Olefin Inversion. 1. Reaction of Aliphatic Epoxides with Triphenylphosphine Dihalides

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Triphenylphosphine dibromide and dichloride (Ph_3PBr_2 and Ph_3PCl_2) reacted with epoxides to produce the corresponding *vic*-dihalides in excellent yields. Ph_3PBr_2 reacted with cis epoxides in benzene to produce erythro dibromides exclusively, but less selectively with trans epoxides to give mixtures of threo and erythro dibromides. Ph_3PCl_2 reacted stereospecifically with both cis and trans epoxides in benzene or methylene chloride, in each case providing the dichloride derived from SN2 displacement on each C–O bond. By reacting epoxides first with hydrochloric acid and then with Ph_3PBr_2, it was possible to stereospecifically prepare *vic*-bromochlorides that were also products of two SN2 displacements. Zinc reduction of erythro dibromides was stereospecifically trans; thus the process (1) epoxidation, (2) Ph_3PBr_2 bromination, (3) Zn reduction affected a clean overall inversion of olefin geometry from *Z* to *E*. Reduction of threo bromochlorides to *Z* olefins could be made approximately 90% selective if carried out at 0–5 °C in dimethylformamide.

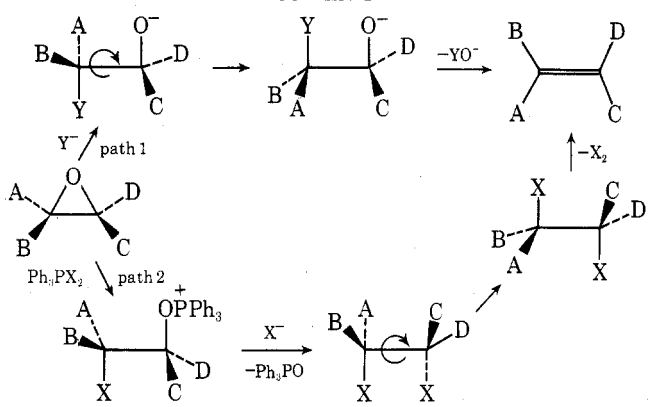
The ability to control and invert olefin geometry deservedly receives continuing attention in the chemical literature. Our own interest in such processes stems from the frequent uncertainty of the exact geometry of insect sex pheromones. The identities of pheromone components may be assigned by classical isolation–identification methods, or logical screening of synthetics,[1] but, in extreme cases, final adjustments have had to be made following ambiguous, or unsatisfactory, field tests.[2] Currently it is not clear whether the best use of a sex pheromone involves mimicking the exact composition of the natural product, or whether some other ratio of components might be more useful in an attempted disruption of mating processes. A convenient method of converting a sex pheromone, often an unsaturated acetate, to a geometric isomer would expedite the processes of determining pheromone isomer content and optimizing insect behavioral responses.

An elegant method of inverting olefin geometry has been described by Vedejs and Fuchs.[5] Epoxides were allowed to react with lithium diphenylphosphide, and the resulting oxy anions were alkylated on phosphorus with methyl iodide to produce betaines which, in turn, underwent cis eliminations to produce olefins of geometry opposite to those of the starting epoxides. A related method, described by Bridges and Whitham,[6] involved hydrogen peroxide oxidation of the same oxyanions; the resulting anions then eliminated the water-soluble lithium diphenylphosphinate. Very recent literature describes inversion via epoxides employing potassium selenocyanate,[7a] or hexamethyldisilazane/KOMe,[7b] and inversion via seleniranes and thiiranes.[7c] These processes involve addition of a single reagent to an epoxide (selenirane, thiirane in one case), with a stereochemical inversion, followed by cis eliminations from the initial adducts (Scheme I, path 1). A logical alternative would be a net cis addition (zero or two inversions) followed by trans elimination of the added groups (Scheme I, path 2). We describe here a route for olefin inversion via epoxides that is based on the latter principle and is thus complementary to those described earlier.

Results and Discussion

Prior literature concerning reactions of epoxides with triphenylphosphine dihalides is sparse; information on stereochemistry is lacking, and indications were that mixtures of dihalides, haloalkenes, and other materials could be expected.[8] The few reaction conditions reported, however, had been quite

Scheme I[a]



[a] Path 1: one inversion, cis elimination. Path 2: two inversions, trans elimination.

vigorous. We recently observed that tetrahydropyranyl ethers were smoothly converted by triphenylphosphine dibromide (Ph_3PBr_2) to the corresponding bromides within minutes at room temperature,[9] and thus anticipated that milder conditions might be advisable in the application of this reagent to epoxides. The epoxide of (*Z*)-9-pentacosene (95% cis by ir, 965 cm^{-1} band) was therefore exposed to a slurry of Ph_3PBr_2 in benzene for 4 h. A dibromide was obtained nearly quantitatively; treatment with zinc in acetic (or propionic) acid produced (*E*)-9-pentacosene (94% trans by ir). The overall yield, olefin–olefin, was ca. 75%, and, within the limits of error of the infrared method of analysis, the transformations were stereospecific. Assuming that the elimination of bromine was trans,[10] the dibromide must have been the erythro isomer.

