanols at C-3,[11b] followed by tosylation and alkylative rearrangement. The principal advantage of this approach is the ready accessibility of all four stereoisomers of 1,2-epoxy-3-alkanols by two Sharpless epoxidation reactions of the same 1-alken-3-ol. Sharpless epoxidation approaches to all four stereoisomers of a 2,3-epoxy-1-alkanol from a 2-alken-1-ol require both geometric isomers of the alkene and a total of four epoxidation reactions. Our results also show that the alkylative rearrangement of 1,2-epoxy-3-alkanol tosylates complements existing methods for the stereoselective synthesis of epoxides, such as Payne rearrangement (Figure 2) and Sharpless epoxidation.

Experimental Section

General. All reactions involving reagents that are sensitive to air or moisture were performed under an atmosphere of N_2 or Ar. Reactions were stirred magnetically unless otherwise indicated. Solutions were transferred either with double-ended needles or with hypodermic syringes. Most commercially obtained reagents were distilled or recrystallized and stored under N_2 prior to use. Solutions of *n*-butyllithium in hexane were titrated to a bright red endpoint using 2,5-dimethoxybenzyl alcohol as an indicator.[36] All Grignard reagents were titrated with *sec*-butyl alchol using the method described by Watson and Eastham.[37] Anhydrous solvents were prepared as follows: THF

(35) Determined by NMR analysis of the (−)-MTPA ester of the corresponding *trans*-2,3-epoxy-5-alkyn-1-ol, assuming no loss of optical activity during the iodination/alkylation sequence.[13]

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and diethyl ether were freshly distilled under N_2 from Na/benzophenone; MeOH was refluxed over Mg turnings, distilled under N_2 and stored over 3 Å molecular sieves; CH_2Cl_2 and $CHCl_3$ were passed through a short column of activity I basic alumina (Woelm) or distilled from CaH_2 under N_2; dimethyl sulfide was distilled from sodium metal under N_2; pyridine was distilled from BaO and stored over KOH. Copper(I) halides were purified by dissolving them in a saturated solution of the corresponding potassium halide followed by treatment with animal charcoal, filtration, and dilution with distilled water to precipitate the salt. The salts were then washed sequentially with acetone and ether and dried under vacuum in the dark. "Ether extractive workup" refers to dilution of the reaction mixture with a 1:1 mixture of ether and distilled water, followed by repeated extraction of the aqueous layer with ether. The combined ether solutions were dried over $MgSO_4$ or Na_2SO_4, filtered, and evaporated under vacuum. ^1H NMR spectra were recorded at 60, 80, or 300 MHz, and chemical shifts were measured relative to internal TMS or residual solvent resonances (δ ($CHCl_3$) = 7.26, δ (DMSO) = 2.49). All coupling constants are reported in Hz. ^{13}C NMR spectra were recorded at approximately 20 or 75 MHz, and chemical shifts were measured relative to residual solvent resonances (δ ($CDCl_3$) = 77.00, δ (DMSO) = 39.5). Mass spectra were obtained by electron impact ionization at 70 eV. Melting points were determined on a Thomas-Hoover apparatus and are uncorrected. Analytical GC was performed with flame ionization detection, and capillary GC was performed using a DB-5 fused silica column (30 m × 0.25 mm). Analytical TLC was performed using Machery-Nagel 0.2-mm silica-coated plastic sheets, and spots were visualized either by UV or by treatment with I_2, 10% phosphomolybdic acid (PMA) in ethanol, or with a solution of vanillin (9g) and H_2SO_4 (1 mL) in ethanol (300 mL). Flash chromatography[17] employed Merck silica gel 60 (230–400 mesh). Elemental microanalyses were performed by Desert Analytics on chromatographed and/or recrystallized samples.

(±)-1-Tetradecen-3-ol (1). A solution of 1.42 M vinylmagnesium bromide in ether (150 mL, 0.21 mol) was stirred under argon as a solution of dodecanal (37 g, 0.20 mol) in 20 mL of anhydrous THF was added dropwise over 35 min. The reaction mixture was stirred under reflux for 3 h, cooled to 0 °C, and quenched by addition of saturated aqueous ammonium chloride (30 mL). The resulting viscous suspension was stirred for several minutes at room temperature and filtered, and then the sticky white precipitate was washed with small portions of diethyl ether. The combined filtrates were dried with Na_2SO_4 overnight and filtered, and the solvent was evaporated *in vacuo* to afford a yellow oil. Distillation gave 36.3 g (85%) of a colorless oil: bp 85–87 °C (0.1 mmHg); ^1H NMR ($CDCl_3$) δ 5.87 (ddd, $^3J_{cis}$ = 10, $^3J_{trans}$ = 17, ^3J = 6.3, 1 H, CH_2=C*H*), 5.23 (ddd, ^2J = ^4J = 1.4, $^3J_{trans}$ = 17, 1 H, C*H*H=CH), 5.10 (ddd, ^2J = 1.4 or 1.2, $^3J_{cis}$ = 10, ^4J = 1.2 or 1.4, 1 H, CH*H*=CH), 4.10 (dt, ^3J = 6.3, 1 H, C*H*OH), 1.50 (m, 2 H, CH_2CHOH), 1.26 (br s, 18 H, $(CH_2)_9$), 0.89 (t, J = 7, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 141.4, 114.3, 73.2, 37.0, 31.9, 29.3, 25.3, 22.6, 14.0; MS (m/z) 183 ($M^+ - C_2H_5$, 1.5), 166 (0.2), 85 (15.9), 72 (26), 57 (100); IR (neat) 3350 (OH), 2900 (CH) cm^{-1}. Anal. Calcd for $C_{14}H_{28}O$: C, 79.18; H, 13.29. Found: C, 79.19; H, 13.68.

(±)-1,2-Epoxy-3-tetradecanol (2). A solution of 1-tetradecen-3-ol (1.50 g, 7.06 mmol) in ca. 10 mL of anhydrous CH_2Cl_2 was cooled to 0 °C under an atmosphere of argon. A solution of *m*-CPBA (1.54 g, 7.58 mmol; Lancaster Synthesis, 85%) in ca. 7 mL of anhydrous CH_2Cl_2 was added dropwise over 10 min to the vigorously stirred solution. The resulting white mixture was slowly warmed to room temperature and stirred for 16 h. TLC (25% ethyl acetate in hexanes, PMA) showed a minor spot at R_f 0.6, corresponding to **1**, and a major spot at R_f 0.4, corresponding to epoxy alcohol **2**. The mixture was again cooled to 0 °C, and 85% *m*-CPBA (0.30 g, 1.48 mmol) was added. After several min at 0 °C the mixture was warmed to room temperature and stirred for another 1 h. The solution was filtered and washed with three 20-mL portions of saturated aqueous $NaHCO_3$. The aqueous layer was extracted with CH_2Cl_2 (2 × 10 mL), and the combined organic layers were dried with anhydrous Na_2SO_4. After filtration of the drying agent, the solvent was evaporated to afford 1.27 g (79%) of a clear, colorless oil which solidified upon exposure to vacuum (0.1 mm Hg). The ratio of threo to erythro epoxy alcohols was determined to be ca. 3:2 by ^1H NMR integration of the carbinol methine resonances and by comparison of the corresponding ^{13}C NMR peak heights. The threo isomer could be enriched by recrystallization from cold pentane. Alternatively, the diastereomers could be separated by large-scale HPLC on silica gel using a Waters preparative LC500 with dioxane/CH_2Cl_2 elution. ***threo*-2**: mp 50–52 °C; ^1H NMR ($CDCl_3$) δ 3.44 (br m, 1 H, C*H*OH), 2.99 (m, 1 H, oxirane CH), 2.83 (dd, ^2J = 4.8, ^3J = 4.2, 1 H, oxirane CH_2), 2.72 (dd, ^2J = 4.8, ^3J = 2.7, 1 H, oxirane CH_2), 1.5 (m, 2 H, CH_2CHOH), 1.26 (br s, 18 H, $(CH_2)_9$), 0.89 (t, J = 7, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 71.7, 55.5, 45.0, 34.2, 31.8, 29.5, 29.2, 25.5, 25.2, 13.9. ***erythro*-2**: mp 39–40 °C; ^1H NMR ($CDCl_3$) δ 3.85 (br m, 1 H, C*H*OH), 3.02 (dd, J = 3.0, 3.9, 1 H, oxirane CH), 2.82 (dd, ^2J = 5, ^3J = 2.7, 1 H, oxirane CH_2), 2.74 (dd, ^2J = 5, ^3J = 4.2, 1 H, oxirane CH_2), 1.5 (m, 2 H, CH_2CHOH), 1.26 (br s, 18 H, $(CH_2)_9$), 0.89 (t, J = 7, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 68.5, 54.6, 43.4, 33.5, 31.8, 29.7, 29.5, 25.2, 22.5, 13.9. Mixture of threo **2** and erythro **2**: MS (m/z) 185 ($M^+ - C_3H_7$, 5.5), 111 (40), 97 (89), 83 (100), 69 (93), 57 (75); IR (neat) 3300 (OH), 2900 (CH) cm^{-1}. Anal. Calcd for $C_{14}H_{28}O_2$: C, 73.63; H, 12.36. Found: C, 73.59; H, 12.73.

