fect on the ketone. We will now consider the arguments in favor of the first hypothesis. The increase of pK_{CH} with the degree of branching is expected since the enolate has greater steric requirements than the ketone. The constancy of k_{23} and the variation of k_{32} with pK_{CH} are explicable if the steric requirements of the enolate are the same as those of the transition state. This is expected, since only a flat transition state will allow conjugation with the carbonyl oxygens. Unfortunately, we have practically no knowledge of the structure of the keto form (all we know is that the dipole moment is greater for the ketone than for the enol) and it does not seem certain to us that the effect, if it is steric, would be more important on the enolate than on the ketone. Moreover, the probability of an isosteric effect on the enol, enolate, and ketonic transition state appears difficult to accept; the condition of simultaneous coplanarity is not sufficient to reach such a conclusion. The following considerations lead us to believe that an electronic effect operating principally on the keto form is the most probable.

(1) The correlations pK_{CH}, log K_T, and log $k_{32} = f(\sigma^*)$ do not support a steric effect interpretation.

(2) Ingold,[19] quoting Hughes, concludes that the +I effect of alkyl groups would lead to an increase in the thermodynamic stability of the ketone.

(3) The coupling constant between the methyl and acidic protons is not affected by alkyl substitution, probably indicating a constant planar geometry for the enol form.

(4) The variation of the enol content with respect to R = H corresponds to a decrease for electron-donating substituents and an increase for electron-withdrawing substituents.

Acknowledgments. We would like to express our appreciation to Dr. F. Garnier and the late Dr. P. Alcais, who assisted in the production of this article through numerous fruitful discussions. The authors are grateful to J. Y. Dugast for his participation in the experimental work.

Registry No.—I, 141-97-9; II, 609-14-3; III, 607-97-6; IV, 1540-28-9; V, 1540-29-0; VI, 1522-46-9; VII, 1540-31-4.

References and Notes

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A Study of Acetate Participation in Acyclic Epoxide Systems. Acid-Catalyzed Rearrangements of *trans*- and *cis*-1-Acetoxy-3,4-epoxypentanes, -4,5-epoxyhexanes, and -5,6-epoxyheptanes

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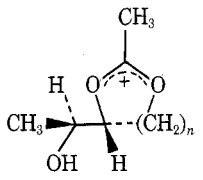
Received April 13, 1973

Acid-catalyzed rearrangements of *trans*- and *cis*-1-acetoxy-3,4-expoypentanes gave, respectively, *cis*- and *trans*-2-methyl-3-acetoxytetrahydrofuran. Similar reaction of *cis*- and *trans*-1-acetoxy-4,5-epoxyhexane gave *threo*- and *erythro*-2-(1-acetoxyethyl)tetrahydrofuran. In the course of these rearrangements the configuration at the epoxide carbons is retained. The mechanism of these rearrangements, elucidated by ^{18}O-labeling experiments, is consistent with the intermediacy of ortho esters. When the ester group is further removed from the epoxide moiety no participation is observed.

The present investigation, as part of a general study of the chemistry of epoxides, was prompted by the possibility of forming bicyclic ortho esters 2 by intramolecular hydroxyl attack on 1,3-dioxolenium ions 1.

Neighboring-group participation by ester groups to give 1,3-dioxolenium ions is now well established.[1] In 1942 Winstein and Buckles[2] found that solvolysis of 2-acetoxy-3-bromobutanes in dry acetic acid–silver acetate takes place with retention of configuration, threo bromo acetate giving the *dl* diacetate and the erythro bromo acetate giving meso diacetate. The postulated 1,3-dioxolenium ion intermediate 4 was later observed[3] by nmr spectroscopy whan 3-acetoxy-2-chloro-2,3-dimethylbutane (3) was dissolved in SbF_5–SO_2 or SbF_5–FSO_3H–SO_2 at −60°. Meer-



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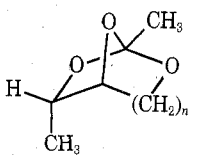

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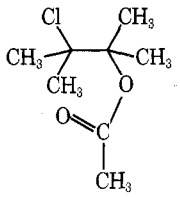
wein, *et al.*,[4] were able to prepare stable 1,3-dioxolenium salts **6** by reaction of fluoro esters **5** with boron trifluoride.



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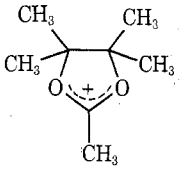

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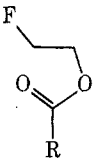

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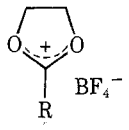

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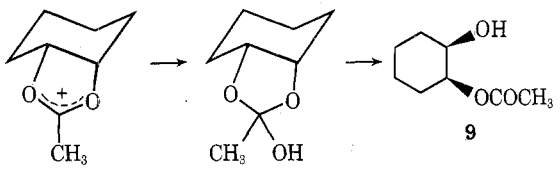
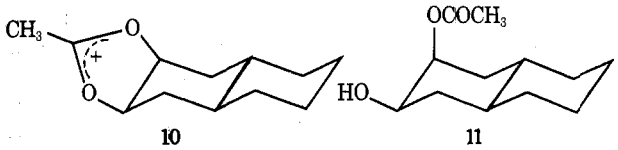
1,3-Dioxolenium ions react with anionic nucleophiles and with water or alcohols. For reaction with water, ring opening occurs *via* an ortho ester **8** rather than attack by water at a C–C carbon.[5] This is demonstrated by reaction of acetonium ion **7** with water to give the cis alcohol ester **9**.



7 8 9

Ring opening of ortho esters takes place with remarkable stereospecificity.[6] The 1,3-dioxolenium ion **10** in moist acetic acid gives the thermodynamically less stable acetoxy alcohol **11**.

Partial hydrolysis of the ortho ester **12** under mild conditions gives almost exclusively axial ester **11**. Ortho esters can be prepared by reaction of 1,3-dioxolenium ions



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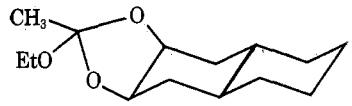

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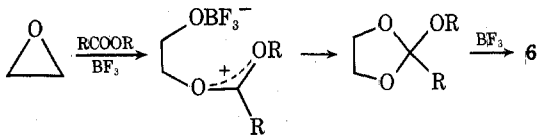