The diastereomeric threo dibromide formed in considerable proportion, however, if more polar solvents were used for the Ph_3PBr_2 treatment. Thus when methylene chloride was substituted for benzene, the ultimate product was a 61:39 mixture of (*E*)- and (*Z*)-9-pentacosenes; a 48:52 *E*:*Z* mixture of alkenes was ultimately derived from reaction in acetonitrile.

Although pentacosenes were of interest to use [the sex pheromone of the "little housefly", *Fannia canicularis* (L.), is (*Z*)-9-pentacosene],[11] greater precision in measuring isomer content would be realized if olefins were used the epoxides of which could be examined by gas chromatography; all data described hereafter were obtained in that manner.

Epoxidation of (*Z*)-7-octadecene[12] with *m*-chloroperbenzoic acid gave the corresponding epoxide (90% cis) which was converted under the conditions described (Ph_3PBr_2 in benzene, Zn/HOAc, *m*-chloroperoxybenzoic acid) to give 7,8-

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epoxyoctadecane which was 94% trans. The sex pheromone of the gypsy moth, *Lymantria dispar* (L.), (*Z*)-7,8-epoxy-2-methyloctadecene (95% cis),[13] similarly gave the epoxide of opposite geometry (97.5% trans). A sample of 85% *cis*-7,8-epoxy-2-methyloctadecane provided 93% trans epoxide. The apparent stereoselectivity of >100%, while gratifying, was suspicious and was subsequently traced to a lack of selectivity in the conversion of the few percent of trans epoxides present in the starting cis epoxides.

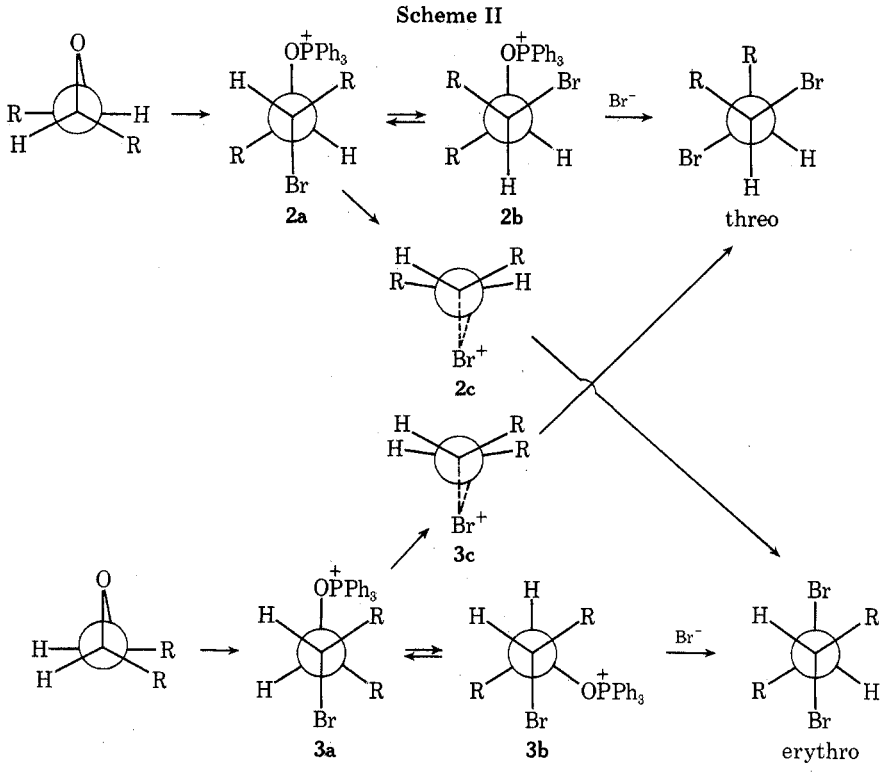
Two trans epoxides were then subjected to the three-step sequence: *trans*-7,8-epoxyoctadecene (94% trans) gave an epoxide mixture that was only 65% cis; *trans*-7,8-epoxy-2-methyloctadecane (97.5% trans) produced a 1:1 mixture of the cis and trans epoxides. The conditions of bromination and debromination were as stated, and overall yields were good (70–80%), but the stereoselectivity, if any, was clearly inadequate to be useful for *E*–*Z* conversions of olefins.

