

The reactions proceeded cleanly in every case to produce a single product. In the case of norbornen-7-one (9), the NMR spectra after five reaction half-lives was consistent with the formation of $99 \pm 4\%$ cyclohexadiene. No other products were observed. Ketone 2 produced $101 \pm 4\%$ cyclooctatetraene after eight reaction half-lives, and bicyclo[4.2.1]nona-2,4,7-trien-9-one (10) produced $100 \pm 4\%$ cyclooctatetraene after five reaction

half-lives.

Registry No. 1, 14725-99-6; 2, 38440-48-1; 3, 17876-06-1; 6, 4011-16-9; 7, 6572-53-8; 8, 629-20-9; 9, 694-71-3; 10, 34733-74-9; cyclohexadiene, 29797-09-9; *endo*-tricyclo[4.2.1.0^{2,5}]nona-7-en-9-one, 42948-87-8; (1 α ,4 α ,4 $\alpha\beta$,5 β ,8 β ,8 $\alpha\beta$)-1,2,3,4,4a,5,8,8a-octahydro-1,4:5,8-dimethanonaphthalen-9-one, 15914-93-9.

Olefin Inversion. 3. Preparations and Reductions of *vic*-Halohydrin Trifluoroacetates

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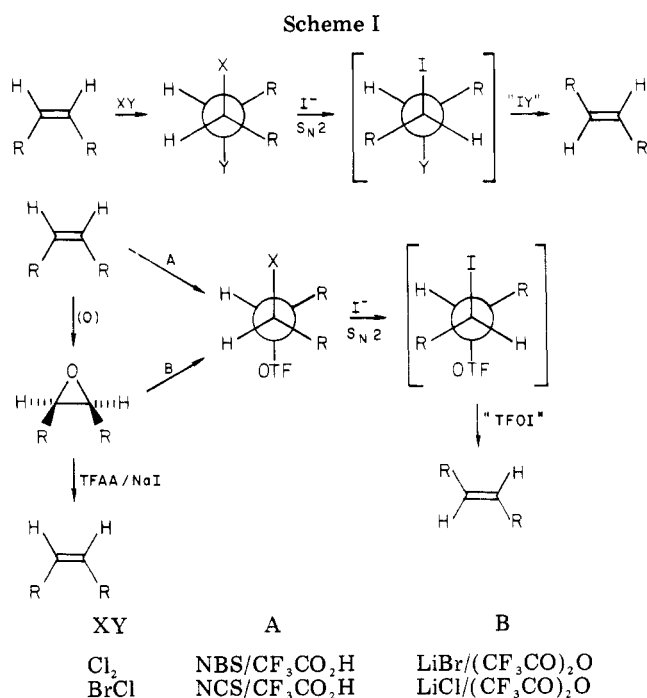
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Treatment of alkenes with *N*-bromo- and *N*-chlorosuccinimide in trifluoroacetic acid resulted in stereospecific anti addition of the elements of trifluoroacetyl hypobromite and hypochlorite, respectively. Heating the *vic*-bromo- or -chlorohydrin trifluoroacetates with NaI in DMF produced olefins with inversion of geometry. Treatment of the adducts with Zn in DMF reduced them to olefins with retention of geometry. Reductive transformations involving the chlorohydrin trifluoroacetates were virtually stereospecific, whereas those involving the bromohydrin trifluoroacetates were $>90\%$ stereoselective for NaI reductions and only 60-90% stereoselective for reductions by Zn.