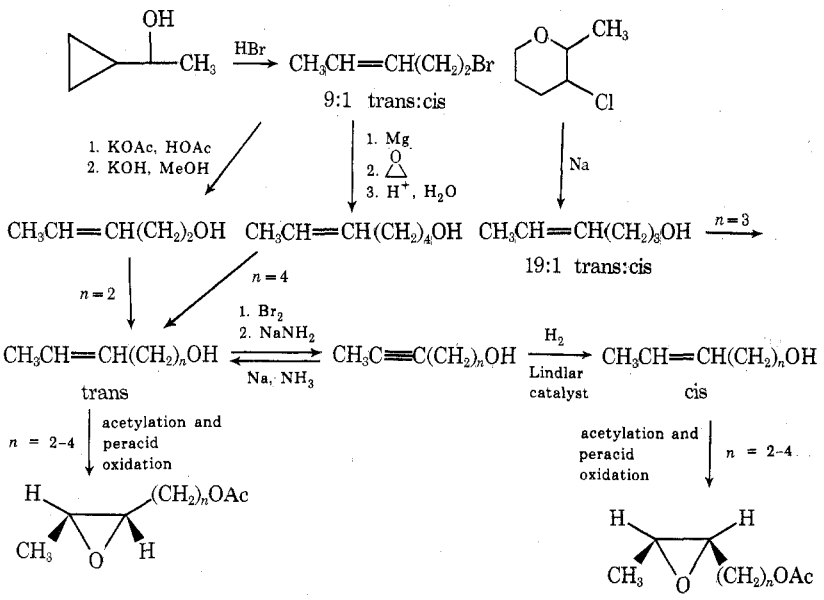
with alcohols or by reaction of epoxides with carboxylic esters in the presence of catalytic amounts of BF_3. In the presence of greater amounts of BF_3 only the 1,3-dioxolenium salt **6** is observed.

Results

We now report the preparation (Scheme I) and acid-catalyzed reactions of *cis*- and *trans*-1-acetoxy-3,4-epoxypentanes (**13** and **15**), -1-acetoxy-4,5-epoxyhexanes (**17** and **21**), and -1-acetoxy-5,6-epoxyheptanes (**25** and **28**).

The common intermediate to the synthesis of *trans*-pent-3-en-1-ol, -hex-4-en-1-ol, and -hept-5-en-1-ol, precursors to the required trans epoxides, was *trans*-1-bromopent-3-ene.[7] A 1:9 mixtures of *cis*- and *trans*-1-bromopent-3-ene was prepared by reaction of cyclopropylcarbinol with hydrogen bromide. The pure *trans*-1-bromopent-3-ene could not be separated from this mixture by distillation. The 1-acetoxypent-3-enes prepared by reaction of the mixed 1-bromopent-3-enes with potassium acetate in glacial acetic acid were similarly inseparable. After alkaline hydrolysis *trans*-pent-3-en-1-ol could be purified by distillation. The required *trans*-1-acetoxy-3,4-epoxypentane was prepared by oxidation of *trans*-1-acetoxypent-3-ene with monoperoxyphthalic acid. The acetoxy olefin was prepared by acetylation of the corresponding hydroxy olefin. The *cis*-pent-3-en-1-ol was prepared from the mixed pent-3-en-1-ols by bromination and dehydrobromination with sodium amide to give pent-3-yn-1-ol.[8] The yield was low (13%) and extensive variation of reaction conditions failed to improve the yield. Hydrogenation of pent-3-yn-1-ol to *cis*-pent-3-en-ol was carried out over Lindlar cata-

Scheme I

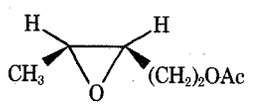


lyst. The *cis*-pent-3-en-1-ol was acetylated with acetic anhydride–pyridine and epoxidized with monoperoxyphthalic acid to give *cis*-1-acetoxy-3,4-epoxypentane (**13**).

A mixture of *cis*- and *trans*-hex-4-en-1-ol was prepared by addition of formaldehyde to the Grignard reagent formed from *cis*- and *trans*-1-bromopent-3-enes. The reaction was, however, inefficient and the mixture of alcohols could not be separated by preparative glc. An alternative reaction pathway[9] involving reaction of 3-chloro-2-methyltetrahydropyran with sodium afforded a 1:19 mixture of *cis*- and *trans*-hex-4-en-1-ol. The mixed hydroxy alkenes were brominated and dehydrobrominated to give hex-4-yn-1-ol in good yield. Reduction of hex-4-yn-1-ol with sodium in liquid ammonia afforded pure *trans*-hex-4-en-1-ol, which after acetylation followed by epoxidation with monoperoxyphthalic acid gave *trans*-1-acetoxy-4,5-epoxyhexane (**21**). Hydrogenation of hex-4-yn-1-ol over Lindlar catalyst gave *cis*-hex-4-en-1-ol. The alkene was converted into *cis*-1-acetoxy-4,5-epoxyhexene (**17**) in the usual manner.

A 1:9 mixture of *cis*- and *trans*-hept-5-en-1-ols was prepared by reaction of the Grignard reagent prepared from the *cis*- and *trans*-1-bromopent-3-ene mixture with ethylene oxide.[10] The *cis*- and *trans*-hept-5-en-1-ols could not be separated by preparative glc and were prepared in a similar manner to the hexenols.

Rearrangements of Epoxy Acetates. Reaction of *cis*-1-acetoxy-3,4-epoxypentane (**13**) with boron trifluoride etherate in ether as solvent gave *trans*-3-acetoxy-2-methyltetrahydrofuran (**14**) in 40% yield. The identity of this



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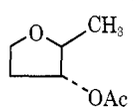

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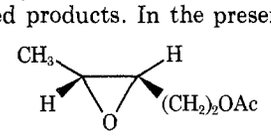
product follows from the nmr spectra and from its identity after hydrolysis with the major product from reduction of dihydro-2-methylfuran-3(2*H*)-one with sodium in moist ether. Reduction of dihydro-2-methylfuran-3(2*H*)-one under these reaction conditions favors the formation of the thermodynamically more stable trans isomer. Reaction of *trans*-1-acetoxy-3,4-epoxypentane (**15**) with boron trifluoride etherate in ether gave the isomeric furan, *cis*-3-acetoxy-2-methyltetrahydrofuran (**16**), but in higher yield (68%). Reduction with $LiAlH_4$ gave *cis*-2-methyltetrahydrofuran-3-ol, identical with the minor product obtained with sodium–moist ether reduction of dihydro-2-methylfuran-3(2*H*)-one. The configuration of the 2-methyltetrahydrofuran-3-ols was further established in that the methyl group for the cis isomer was deshielded (δ 1.25) in the nmr spectra relative to the trans isomer (δ 1.18), consistent with the proximity of the methyl and hydroxyl groups in the former compound.[11] The *cis*- and *trans*-1-acetoxy-3,4-epoxypentanes (**13** and **14**) also gave the corresponding *trans*- and *cis*-3-acetoxy-2-methyltetrahydrofurans (**14** and **16**) when the reaction was carried out using *p*-toluenesulfonic acid or trifluoroacetic acid in ether. The formation of the rearranged furans in the *p*-toluenesulfonic acid and trifluoroacetic acid reactions excludes the possible intermediacy of fluorohydrins in the analogous reaction using boron trifluoride etherate. On reaction with *p*-toluenesulfonic acid the cis epoxide **13** gave a mixture of trans (**14**, 64%) and cis furans (**16**, 24%)[12] and two unidentified products. In the presence of trifluoroacetic acid,



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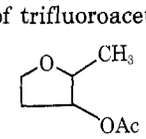

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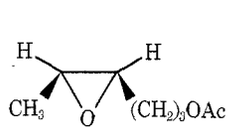
the major product detected by glc was trans furan (**14**, 97%). Only a trace of the cis furan **16** could be detected. Similar reaction of trans epoxide **15** with *p*-toluenesulfonic acid or trifluoroacetic acid gave mixtures containing 10% trans furan **14** and 80% cis furan **16** and 5% trans furan **14** and 95% cis furan **16**, respectively.