Since we had evaluated only the end product of a three-reaction sequence (Ph_3PBr_2 bromination, Zn/HOAc reduction, and peracid epoxidation), we now had to ascertain at what point the loss of specificity had occurred. Epoxidation with peracids is known to be highly selectively cis,[14] and we had encountered no exception in performing the oxidations of olefins with known geometry. Also reductive debromination with zinc in acetic acid is generally accepted to proceed trans, though Young and co-workers[10] had observed a few percent of diastereomer formation in their studies of zinc debromination–rebromination. To evaluate the zinc reduction under our conditions, we added bromine to (*Z*)-7-octadecene (90% cis) to produce the threo dibromide that we had sought to obtain from *trans*-7-octadecene oxide and Ph_3PBr_2. Zinc/acetic acid reduction of this threo dibromide and epoxidation of the product gave the cis epoxide (80% cis). Thus, as the earlier work had demonstrated,[10] the bromination, zinc–debromination sequence was not completely stereospecific for the threo dibromide. However, the deviation from specificity was insufficient to explain the results of our attempted trans–cis conversions.

We also examined the stereochemical stability of the *threo*-7,8-dibromooctadecane under the Ph_3PBr_2 bromination conditions. 5α,6β-Dibromocholesterol and some of its derivatives (trans-diaxial bromines) are known to isomerize spontaneously to the more stable 5α,6β-coprostane isomers,[15] but this type of isomerization is believed to involve a β-bromine-assisted ionization[15] and does not seem to have been considered important for aliphatic dibromides. When a sample of our *threo*-7,8-dibromooctadecane was exposed to a mixture of Ph_3PBr_2 and triphenylphosphine oxide in benzene for 24 h, reduction with zinc followed by epoxidation gave epoxide that was 73% cis. Whether the difference between the 80% cis realized earlier and the 73% cis obtained in this case was the result of dibromide isomerization or whether it indicated some limit of reproducibility in the reduction was not determined. What did become apparent was that the major stereochemical problem was encountered in the reaction of trans epoxides with Ph_3PBr_2, and not in the Zn reduction.

The reactions of cis and trans epoxides with Ph_3PBr_2 in benzene may be envisioned as shown in Scheme II. The trans epoxide reacts to produce the phosphorylated bromide **2a**. Direct SN2 displacement of triphenylphosphine oxide is possible, perhaps after an internal rotation to the more crowded rotamer **2b** in order to avoid eclipsing of bromine by incoming bromide; this would produce the threo dibromide. Alternatively, the triphenylphosphine oxide can be lost solvolytically with assistance from the adjacent bromine atom, generating a bromonium ion **2c** that would produce the erythro dibromide (a net front-side replacement of oxygen and thus a single inversion of configuration). The rotamer **2a** from which bromonium ion formation would be anticipated is probably more favored sterically than **2b**. The initial intermediate obtained from the cis epoxide, on the other hand, is the less sterically favored one **3a**; rotation to **3b** relieves crowding and also avoids potential eclipsing of bromine and incoming bromide. However, the functionalities of **3b** are not aligned for bromine-assisted solvolysis of triphenylphosphine oxide, and, in nonpolar solvents, the SN2 displacement occurs cleanly to provide the erythro dibromide. The loss of stereospecificity observed in the cis–trans isomerizations in the more polar solvents presumably results from the formation of the cisoid bromonium ion **3c** under those conditions.