Reductive elimination of vicinal disubstituted compounds employing a wide range of reducing agents has received considerable attention for many years.¹ In particular, sodium iodide induced the elimination of vicinal dibromides,² bromochlorides,³ dichlorides,³ ditosylates,² and dimesylates.² The reductions of *vic*-dibromides proceeded with predominant anti stereochemistry,⁴ and very exacting kinetic studies suggested that the elimination reactions induced by iodide (and other charged nucleophiles) should be viewed reciprocally with electrophilic addition.⁵ If one of the bromine atoms was on a primary (deuterated) carbon, however, S_N2 displacement of bromide by iodide on carbon occurred,⁶ followed by anti elimination of IBr. The resulting deuterated olefin was then the product of a (net) syn elimination. The presumed intermediate iodobromide evidently collapsed by an anti elimination faster than iodide ion could perform another displacement on bound iodine since the product geometry would not otherwise have been preserved. Similarly, diastereomerically pure dichlorides and bromochlorides treated with iodide in DMF resulted in olefins that were the product of (net) syn elimination.³

Additions of halogen to 1,2-disubstituted olefins generally involve clean anti addition. The intervention of a Walden inversion between an anti addition and an anti



elimination constitutes an odd number of inversions and will yield an olefin of opposite configuration (Scheme I). The utility of this route for olefin inversion employing dichlorides and dibromides has been investigated.³ The observation that *vic*-iodohydrin trifluoroacetates eliminated cleanly with anti stereochemistry in the presence of sodium iodide at room temperature⁷ prompted a study of the preparations and reductions of *vic*-bromo- and -chlorohydrin trifluoroacetates. In particular, we wished to know the stereochemistry of iodide- and zinc-promoted

(1) I. T. Harrison and S. Harrison, "Compendium of Organic Synthetic Methods", Wiley-Interscience, New York, 1971, p 510.

(2) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Vol. 1, Wiley, New York, 1967, p 1089.

(3) P. E. Sonnet and J. E. Oliver, *J. Org. Chem.*, **41**, 3284 (1976).

(4) S. Winstein, D. Pressman, and W. G. Young, *J. Am. Chem. Soc.*, **61**, 1645 (1939).

(5) C. S. Tsai Lee, I. M. Mathai, and S. I. Miller, *J. Am. Chem. Soc.*, **92**, 4602 (1970). For related studies of iodide-induced elimination see: I. M. Mathai, K. Schug, and S. I. Miller, *J. Org. Chem.*, **35**, 1733 (1970); I. M. Mathai, *ibid.*, 3416 (1970); W. K. Kwok, I. M. Mathai, and S. I. Miller, *ibid.*, 3420 (1970).

(6) (a) J. Hine and W. H. Brader, Jr., *J. Am. Chem. Soc.*, **77**, 361 (1955); (b) W. M. Schubert, H. Steadly, and B. S. Rabinovitch, *ibid.*, **77**, 5755 (1955).

(7) P. E. Sonnet, *J. Org. Chem.*, **43**, 1841 (1978).

Table I. Deoxygenation of Epoxides with Inversion of Geometry^a

reactant	geometry ^b	product	geometry ^b	method ^d
4,5-epoxyoctane	96% <i>Z</i>	4-octene	96% <i>E</i>	A
4,5-epoxyoctane	99% <i>E</i>	4-octene	99% <i>Z</i>	A
4,5-epoxydecane	93% <i>Z</i>	4-decene	92% <i>E</i>	A
5,6-epoxydecane	94% <i>E</i>	5-decene	>90% <i>Z</i> ^c	A
7,8-epoxy-2-methyloctadecane	97.5% <i>Z</i>	2-methyl-7-octadecene	98% <i>E</i>	A
7,8-epoxy-2-methyloctadecane	97.5% <i>E</i>	2-methyl-7-octadecene	95% <i>Z</i>	A
4,5-epoxyoctane	96% <i>Z</i>	4-octene	98% <i>E</i>	B
4,5-epoxyoctane	99% <i>E</i>	4-octene	>93% <i>E</i> ^c	B
7,8-epoxy-2-methyloctadecane	97.5% <i>Z</i>	2-methyl-7-octadecene	92% <i>E</i>	B
7,8-epoxy-2-methyloctadecane	97.5% <i>E</i>	2-methyl-7-octadecene	96% <i>Z</i>	B