Reaction of *cis*- and *trans*-1-acetoxy-4,5-epoxyhexane (**17**) with boron trifluoride etherate in ether was slower than reaction of the corresponding epoxypentanes and gave from the cis epoxide **17** *erythro*-2-(1-acetoxyethyl)tetrahydrofuran (**18**, 30%), *threo*-1-acetoxy-5-fluorohexan-4-ol (**19**, 14%), *threo*-1-acetoxy-4-fluorohexan-5-ol (**20**, 7%), 1-acetoxyhexan-5-one (14%), and 1-acetoxyhexan-4-one (30%); and from the trans epoxide **21** *threo*-2-(1-acetoxyethyl)tetrahydrofuran (**22**, 62%), *erythro*-1-acetoxy-5-fluorohexan-4-ol (**23**, 17%), *erythro*-1-acetoxy-4-fluorohexan-5-ol (**24**, 13%), 1-acetoxyhexan-5-one (trace), and 1-acetoxyhexan-4-one (3%). The structures of the 2-(1-acetoxyethyl)tetrahydrofurans (**18** and **22**) were established from the nmr spectra and from the conversion of the acetates into known threo and erythro alcohols by reaction with $LiAlH_4$. Solution infrared spectra of these alcohols established the configuration, intramolecular hydrogen bonding being less favored for the erythro isomer than for the threo isomer.[13] The configuration of the fluorohydrins follows from the known preference for opening of epoxides with inversion[14] of configuration at the site of nucleophilic attack and from reaction with KO-*t*-Bu-*t*-BuOH.[15]



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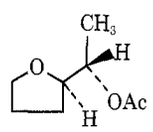

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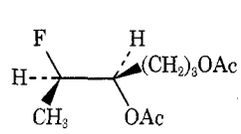

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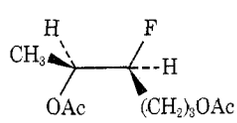

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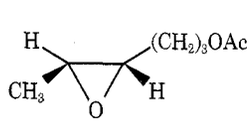

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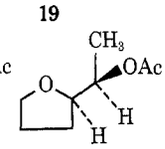

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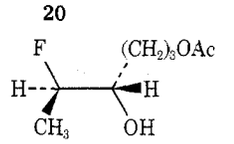

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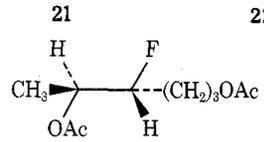

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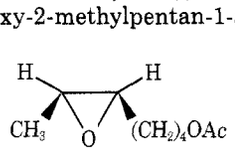
Reaction of *cis*- and *trans*-1-acetoxy-5,6-epoxyheptanes (**25** and **28**) with boron trifluoride etherate in ether is slow and gives from the cis epoxide **25** 1-acetoxyheptan-5-one (35%), 1-acetoxyheptan-6-one (25%), *threo*-1-acetoxy-6-fluoroheptan-5-ol (**26**, 13%), and *threo*-1-acetoxy-5-fluoroheptan-6-ol (**27**, 10%); and from the trans epoxide **28** 5-acetoxy-2-methylpentan-1-al (**29**, 5%), 1-acetoxyheptan-



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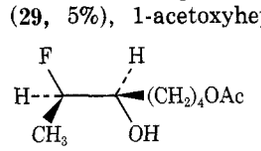

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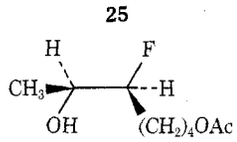

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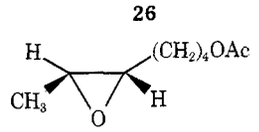

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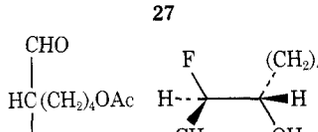

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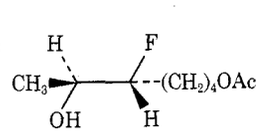

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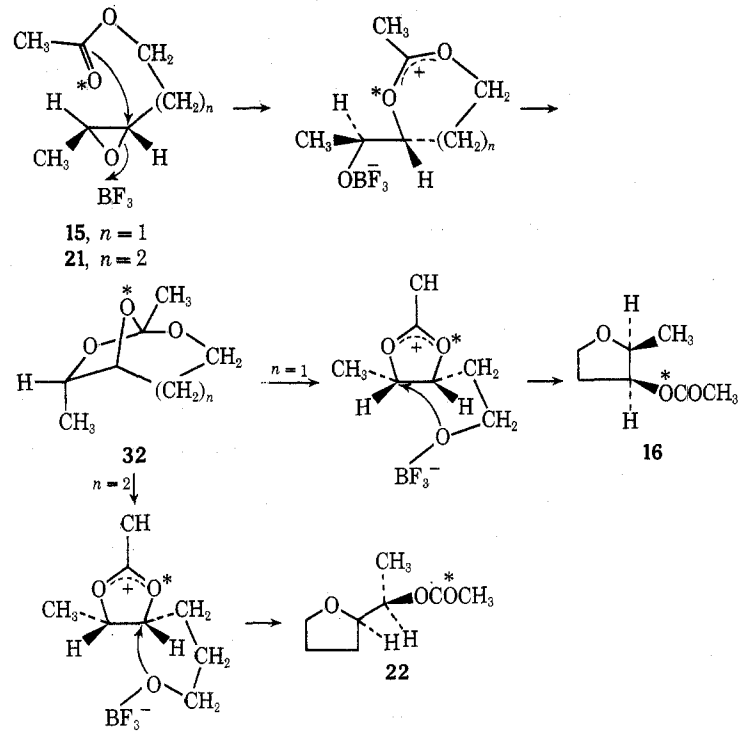
Scheme II



5-one (11%), 1-acetoxyheptan-6-one (8%), *erythro*-1-acetoxy-6-fluoroheptan-5-ol (**30**, 36%), and *erythro*-5-fluoroheptan-6-ol (**33**, 35%).

Discussion

The acid-catalyzed reactions of *trans*- and *cis*-1-acetoxy-3,4-epoxypentanes and -1-acetoxy-4,5-epoxyhexanes gave products that can only arise from intramolecular acetate participation with epoxide C–O bond cleavage. The reaction of *cis*- and *trans*-1-acetoxy-5,6-epoxyheptanes (**17**, and **21**) with boron trifluoride etherate is, however, dominated by two reaction processes which do not involve intramolecular ester participation. Attack by a fluoride-containing nucleophile occurs with consequent fluorohydrin formation and hydride migration occurs with rearrangement to ketone products. For both the *cis*- and *trans*-1-acetoxy-5,6-epoxyheptanes little discrimination is observed between the epoxide carbons for the site of nucleophilic attack. Attack by fluoride is the dominant reaction path for the trans epoxide; however ketone formation predominates from the cis epoxide. The fluorohydrin products were shown by separate experiment to be stable under the reaction conditions and are therefore not intermediates in the formation of ketone products.