(±)-1,2-Epoxy-3-(tosyloxy)tetradecane (3 and 4). A solution of 2.0 g (8.8 mmol) of epoxy alcohol **2** (ca. 3:2 threo/erythro) in 10 mL of anhydrous pyridine was stirred under argon at 0 °C, as a solution of TsCl (2.50 g, 13.0 mmol, recrystallized from petroleum ether) in 2 mL of pyridine was added dropwise over several min. The reaction mixture was stirred at 5 °C for 41 h and diluted with an equal volume of cold water. Extraction by diethyl ether gave 2.98 g (89%) of a beige solid. TLC of the crude product (4:1 hexanes/ethyl acetate, v/v) showed spots at R_f 0.55 and 0.40 corresponding to **4** and **3**, respectively. Purification by flash chromatography (15 × 51 cm) eluting with a mixture of hexanes and ethyl acetate (first 8:1 then 4:1, v/v) afforded 1.76 g of **3** as a white solid and 0.41 g of **4** as a clear colorless oil. ***threo*-3**: recrystallization from cold pentane afforded 1.3 g of fine white needles, mp 53–56 °C; ^1H NMR ($CDCl_3$) δ 7.82 (d, J = 8.4, 2 H, 2,6-Ar), 7.33 (d, J = 8.4, 2 H, 3,5-Ar), 4.34 (dt, J = 6.6, 7.2, 1 H, C*H*OSO_2), 3.05 (m, 1 H, oxirane CH), 2.78 (dd, ^2J = 4.8, ^3J = 4.5, 1 H, oxirane CH_2), 2.63 (dd, ^2J = 4.8, ^3J = 2.7, 1 H, oxirane CH_2), 2.44 (s, 3 H, $ArCH_3$), 1.70 (m, 2 H, CH_2CHOSO_2), 1.26 (br s, 18 H, $(CH_2)_9$), 0.89 (t, J = 6.9, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 144.7, 134.3, 129.6, 127.8, 83.4, 52.7, 44.9, 31.93, 31.85, 29.6, 29.5, 29.4, 29.3, 24.8, 22.7, 21.7, 14.1; MS (m/z) 227 ($M^+ - C_{11}H_{23}$, 1.5), 197 (1.2), 173 (18), 155 (100), 91 (58); IR (neat) 3050 (Ar CH), 2925 (CH), 1595 (Ar), 1350 (SO) cm^{-1}. Anal. Calcd for $C_{21}H_{34}SO_4$: C, 65.93; H, 8.96; S, 8.38. Found: C, 66.24; H, 8.99; S, 8.11. ***erythro*-4**: ^1H NMR ($CDCl_3$) δ 7.78 (d, J = 8.4, 2 H, 2,6-Ar), 7.34 (d, J = 8.4, 2 H, 3,5-Ar), 4.18 (dt, J = 6.3, 1 H, C*H*OSO_2), 2.98 (m, 1 H, oxirane CH), 2.71 (dd, ^2J = 4.8, ^3J = 4.0, 1 H, oxirane CH_2), 2.60 (dd, ^2J = 4.8, ^3J = 2.4, 1 H, oxirane CH_2), 2.45 (s, 3 H, $ArCH_3$) 1.69 (m, 2 H, CH_2CHOSO_2), 1.25 (br s, 18 H, $(CH_2)_9$), 0.88 (t, J = 6.6, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 144.8, 134.1, 129.7, 127.8, 82.2, 52.1, 46.4, 32.3, 31.9, 29.6, 29.3, 29.1, 24.4, 22.7, 21.6, 14.1; MS (m/z) 241 ($M^+ - C_{10}H_{21}$, 0.1), 227 (0.2), 173 (18), 155 (100), 91 (61); IR (neat) 3050 (Ar CH), 2930 (CH), 1595 (Ar), 1350 (SO) cm^{-1}. Anal. Calcd for $C_{21}H_{34}SO_4$: C, 65.93, H, 8.96; S, 8.38. Found: C, 65.95; H, 8.97; S, 8.42.

1-Iodo-1,4-heptadiyne (5). The procedure described by Corey and Kang was followed.[38] To a solution of 1,4-heptadiyne (5.0 g, 54 mmol) in anhydrous ether (75 mL) cooled to −50 °C was added a solution of ethylmagnesium bromide in ether (19.6 mL, 2.76 M, 5.40 mmol) in four small portions via syringe. During the addition, the temperature was maintained below −35 °C, and then the mixture was slowly warmed to room temperature and stirred for 2.25 h. The mixture was cooled to −30 °C, and pulverized iodine (16.5 g, 54.0 mmol) was added to the dark amber solution. After the mixture was warmed to room temperature and stirred for 1 h, most of the iodine had reacted and the mixture was poured into a separatory funnel containing 50 mL of 10% aqueous sodium thiosulfate. The layers were separated, the aqueous layer was extracted with ether, and the combined ether solutions were dried and evaporated to afford 10 g of a dark brown liquid. TLC (10% ethyl acetate in hexanes) revealed a large, UV-active spot at R_f 0.73 corresponding to product and a smaller spot at R_f 0.42 corresponding to 1,4-heptadiyne. The

(38) Corey, E. J.; Kang, J. *Tetrahedron Lett.* **1982**, *23*, 1651.

crude product was purified on a silica gel column to afford 5.4 g (46%) of **5** as an unstable, clear purple liquid: ^{1}H NMR ($CDCl_3$) δ 3.31 (t, J = 2.4, 2 H, C≡CCH_2C≡C), 2.19 (br q, J = 7.2, 2 H, CH_2CH_3), 1.11 (t, J = 7.2, 3 H, CH_3); MS (m/z) 218 (M^+, 100), 189 (10), 127 (22.1), 91 (51.9), 65 (47.2).

1-Bromo-1,4-heptadiyne (6). The procedure described by Hofmeister *et al.* was followed.[20] To a stirred solution of 1,4-heptadiyne (1.50 g, 16.3 mmol) in anhydrous acetone was added NBS (3.38 g, 19.0 mmol) along with $AgNO_3$ (272 mg, 1.60 mmol). The reaction was 97% complete after 15 min as determined by analytical GC (3% DEGS) of an aliquot (0.2 mL) which was quenched with cold distilled water (0.5 mL) and extracted with hexanes (0.5 mL). After the mixture had stirred for 45 min at rt, ether extractive workup afforded 2.68 g (98%) of **6** as an amber liquid (97% pure by GC, 3% DEGS): ^{1}H NMR ($CDCl_3$) δ 3.16 (t, ^5J = 2.4, 2 H, C≡CCH_2C≡C), 2.17 (q, ^3J = 7.2 2 H, CH_2CH_3), 1.11 (t, ^3J = 7.2, 3 H, CH_3).

(*Z,Z*)-1-Iodo-1,4-heptadiene (7). The procedure described by Corey and Kang was followed.[38] A solution of 1-iodo-1,4-heptadiyne (0.50 g, 2.3 mmol) in 5 mL of THF was cooled to −10 °C and stirred under argon. A solution of disiamylborane in THF (8.0 mL, 5.3 mmol)[39] was added by syringe over 5 min. The resulting clear orange solution was stirred under argon for 3.5 h at 0 °C and then for 2 h at room temperature. Glacial acetic acid (2.6 mL, 46 mmol) was added dropwise, and the mixture was stirred for a further 16 h at rt. The reaction mixture was then carefully poured into a separatory funnel containing 50 mL of saturated aqueous $NaHCO_3$. The organic layer was repeatedly washed with aqueous $NaHCO_3$ (4 × 20 mL), dried over Na_2SO_4 and concentrated *in vacuo* to afford 1.35 g of a light orange liquid. Chromatography (silica, hexanes) gave 288 mg (57%) of the iododiene **7** as a clear, light purple liquid: ^{1}H NMR ($CDCl_3$) δ 6.19 (m, 2 H, CH_2CH=CHI), 5.41 (m, 2 H, CH_2CH=$CHCH_2$), 2.89 (dd, J = 6.8, 2 H, C=CCH_2C=C), 2.11 (dq, ^3J = 7.2, 2 H, CH_2CH_3), 0.99 (t, J = 7.6, 3 H, CH_3); MS (m/z) 222 (M^+, 31), 193 (7), 180 (98), 127 (21), 95 (100), 55 (27).