^a Yields were >85% as determined with 1-decene ISTD by GLC for octenes and decenes and as determined by weight of crude olefin after column chromatography for methyloctadecenes. ^b See Experimental Section for details. ^c Interference in the GLC peak of the *Z* component. ^d Method A: TFAA/LiCl in DMF, room temperature, followed by NaI, 130 °C, 24 h. Method B: TFAA/LiBr in DMF, room temperature, followed by NaI, 90 °C, 24 h.

eliminations of the diastereomeric halohydrin esters.⁸

Results and Discussion

Solutions containing lithium halide and trifluoroacetic anhydride (TFAA) reacted with epoxides as if they contained the trifluoroacetyl halide. Lithium iodide and TFAA were brought together initially in THF, and after 15 min an equal volume of hexane was added. Filtration of a precipitate (lithium trifluoroacetate presumably) produced a solution (IR: 1783 cm⁻¹) that reacted with (*E*)-3,4-epoxyoctane to produce an *erythro*-iodohydrin trifluoroacetate (mixture of positional isomers) identical with the one obtained by conducting the reaction homogeneously in THF-acetonitrile.^{7,9} The reactive species therefore appears to be the acid iodide. The reactions of the analogously prepared trifluoroacetyl chloride and bromide with 1,2-dialkyl epoxides succeeded in high yield (Scheme I). The products were formed stereospecifically as judged by GLC analyses (the diastereomers were readily separated, but the positional isomers obtained from unsymmetrically substituted epoxides were not resolved). Because the products were stereochemically homogeneous, they were presumed to arise from trans opening of the epoxide ring. Generally the reaction of a *cis*-epoxide in dry DMF was complete in 2 h at room temperature; *trans*-epoxides required longer times (~16 h). The same bromo- and chlorohydrin trifluoroacetates were prepared directly from the alkenes by (the expected¹⁰) anti addition stereospecifically using *N*-halosuccinimides in trifluoroacetic acid solvent. These reactions were complete within minutes, and the products of these additions served as a confirmation of the stereochemistry of the epoxide reactions. It is noteworthy that although NBS reacted in acetic acid with olefins producing *vic*-haloacetates,¹⁰ additions of NCS to olefins appear to have been much less studied. Also, no reaction occurred when a 1,2-dialkyl epoxide was exposed to sodium iodide and acetic anhydride in THF-CH₃CN even under reflux for 24 h. However, reaction with trifluoroacetyl iodide (NaI, TFAA), on the other hand, was exothermic at room temperature in this solvent.

The halohydrin trifluoroacetates were treated with sodium iodide in DMF (Scheme I). The bromides were

reduced to olefins at 90 °C; the chlorides required higher temperatures (130 °C) to effect reduction. The reduction proceeded with (net) *syn* elimination and was stereospecific for the chlorohydrin trifluoroacetates and about 93–94% selective for the bromides (Table I). Analyses of the product alkenes were conducted on the dibromides or the chlorohydrin trifluoroacetates prepared as just described. At higher temperatures, reduction of the bromoester became yet less stereoselective.

These results parallel the reductions of *vic*-dichlorides and -bromochlorides in that vicinal adducts in which one substituent was bromine reduced faster and less stereoselectively than those adducts without bromine. Hence, the reductive eliminations are viewed as analogous to those of the dihalides in that an initial displacement of halogen occurred (Br from the bromo ester, Cl from the chloro ester) followed by rapid anti elimination. The deviation from overall *syn* elimination evidently was not associated with the anti elimination step, since the transformation of the chloro esters to olefins, which was conducted at the higher temperature, would have been expected to be less specific than the corresponding reaction of the bromo ester. Therefore, the elimination of *vic*-iodohydrin trifluoroacetates and *vic*-iodochlorides⁷ (the latter being intermediates in the reduction of *vic*-dichlorides) must be very stereospecific. Parenthetically, iodochlorides and iodobromides, though known,¹¹ have apparently not been studied much.