The same features of reaction were observed for reaction of *cis*- and *trans*-1-acetoxy-4,5-epoxyhexanes (**17** and **21**) with boron trifluoride etherate. Fluorohydrin formation was favored from the trans epoxide **21** and hydride migration was favored from the cis epoxide **17**. The most notable feature[16] of the reaction of the hexane epoxides was the stereoselective formation of *threo*- and *erythro*-2-(1-acetoxyethyl)tetrahydrofuran (**22** and **18**). Products analogous to these furans were isolated from the reaction of *cis*- and *trans*-1-acetoxy-3,4-epoxypentane (**13** and **15**).

The formation of these furans **14** and **16** from epoxides **13** and **15** and **18** and **22** from epoxides **17** and **21** can be accounted for as shown in Scheme II for the trans epoxides. Participation by the terminal acetate with cleavage of the epoxide C–O bond results in formation of a dioxolenium ion which by attack with the OBF_3^- moiety gives the ortho ester **32**. The ortho ester can rearrange intramolecularly to give, when $n = 1$, the furan **16** and, when $n = 2$, furan **22**.

The validity of the reaction scheme was demonstrated by ^{18}O-labeling experiments. Rearrangement of *trans*-1-acetoxy-3,4-epoxypentane (**15**), ^{18}O enriched at the acetate carbonyl, gave *cis*-3-acetoxy-2-methyltetrahydrofuran (**16**, 21.5% ^{18}O) which on hydrolysis to the alcohol showed no significant loss of oxygen label (20% ^{18}O). The carbonyl oxygen of the starting acetate must therefore be present as the ether or hydroxyl oxygen in the product. Reaction of *trans*-1-acetoxy-4,5-epoxyhexane (**21**) labeled at the carbonyl oxygen with ^{18}O gave labeled *threo*-2-(1-acetoxyethyl)tetrahydrofuran (**22**, 21% ^{18}O) which on hydrolysis gave *threo*-2-(1-hydroxyethyl)tetrahydrofuran with complete loss of oxygen label.

Experimental Section

***trans*-1-Bromopent-3-ene.** The procedure of Julia, *et al.*,[7] was used in the preparation of this material. A mixture of 32.5 g of α-methylcyclopropanemethanol and 150 ml of 48% hydrobromic acid was stirred rapidly for 10 min. The reaction mixture was extracted with light petroleum ether, neutralized with sodium bicarbonate solution, and dried with sodium sulfate. The solvent was removed to give a 1:9 mixture of *cis*- and *trans*-1-bromopent-3-ene: bp 125°; ν_{max} 970 cm^{-1}; nmr δ 5.45 ($W_{1/2}$ = 60 Hz, C^3 H, C^4 H), 3.30 (apparent t, J = 7 Hz, $-CH_2Br$), 2.83–2.25 (C^2 H_2), 1.65 (d, J = 4.5 Hz, C^5 H_3).

***trans*-1-Acetoxypent-3-ene.** The method of Julia *et al.*,[7] was used. A solution of 70 g of *cis*- and *trans*-1-bromopent-3-ene and 146 g of potassium acetate in 300 ml of acetic acid was heated under reflux for 12 hr. The product was extracted into ether, washed with aqueous sodium bicarbonate, and dried with anhydrous sodium carbonate. After removal of solvent, distillation gave a 1:9 mixture of *cis*- and *trans*-1-acetoxypent-3-ene (53 g): bp 92° (100 mm); ν_{max} 1745, 1360, 1345, and 965 cm^{-1}; nmr δ 5.46 ($W_{1/2}$ = 48 Hz, C^3 H, C^4 H), 4.05 (apparent t, J = 7 Hz, $-CH_2OAc$), 2.50–2.10 (C^2 H_2), 2.02 ($-COCH_3$), 1.63 (d, J = 4.5 Hz, C^5 H_3).

***trans*-Pent-3-en-5-ol.** A solution of 42 g (1:9) of *cis*- and *trans*-1-acetoxypent-3-ene and 56 g of potassium hydroxide in 200 ml of methanol was heated under reflux for 1 hr. The hydroxy olefin was extracted into ether washed with water and dried. After removal of solvent the mixture was carefully distilled through an annular teflon spinning band distillation column to give *trans*-pent-3-en-1-ol free of the cis isomer: bp 78–79° (88 mm); ν_{max}

3375 and 965 cm^{-1}; nmr δ 5.50 ($W_{1/2}$ = 48 Hz, C^3 H, C^4 H), 3.60 (apparent t, J = 6.5 Hz, $-CH_2OH$), 2.47–2.05 (C^2 H_2), 1.67 (d, J = 4.5 Hz, C^5 H_3). Acetylation of *trans*-pent-3-en-1-ol in acetic anhydride–pyridine gave *trans*-1-acetoxypent-3-ene.

***trans*-Acetoxy-3,4-epoxypentane (15).** A solution of 1.28 g of *trans*-1-acetoxypent-3-ene in 50 ml of a 0.35 *M* monoperoxyphthalic acid–ether solution was kept at 5° for 1 week. Excess anhydrous potassium carbonate was added and the mixture was filtered. After the ether was removed by distillation, preparative glc gave *trans*-1-acetoxy-3,4-epoxypentane (15, 0.86 g): ν_{max} 1745, 1360, 1350 cm^{-1}; nmr δ 4.18 (apparent t, J = 6 Hz, $-CH_2OAc$), 2.93–2.58 (C^3 H, C^4 H), 2.12–1.65 (C^2 H_2), 2.03 ($-COCH_3$), 1.28 (d, J = 5 Hz, C^5 H_3).

Anal. Calcd for $C_7H_{12}O_3$: C, 58.3; H, 8.4. Found: C, 57.8; H, 8.4.

Pent-3-yn-1-ol. The procedure of Crombie and Harper[8] was used in the preparation of this material. To a solution of 30 g of *trans*-pent-3-en-1-ol in 100 ml of ether was added 1 molar equiv of bromine. After removal of ether the dibromo alcohol was added to a solution prepared by the addition of 50 g of sodium to 1.5 l. of ammonia liquid to which 0.25 g of ferric chloride had been added. After 30 min ammonium chloride was added and the ammonia was allowed to evaporate. The product was extracted into ether, washed with water, and dried. After removal of solvent, pent-3-yn-1-ol was isolated by preparative glc. The maximum yield of product that could be isolated was 13%: bp 154–157°; ν_{max} 3375 cm^{-1}; nmr δ 3.67 (apparent t, J = 6 Hz, $-CH_2OH$), 2.55–2.20 (C^2 H_2), 1.78 (t, J = 2.5 Hz, C^5 H_3).