(*Z,Z*)-1-Bromo-1,4-heptadiene (8). Employing the same procedure used for the preparation of **7**, hydroboration of **6** (1.23 g, 7.23 mmol) with a solution of $(Sia)_2BH$ (16.6 mmol) in anhydrous THF, followed by protonolysis with glacial acetic acid (45 mmol), gave 2.27 g of a crude amber liquid. Chromatography (silica, hexanes) afforded 257 mg (20%) of bromo diene **8** as a clear, light amber liquid: ^{1}H NMR ($CDCl_3$) δ 6.15 (m, 2 H, CH_2CH=$CHBr$), 5.40 (m, 2 H, CH_2CH=$CHCH_2$), 2.94 (dd, J = 5.6, 2 H, C=CCH_2C=C), 2.10 (dq, J = 7.2, 2 H, CH_2CH_3), 1.00 (t, J = 8, 3 H, CH_3); MS (m/z) 176 (M^+, 10), 134 (47), 95 (M − Br, 100).

Reaction of (±)-3 with Lithium Bis((*Z,Z*)-1,4-heptadienyl)copper Dimethyl Sulfide Complex. A solution of iodo diene **7** (10 mg, 0.49 mmol) in 4 mL of THF, 1 mL of ether, and 1 mL of pentane was cooled to −130 °C under argon. A solution of *t*-BuLi in pentane (0.58 mL, 1.7 M, 0.98 mmol) was added dropwise via syringe, and the resulting yellow solution was stirred for 1 h at −130 to −140 °C. The dimethyl sulfide complex of copper(I) iodide (66 mg, 0.26 mmol) was added at −100 °C, and then the mixture was slowly warmed to −45 °C and stirred for 1.2 h. A solution of (±)-**3** (50 mg, 0.13 mmol) in 1.5 mL of THF was added by syringe over 2 min to the dark green slurry. The mixture was warmed slowly to −5 °C and stirred at this temperature for 16 h. The reaction mixture was treated with an equal volume of water and extracted with ether to give 46 mg of an amber oil. Chromatography (silica) gave 2 mg of (±)-**3** along with 28 mg (64%) of 2-(iodomethyl)-3-undecyloxirane (**9**): ^{1}H NMR ($CDCl_3$) δ 3.3 (m, 2 H, CH_2I), 3.0 (m, 2 H, oxirane CH), 1.31 (m, 20 H, $(CH_2)_{10}$), 0.92 (t, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 60.0, 56.8, 31.9, 22.7, 14.2, 1.4 (CH_2I); MS (m/z) 211 (M^+ − I, 10), 197 (3), 183 (5), 155 (11), 127 (6), 83 (95), 69 (100).

Reaction of (±)-3 with Lithium Di(*n*-butyl)copper. A solution of *n*-BuLi in hexanes (0.19 mL, 1.55 M, 0.29 mmol) was added by syringe to a suspension of copper(I) iodide (27 mg, 0.14 mmol), which was stirred at −50 to −60 °C in diethyl ether. After 25 min, the brown mixture was cooled to −78 °C, and a solution of (±)-**3** (50 mg, 0.13 mmol) in ether was added by syringe; the mixture was then stirred for 2 h and 10 min at −78 °C. Dilution with water and ether extraction gave 42 mg of a white solid. Purification by flash chromatography[17] (9:2 hexanes/ethyl acetate, v/v) afforded 14 mg (40%) of 6-octadecanone (**11**) as a white solid, mp 35–37 °C. This product was spectroscopically and chromatographically identical with a sample prepared by PCC oxidation of 6-octadecanol: ^{1}H NMR ($CDCl_3$) δ 2.37 (t, J = 7.2, 4 H, $CH_2C(O)CH_2$), 1.25 (br s, 26 H, $(CH_2)_{10}$, $(CH_2)_3$) 0.87 (t, J = 5.7, 6 H, $(CH_3)_2$); ^{13}C NMR ($CDCl_3$) δ 211.6, 42.8, 42.8, 31.9, 31.5, 29.6, 29.3, 23.9, 23.6, 22.7, 22.5, 14.1, 13.9; MS (m/z) 268 (M^+, 0.7), 239 (1.4), 225 (3), 197 (47), 99 (78), 71 (100); IR (neat) 2900 (CH), 1710 (CO) cm^{-1}.

Reaction of (±)-3 with Triethylaluminum. The method described by Suzuki *et al.* was followed.[40] A solution of (±)-**3** (78 mg, 0.20 mmol) was stirred in CH_2Cl_2 at 0 °C as a solution of triethylaluminum in hexane (0.24 mL, 1.45 M, 0.35 mmol) was added by syringe. After 1.5 h at 0 °C more triethylaluminum in hexane was added (0.22 mL, 1.45 M, 0.32 mmol), and the resulting mixture was stirred overnight at 3 °C. Ether extractive workup gave 48 mg of a clear oil. Flash chromatography[17] (15 × 1 cm column, 4:1 hexanes/ethyl acetate, v/v) afforded 21 mg (39%) of 4-ethyl-4-hexadecanol (**13**) as a clear, colorless oil: ^{1}H NMR ($CDCl_3$) δ 1.25 (m, 28 H, $(CH_2)_{11}$, $(CH_2)_2$, CH_2), 0.85 (m, 9 H, $(CH_3)_2$); MS (m/z) 252 (M − H_2O, 0.2), 241 (M − C_2H_5, 17), 227 (M − C_3H_7, 21), 101 (100).

(±)-*cis*-2-(2,5-Octadiynyl)-3-undecyloxirane (15). A solution of 1,4-heptadiyne (133 mg, 1.44 mmol) in 3 mL of anhydrous THF was stirred at −78 °C as a solution of *n*-BuLi in hexanes (0.50 mL, 1.45 M, 0.72 mmol) was added dropwise. The resulting dark orange solution was stirred for 20 min, and then BF_3·Et_2O (0.90 mL, 0.72 mmol) was added by syringe. After another 20 min, a solution of (±)-**3** (100 mg, 0.26 mmol) in 1 mL of THF was added via syringe, and the reaction mixture was stirred for 4.5 h at −78 °C. After addition of several mL of saturated aqueous NH_4Cl, extraction with ether afforded a dark brown residue. This crude sample of **14** was redissolved in anhydrous methanol (3 mL) and treated with anhydrous K_2CO_3 (79 mg, 0.57 mmol) with vigorous stirring at room temperature. The cloudy orange reaction mixture was stirred for 3.5 h, and then several mL of saturated aqueous NH_4Cl was added. Ether extractive workup gave 84 mg of a dark brown solid. Flash chromatography[17] (15 × 1 cm, 11:1 hexanes/ethyl acetate, v/v) afforded 44 mg (56%) of (±)-**15** as a clear oil which solidified below room temperature: ^{1}H NMR ($CDCl_3$) δ 3.14 (m, 3 H, C≡CCH_2C≡C, oxirane CH), 2.95 (dt, ^3J = 4.5, 5.5, 1 H, oxirane CH), 2.57 (ddt, ^2J = 17.1, ^3J = 5.4, ^5J = 2.7, 1 H, CH*H*CH(O)CH), 2.27 (ddt, ^2J = 17.1, ^3J = 7.2, ^5J = 2.1, 1 H, C*H*HCH(O)CH), 2.18 (qt, ^3J = 7.5, ^5J = 2.4, 2 H, CH_3CH_2C≡C), 1.57 (br m, 2 H, CH(O)HCH_2), 1.26 (br s, 18 H, $(CH_2)_9$), 1.12 (t, J = 7.5, 3 H, CH_3CH_2C≡C), 0.88 (t, J = 6.9, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 81.9, 76.6, 75.2, 73.2, 60.0, 54.9, 31.8, 29.6, 29.5, 29.3, 27.5, 26.4, 22.6, 19.5, 18.7, 14.0, 13.8, 12.3, 9.6; MS (m/z) 302 (M^+, 0.8), 287 (0.8), 273 (1.6), 235 (17), 161 (20), 91 (100), 81 (78), 67 (86), 55 (89%); IR (neat) 2925 (CH), 2200 (C≡C, weak), 1460 cm^{-1}; HRMS (m/z) calcd for $C_{21}H_{34}O$ 302.2601, found 302.2614.