In practice, the conversion of an olefin from one geometry to the other can be accomplished in a variety of ways.¹² Employing halohydrin trifluoroacetates, the sequence is essentially accomplished in two steps either by (1) reaction of the olefin with NCS or NBS in trifluoroacetic acid followed by (2) reduction with NaI or by (1) epoxidation followed by (2) exposure to trifluoroacetyl chloride or bromide and (without isolation) further treatment with NaI.

Neither the epoxide of 1-methylcyclohexene nor the trisubstituted alkene itself reacted cleanly to form a *vic*-halohydrin trifluoroacetate (addition of halogen to trisubstituted olefins likewise produces mixtures).^{3,13} Similarly, neither citronellyl acetate nor its epoxide provided a clean addition product. Thus, the scope of this sequence will apparently not encompass trisubstituted alkenes. Additionally, attempts to prepare the highly strained *trans*-cyclooctene by (1) bromochlorination of *cis*-cyclooctene and (2) NaI produced only *cis*-cyclooctene.¹⁴ These

(8) Presented in part at the 175th National Meeting of the American Chemical Society, Anaheim, CA, March 11, 1978.

(9) Iodotrifluoroacetates have been prepared by the silver salt and I₂ method (M. Adinolfi, M. Parrilli, G. Barone, G. Leonigro, and L. Mangoni, *Gazz. Chim. Ital.*, **105**, 1259 (1975); R. C. Camlie, B. G. Lindsay, P. S. Rutledge, and P. D. Woodgate, *J. Chem. Soc., Chem. Commun.*, 919 (1978)) and also from alkenes with iodine tris(trifluoroacetate): J. Budrus, *Angew. Chem., Int. Ed. Engl.*, **12**, 163 (1973). Bromo- and chlorotrifluoroacetates have apparently not been described.

(10) H. O. House, "Modern Synthetic Reactions", 2nd ed., W. A. Benjamin, Menlo Park, CA, 1972, p 432.

(11) W. C. Baird, J. H. Surridge, and M. Buza, *J. Org. Chem.*, **36**, 3324 (1971).

(12) E. Vedejs and P. L. Fuchs, *J. Am. Chem. Soc.*, **95**, 822 (1973), and references cited; P. E. Sonnet, *Tetrahedron*, in press.

(13) M. L. Poutsma, *Science*, **157**, 997 (1967).

Table II. Additional Examples of Olefin Inversion

reactant (geometry) ^a	product yield, geometry ^a	method ^c
(<i>Z</i>)-9-tetradecen-1-ol acetate (97%)	86%, 96% <i>E</i>	1
(<i>Z</i>)-3-tetradecen-1-ol acetate (89%)	64%, 90% <i>E</i>	1
(<i>Z,Z</i>)-1,7,13-pentacosatriene (~92%)	68%, 94-95% <i>E</i>	2
(<i>Z,E</i>)-1,7,13-pentacosatriene (~97%)	44%, 96% <i>E,E</i>	2 ^b
(<i>Z,E</i>)-1,7,13-pentacosatriene (~97%)	80%, ~97% <i>E,Z</i>	1 ^b

^a See Experimental Section. ^b P. E. Sonnet, *J. Chem. Ecol.*, in press. Method 1 = (1) epoxidation, (2) reaction with trifluoroacetyl chloride, (3) NaI. Method 2 = (1) epoxidation, (2) reaction with triphenylphosphine dibromide, (3) Zn-HOAc.

reactions also would not be suitable for inversion of conjugated dienes, nor would these reactions be expected to have utility for the generation of systems which would isomerize the olefins under the reaction conditions that produced them, e.g., *cis*- α,β -unsaturated carbonyl compounds, etc.