***cis*-Pent-3-en-1-ol.** The method of Crombie and Harper[8] was used. A mixture of pent-3-yn-1-ol and 50 mg of Lindlar catalyst was stirred in a hydrogen atmosphere until 1 mol of hydrogen had been adsorbed. The reaction was slow and the catalyst was changed several times. After filtration to remove the catalyst and evaporation of the solvent, *cis*-pent-3-en-1-ol was isolated by preparative glc: ν_{max} 3350 and 710 cm^{-1}; nmr δ 5.54 ($W_{1/2}$ = 48 Hz, C^3 H, C^4 H), 3.60 (apparent t, J = 6 Hz, $-CH_2OH$), 2.55–2.11 (C^2 H_2), 1.63 (d, J = 5 Hz, C^5 H_3).

***cis*-1-Acetoxy-3,4-epoxypentane (13).** A solution of 0.5 g of *cis*-pent-3-en-1-ol in 2.5 ml of pyridine and 0.6 ml of acetic anhydride was kept at room temperature overnight. Ether was added and the pyridine was removed by washing with dilute aqueous acid. After removal of solvent the residue was epoxidized with monoperoxyphthalic acid in the usual manner. The product, *cis*-1-acetoxy-3,4-epoxypentane (13, 0.49 g) was obtained pure by preparative glc: ν_{max} 1740, 1370, and 1360 cm^{-1}; nmr δ 4.22 (apparent t, J = 6 Hz, $-CH_2OAc$), 3.27–2.83 (C^3 H, C^4 H), 2.05 ($-OCOCH_3$), 1.92 (m, $J_{1,2} = J_{2,3} \cong 6$ Hz, C^2 H_2), 1.28 (d, J = 5.5 Hz, C^5 H_3).

Anal. Calcd for $C_7H_{12}O_3$: C, 58.3; H, 8.4. Found: C, 58.1; H, 8.4.

***trans*-Hex-4-en-1-ol.** The method of Crombie and Harper[9] was used. A solution of 2440 g of *cis*- and *trans*-3-chloro-3-methyltetrahydropyran in 1 l. of ether was treated with 92 g of sodium. After all the sodium had reacted the mixture was washed with water and the solvent was removed by distillation. After distillation of 1:9 mixture of *cis*- and *trans*-hex-4-en-1-ol was obtained: bp 68° (15 mm); ν_{max} 3350 and 960 cm^{-1}; nmr δ 5.44 ($W_{1/2}$ = 16 Hz, C^4 H, C^5 H), 3.60 (apparent t, J = 6 Hz, $-CH_2OH$), 2.27–1.85 (C^3 H_2), 1.85–1.30 (C^2 H_2), 1.63 (d, J = 5.5 Hz, C^6 H_3).

***trans*-1-Acetoxy-4,5-epoxyhexane (21).** A solution of 2 g of mixed *cis*- and *trans*-hex-4-en-1-ols in 10 ml of pyridine and 2 ml of acetic anhydride was kept at room temperature overnight. The product was isolated and epoxidized with monoperoxyphthalic acid. Preparative glc gave 1.9 g of pure *trans*-1-acetoxy-4,5-epoxyhexane (21): ν_{max} 1725, 1370, and 1360 cm^{-1}; nmr δ 4.10 (apparent t, J = 6 Hz, $-CH_2OAc$), 2.92–2.52 (C^4 H, C^5 H), 2.02 ($-OCOCH_3$), 1.97–1.40 (C^2 H_2, C^3 H_2), 1.28 (d, J = Hz, C^6 H_3).

Anal. Calcd for $C_8H_{14}O_3$: C, 60.7; H, 8.9. Found: C, 60.7, H, 8.9.

***cis*-Hex-4-en-1-ol.** To a solution of 30 g of *trans*-hex-4-en-1-ol in 100 ml of ether was added 1 molar equiv of bromine. After removal of excess bromine the dibromo alcohol was added to a solution prepared by addition of 50 g of sodium to 1.5 l. of liquid ammonia to which 0.25 g of ferric chloride had been added. The product hex-4-yn-1-ol was purified and then hydrogenated over Lindlar catalyst. The reaction product was purified by preparative glc to give 3.9 g of *cis*-hex-4-en-1-ol: ν_{max} 3350 and 710 cm^{-1}; nmr δ 5.45 ($W_{1/2}$ = 40 Hz, C^4 H, C^5 H), 3.63 (apparent t, J = 6 Hz, $-CH_2OH$), 2.38–1.86 (C^3 H_2), 1.86–1.35 (C^2 H_2), 1.62 (d, J = 5 Hz, C^6 H_3).

***cis*-1-Acetoxy-4,5-epoxyhexane (17).** A solution of 1 g of *cis*-hex-4-en-1-ol in 50 ml of pyridine and 1 ml of acetic anhydride was kept at room temperature overnight. The product was isolated in the usual manner and epoxidized with monoperoxyphthalic acid. The reaction product was purified by preparative glc to give 0.95 g of *cis*-1-acetoxy-4,5-epoxyhexane (17): ν_{max} 1740, 1375, and 1350 cm^{-1}; nmr δ 4.13 (apparent t, J = 6 Hz, $-CH_2OAc$), 3.27–2.75 (C^4 H, C^5 H), 2.03 ($OCOCH_3$), 2.00–1.38 (C^2 H_2, C^3 H_2), 1.27 (d, J = 5 Hz, C^6 H_3).

Anal. Calcd for $C_8H_{14}O_3$: C, 60.7; H, 8.9. Found: C, 60.7; H, 8.9.

***trans*-Hept-5-en-1-ol.** The procedure of Dreger[10] was used in the preparation of this compound. The magnesium derivative of 27.5 g of a 1:9 mixture of *cis*- and *trans*-1-bromopent-3-ene was prepared in 90 ml of ether and allowed to react with an excess of ethylene oxide. The product was isolated in the usual manner and distillation on a spinning band column gave 20 g of a 1:9 mixture of *cis*- and *trans*-hept-5-en-1-ol: ν_{max} 3340 and 960 cm^{-1}; nmr δ 5.37 ($W_{1/2}$ = 15 Hz, C^5 H, C^6 H), 3.50 (apparent t, J = 6 Hz, $-CH_2OH$), 2.20–1.77 (C^4 H_2), 1.77–1.17 (m, C^3 H_2, C^4 H_2, C^7 H_3).

***trans*-1-Acetoxy-5,6-epoxyheptane (28).** A solution of 2 g of a 1:9 mixture of *cis*- and *trans*-hept-5-en-1-ols in 10 ml of pyridine and 2 ml of acetic anhydride was kept at room temperature overnight. The product was isolated in the usual manner and epoxidized with monoperophthalic acid. The reaction product was purified by preparative glc to remove the cis isomer and gave 1.8 g of *trans*-1-acetoxy-5,6-epoxyheptane (28): ν_{max} 1740, 1370, and 1355 cm^{-1}; nmr δ 4.07 (apparent t, J = 6 Hz, $-CH_2OAc$), 2.94–2.50 (C^5 H, C^6 H), 2.05 ($-OCOCH_3$), 1.83–1.43 (C^2 H_2, C^3 H_2, C^4 H_2), 1.28 (d, J = 5 Hz, C^7 H_3).