(*Z,Z*)-(±)-*cis*-2-(2,5-Octadiynyl)-3-undecyloxirane (16). Lindlar's catalyst (5% palladium on $CaCO_3$ poisoned with lead, 12 mg) and quinoline (4 mg) were placed in a 25-mL flask equipped with a side arm and a rubber septum. The flask was alternately evacuated (0.1 mmHg) and filled with hydrogen several times. A solution of (±)-**15** (122 mg, 4.0 mmol) in 3 mL of pentane was added through the septum via syringe, and the suspension was stirred at room temperature. After 1.5 h the reaction mixture was filtered through a 1.5-in. plug of activity III silica gel, eluting with 11:1 (v/v) hexanes/ethyl acetate. The combined fractions were dried over anhydrous $MgSO_4$ and filtered, and the solvent was removed *in vacuo* to afford 116 mg (91%) of (±)-**16** as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 5.50–5.32 (m, 4 H, olefinic), 2.94 (m, 2 H, oxirane CH), 2.81 (dd, J = 6.3, 2 H, C=CCH_2C=C), 2.42 (dt, ^2J = 19.5, ^3J = 6.3, 1 H, CH=CHC*H*HCH(O)CH), 2.24 (dt, ^2J = 19.5, ^3J = 6.3, 1 H, CH=CHCH*H*CH(O)CH), 2.08 (dq, J = 6.9, 2 H, CH_3CH_2CH=CH), 1.55 (br m, 2 H, CH(O)CHCH_2), 1.26 (br s, 18 H, $(CH_2)_9$), 0.98 (t, J = 7.5, 3 H, CH_3CH_2CH=CH), 0.88 (t, J = 6.9, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 132.1, 130.7, 126.6, 124.2, 57.1, 31.9, 29.6, 29.3, 27.8, 26.6, 26.3, 25.7, 22.7, 20.6, 14.2,

(39) Brown, H. C. *Organic Syntheses via Boranes*; John Wiley and Sons: New York, 1975.

(40) Suzuki, T.; Hiroyuki, S.; Tomioka, H.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1982**, *23*, 3597.

14.1; MS (*m/z*) 306 (M^+, 0.1), 108 (52), 79 (100); IR (neat) 2925 (CH), 1650 (C=C), 1460, 1380, 1260 cm^{-1}. Synthetic (±)-**16** was found to be chromatographically identical with samples of the natural pheromone isolated from sex glands of *C. gangis* females.[26] The only spectroscopic difference was that synthetic samples gave additional ^{13}C NMR resonances in the expanded olefinic region attributed to 15–20% of the *E,Z* and *E,E* isomers.

(±)-*trans*-2-(2,5-Octadiynyl)-3-undecyloxirane (17). The same procedure was followed as described for the preparation of (±)-**15**. Epoxy tosylate (±)-**4** (246 mg, 6.43 mmol) yielded (±)-**17** (94 mg, 49%; 54% based on recovered (±)-**4**) as an amber oil which solidified just below room temperature. Purification was accomplished by flash chromatography[17] (15 × 1 cm, hexanes/ethyl acetate): ^1H NMR ($CDCl_3$) δ 3.12 (quint, J = 2.4, 2 H, $C{\equiv}CCH_2C{\equiv}C$), 2.83 (m, 2 H, oxirane CH), 2.57 (ddt, ^2J = 17.1, ^3J = 5.1, ^5J = 2.1, 1 H, $C{\equiv}CCHHCH(O)CH$), 2.39 (ddt, ^2J = 17.1, ^3J = 5.1, ^5J = 2.7, 1 H, $C{\equiv}CCHHCH(O)CH$), 2.16 (qt, ^3J = 7.5, ^5J = 2.4, 2 H, $CH_3CH_2C{\equiv}C$), 1.55 (br m, 2 H, $CH(O)CHCH_2$), 1.25 (br s, 18 H, $(CH_2)_9$), 1.11 (t, J = 7.5, 3 H, $CH_3CH_2C{\equiv}C$), 0.87 (t, J = 6.6, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 82.0, 76.8, 74.9, 73.3, 58.5, 56.2, 31.9, 31.6, 29.63, 29.64, 29.4, 25.9, 22.7, 22.3, 14.1, 13.9, 12.4, 9.8; MS (*m/z*) 211 ($M - C_7H_7$, 1.2), 111 (20), 97 (50), 83 (60), 69 (90), 55 (100); IR (neat) 2890 (CH), 2217 (C≡C, weak), 1462, 1377, 1322 cm^{-1}.

(*Z,Z*)-(±)-*trans*-2-(2,5-Octadienyl)-3-undecyloxirane (18). The same procedure was followed as described for the catalytic hydrogenation of (±)-**15**. Trans epoxy diyne (±)-**17** (94 mg, 0.31 mmol) yielded 88 mg (93%) of (±)-**18** as a colorless liquid: ^1H NMR ($CDCl_3$) δ 5.50–5.32 (m, 4 H, olefinic), 2.79 (t, J = 6.9, 2 H, $C{=}CCH_2C{=}C$), 2.71 (t, J = 5.1, 2 H, oxirane CH), 2.44 (dt, ^2J = 19.5, 1 H, $CH{=}CHCHHCH(O)CH$), 2.26 (dt, ^2J = 19.5, 1 H, $CH{=}CHCHHCH(O)CH$), 2.07 (quint, J = 7.8, 2 H, CH_3CH_2-$CH{=}CH$), 1.50 (br m, 2 H, $CH(O)CHCH_2$), 1.26 (br s, 18 H, $(CH_2)_9$), 0.98 (t, J = 7.8, 3 H, $CH_3CH_2CH{=}CH$), 0.88 (t, J = 6.9, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 132.1, 130.9, 126.7, 123.6, 58.4, 57.9, 31.9, 30.0, 29.6, 29.5, 29.39, 29.35, 26.0, 25.6, 22.7, 20.5, 14.2, 14.1; MS (*m/z*) 288 ($M - H_2O$, 0.4), 108 (55), 93 (44), 79 (100); IR (neat) 2925 (CH), 1650 (C=C), 1460 cm^{-1}; HRMS (*m/z*) calcd for $C_{21}H_{36}$ ($M - H_2O$) 288.2817, found 288.2848. The product contained no (±)-**16** (and *vice versa*) according to capillary GC analysis (DB-5, 29 m × 0.25 mm, 50–250 °C, retention times: (±)-**16**, 41.7;(±)-**18**, 41.5 m).

(±)-*cis*-2-(2-Octynyl-3-undecyloxirane (19). The same procedure was followed as described for the preparation of (±)-**15** using 1-heptyne (100 mg, 1.04 mmol), *n*-butyllithium in hexanes (0.36 mL, 1.45 M, 0.25 mmol), and $BF_3{\cdot}Et_2O$ (0.65 mL, 0.52 mmol). Reaction of (±)-**3** (71 mg, 0.19 mmol) gave 32 mg (56%) of (±)-**19** as a waxy, yellow solid. Purification was accomplished by flash chromatography[17] (15 × 1 cm, 8:1 hexanes/ethyl acetate, v/v): ^1H NMR ($CDCl_3$) δ 3.10 (m, 1 H, oxirane CH), 2.95 (dt, J = 5.7, 1 H, oxirane CH), 2.56 (ddt, ^2J = 16.5, ^3J = 5.4, ^5J = 2.1, 1 H, $C{\equiv}CCHHCH(O)CH$), 2.22 (ddt, ^2J = 16.5, ^3J = 7.5, ^5J = 2.4, 1 H, $C{\equiv}CCHHCH(O)CH$), 2.15 (tt, ^3J = 7.2, ^5J = 2.1, 2 H, $CH_2CH_2C{\equiv}C$), 1.50 (br m, 2 H, $CH(O)CHCH_2$), 1.26 (br s, 18 H, $(CH_2)_9$), 0.89 (t, J = 6.9, 3 H, CH_3), 0.88 (t, J = 6.9, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 82.5, 74.8, 57.1, 55.4, 31.9, 31.1, 29.56, 29.46, 29.4, 28.6, 27.6, 26.5, 22.7, 22.2, 18.8, 18.7, 14.1, 14.0; MS (*m/z*) 263 ($M - C_3H_7$, 2.2), 235 (2), 179 (10), 165 (19), 151 (25), 81 (71), 67 (79), 55 (100); IR (neat) 2920 (CH), 2210 (C≡C, weak), 1460 cm^{-1}.