On the other hand, the reagents employed for this inversion route are readily available, and compatibility with a variety of functional groups can be expected. Our own specific interest is in the area of insect sex pheromones, and the halohydrin trifluoroacetate-iodide inversion was applied to several suitable structures (Table II). Epoxidation of (*Z*)-9-tetradecen-1-ol acetate followed by trifluoroacetyl chloride generated in situ, and then by NaI, produced the *E* isomer in 80% yield. Similarly, the 1,5-diene, (*Z,E*)-7,11-tetradecadien-1-ol acetate was inverted to the *E,Z* isomer, although in only 50% yield. Both inversions were >98% stereoselective. The homoallylic ester, (*Z*)-3-tetradecen-1-ol acetate (that was 89% *cis*), provided a product via the halo ester route in 64% yield that was 90% *E*. A route employing Ph₃P·Br₂ treatment of the epoxide followed by Zn reduction¹⁵ gave a 94-95% *E* ester in 68% yield. The *E* → *Z* conversion by that latter route was not stereospecific,¹⁴ so its application to a *Z* → *E* conversion had the observed positive affect on the isomer ratio. The allylic ester, (*E*)-2-dodecen-1-ol acetate, when subjected to the halo ester inversion sequence, underwent a more complex set of transformations, culminating in a product rich in (*E*)-1,3-dodecadiene (IR 985 cm⁻¹; mass spectrum, P⁺ = 138).

The reducing agent that promoted anti elimination most effectively for *vic*-dichlorides and -bromochlorides was NaI/DMF.³ Activated zinc¹⁶ was somewhat less selective; threo dichlorides were less specifically reduced than erythro dichlorides, and the reduction of bromochlorides was still less stereospecific. The deviation from strictly anti elimination of Zn reductions with aliphatic dibromides is well-known,¹⁷ and the specificity of metal reductions (including Zn) of stilbene dibromides has been discussed as a possible surface radical process.^{17c} The halohydrin trifluoroacetates of the 4-octenes were treated with activated Zn in DMF at 0 °C (Table III). Although both diastereomeric chlorotrifluoroacetates were reduced essentially completely anti, the bromo- and iodotrifluoroacetates were less selectively reduced and the threo compounds under-

Table III. Reductions of *vic*-Halotrifluoroacetates of 4-Octenes with Zinc-HOAc (0 °C)

reactant ^a	product, <i>E:Z</i> ^a	% anti elimination (approx)
5-Cl,4-OTF (erythro)	>98:2	100
5-Cl,4-OTF (threo)	4:96	100
5-Br,4-OTF (erythro)	88:12	90
5-Br,4-OTF (threo)	36:64	60
5-I,4-OTF (threo)	39:61	60

^a Halogen trifluoroacetate addition to the 4-octenes was exclusively *trans*. Hence, the threo adducts were 98-99% pure; the erythro adducts were 96% pure. See Experimental Section for details of the analyses.

went the greatest amount of inversion of geometry during reduction. That the threo isomers reduce less stereospecifically (in general with any reducing agent) has already been explained.^{17c} The variation in stereoselectivity with the nature of the halogen noted in these reductions could be rationalized in several ways, and more definitive experiments are required.

erythro-4-Acetoxy-5-iodooctane was prepared by the silver salt-I₂ method.¹⁸ Treatment with excess sodium iodide in DMF produced no octene. When the reaction was heated at 90 °C for 24 h, the only product was the glycol monoester due to adventitious moisture. Thus *vic*-iodoacetates may apparently be subject exclusively to expulsion of iodide by neighboring acetate (the Prevost reaction¹⁸), whereas the nature of the trifluoroacetate group renders a *vis*-iodotrifluoroacetate subject to reductive elimination, i.e., expulsion of the ester group by neighboring iodine.