Anal. Calcd for $C_9H_{16}O_3$: C, 62.8; H, 9.4. Found: C, 62.9; H, 9.3.

***cis*-Hept-5-en-1-ol.** To a solution of 30 g of a 1:9 mixture of *cis*- and *trans*-hept-5-en-1-ols in 100 ml of ether was added 1 molar equiv of bromine. After removal of excess bromine the dibromo alcohol was added to a solution prepared by addition of 50 g of sodium to 1.5 l. of ammonia in the presence of catalytic amounts of ferric chloride. The product hept-5-yn-1-ol was purified by preparative glc and then hydrogenated over Lindlar catalyst to give 5.8 g of *cis*-hept-5-en-1-ol: ν_{max} 3350 and 710 cm^{-1}; nmr δ 5.42 ($W_{1/2}$ = 30 Hz, C^5 H, C^6 H), 3.65 (apparent t, J = 6 Hz, $-CH_2OH$), 2.42–1.86 (C^4 H_2), 1.77–1.10 (C^2 H_2, C^3 H_2), 1.62 (d, J = 5 Hz, C^7 H_3).

***cis*-1-Acetoxy-5,6-epoxyheptane (25).** *cis*-Hept-5-en-1-ol (1 g) was acetylated and epoxidized with monoperoxyphthalic acid in the usual manner. The final reaction product was purified by preparative glc to give 0.90 g of *cis*-1-acetoxy-5,6-epoxyheptane (25): ν_{max} 1740, 1380, and 1365 cm^{-1}; nmr δ 4.09 (apparent t, J = 6 Hz, $-CH_2OAc$), 3.23–2.73 (C^5 H, C^6 H), 2.03 ($-OCOCH_3$), 1.97–1.40 (C^2 H_2, C^3 H_2, C^4 H_2), 1.27 (d, J = 5 Hz, C^7 H_3).

Anal. Calcd for $C_9H_{16}O_3$: C, 62.8; H, 9.4. Found: C, 62.8; H, 9.3.

Rearrangement of *cis*-1-Acetoxy-3,4-epoxypentane (13) with Boron Trifluoride Etherate in Ether. A solution of 120.1 mg of *cis*-1-acetoxy-3,4-epoxypentane in 120 ml of sodium-dried ether was stirred and 430 mg of boron trifluoride etherate was added. After 2.5 hr at room temperature the reaction was quenched by adding 0.5 ml of a saturated potassium carbonate solution. After the mixture was stirred for 15 min, 118.2 mg of tetrahydrofurfuryl acetate was added as an internal standard for glc analysis. Anhydrous potassium carbonate was added to remove the water and the mixture was filtered. The crude reaction product was shown by glc to contain 40% *trans*-3-acetoxy-2-methyltetrahydrofuran and traces of two compounds that had retention times characteristic of ketone products. No other low-boiling compounds or fluorohydrins were found. The reaction was carried out in duplicate.

trans-3-Acetoxy-2-methyltetrahydrofuran (14) was isolated by preparative glc from a reaction carried out using 0.5 g of epoxide 15: ν_{max} 1735, 1365, and 1350 cm^{-1}; nmr δ 4.86 (m, $J_{3,4}$ = 3, $J_{3,2}$ = 6 Hz, C^3 H), 4.15–3.70 (C^2 H, C^5 H_2), 2.57–1.50 (C^4 H_2), 2.03 ($-OCOCH_3$), 1.22 (d, J = 6 Hz, C^2 CH_3).

Anal. Calcd for $C_7H_{12}O_3$: C, 58.3; H, 8.4. Found: C, 58.1; H, 8.3.

Rearrangement of *trans*-1-Acetoxy-3,4-epoxypentane (15) with Boron Trifluoride Etherate in Ether. Rearrangement of *trans*-1-acetoxy-3,4-epoxypentane (15) was carried out as above for the cis isomer. The crude reaction product was shown by glc using tetrahydrofurfuryl acetate as internal standard to contain *cis*-3-acetoxy-2-methyltetrahydrofuran (16) in 68% yield and traces of three compounds that had retention times characteristic of ketone products. The latter of these compounds had the same retention time as one of the trace products from rearrangement of

cis epoxide. No products with retention times characteristic of fluorohydrins were found.

cis-3-Acetoxy-2-methyltetrahydrofuran (**16**) was isolated by preparative glc from a reaction carried out on 1 g of *trans*-1-acetoxy-3,4-epoxypentane: ν_{max} 1740 and 1360 cm^{-1}; nmr δ 5.27 (m, J = 5.5, 2.2, 3.7 Hz, C^3 H), 4.25–3.52 (C^2 H, C^5 H_2), 2.67–1.67 (C^4 H_2), 2.07 ($-OCOCH_3$), 1.20 (d, J = 6 Hz, C^2 CH_3).

Anal. Calcd for $C_7H_{12}O_3$: C, 58.3; H, 8.4. Found; C, 58.2; H, 8.3.

Rearrangement of *cis*-1-Acetoxy-3,4-epoxypentane (13) with *p*-Toluenesulfonic Acid and Trifluoroacetic Acid in Ether. The reaction was carried out as for the boron trifluoride etherate catalyzed reaction but using an equivalent amount of an azeotropically dried solution of 4.7 g of *p*-toluenesulfonic acid in 1 l. of ether. The reaction product was isolated in the usual manner and shown by glc to be a mixture of *trans*-3-acetoxy-2-methyltetrahydrofuran (**14**, 64%), *cis*-3-acetoxy-2-methyltetrahydrofuran (**16**, 24%), and two unknown products (6% each). The reaction was carried out in the usual manner but with an equivalent amount of a solution of trifluoroacetic acid in ether as the acid catalyst. The reaction product, volatile to glc, contained *trans*-3-acetoxy-2-methyltetrahydrofuran (**14**, 97%) and a trace of *cis*-3-acetoxy-2-methyltetrahydrofuran (**16**).

Rearrangement of *trans*-1-Acetoxy-3,4-epoxypentane (15) with *p*-Toluenesulfonic Acid and Trifluoroacetic Acid in Ether. The reaction was carried out as above but with *p*-toluenesulfonic acid as catalyst. The crude reaction product was shown by glc to contain *trans*-3-acetoxy-2-methyltetrahydrofuran (**14**, 10%), *cis*-3-acetoxy-2-methyltetrahydrofuran (**16**, 80%), and two unidentified compounds (6 and 4%). When trifluoroacetic acid was used as catalyst, the reaction product was *cis*-3-acetoxy-2-methyltetrahydrofuran (**16**, 95%) and *trans*-3-acetoxy-2-methyltetrahydrofuran (**14**, 5%).