Scheme II

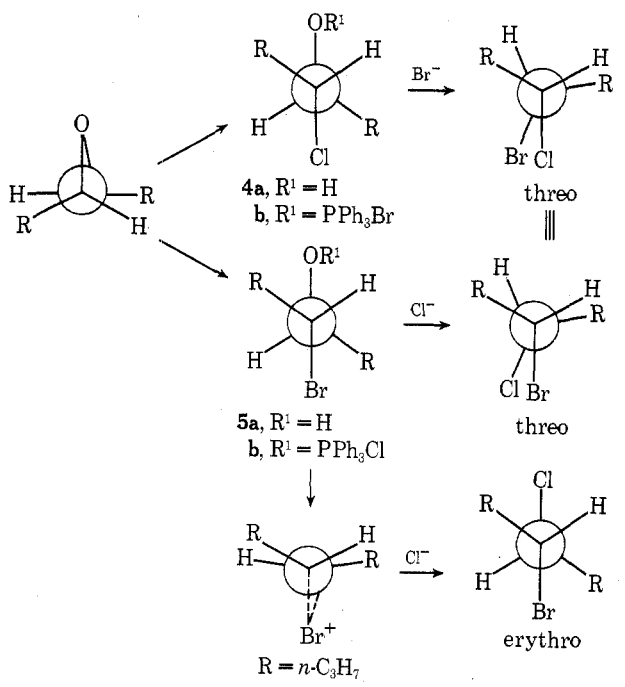


We next treated *trans*-7,8-epoxy-2-methyloctadecane with 48% hydrobromic acid in tetrahydrofuran. The resulting bromohydrin, presumed to be erythro resulting from SN2 attack by bromide on the protonated oxirane,[16] was reacted with Ph_3PBr_2 in benzene. The resulting dibromide was reduced with zinc, and the olefin was epoxidized; the resulting epoxide was only 23% cis. The erythro bromohydrin would also be expected to form an intermediate of the type **2a.** Formation of the bromonium ion **2c** seems to account for more of the product in this case, perhaps because of the presence of HBr in the reaction mixture.

Subsequent experiments further supported the idea of the bromonium intermediate. Since it is generally accepted that chloronium ions are of considerably higher energy than bromonium ions,[17] dichloride formation from epoxides and triphenylphosphine dichloride (Ph_3PCl_2) might be expected to be stereochemically more specific than the corresponding reactions in the Ph_3PBr_2 series. Indeed this was the case. We chose as models the *cis*- and *trans*-4,5-epoxyoctanes because we could analyze the dihalides directly by gas chromatography. In these cases, each epoxide reacted with Ph_3PCl_2 in either benzene or methylene chloride to produce a single dichloride; the dichlorides from the cis and trans epoxides corresponded to those obtained by direct (trans) addition of chlorine to the trans and cis olefins, respectively. Thus the reaction of the 1,2-disubstituted aliphatic epoxides with Ph_3PCl_2 had proceeded with the anticipated *back-side* displacement of *both* C–O bonds to give the equivalent of cis addition of chlorine to the alkenes. Chloronium ions evidently did not occur as intermediates.

The intermediacy of bromonium, but not chloronium, ions was further emphasized by converting *trans*-4,5-epoxyoctane to 4-bromo-5-chlorooctane. Samples of the trans epoxide were treated with hydrochloric and hydrobromic acids to give the erythro chlorohydrin **4a** and bromohydrin **5a,** respectively (Scheme III). The chlorohydrin **4a** was then treated with

Scheme III



Ph_3PBr_2 and the bromohydrin **5a** with Ph_3PCl_2. The bromochloride obtained from **4a** via **4b** was entirely threo (no chloronium ion participation), whereas that from **5a** via **5b** consisted of approximately equal parts of erythro and threo isomers (bromonium ion participation).

The reactions of triphenylphosphine dihalides with 1,2-epoxycyclohexane were also briefly examined. The epoxide reacted with Ph_3PBr_2 in such solvents as acetonitrile, benzene, and chlorobenzene to produce various mixtures of *cis*- and *trans*-1,2-dibromocyclohexane that often also contained some *trans*-1,2-bromohydrin. The latter could possibly be avoided by proper manipulation of reaction conditions, e.g., by using excess phosphorane, but a mixture of dibromides seemed unavoidable. On the other hand, Ph_3PCl_2 and cyclohexane epoxide in benzene or carbon tetrachloride produced *cis*-1,2-dichlorocyclohexane uncontaminated by the trans isomer. This reaction appears to be superior to the reported[18] conversion of cyclohexane epoxide to *cis*-1,2-dichlorocyclohexane with sulfuryl chloride in that the yields are better and the stereospecificity is much less subject to minor variations in the reaction conditions.

Since the means of converting epoxides to dichlorides with the required two inversions of configuration was now available, we turned our attention to reductive eliminations of the threo dichlorides. *trans*-7,8-Epoxyoctadecane was converted to the threo dichloride, and a variety of reaction conditions were investigated to effect a trans elimination. The dichloride required more vigorous reduction conditions than had the dibromides, and in all cases the reaction failed to exhibit the desired stereospecificity (Table I). Interestingly, sodium iodide in refluxing dimethylformamide (DMF) converted the threo dichloride to an olefin the epoxide of which was 91% trans; thus a cis elimination had occurred. This reaction and its potential for olefin interconversions are described in an accompanying paper.[19]

Since the transformations of epoxide to chlorohydrin to bromochloride with triphenylphosphine dibromide were proven to be stereospecific, threo bromochlorides were prepared from both *trans*-7,8-epoxyoctadecane and *trans*-7,8-epoxy-2-methyloctadecane in this manner. Various reduction procedures were studied and the results are given in Table I. The reductions of the bromochlorides proceeded under less vigorous conditions than those required for dichlorides but were still not completely stereospecific. To date the best procedure for converting trans epoxides to cis olefins via threo