(*Z*)-(±)-*cis*-2-(2-Octynyl)-3-undecyloxirane (20). The same procedure was followed as described for the catalytic hydrogenation of (±)-**16**. Epoxyalkyne **19** (44 mg, 0.14 mmol) gave 39 mg (89%) of (±)-**20** as a clear, colorless oil, which was purified by flash chromatography[17] (15-in. × 1 cm, 11:1 hexanes/ethyl acetate): ^1H NMR ($CDCl_3$) δ 5.6–5.3 (m, 2 H, olefinic), 2.93 (br m, 2 H, oxirane CH), 2.37 (dt, ^2J = 15.3, ^3J = 6.6, 1 H, $CH{=}CHCHHCH(O)CH$), 2.18 (dt, ^2J = 15.3, ^3J = 7.5, 1 H, $CH{=}CHCHHCH(O)CH$), 2.04 (m, 2 H, $CH_2CH_2CH{=}CH$), 1.53 (br m, 2 H, $CH(O)CHCH_2$), 1.27 (br s, 24 H, $(CH_2)_3$, $(CH_2)_9$), 0.89 (t, J = 6.7, 3 H, CH_3), 0.88 (t, J = 6.6, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 132.7, 123.8, 57.2, 56.6, 31.9, 31.5, 29.7, 29.6, 29.4, 29.3, 27.8, 27.5, 26.6, 26.3, 22.7, 22.6, 14.11, 14.06; MS (*m/z*) 251 ($M - C_4H_9$, 0.6), 237 (1.6), 211 (0.2), 197 (0.5), 153 (5), 81 (76), 69 (88), 55 (100%); IR (neat) 2890 (CH), 1654 (C=O), 1466, 1261 cm^{-1}.

(2*R*,3*R*,*S*)-1,2-*O*-Isopropylidene-1,2,3-tetradecanetriol (22). A solution of (*R*)-glyceraldehyde acetonide (**21**) (10.3 g, 79.0 mmol) in 20 mL of anhydrous ether was cooled to 0 °C, and a solution of undecylmagnesium bromide in ether (215 mL, 0.46 M, 99 mmol) was added. The clear, bronze-colored mixture was stirred for 3 h at 0 °C and then placed in a refrigerator (8 °C) overnight. After the excess Grignard reagent was destroyed by addition of 200 mL of saturated aqueous NH_4Cl, ether extractive workup afforded 30.9 g of a clear, colorless oil. Vacuum distillation gave 10.8 g (50%) of a 3:1 mixture of erythro/threo alcohols as a clear, colorless oil (bp 131–135 °C, 0.1 mmHg). A portion of the distilled alcohol (1.30 g) was purified by flash chromatography[17] (15-in. × 4 cm, 13% ethyl acetate in CH_2Cl_2) to afford 132 mg of *threo*-**22** (R_f 0.75) and 498 mg of *erythro*-**22** (R_f 0.69) as colorless oils. ***threo*-22**: ^1H NMR ($CDCl_3$) δ 3.97 (m, 2 H, $CH_2(O)CHO$), 3.70 (m, 1 H, $CH_2(O)CHO$), 3.46 (m, 1 H, $CHOH$), 1.40 (s, 3 H, CH_3), 1.34 (s, 3 H, CH_3), 1.23 (br s, 20 H, $(CH_2)_9$), 0.85 (t, J = 6, 3 H, CH_2CH_3); ^{13}C NMR ($CDCl_3$) δ 109.3, 79.2, 72.2, 66.1, 33.6, 31.9, 29.6, 29.5, 29.3, 26.6, 25.5, 25.3, 22.6, 14.1; IR (neat) 3478 (OH), 2900 (CH), 1467, 1370, 1068 cm^{-1}; $[\alpha]^{23}_D$ = +12.2° (*c* 5, $CHCl_3$). Anal. Calcd for $C_{17}H_{34}O_3$: C, 71.28; H, 11.96. Found: C, 71.47; H, 12.31. ***erythro*-22**: ^1H NMR ($CDCl_3$) δ 3.93 (m, 3 H, $CH_2(O)CHO$), 3.72 (br m, 1 H, $CHOH$), 1.39 (s, 3 H, CH_3), 1.33 (s, 3 H, CH_3), 1.23 (br s, 20 H, $(CH_2)_9$), 0.84 (t, J = 7, 3 H, CH_2CH_3); ^{13}C NMR ($CDCl_3$) δ 108.3, 78.7, 70.6, 64.5, 32.6, 31.9, 29.54, 29.48, 29.3, 29.2, 26.4, 25.7, 25.3, 22.6, 14.1; IR (neat) 3450 (OH), 2925 (CH), 1460, 1375 cm^{-1}; $[\alpha]^{23}_D$ = +9.2° (*c* 5, $CHCl_3$). Anal. Calcd for $C_{17}H_{34}O_3$: C, 71.28; H, 11.96. Found: C, 71.14; H, 12.30.

(2*R*,3*R*,*S*)-1,2,3-Tetradecanetriol (23). A distilled mixture of erythro and threo alcohols (**22**) (9.86 g, 34.0 mmol) was dissolved in 164 mL of THF, and 164 mL of 1 N HCl was added. The cloudy mixture was stirred at room temperature for 3.75 h and neutralized by stirring with 250 mL of saturated aqueous $NaHCO_3$. Ether extractive workup gave 8.08 g (97%) of the crude triol as a white solid. Recrystallization from 140 mL of ethyl acetate afforded 6.70 g (80%) of a fluffy white solid, mp 76–98 °C: ^1H NMR (DMSO-d_6) δ 4.30 (m, 1 H, $CH_2(OH)$-$CHOH$), 4.05 (d, J = 6, 1 H, OH), 3.30 (m, 3 H, $CH_2(OH)CH(OH)CHOH$), 1.24 (br s, 20 H, 2 OH, $(CH_2)_9$), 0.85 (t, J = 6.6, 3 H, CH_3); ^{13}C NMR (DMSO-d_6) δ 74.8 (erythro), 74.0 (threo), 71.5 (erythro), 70.5 (threo), 63.6 (erythro), 62.9 (threo), 32.8, 31.4, 29.4, 29.3, 29.19, 29.15, 28.8, 25.7, 25.3, 22.2, 13.9; MS (*m/z*) 299 ($M - H_2O$, 4.5), 215 (8), 185 (25), 111 (100), 97 (93); IR (neat) 3250 (OH), 2900 (CH), 1460 cm^{-1}; $[\alpha]^{23}_D$ = −8.4° (*c* 5, absolute EtOH). Anal. Calcd for $C_{14}H_{30}O_3$: C, 68.25; H, 12.27. Found: C, 68.60; H, 12.60.

(2*R*,3*S*)-1-(Tosyloxy)-2,3-tetradecanediol (24). A solution of triol **23** (6.30 g, 25.6 mmol) in 10 mL of anhydrous pyridine was cooled to 0 °C, and TsCl (5.11 g, 25.6 mmol) was added in small portions over several minutes. The resulting clear, yellow mixture was stirred for three days at 5 °C and then treated with an equal volume of water. Ether extractive workup afforded 9.70 g of a white solid, which was purified by flash chromatography[17] (1:1 hexanes/ethyl acetate, v/v) and crystallization from cold pentane, yielding 5.42 g (53%) of a white solid, mp 52–55 °C: ^1H NMR ($CDCl_3$) δ 7.80 (d, J = 9, 2 H, Ar), 7.35 (d, J = 9, 2 H, Ar), 4.17 (m, 2 H, CH_2OTs), 3.72 (br m, 2 H, $CH(OH)$-$CHOH$), 2.44 (s, 3 H, $ArCH_3$), 1.25 (br s, 20 H, 2 OH, $(CH_2)_9$), 0.87 (t, J = 6.9, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 145.0, 132.3, 129.9, 127.9, 72.1, 72.0, 32.3, 31.8, 29.53, 29.49, 29.3, 25.7, 22.6, 22.5, 14.0; MS (*m/z*) 215 (2.6), 197 (0.5), 173 (100), 155 (36), 91 (48); IR (neat) 3450 (OH), 3050 (ArH), 2925 (CH), 1596 (C=C) cm^{-1}; $[\alpha]^{23}_D$ = +4.4° (*c* 5, $CHCl_3$). Anal. Calcd for $C_{21}H_{36}O_5S$: C, 62.97; H, 9.06; S, 8.00. Found: C, 63.15; H, 9.30; S, 8.22.

(2*R*,3*S*)-1,2-Epoxy-3-(tosyloxy)tetradecane (26). A solution of monotosylated triol **24** (1.00 g, 2.5 mmol) in anhydrous MeOH was stirred at 0 °C, anhydrous K_2CO_3 (695 mg, 5.0 mmol) was added, and the mixture was slowly warmed to room temperature. After 3.5 h the mixture was treated with an equal volume of water, and ether extractive workup afforded 504 mg (88%) of a white solid: mp 78–80 °C; $[\alpha]^{23}_D$ = +9° (*c* 2, $CHCl_3$). A sample of crude epoxy alcohol (**25**) was treated according to the procedure for preparation of (±)-**3**, yielding 710 mg (41%) of erythro epoxy tosylate **26** as a clear, colorless oil after purification by flash chromatography; $[\alpha]^{23}_D$ = −9.7° (*c* 10, $CHCl_3$). This product was spectroscopically and chromatographically indistinguishable from a sample of (±)-**4**.