Attempts to extend the reactions of trifluoroacetyl halides to pseudohalogens failed. Neither trifluoroacetyl cyanide (TFAA, NaCN; IR 2267, 1850 cm⁻¹) nor combination of TFAA and NaN₃ reacted with epoxides. Extension of the reaction to other (noncarboxylic) acid halides, the products from which would be formally subject to reductive elimination, likewise failed. Methanesulfonyl chloride reacted negligibly with epoxides at room temperature in DMF, and the product of the reaction of trifluoromethanesulfonyl chloride in DMF with an epoxide was the formate ester of the chlorohydrin (IR 1720 cm⁻¹; ¹H NMR (CCl₄) δ 3.96 (CHCl), 5.18 (HCO), 8.13 (O=CH)). Trifluoroacetylhalides were also capable of reacting with solvent (THF yielded the trifluoroacetate of 4-iodobutan-1-ol), but in the presence of an epoxide the reaction was exclusively with that substrate (in THF or DMF).

Experimental Section¹⁹

Gas-liquid chromatography was performed with a Varian 2400 instrument employing the following columns: (1) UCW-982 column, 10% on 80-100 WAW-DMCS, 3.2 mm × 51 cm; (2) DEGS, 4 mm × 46 m WCOT column that was used to characterize the geometry of alkenes as their epoxides; and (3) Ultrabond II, 3.2 mm × 1.5 m, that served to characterize the geometry of alkenes as their diastereomeric addition products (see below). Mass spectral data were obtained with a Finnigan Model 105C chemical ionization mass spectrometer that was equipped with a chromatographic inlet (Varian Model 1400) served by a 3% OV-101 column, 3.2 mm × 1.5 m (Table IV). Infrared data were obtained with either a Perkin-Elmer 467 grating infrared spectrophotometer (CCl₄ solutions) or a Nicolet 1180 data system, and ¹H and ¹³C NMR data were obtained with a Bruker WHX-90

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(15) P. E. Sonnet and J. E. Oliver, *J. Org. Chem.*, **41**, 3279 (1976).

(16) K. Tsuda, E. Ohki, and S. Nozoe, *J. Org. Chem.*, **28**, 783 (1963).

(17) (a) W. G. Young, S. J. Cristol, and T. Skei, *J. Am. Chem. Soc.*, **65**, 2099 (1943). (b) ref 2, p 1276. (c) I. M. Mathai, K. Schug, and S. I. Miller, *J. Org. Chem.*, **35**, 1733 (1970).

(18) Reference 10, pp 438-441.

(19) Mention of commercial company or proprietary product in this paper does not constitute endorsement of that product or company by the USDA.

Table IV. Chemical Ionization Mass Spectral^a Data for Bromo- and Chlorohydrin Trifluoroacetates

entry	octane	I	II
1	5-Cl-4-OTF, ^b erythro	147, 149	111
2	5-Cl-4-OTF, threo	147, 149	111
3	5-Br-4-OTF, erythro	191, 193	111
4	5-Br-4-OTF, threo	191, 193	111

^a See Experimental Section for details. Parent ion peaks were not observed. Isotope peaks were observed in the appropriate ratios. In addition, 4,5-dichlorooctane (erythro) gave the same fragment ions as did entries 1 and 2; 4,5-dibromooctane (erythro) gave the same fragment ions as did entries 3 and 4; and 4-bromo-5-chlorooctane (erythro) gave all of the peaks listed. ^b Y = OTF = trifluoroacetate.

Table V. ¹³C Chemical Shifts^a for Diastereomeric Bromo- and Chlorohydrin Trifluoroacetates

octane	δ			
	C-OTF	C-(X)	CH ₂ -COTF	CH ₂ CX
5-Cl-4-OTF, erythro	81.38	62.91 (Cl)	35.69	32.85
5-Cl-4-OTF, threo	80.75	62.91 (Cl)	36.85	33.69
(7,8)-Cl,OTF-2-Me, erythro	81.16	62.77 (Cl)	33.56	30.55
(7,8)-Cl,OTF-2-Me, threo	80.69	62.86 (Cl)	34.65	31.40
5-Br-4-OTF, erythro	81.26	55.69 (Br)	36.14	33.72
5-Br-4-OTF, threo	80.58	55.69 (Br)	37.37	34.41
(7,8)-Br,OTF-2-Me, erythro	81.23	55.71 (Br)	34.20	31.67
(7,8)-Br,OTF-2-Me, threo	80.57	55.71 (Br)	35.22	32.16