Table I. Reductions of *vic*-Dichlorides and Bromochlorides

Dihalide (diastereomer content, %)[a]	Reduction conditions[b]	Isomer ratio (*E*:*Z*)[c]
threo-(7,8)-Dichloro-octadecane (94)	$LiAlH_4$, THF, reflux	30:70
	NaI, DMF, reflux	91:9
	Zn, HOAc, reflux	52:48
	Zn, DMF, 140 °C	30:70
threo-(7,8)-Bromo-chloroctadecane (90)[d]	Zn*,[e] DMF, H^+, 0–5 °C	28:72
threo-(7,8)-Bromo-chloro-2-methyl-octadecane (95)[d]	$LiAlH_4$, THF, reflux	48:52
	Zn, $C_2H_5CO_2H$, 25 °C	40:60
	Zn, DMF, 70 °C	24:76
	Zn*,DMF, H^+, 60–70 °C	18:82
	Zn*,DMF, H^+, 0–5 °C	13:87

[a] Estimated from purity of epoxides from which the dihalides were derived. [b] These conditions were for the most part approximately the mildest that would permit complete reduction in less than 24 h. Aliquots were worked up and examined by GLC; hence yields were not calculated except for the activated zinc reduction, which gave 80–87% yields. [c] Determined by GLC data using the epoxides. [d] Mixtures of 7-bromo-8-chloro and 7-chloro-8-bromo compounds. [e] Zinc was activated by brief treatment with dilute HCl as described by Tsuda et al.,[20] and 3 drops of acetic acid/5 ml of DMF was required to catalyze the reduction.

dihalides appears to be the activated zinc[20]–DMF treatment of bromochlorides which, at 0–5 °C, produced 87% cis alkene from 97.5% trans (ca. 90% selectivity).

The procedures thus far developed for inverting double bonds were then extended to unsaturated esters by examining their application to (*Z*)- and (*E*)-11-tetradecen-1-ol acetates. These two esters, which have been implicated repeatedly as sex attractants for lepidoptera,[21] were epoxidized (*m*-chloroperbenzoic acid). The trans epoxide was converted to the threo bromochloride via the two-step procedure (1) HCl/THF, (2) PPh_3·Br_2/CH_2Cl_2); and the cis isomer was treated directly with PPh_3·Br_2/benzene to give the erythro dibromide. Each dihalide was then reduced with activated zinc in DMF at 0–5 °C; the resulting unsaturated acetates were analyzed by GLC. The trans ester (99+% trans) gave the cis ester (92% cis); the cis ester (94% cis) gave the trans ester (>96% trans). The overall yields of these conversions were 70–80%.

Since the sensitivity of esters to lithium diphenylphosphide[5] appears to require protection of that group before an attempted olefin inversion via epoxide, the use of triphenylphosphine dihalides followed by zinc reduction of the resulting *vic*-dihalides should have considerable application. Triphenylphosphine dibromide is the reagent of choice when the object is to convert a *Z* alkene to a *E* isomer. Inversion in the opposite direction is best accomplished with HCl cleavage of the trans epoxide followed by reaction of the resulting chlorohydrin with triphenylphosphine dibromide. The *vic*-bromochloride may then be reduced with zinc–DMF at 0–5 °C with stereoselectivity of about 90%.

Experimental Section[22]

Infrared spectra were obtained with a Perkin-Elmer 457A spectrophotometer as 3% carbon tetrachloride solutions. More concentrated solutions were employed to estimate trans olefin content. NMR spectra were obtained with a Varian Associates T60 spectrometer; resonance frequencies were determined relative to internal Me_4Si. Gas chromatograms were obtained with Varian Aerograph 1520B, Hewlett-Packard 5700A, and Perkin-Elmer 3920 instruments. The following columns were employed: (1) SE-30, 5% on Chromosorb W (ABS), 92 cm × 6 mm; (2) Carbowax 20M, 5% on Chromosorb W (ABS), 1.83 m × 6 mm; (3) DEGS, 10% on Chromosorb W (AW), 1.83 m × 6 mm; (4) EGGS-X SCOT column, 15 m × 0.5 mm. Column chromatography was monitored with thin layer chromatography by using Brinkmann Instruments plates precoated with 0.25 mm of Sil G-25 UV_{254} and employing 15% ether/85% petroleum ether as the eluting solvent. Samples of (*Z*) and (*E*)-4-octenes were obtained commercially; (*Z*)-9-pentacosene[11] and (*Z*)-7-octadecene[12] were synthesized by Wittig condensation of an appropriate phosphorane with an aldehyde using HMPA–THF solvent to maximize the *Z*:*E* ratio.[23] Chemical analyses were performed by Galbraith Laboratories Inc., Knoxville, Tenn.