(2*R*)-1,2-*O*-Isopropylidene-1,2-dihydroxy-3-tetradecanone (27). Procedure A.[31b] Anhydrous DMSO (5.6 mL, 6.13

g, 78.4 mmol) and P_2O_5 (11.1 g, 78.4 mmol) were added to a stirred solution of alcohol **22** (5.62 g, 19.6 mmol) in 70 mL of anhydrous CH_2Cl_2 at 0 °C. The white slurry was slowly warmed to room temperature, and stirred for 24 h, and then cooled to 0 °C, and triethylamine (14.0 mL, 9.92 g, 98.0 mmol) was added. The resulting clear, light orange mixture was stirred at 0 °C for 3 h and then stirred at rt for 2.5 h. Ether extractive workup and vacuum filtration of the ether solution through Celite/silica gel (1:1) gave 3.62 g (65%) of the desired ketone, which partially solidified. ^{1}H NMR ($CDCl_3$) δ 4.43 (m, 1 H, $CH_2(O)CHO$), 4.22 (m, 1 H, $CHH(O)CHO$), 3.97 (m, 1 H, $CHH(O)CHO$), 2.60 (t, J = 7, 2 H, $C(O)CH_2$), 1.48 (s, 3 H, CH_3), 1.39 (s, 3 H, CH_3), 1.26 (br s, 18 H, $(CH_2)_9$), 0.88 (t, J = 7, 3 H, CH_2CH_3); ^{13}C NMR ($CDCl_3$) δ 210.7, 110.7, 80.2, 66.4, 38.5, 31.9, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 25.9, 24.9, 22.9, 22.6, 14.0; MS m/z 296 (M − CH_3, 1.6), 101 (100), 73 (4.8), 43 (12.4); IR (neat) 2900 (CH), 1718 (CO), 1450, 1375 cm^{-1}. **Procedure B.**[31a] Anhydrous DMSO (5.50 mL, 6.09 g, 78.0 mmol) was added to a stirred solution of oxalyl chloride (3.4 mL, 4.92 g, 39.0 mmol) in anhydrous CH_2Cl_2 at −55 to −60 °C. A solution of alcohol **22** (10.2 g, 35.4 mmol) in 30 mL of CH_2Cl_2 was then added over 15 min followed by an additional 20 mL of CH_2Cl_2, and the resulting viscous, white mixture was stirred for 1 h at −50 to −60 °C. Triethylamine (25.0 mL, 18.0 g, 178 mmol) was added, and the mixture was slowly warmed to room temperature over 3 h and then diluted with H_2O. Ether extractive workup afforded 7.85 g (75%) of the desired ketone that was spectroscopically and chromatographically identical to the product obtained by procedure A.

(2*R*,3*R*)-1,2-*O*-Isopropylidene-1,2,3-tetradecanetriol (*threo*-22). A solution of lithium tri-*sec*-butylborohydride in THF (L-Selectride, Aldrich; 53 mL, 1.0 M) was added over 25 min to a stirred solution of crude ketone **27** (10.0 g, 35.6 mmol) in 40 mL of anhydrous THF at −78 °C. The mixture was warmed to room temperature over 5 h and then stirred overnight. Oxidation of the organoborane byproduct was accomplished by treating the clear, amber solution with 55 mL of 3 M NaOH and 50 mL of 30% H_2O_2, maintaining the temperature below 50 °C. The resulting mixture was stirred for 6 h at 35 °C. Ether extractive workup afforded the mixture of diastereomeric alcohols as a clear, yellow oil (8.51 g, 83%) exhibiting the same spectroscopic and chromatographic properties as the sample obtained by Grignard reaction of undecylmagnesium bromide with (*S*)-glyceraldehyde acetonide. The threo/erythro ratio was estimated as approximately 10:1 by comparison of ^{13}C NMR peak heights.

(2*R*,3*R*)-1,2,3-Tetradecanetriol (28). According to the procedure described for the preparation of **23**, alcohol **22** (10:1 threo/erythro; 8.51 g, 29.7 mmol) gave 5.39 g (74%) of triol **28** as a fluffy, slightly yellow crystalline solid after recrystallization from ethyl acetate, mp 63–68 °C; $[\alpha]^{23}_D$ = +8.7° (*c* 1.0, EtOH). No peaks for the erythro diastereomer were observed in the ^{13}C NMR spectrum (DMSO-d_6); all other spectroscopic properties were almost identical to those observed for **23**.

(2*R*,3*R*)-1-(Tosyloxy)-2,3-tetradecanediol (29). According to the procedure described for the preparation of **24**, triol **28** (3.00 g, 12.2 mmol) gave 1.85 g (38%) of a white solid, mp 72–74 °C; ^{1}H NMR ($CDCl_3$) δ 7.79 (d, J = 8, 2 H, Ar), 7.34 (d, J = 8, 2 H, Ar), 4.07 (m, 2 H, CH_2OTs), 3.68 (br m, 1 H, $CHOH$), 3.56 (br m, 1 H, $CHOH$), 2.85 (d, J = 6, 1 H, OH), 2.33 (d, J = 6, 1 H, OH), 2.44 (s, 3 H, $ArCH_3$), 1.24 (br s, 20 H, $(CH_2)_{10}$), 0.87 (t, J = 7, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 145.1, 132.5, 129.9, 127.9, 71.4, 70.8, 33.4, 31.9, 29.6, 29.5, 29.3, 25.5, 22.6, 21.6, 14.1; $[\alpha]^{23}_D$ = +7.2° (*c* 3.2, $CHCl_3$); MS and IR spectra were almost identical to those obtained for the erythro diastereomer **24**.

(2*R*,3*R*)-1,2-Epoxy-3-tetradecanol (30). According to the procedure described for preparation of **25**, tosylate **29** (1.80 g, 4.49 mmol) afforded 717 mg (70%) of **30** as a white solid after recrystallization from pentane, mp 41–42 °C: $[\alpha]^{23}_D$ = +4.1° (*c* 2.7, EtOH). This material was spectroscopically and chromatographically identical to samples of (±)-*threo*-**2**.

(2*R*,3*R*)-1,2-Epoxy-3-(tosyloxy)tetradecane (31). According to the procedure described for the preparation of (±)-**3**, threo epoxy alcohol **30** (651 mg, 2.85 mmol) afforded 242 mg (22%) of **31** as a white crystalline solid, mp 53–54 °C, which was spectroscopically and chromatographically identical to (±)-**3**: $[\alpha]^{23}_D$ = −7.3° (*c* 1, CCl_4).

(2*S*,3*S*)-2,3-*O*-Isopropylidene-1,2,3,4-butanetetrol *tert*-Butyldimethylsilyl Ether (33). According to the method of McDougal *et al.*,[41] a solution of diol **32** (14.1 g, 86.6 mmol) in 10 mL of anhydrous THF was added to a vigorously stirred suspension of NaH (3.45 g, 86.3 mmol; 60% dispersion in mineral oil, washed twice with pentane) in 100 mL of anhydrous THF. After 1 h, the resulting light brown gelatinous mass was treated with *tert*-butyldimethylsilyl chloride (13.0 g, 86.3 mmol), and the mixture became a cloudy brown liquid. After the mixture was stirred for 3 h, dilution with water and ether extractive workup afforded 22.3 g of a clear, yellow liquid. The crude product was dissolved in hexanes and filtered through silica gel, which was then washed with 2:1 (v/v) hexanes/ethyl acetate. Evaporation of the combined filtrates gave 15.2 g (64%) of the monosilylated diol as a clear, colorless liquid: ^{1}H NMR ($CDCl_3$) δ 3.70 (m, 6 H, CH, CH_2), 1.37 (s, 3 H, CH_3), 1.35 (s, 3 H, CH_3), 0.86 (s, 9 H, $SiC(CH_3)_3$), 0.04 (s, 6 H, $Si(CH_3)_2$); ^{13}C NMR ($CDCl_3$) δ 109.4, 80.1, 78.0, 63.6, 62.7, 27.0, 26.8, 25.8, 18.3, −5.5; MS (m/z) 261 (M − CH_3, 3.5), 219 (2), 161 (20), 131 (76.4), 117 (34.5), 75 (100), 73 (48.4), 59 (31); IR (neat) 3450 (OH), 2950 (CH), 1460, 1375 cm^{-1}; $[\alpha]^{23}_D$ = +8.1° (*c* 10, CCl_4).