^a See Experimental Section for details.

spectrometer (acetone-*d*₆). The ¹³C data were collected by using a pulse width of 8 μ s and 8K data points (Table V). Alkenes and alkene acetates were obtained from Chemical Samples Co. (Columbus, OH 43220) or Farchan Chemical Co. (Willoughby, OH 44094).²⁰

Additions of Halogen Trifluoroacetate to Alkenes. The following procedure was typical. *trans*-4-Octene (1.12 g, 10 mmol) was added neat dropwise to a chilled (5 °C) solution of *N*-bromosuccinimide (2.14 g, 12 mmol) in 15 mL of trifluoroacetic acid protected with a drying tube. The reaction was exothermic,

(20) *cis*-7,8-Epoxy-2-methyloctadecane is the sex pheromone of the gypsy moth, *Lymantria dispar* (L.) (B. A. Bierl, M. Beroza, and C. W. Collier, *Science*, **170**, 87 (1970)); (*Z*)- and (*E*)-9-tetradecen-1-ol acetates are portions of the sex pheromones of several moth species (M. S. Mayer and J. R. McLaughlin, *Fl. Agric. Exp. St. Monogr. Ser.*, **6** (1975)); (*Z*)-, (*E*)-7,11-hexadecadien-1-ol acetate is the sex pheromone of the Angoumois grain moth, *Sitotroga cerealella* (K. W. Vick, H. C. F. Su, L. L. Sower, P. G. Muhany, and D. C. Drummond, *Experientia*, **30**, 17 (1974)) and is a component of the sex pheromone of the pink bollworm moth, *Pectinophora gossypiella* (H. E. Hummel, L. K. Gaston, H. H. Shorey, R. S. Kaae, K. S. Byrne, and R. M. Silverstein, *Science*, **181**, 873 (1973)); B. A. Bierl, M. Beroza, R. T. Staten, P. E. Sonnet, and V. E. Adler, *J. Econ. Entomol.*, **67**, 211 (1974)).

and the addition was controlled to keep the temperature ≤ 20 °C. The resulting solution was stirred without external cooling for 15 min and was then worked up by dilution with water and hexane extraction. The organic phase was washed several times with water and dried (MgSO₄). The product was distilled bulb-to-bulb and gave 2.75 g (90%) of the *erythro*-5-bromo-4-octanol trifluoroacetate: bp 100–110 °C (25 mm); IR (CCl₄) 1785 (CF₃C=O) cm⁻¹; ¹H NMR (acetone-*d*₆) δ 3.94 (m, 1, CHBr), 5.07 (m, 1, CHOTF); ¹³C NMR and CI mass spectra discussed in the text. The *erythro*- and *threo*-bromo- and -chlorohydrin trifluoroacetates were prepared in 70–90% distilled yields. Relative retention times for diastereomeric pairs of octanes using column 3 were the following (compound, temperature, threo:erythro): 5-Cl-4-OTF, 65 °C, 1.14; 5-Br-4-OTF, 65 °C, 1.18; 5-Br-4-Cl, 65 °C, 1.13; 7(8)-Cl-8(7)-OTF-2-Me, 160 °C, 1.09; 7(8)-Br-8(7)-OTF-2-Me, 160 °C, 1.06; for tetradecan-1-ol acetate, 9(10)-Cl-10(9)-OTF, 155 °C, 1.13.

Additions of Trifluoroacetyl Halides to Epoxides. The alkenes were epoxidized with 1.5 equiv of *m*-chloroperbenzoic acid in CH₂Cl₂ in the usual way. Crude epoxidation products were employed directly. Trifluoroacetic anhydride (0.6 mL, 4.0 mmol) was added to a stirred solution of LiCl (0.2 g, 4.5 mmol) that had been dried at 130 °C for 24 h in 10 mL of dry DMF (drying tube).