Epoxidations with *m*-Chloroperbenzoic Acid. The following procedure was typical. (*Z*)-9-Pentacosene (6.0 g, 17 mmol) was added to a stirred and ice-cooled solution of 85% *m*-chloroperbenzoic acid (4.1 g, 20 mmol) in methylene chloride (50 ml). The mixture was allowed to attain room temperature and, after 4 h, was washed with 25 ml of 5% NaOH and 25 ml of H_2O. The solution was dried ($MgSO_4$), and the solvent was removed yielding (*Z*)-9,10-epoxypentacosane (5.3 g, 86%). Recrystallization from petroleum ether provided a sample: mp 40–42 °C; NMR δ 0.90 (t, 6, CH_3), 2.68 (bs, 2, CHO). Anal. Calcd for $C_{25}H_{50}O$: C, 81.89; H, 13.75, Found: C, 82.20; H, 13.98.

Epoxides of (*Z*)- and (*E*)-4-octenes (96% *Z* and 99% *E*, respectively) were similarly prepared. The (*E*)-7-octadecene was synthesized from the *Z* isomer as described below. Relative GLC retention for (*Z*)- and (*E*)-4,5-epoxyoctanes using column 2 at 100 °C was 1.25:1.00; for (*Z*)- and (*E*)-7,8-epoxyoctadecanes using column 4 at 160 °C, it was 1.11:1.00; for (*Z*)- and (*E*)-7,8-epoxy-2-methyloctadecane[13] using column 4 at 160 °C, it was 1.10:1.00. These epoxides were sufficiently pure to be used directly for subsequent reactions.

Reactions of Epoxides with Triphenylphosphine Dibromide. The following procedure was typical. Bromine (2.7 g, 16.5 mmol) was added dropwise as a solution in CH_2Cl_2 (10 ml) to a stirred, ice-cooled solution of triphenylphosphine (4.4 g, 16.5 mmol) in CH_2Cl_2 (50 ml). Use of methylene chloride gave a visual end point, and the phosphine could be titrated with the bromine which obviated an exact weighing of the latter and produced a homogeneous solution. The solvent was removed and replaced with benzene (60 ml) to which was then added (*Z*)-9,10-epoxypentacosane (5.5 g, 15 mmol). The resulting slurry was stirred at room temperature for 4 h during which time the solid markedly changed character. The solvent was removed and the residue broken up under petroleum ether. Most of the triphenylphosphine oxide was removed by suction filtration. Removal of petroleum ether from the filtrate and recrystallization from petroleum ether (bp 30–60 °C) gave *erythro*-9,10-dibromopentacosane (6.5 g, 85%): mp 48–49 °C; NMR δ 4.02 (m, 2, CHBr). The CHBr resonance is consistent with an erythro as opposed to threo diastereomer.[24] Anal. Calcd for $C_{25}H_{50}Br_2$: C, 58.82; H, 9.87; Br, 31.31. Found: C, 58.92; H, 10.04; Br, 31.15.

erythro-7,8-Dibromo-2-methyloctadecane and *erythro*-7,8-dibromooctadecane were prepared similarly. Each was obtained as a liquid and was purified by passage through silica gel (~10 g/g dibromide) by elution with petroleum ether. After the solvent was removed and the purity was confirmed by TLC and GLC (column 1 at 250 °C), each was employed directly for reduction. A sample of *erythro*-7,8-dibromo-2-methyloctadecane was further purified by bulb-to-bulb distillation: bp 160 °C (0.02 mm); $n^{25}D$ 1.4803. Anal. Calcd for $C_{19}H_{38}Br_2$: C, 53.53; H, 8.98; Br, 37.49. Found: C, 53.86; H, 9.15; Br, 37.34.

Conversion of Epoxides to *vic*-Dichlorides with Triphenylphosphine Dichloride. The reactions of (*E*)- and (*Z*)-4,5-epoxyoctanes are typical. A 100-ml, three-necked flask fitted with a dry ice condenser, gas inlet, and addition funnel was charged with a solution of triphenylphosphine (2.0 g, 7.6 mmol) in anhydrous benzene (20 ml). The solution was stirred magnetically with external cooling (ice–water) and chlorine was admitted through the gas inlet until the mixture developed a permanent yellow color. A solution of the epoxide (0.64 g, 5 mmol) in benzene (5 ml) was added dropwise, then the dry ice condenser was replaced by a water-cooled condenser and the mixture was refluxed for 3.5 h. It was then cooled and treated with a little methanol to destroy excess Ph_3PCl_2. The benzene was stripped and replaced with petroleum ether (bp 30–60 °C) which caused the precipitation of triphenylphosphine oxide that was removed by filtration. The filtrate was concentrated, and the residue was added to a column of silica gel (15 g) and eluted with 100 ml of a solution of 15% ether in petroleum ether. Consentration of the eluate gave the 4,5-dichlorooctanes in 50–60% yields. The two dichlorooctanes were conveniently examined by gas chromatography on column 3. Each of the two products (from the isomeric epoxides) contained three minor, longer retention time impurities, but each was free from the isomeric dichloride. Samples of the two dichlorides were also prepared by chlorinating (*E*)- and (*Z*)-4-octenes with Cl_2 in CH_2Cl_2 at −78 °C; the chlorination product of the *E* olefin corresponded to the dichloride from the *Z* epoxide, and vice versa.