(2*S*,3*S*)-2,3-*O*-Isopropylidene-2,3,4-trihydroxybutanal *tert*-Butyldimethylsilyl Ether (34). According to procedure B described for the oxidation of alcohol **22**, monosilylated diol **33** (15.2 g, 55.1 mmol) afforded 8.49 g (56%) of aldehyde **34** as a clear, yellowish oil after vacuum distillation (bp 93–95 °C, 0.4 mmHg): ^{1}H NMR ($CDCl_3$) δ 9.64 (d, J = 1.5, 1 H, CHO), 4.19 (dd, ^3J = 7, 1.5, 1 H, $CHCHO$), 3.98 (dt, ^3J = 7, 4.5, 1 H, $CH(O)CH(O)CHO$), 3.68 (dd, ^2J = 11, ^3J = 4.5, 1 H, $CHHOSi$), 3.66 (dd, ^2J = 11, ^3J = 4.5, 1 H, $CHHOSi$), 1.34 (s, 3 H, CH_3), 1.29 (s, 3 H, CH_3), 0.77 (s, 9 H, $SiC(CH_3)_3$), −0.04 (s, 6 H, $Si(CH_3)_3$); ^{13}C NMR ($CDCl_3$) δ 200.5, 111.2, 81.8, 77.4, 62.8, 26.7, 25.9, 25.7, 18.2, −5.5; MS m/z 259 (M − CH_3, 2.0), 245 (2.8), 217 (3), 159 (30), 129 (45), 117 (100), 101 (53.7), 89 (55), 75 (82.8), 73 (63.6); IR (neat) 2950 (CH), 1735 (CO), 1460, 1375 cm^{-1}; $[\alpha]^{23}_D$ = +8.9 (*c* 8.5, $CHCl_3$); HRMS (m/z) calcd for $C_{12}H_{23}O_4Si$ (M − CH_3) 259.1359; found 259.1358 (3.1%).

(4*E*,*Z*)-(2*S*,3*S*)-2,3-*O*-Isopropylidene-4-tetradecene-1,2,3-triol *tert*-Butyldimethylsilyl Ether (35). A solution of *n*-decyltriphenylphosphonium bromide[34] in anhydrous THF (15.6 mL, 0.90 M, 14.0 mmol) was added to a flask containing 40 mL of anhydrous THF. This solution was stirred at −78 °C, and a solution of *n*-BuLi in hexanes (5.5 mL, 2.55 M, 15.0 mmol) was added. The reaction mixture was warmed to room temperature overnight, and 15 mL of absolute ethanol was added to quench any unreacted *n*-BuLi. The resulting burgundy-colored solution was concentrated *in vacuo*, and the residue was purified by silica chromatography (5:1 hexanes/ethyl acetate, v/v) to afford 3.48 g (77%) of the olefin as a clear, yellowish oil: ^{1}H NMR ($CDCl_3$) δ 5.65 (m, 1 H, olefinic), 5.40 (m, 1 H, olefinic), 4.78 (dd, 1 H, $CH(O)CH{=}CH$), 3.78 (m, 1 H, $CH(O)CH(O)CH{=}CH$), 3.64 (m, 2 H, CH_2OSi), 2.10 (br m, 2 H, $C{=}CCH_2$), 1.43 (s, 3 H, CH_3), 1.42 (s, 3 H, CH_3), 1.26 (br s, 14 H, CH_2), 0.90 (s, 9 H, $SiC(CH_3)_3$), 0.88 (t, J = 7, 3 H, CH_2CH_3), 0.07 (s, 3 H, $SiCH_3$), 0.06 (s, 3 H, $SiCH_3$); ^{13}C NMR ($CDCl_3$) δ 136.1, 126.4, 108.7, 81.8, 72.8, 61.5, 31.9, 29.7, 29.5, 29.3, 27.8, 27.3, 26.9, 25.9, 14.1, −5.48; MS (m/z) 283 (M − $Si(CH_3)_2C(CH_3)_3$, 25), 209 (14), 173 (20), 143 (30), 117 (100), 89 (56.8), 75 (71), 73 (62); IR (neat) 3025 (CH=CH), 2950 (CH), 1660 (C=C), 1460, 1375 cm^{-1}; $[\alpha]^{23}_D$ = −3.3° (*c* 10, $CHCl_3$).

(4*E*,*Z*)-(2*S*,3*S*)-2,3-*O*-Isopropylidene-4-tetradecene-1,2,3-triol 1-*O*-Benzyl Ether (41). Aldehyde **40** was prepared by oxidation of alcohol **39**[11a] according to procedure B described for oxidation of alcohol **22**. According to the procedure described for the preparation of **35**, aldehyde **40** (1.37 g, 5.47 mmol) was converted to 1.17 g (57%) of olefin **41** after silica chromatography (hexanes/ethyl acetate): ^{1}H NMR ($CDCl_3$) δ 7.27 (m, 5 H, Ar), 5.60 (dt, J = 12, 9, 1 H, olefinic), 5.32 (m, 1 H, olefinic), 4.58 (m, 1 H, $CH(O)CH{=}CH$), 4.52 (s, 2 H, CH_2OCH_2Ph), 3.80 (m, 1 H, $CH(O)CH(O)CH{=}CH$), 3.53 (m, 2 H, CH_2OCH_2Ph), 2.00 (m, 2 H, $C{=}CCH_2$), 1.38 (s, 6 H, $O_2C(CH_3)_2$), 1.20 (br s, 14 H, $(CH_2)_7$), 0.82 (t, J = 6, 3 H, CH_2CH_3); ^{13}C NMR ($CDCl_3$) δ 137.9, 136.3, 133.7, 128.2, 127.5, 126.1, 109.0, 80.4, 73.5, 69.1, 31.8, 29.51, 29.46, 29.4, 29.24, 29.15, 27.7, 27.1, 26.9, 22.6, 14.0; MS (m/z) 253 (M − CH_2OCH_2Ph, 0.7), 224 (8), 209 (11), 97 (30), 91 (100); IR (neat) 3050 (ArCH), 2925 (CH), 1650 (C=C), 1450, 1375 cm^{-1}; $[\alpha]^{23}_D$ = +2.1° (*c* 10, $CHCl_3$).

(41) McDougal, P. G.; Rico, J. G.; Young-Im, O.; Condon, B. D. *J. Org. Chem.* **1986**, *51*, 3388.

(2*S*,3*S*)-2,3-*O*-Isopropylidene-1,2,3-tetradecanetriol (36). Method A. To a stirred solution of silyl ether **35** (3.47 g, 8.70 mmol) in 40 mL of anhydrous THF was added $(n\text{-Bu})_4NF{\cdot}3H_2O$ (8.24 g, 26.1 mmol). Ether extractive workup gave 3.51 g of an amber liquid. Silica chromatography afforded 2.25 g (91%) of the unsaturated alcohol as a clear, slightly yellow oil. IR (neat) 3450 (OH), 3025 (CH=CH), 2950 (CH), 1650 (C=C), 1460, 1375 cm^{-1}. A solution of the unsaturated alcohol (226 mg, 0.79 mmol) in 22 mL of EtOH was hydrogenated at 38 psi over 190 mg of 5% palladium on carbon. Filtration of the reaction mixture through a 2 in. plug of activity III silica gel with ether elution and concentration of the filtrate *in vacuo* gave 180 mg (80%) of **36** as a clear, yellow oil: ^1H NMR ($CDCl_3$) δ 3.75 (m, 4 H, CH(O), CH_2O), 1.42 (br s, 6 H, $O_2C(CH_3)_2$), 1.27 (br s, 20 H, $(CH_2)_{10}$), 0.89 (t, J = 7, 3 H, CH_2CH_3); ^{13}C NMR (C_6D_6) δ 108.6, 82.3, 77.7, 63.5, 33.6, 32.3, 30.10, 30.05, 30.0, 29.8, 27.7, 27.3, 26.6, 23.1, 14.3; MS (m/z) 271 (M − CH_3, 43), 255 (7), 109 (30), 95 (53), 81 (40), 59 (100), 43 (53); IR (neat) 3425 (OH), 2925 (CH), 1460, 1360 cm^{-1}. **Method B.** Hydrogenolysis–hydrogenation of **41** (1.38 g, 3.70 mmol) was carried out under the conditions described above to yield 0.89 g (85%) of **36** as a semisolid which was spectroscopically and chromatographically identical to the sample prepared from **35**.