Rearrangement of *cis*-1-Acetoxy-4,5-epoxyhexane (17) with Boron Trifluoride Etherate in Ether. The reaction of *cis*-1-acetoxy-4,5-epoxyhexane (**17**) with boron trifluoride etherate in ether was carried out as for *cis*-1-acetoxy-3,4-epoxypentane above. Cyclohexanol was used as the internal standard for glc analysis. The crude reaction product was shown to contain *erythro*-2-(1-acetoxyethyl)tetrahydrofuran (**18**, 30%), 1-acetoxyhexan-4-one (30%), 1-acetoxyhexan-5-one (14%), *threo*-1-acetoxy-5-fluoro-4-hydroxyhexane (**19**, 14%), and *threo*-1-acetoxy-4-fluoro-5-hydroxyhexane (**20**, 7%). The fluorohydrins were unstable to preparative glc and were converted by reaction with acetyl chloride in pyridine to the corresponding fluoro diacetates. The components were separated by preparative glc. *erythro*-2-(1-Acetoxyethyl)tetrahydrofuran (**18**) had ν_{max} 1740 and 1350 cm^{-1}; nmr δ 4.90 (m, $J_{Me,H}$ = 6, $J_{H,C2H}$ = 4.5 Hz, CHOAc), 4.70–3.60 (C^5 H_2), 2.13–1.53 (C^3 H_2, C^4 H_2), 2.03 ($-OOCOCH_3$), 1.22 [d, J = 6 Hz, $-CH(OAc)CH_3$]. Hydrolysis by $LiAlH_4$ gave *erythro*-2-(1-hydroxyethyl)tetrahydrofuran: ν_{max} (CCl_4) 3560 and 3588 cm^{-1}; nmr δ 4.12–2.50 (C^2 H, CHOH, C^5 H_2), 2.03–1.67 (C^3 H_2, C^4 H_2), 1.13 [d, $J_{CH,Me}$ = 6 Hz, $CH(OH)CH_3$].

1-Acetoxyhexan-4-one had ν_{max} 1740, 1718, and 1350 cm^{-1}; nmr δ 4.07 (apparent t, J = 6 Hz, $-CH_2OAc$), 2.50 (t, $J_{2,3}$ = 6 Hz, C^3 H_2), 2.45 (q, $J_{5,6}$ = 7 Hz, C^5 H_2), 2.2–1.5 (C^2 H_2), 2.03 ($-OCOCH_3$), 1.05 (t, $J_{5,6}$ = 7 Hz, C^6 H_3).

Anal. Calcd for $C_8H_{14}O_3$: C, 60.8; H, 8.9. Found: C, 60.8; H, 8.8.

1-Acetoxyhexan-5-one had ν_{max} 1740, 1720, and 1350 cm^{-1}; nmr δ 4.07 (apparent t, $J_{1,2}$ = 6 Hz, $-CH_2OAc$), 2.48 ($W_{1/2}$ = 15 Hz, C^4 H_2), 2.13 ($COCH_3$), 2.03 ($-OCOCH_3$), 1.77–1.48 (C^2 H_2, C^3 H_2).

Anal. Calcd for $C_8H_{14}O_3$: C, 60.7; H, 8.9. Found: C, 60.8; H, 8.9.

threo-1-4,Diacetoxy-5-fluorohexane (**19**) had ν_{max} 1740 and 1350 cm^{-1}; nmr δ 4.95 (m, $J_{4,F} \cong 17$, $J_{4,5} \cong 4$ Hz, $J_{4,3}$ not determined, C^4 H), 4.65 (m, $J_{5,F} \cong 49$, $J_{5,6}$ = 6, $J_{5,4} \cong 4$ Hz, C^5 H), 4.08 (apparent t, $J_{1,2}$ = 6 Hz, $-CH_2OAc$), 2.10 (C^4 $OCOCH_3$), 2.03 (C^1 $OCOCH_3$), 1.92–1.10 (C^2 H_2, C^3 H_2), 1.30 (d of d, $J_{6,F}$ = 24, $J_{6,5}$ = 6 Hz, C^6 H_3).

Anal. Calcd for $C_{10}H_{17}FO_4$: C, 54.5; H, 7.8; F, 8.6. Found: C, 54.1; H, 7.9; F, 8.8.

threo-1,5-Diacetoxy-4-fluorohexane (**20**) had ν_{max} 1740 and 1350 cm^{-1}; nmr δ 5.02 (m, $J_{5,F} \cong 22$, $J_{5,6}$ = 6, $J_{5,4} \cong 4$ Hz, C^5 H), 4.35 (m, $J_{4,F} \cong 47$, $J_{4,5} \cong 4$ Hz, $J_{4,3}$ not determined, C^4 H), 4.10 (apparent t, $J_{1,2}$ = 6 Hz, $-CH_2OAc$), 2.07 (C^5 $OCOCH_3$), 2.03 (C^1 $OCOCH_3$), 2.00–1.10 (C^2 H_2, C^3 H_2), 1.27 (d, J = 6 Hz, C^6 H_3).

Anal. Calcd for $C_{10}H_{17}FO_4$: C, 54.5; H, 7.8; F, 8.6. Found: C, 54.1; H, 8.0; F, 9.1.

Rearrangement of *trans*-1-Acetoxy-4,5-epoxyhexane (21) with Boron Trifluoride Etherate in Ether. The reaction of *trans*-1-acetoxy-4,5-epoxyhexane (**21**) with boron trifluoride etherate in ether was carried out under similar reaction conditions to that of the cis isomer. Cyclohexanol was used as the internal standard for glc analysis. The crude reaction product was shown to contain *threo*-2-(1-acetoxyethyl)tetrahydrofuran (**22**, 62%), 1-acetoxyhexan-4-one (3%), 1-acetoxyhexan-5-one (trace), *erythro*-1-acetoxy-5-fluorohexan-4-ol (**23**, 17%), and *erythro*-1-acetoxy-4-fluorohexan-5-ol (**24**, 13%). The fluorohydrins were unstable to preparative glc and were converted, by reaction with acetyl chloride in pyridine, to the corresponding fluoro diacetates. The products were then separated by preparative glc.

threo-2-(1-Acetoxyethyl)tetrahydrofuran (**22**) had ν_{max} 1735 and 1350 cm^{-1}; nmr δ 4.85 [m, $J_{H,2}$ = 6, $J_{H,Me}$ = 6 Hz, $-CH(CH_3)OAc$], 4.05–3.58 (C^2 H, C^5 H_2), 2.25–1.50 (C^3 H_2, C^4 H_2), 2.05 ($-OCOCH_3$), 1.20 [d, J = 6 Hz, $-CH(OAc)CH_3$]. Hydrolysis by reaction with $LiAlH_4$ gave *threo*-2-(1-hydroxyethyl)tetrahydrofuran: ν_{max} (CCl_4) 3578 cm^{-1}; nmr δ 4.23–2.87 (C^2 H, CHOH, C^6 H_2), 2.05–1.23 (C^3 H_2, C^4 H_2, C^5 H_2), 1.12 [d, $J_{CH,Me}$ = 6 Hz, $-CH(OH)CH_3$].

erythro-1,4-Diacetoxy-5-fluorohexane (**24**) had ν_{max} 1742, 1736, and 1355 cm^{-1}; nmr δ 4.95 (m, $J_{5,F}$ = 19, $J_{5,6}$ = 6, $J_{5,4} \cong 4$ Hz, C^5 H), 4.45 (m, $J_{4,F}$ = 49, $J_{4,5} \cong 4$, Hz, $J_{4,3}$ not determined, C^4 H), 4.10 (apparent t, $J_{1,2}$ = 6 Hz, $-CH_2OAc$), 2.07 (C^5 $OCOCH_3$), 2.03 (C^1 $OCOCH_3$), 1.97–0.92 (C^2 H_2, C^3 H_2), 1.25 (m, $J_{6,5}$ = 6, $J_{6,F}$ = 1.2 Hz, C^6 H_3).