Conversions of Epoxides to Bromochlorides. A solution of (*Z*)-4,5-epoxyoctane (0.50 g, 3.9 mmol) in tetrahydrofuran (THF, 5 ml) was chilled to 0–5 °C. Concentrated HCl (0.5 ml) was added, and the solution was allowed to stand for 3 h at room temperature. The mixture was diluted with water and extracted thoroughly with ether. The extract was dried ($MgSO_4$) and concentrated to give the crude chlorohydrin which was then added to a solution of triphenylphosphine dibromide (6 mmol) in CH_2Cl_2 (20 ml) prepared as described previously. The resulting mixture was stirred overnight at ambient temperature, concentrated, and worked up with petroleum ether as previously described for the *vic*-dibromides. Purification, achieved by passage through silica gel as described for the *vic*-dibromides, gave, after solvent removal, *erythro*-4-bromo-5-chlorooctane (0.60 g, 67%): bulb-to-bulb distillation, bath temperature 125 °C (17 mm); $n^{25}D$ 1.4729; ir and NMR not distinct from those of the threo isomer. Anal. Calcd for C_8H_6BrCl: C, 42.22; H, 7.08; Br, 35.12; Cl, 15.58. Found: C, 42.50; H, 7.10; Br, 34.96; Cl, 15.30.

The threo isomer was similarly prepared (0.55 g, 62%): $n^{25}D$ 1.4714; relative GLC retention using column 2 was 1.15:1.00 (threo:erythro). Anal. Calcd for $C_8H_{16}BrCl$: 42.22; H, 7.08; Br, 35.12; Cl, 15.15. Found: C, 42.48; H, 7.04; Br, 34.95; Cl, 15.32.

The (*E*)- and (*Z*)-4,5-epoxyoctanes were similarly converted to erythro and threo bromohydrin, respectively (distinct from, and free from, each other, GLC column 3, 150 °C), with 48% HBr in dimethoxyethane (THF gave 4-bromo-1-butanol as a by-product that was bothersome to separate). The erythro bromohydrin was treated with a solution of Ph_3PCl_2 in methylene chloride as described for the conversion of epoxides to dichlorides. The product was an approximately equimolar mixture of *erythro*- and *threo*-4-bromo-5-chlorooctanes.

The threo bromochlorides derived from (*E*)-7,8-epoxyoctadecane and (*E*)-7,8-epoxy-2-methyloctadecane were similarly prepared and

purified. Purities were confirmed by TLC and GLC (column 1 at 250 °C).

Reductions of *vic*-Dihalides. A. Zinc–HOAc. The following procedure was typical. *erythro*-7,8-Dibromo-2-methyloctadecane (3.8 g, 8.9 mmol) was dissolved in acetic (or propionic) acid (40 ml). Zinc dust (3.8 g) was added, and the mixture was vigorously stirred. The reaction was mildly exothermic, and stirring was continued for 0.5 h. The mixture was diluted with H_2O and extracted with petroleum ether. The extract was washed with 5% $NaHCO_3$ until the washes were slightly alkaline, dried ($MgSO_4$), and concentrated to give (*E*)-7,2-methyloctadecene (2.16 g, 91%): bulb-to-bulb distillation, bath temperature 105 °C (0.02 mm); $n^{25}D$ 1.4545; ir 965 cm^{-1}; NMR δ 5.3 (m, 2 H, CH=); GLC analysis (column 4) of the epoxide indicated that the product was 97.5% *E*. Anal. Calcd for $C_{19}H_{38}$: C, 85.63; H, 14.37. Found: C, 85.67; H, 14.37. *erythro*-9,10-Dibromopentacosane and *erythro*-7,8-epoxyoctadecane were reduced in the same manner and gave (*E*)-9-pentacosene (95% *E* by ir) and (*E*)-7-octadecene (92% *E* judged by GLC analysis of its epoxide by using column 4 as described above).