(2*S*,3*S*)-1,2-Epoxy-3-tetradecanol (37). Method A. According to the procedure described for the preparation of **24**, alcohol **36** (0.89 g, 3.1 mmol) gave 1.5 g of crude (2*S*,3*S*)-2,3-*O*-isopropylidene-1-(tosyloxy)-2,3-tetradecanediol as a clear yellow oil: ^1H NMR ($CDCl_3$) δ 7.80 (d, J = 8, 2 H, Ar), 7.30 (d, J = 8, 2 H, Ar), 4.06 (m, 2 H, CH_2OTs), 3.25 (m, 2 H, CH(O)C*H*O), 2.44 (s, 3 H, $ArCH_3$), 1.35 (s, 3 H, CH_3), 1.29 (s, 3 H, CH_3), 1.25 (br s, 20 H, $(CH_2)_{10}$), 0.87 (t, J = 7, 3 H, CH_2CH_3). This oil was stirred with 1% methanolic HCl for 1 h; ether extractive workup gave 0.30 g of (2*S*,3*S*)-1-(tosyloxy)-2,3-tetradecanediol as a white solid. The crude monotosylated triol was dissolved in 5 mL of anhydrous MeOH and treated with anhydrous K_2CO_3 (195 mg, 1.40 mmol). The cloudy white mixture was stirred vigorously for 4 h at room temperature, and ether extractive workup afforded 135 mg (84% from **36**) of **37** as a white solid, spectroscopically and chromatographically identical with a sample of (±)-*threo*-**2**. **Method B.** According to the procedure described for the preparation of **23**, alcohol **36** (1.40 g, 4.89 mmol) afforded 1.0 g (84%) of (2*S*,3*S*)-1,2,3-tetradecanetriol as a white, crystalline solid, mp 65–69 °C: ^{13}C NMR (DMSO-d_6) δ 74.0, 70.5, 62.8, 32.8, 31.3, 29.3, 29.2, 29.17, 29.12, 28.8, 25.7, 22.1, 13.9; $[\alpha]^{23}_D$ = −8.2° (*c* 5.0, EtOH). According to the procedure for preparation of **24**, the triol (1.96 g, 7.95 mmol) was converted to 1.16 g (36%) of (2*S*,3*S*)-1-(tosyloxy)-2,3-tetradecanediol, obtained as a white solid: mp 71–73 °C; $[\alpha]^{23}_D$ = −7.5° (*c* 4.4, $CHCl_3$). This material was spectroscopically and chromatographically identical to its enantiomer (**30**) prepared from D-mannitol. The monotosylated triol (1.11 g, 2.77 mmol) was converted to 0.57 g (90%) of the epoxy alcohol according to the procedure described for the preparation of **25**. The product was obtained as a powdery white solid, mp 39–40 °C: $[\alpha]^{23}_D$ = 5.8° (*c* 3.8, EtOH). This material was spectroscopically and chromatographically identical to a sample of (±)-threo epoxy alcohol **2**.

(2*S*,3*S*)-1,2-Epoxy-3-(tosyloxy)tetradecane (38). According to the procedure described for the preparation of (±)-**3**, epoxy alcohol **37** (548 mg, 2.40 mmol) gave 212 mg (23%) of **38** as a crystalline white solid after recrystallization cold pentane, mp 55–58 °C. This material was spectroscopically and chromatographically identical with a sample of (±)-**3**: $[\alpha]^{23}_D$ = +8.7° (*c* 1, CCl_4).

(2*R*,3*R*)-2-(2-Octynyl)-3-undecyloxirane (42). The procedure described for the preparation of (±)-**15** was followed. Erythro epoxy tosylate **26** (200 mg, 0.52 mmol) afforded, after flash chromatography, 83 mg (52%) of **42** as a clear, colorless oil which solidified just below room temperature: ^1H NMR ($CDCl_3$) δ 2.80 (m, 2 H, oxirane CH), 2.56 (ddt, ^2J = 16, ^3J = 6, ^5J = 2.4, 1 H, C*H*HCH(O)CH), 2.33 (ddt, ^2J = 16, ^3J = 5, ^5J = 2.4, 1 H, C≡CCH*H*CH(O)CH), 2.13 (tt, ^3J = 7, ^5J = 2.4, 2 H, C≡CCH_2), 1.50 (m, 2 H, CH(O)CHCH_2), 1.25 (br s, 18 H, $(CH_2)_9$), 0.89 (t, J = 7, 3 H, CH_3), 0.87 (t, J = 7, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 82.5, 74.9, 58.3, 56.5, 31.9, 31.6, 31.0, 29.6, 29.5, 29.3, 28.6, 26.0, 22.7, 22.3, 18.7, 14.1, 14.0; MS (m/z) 306 (M, 0.2), 291 (0.2), 263 (4), 165 (20), 95 (40), 81 (83), 67 (80), 55 (100), 43 (100); IR (neat) 2900 (CH), 2216 (C≡C, weak), 1463 cm^{-1}; $[\alpha]^{23}_D$ = −4.2° (*c* 5.2, CCl_4); HRMS m/z calcd for $C_{21}H_{38}O$ (M^+), 306.2913; found 306.2914 (2.9).

(2*S*,3*R*)-*cis*-2-(2,5-Octadiynyl)-3-undecyloxirane (15). The procedure described for the preparation of (±)-**15** was followed. Threo epoxy tosylate **38** (100 mg, 0.26 mmol) afforded 36 mg (46%) of (2*S*,3*R*)-**15** as a waxy, yellow solid after flash chromatography. This material was spectroscopically and chromatographically identical to a sample of (±)-**15**: $[\alpha]^{23}_D$ = +52.2° (*c* 3.6, CCl_4).

(*Z*,*Z*)-(2*S*,3*R*)-*cis*-2-(2,5-Octadienyl)-3-undecyloxirane (16). The procedure described for the preparation of (±)-**16** was followed. (2*S*,3*R*)-**15** (32 mg, 0.11 mmol) afforded 11 mg (33%) of (*Z*,*Z*)-(2*S*,3*R*)-**16** as a clear oil after 2-fold purification by flash chromatography. This material was spectroscopically and chromatographically identical to a sample of (±)-**16**. Examination of the olefinic carbon region of the expanded ^{13}C NMR spectrum revealed three small signals (123.8, 124.3, 133.2) ca. 10% as intense as those of the major signals, implying geometrical purity >85%: $[\alpha]^{23}_D$ = +7.7° (*c* 1.0, CCl_4).

(2*R*,3*S*)-*cis*-2-(2,5-Octadiynyl)-3-undecyloxirane (15). The procedure described for the preparation of (±)-**15** was followed. Threo epoxy tosylate **31** (110 mg, 0.288 mmol) afforded 28 mg (32%) of (2*R*,3*S*)-**15** as a waxy, yellow solid after flash chromatography. This material spectroscopically and chromatographically identical to a sample of (±)-**15**: $[\alpha]^{23}_D$ = −58.4° (*c* 3.1, CCl_4).

(*Z*,*Z*)-(2*R*,3*S*)-*cis*-2-(2,5-Octadienyl)-3-undecyloxirane (16). The procedure described for the preparation of (±)-**16** was followed. (2*R*,3*S*)-**15** (20 mg, 0.066 mmol) afforded 9 mg (45%) of (*Z*,*Z*)-(2*R*,3*S*)-**16** as a clear oil after purification by flash chromatography. This material was spectroscopically and chromatographically identical to a sample of (±)-**16**: $[\alpha]^{23}_D$ = −7.9° (*c* 1.2, CCl_4).

(2*R*,3*R*)-*trans*-2-(2,5-Octadiynyl)-3-undecyloxirane (17). The procedure described for the preparation of (±)-**15** was followed. Erythro epoxy tosylate **24** (100 mg, 0.261 mmol) afforded 39 mg (49%) of (2*R*,3*R*)-**17** as a waxy, yellow solid after flash chromatography. This material was spectroscopically and chromatographically identical to a sample of (±)-**17**: $[\alpha]^{23}_D$ = −5.0° (*c* 2.0, CCl_4).

(*Z*,*Z*)-(2*R*,3*R*)-*trans*-2-(2,5-Octadienyl)-3-undecyloxirane (18). The procedure described for the preparation of (±)-**16** was followed. (2*R*,3*R*)-**17** (36 mg, 0.12 mmol) afforded 21 mg (58%) of (*Z*,*Z*)-(2*R*,3*R*)-**18** as a clear oil after purification by flash chromatography. This material was spectroscopically and chromatographically identical to a sample of (±)-**18**. Examination of the olefinic carbon region of the expanded ^{13}C NMR spectrum revealed four small signals (125.0, 127.9, 131.7, 131.8) ca. 6% as intense as those of the major signals, implying geometrical purity >90%: $[\alpha]^{23}_D$ = +12.9° (*c* 2.1, CCl_4).

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Supplementary Material Available: ^1H and ^{13}C NMR spectra (20 pages). This material is contained in 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.