After 5 min, the epoxide (3.5 mmol) was injected, and the solution was then stirred at ambient temperature overnight (actually less time was required, as discussed in the text). The reaction mixture was diluted with water, and the halo ester was extracted with hexane. The crude products were obtained in >90% yields, and their diastereomeric constitutions were assessed by GLC comparison with the alkene addition products.

Reduction of *vic*-Halohydrin Trifluoroacetates with NaI. The addition products that were obtained from epoxides in DMF could be reduced directly. Dry NaI (2.4 g, 16 mmol) was added to a solution of the *vic*-halotrifluoroacetate (3.5 mmol), and the mixture was heated in an oil bath for 20–24 h at 130 °C for chloro esters (90 °C for bromo esters). The mixture was cooled, diluted with water containing some NaHSO₃, and extracted with hexane. Efficient cooling was required when octenes were produced. The olefins were then distilled (bulb-to-bulb) and converted to *vic*-chlorohydrin trifluoroacetates (NCS, TFAH) or epoxides for GLC analysis. Alkene esters were analyzed directly with column 2.

Reduction of *vic*-Halohydrin Trifluoroacetates with Zn. The *vic*-halohydrin trifluoroacetates (0.2 g) were dissolved in 5 mL of dry DMF at 0 °C containing 3 drops of HOAc. Activated Zn¹⁶ (0.4 g) was added, and the resultant mixture was stirred at 0 °C overnight. The mixture was diluted with water, and the crude olefinic product was extracted with hexane for analysis as described. Reduction was complete; no byproducts were noted.

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Registry No. *cis*-4,5-epoxyoctane, 1439-06-1; *cis*-4,5-epoxydecane, 60788-60-5; *trans*-5,6-epoxydecane, 2165-61-9; *cis*-7,8-epoxy-2-methyloctadecane, 29804-22-6; (*Z*)-4-octene, 7642-15-1; (*E*)-4-octene, 14850-23-8; (*E*)-4-decene, 19398-89-1; (*Z*)-5-decene, 7433-78-5; (*Z*)-2-methyl-7-octadecene, 35354-39-3; (*E*)-2-methyl-7-octadecene, 40302-56-5; (*Z*)-9-tetradecen-1-ol acetate, 16725-53-4; (*Z*)-3-tetradecen-1-ol acetate, 54897-65-3; (*Z,Z*)-1,7,13-pentacosatriene, 63623-55-2; (*Z,E*)-1,7,13-pentacosatriene, 72032-24-7; (*E*)-9-tetradecen-1-ol acetate, 23192-82-7; (*E*)-3-tetradecen-1-ol acetate, 56221-90-0; (*E,E*)-1,7,13-pentacosatriene, 72032-23-6; (*E,Z*)-1,7,13-pentacosatriene, 72032-22-5; *erythro*-5-chloro-4-octanol trifluoroacetate, 72138-61-5; *threo*-5-chloro-4-octanol trifluoroacetate, 72152-05-7; *erythro*-5-bromo-4-octanol trifluoroacetate, 72138-62-6; *threo*-5-bromo-4-octanol trifluoroacetate, 72138-63-7; *threo*-5-iodo-4-octanol trifluoroacetate, 72138-64-8; *erythro*-7-chloro-2-methyl-8-octadecanol trifluoroacetate, 72138-65-9; *threo*-7-chloro-2-methyl-8-octadecanol trifluoroacetate, 72138-66-0; *erythro*-7-bromo-2-methyl-8-octadecanol trifluoroacetate, 72138-67-1; *threo*-7-bromo-2-methyl-8-octadecanol trifluoroacetate, 72138-68-2; *trans*-4,5-epoxyoctane, 1689-70-9; *trans*-7,8-epoxy-2-methyloctadecane, 42991-03-7.