B. Zinc–Dimethylformamide. The following procedure was employed in an attempt to achieve reduction under as mild conditions as possible. A solution of a *vic*-bromochloride (0.5 g) in dimethylformamide (DMF, 8 ml) was stirred and cooled with an ice bath. Activated[20] zinc dust (0.6 g) was pulverized with a mortar and pestle and added to the solution, then a solution of acetic acid (2–3 drops) in DMF (0.5 ml) was added dropwise (the reduction did not proceed at 0 °C in the absence of the acetic acid). The mixture was stirred magnetically in a refrigerator overnight (0 °C); then the solution was decanted from the metal (which was in the form of small, irregular spheres). Water was added, the product was extracted into hexane, and the hexane solution was washed with water, dried, and concentrated. In a few cases the residual zinc and zinc halides remained rather amorphous; in those instances the reaction mixtures were diluted with cold, dilute HCl, and the products were then extracted in hexane.

Conversion of (*Z*)- to (*E*)-11-Tetradecen-1-yl Acetate. The (*Z*)-11-tetradecen-1-yl acetate[2] was epoxidized by *m*-chloroperbenzoic acid as described. The crude epoxide (1.0 g, 3.7 mmol) was added to a slurry of triphenylphosphine dibromide (5.0 mmol) in benzene (25 ml) prepared as described previously. The mixture was stirred at ambient temperature overnight, concentrated, and worked up with petroleum ether, filtering to remove most of the triphenylphosphine oxide. The filtrate was concentrated, and the crude dibromoacetate was passed through silica gel (20 g) with 60 ml each of petroleum ether, 7.5% ether–petroleum ether, and 15% ether–petroleum ether. The eluate was concentrated, and the compound so obtained was added to a slurry of activated inc[20] (1.0 g) in DMF (10 ml) containing acetic acid (5 drops) at 5–10 °C. Stirring was continued at that temperature for 2 h. The reaction mixture was diluted with H_2O, and the product was obtained by extraction with petroleum ether in the usual manner (0.61 g, 70%). GLC analysis using column 4 (150 °C) indicated >96% *E*; relative retentions of the isomeric 11-tetradecen-1-yl acetates are 1.04:1.00 (*Z*:*E*).

Conversion of (*E*)- to (*Z*)-11-Tetradecen-1-yl Acetate. The *E* ester (99% *E*)[2] was epoxidized in the usual way, and the epoxide was treated sequentially with hydrochloric acid and Ph_3PBr_2 as described earlier. The mixture of bromochlorides was reduced by the zinc/DMF procedure to give 11-tetradecen-1-yl acetate (92:8 *Z*:*E*) in an overall yield of ca. 70%.

Registry No.—*m*-Chloroperbenzoic acid, 937-14-4; (*Z*)-9-pentacosene, 51865-00-0; (*Z*)-9,10-epoxypentacosane, 59906-99-9; (*Z*)-4-octene, 7642-15-1; (*E*)-4-octene, 14850-23-8; (*Z*)-4,5-epoxyoctane, 1439-06-1; (*E*)-4,5-epoxyoctane, 1689-70-9; (*E*)-7-octadecene, 7206-23-7; (*Z*)-7-octadecene, 7206-35-1; (*Z*)-7,8-epoxyoctadecane, 59907-00-5; (*E*)-7,8-epoxyoctadecane, 59907-01-6; (*Z*)-7,8-epoxy-2-methyloctadecane, 29804-22-6; (*E*)-7,8-epoxy-2-methyloctadecane, 42991-03-7; triphenylphosphine dibromide, 1034-39-5; *erythro*-9,10-dibromopentacosane, 59907-02-7; *erythro*-7,8-dibromo-2-methyloctadecane, 59840-28-7; *erythro*-7,8-dibromooctadecane, 59907-03-8; triphenylphosphine dichloride, 2526-64-9; *erythro*-4-bromo-5-chlorooctane, 59840-29-8; *threo*-4-bromo-5-chlorooctane, 59840-30-1; (*E*)-7,2-methyloctadecene, 40302-56-5; (*Z*)-11-tetradecen-1-yl acetate, 20711-10-8; (*E*)-11-tetradecen-1-yl acetate, 33189-72-9; *threo*-7,8-dichlorooctadecane, 59840-26-5; *threo*-7-bromo-8-chlorooctadecane, 59840-21-0; *threo*-7-chloro-8-bromooctadecane, 59840-22-1; *threo*-7-bromo-8-chloro-2-methyloctadecane, 59840-17-4; *threo*-7-chloro-8-bromo-2-methyloctadecane, 59840-18-5; DMF, 68-12-2; zinc, 7440-66-6.

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