Anal. Calcd for $C_{10}H_{17}FO_4$: C, 54.5; H, 7.8; F, 8.6. Found: C, 55.0; H, 8.0; F, 9.0.

The ketones 1-acetoxyhexan-4-one and 1-acetoxyhexan-5-one were identical with samples isolated from rearrangement of cis epoxide **17**.

Rearrangement of *cis*-1-Acetoxy-5,6-epoxyheptane (25) with Boron Trifluoride Etherate in Ether. A solution of 120.2 mg of *cis*-1-acetoxy-5,6-epoxyheptane (**25**) in 120 ml of sodium-dried ether was stirred and 960 mg of boron trifluoride etherate was added in three equal amounts over a period of 2 hr. The reaction was kept at room temperature for 24 hr. The boron trifluoride etherate was quenched by the addition of 1 ml of a saturated potassium carbonate solution. The product was isolated in the usual manner and shown by glc using tetrahydrofurfuryl acetate as standard to contain 1-acetoxyheptan-5-one (35%), 1-acetoxyheptan-6-one (25%), *threo*-1-acetoxy-6-fluoroheptan-5-ol (**26**, 13%), and *threo*-1-acetoxy-5-fluoroheptan-6-ol (**27**, 10%) The products were isolated from a reaction using 1 g of epoxide. The acetoxyfluoro alcohols decompose on preparative glc and so the reaction mixture was acetylated with acetyl chloride–pyridine before chromatography.

1-Acetoxyheptan-5-one had ν_{max} 1740, 1718, and 1350 cm^{-1}; nmr δ 4.05 (apparent t, $J_{2,1}$ = 6 Hz, $-CH_2OAc$), 2.65–2.22 (C^4 H_2, C^6 H_2), 2.03 ($OCOCH_3$), 1.78–1.45 (C^2 H_2, C^3 H_2), 1.05 (t, $J_{6,7}$ = 7 Hz, C^7 H_3).

Anal. Calcd for $C_9H_{16}O_3$: C, 62.8; H, 9.4. Found: C, 62.7; H, 9.3.

1-Acetoxyheptan-6-one had ν_{max} 1740, 1718, and 1350 cm^{-1}; nmr δ 4.03 (apparent t, $J_{2,1}$ = 6 Hz, $-CH_2OAc$), 2.43 (*ca.* t, $J_{5,4}$ = 6 Hz, C^5 H_2), 2.13 ($COCH_3$), 2.03 (C^1 $OCOCH_3$), 1.90–1.17 (C^2 H_2, C^3 H_2, C^4 H_2).

Anal. Calcd for $C_9H_{16}O_3$: C, 62.8; H, 9.4. Found: C, 62.8; H, 9.3.

threo-1,5-Diacetoxy-6-fluoroheptane had ν_{max} 1740 and 1355 cm^{-1}; nmr δ 4.93 (m, $J_{5,F} \cong 17$, $J_{5,6} \cong 4$ Hz, $J_{5,4}$ not determined, C^5 H), 4.67 (m, $J_{6,F}$ = 49, $J_{6,7}$ = 6, $J_{6,5} \cong 4$ Hz, C^6 H), 4.05 (apparent t, $J_{1,2}$ = 6 Hz, CH_2OAc), 2.10 (C^5 $OCOCH_3$), 2.02 (C^1 $OCOCH_3$), 1.92–1.10 (C^2 H_2, C^3 H_2, C^4 H_2), 1.28 (m, $J_{7,F}$ = 24, $J_{7,6}$ = 6 Hz, C^7 H_3).

Anal. Calcd for $C_{11}H_{19}FO_4$: C, 56.4; H, 8.2; F, 8.1. Found: C, 56.1; H, 8.2; F, 8.6.

threo-1,6-Diacetoxy-5-fluoroheptane had ν_{max} 1740 and 1355 cm^{-1}; nmr δ 5.00 (m, $J_{6,F}$ = 22, $J_{6,7}$ = 6, $J_{6,5}$ = 4 Hz, C^6 H), 4.37 (m, $J_{5,F} \cong 47$, $J_{5,6} \cong 4$ Hz, C^5 H), 4.05 (apparent t, $J_{1,2}$ = 6 Hz, CH_2OAc), 2.07 (C^6 $OCOCH_3$), 2.03 (C^1 $OCOCH_3$), 1.95–1.10 (C^2 H_2, C^3 H_2, C^4 H_2), 1.25 (m, $J_{6,7}$ = 6, $J_{7,F}$ = 0.8 Hz, C^7 H_3).

Anal. Calcd for $C_{11}H_{19}FO_4$: C, 56.4; H, 8.2; F, 8.1. Found: C, 56.0; H, 8.1; F, 8.5.

Rearrangement of *trans*-1-Acetoxy-5,6-epoxyheptane (28) with Boron Trifluoride Etherate in Ether. The reaction of *trans*-1-acetoxy-5,6-epoxyheptane (**28**) with boron trifluoride etherate was carried out in duplicate under the same reaction conditions as those of the cis isomer. Tetrahydrofurfuryl acetate was used as the internal standard for glc analysis. The crude reaction product was shown to contain 5-acetoxy-2-methylpentan-1-al (**29**,

5%), 1-acetoxyheptan-5-one (11%), 1-acetoxyheptan-6-one (8%), *erythro*-1-acetoxy-6-fluoroheptan-5-ol (**30**, 36%), and *erythro*-1-acetoxy-5-fluoroheptan-6-ol (**33**, 35%). The products were separated by preparative glc.

5-Acetoxy-2-methylpentan-1-al (**29**) had δ 9.60 (d, J = 2 Hz, CHCHO), 4.05 (apparent t, $J_{5,4}$ = 6 Hz, CH_2OAc), 2.67–2.17 (C^2 H), 2.03 ($OCOCH_3$), 1.85–1.05 (C^2 H_2, C^3 H_2, C^4 H_2), 1.10 (d, $J_{H,Me}$ = 6.5 Hz, $CHOH_3$). The aldehyde decomposed rapidly on storage.

1-Acetoxyheptan-5-one and 1-acetoxyheptan-6-one were identical in all respects with the same ketones obtained from rearrangement of the cis epoxide.

erythro-1-Acetoxy-6-fluoroheptan-5-ol (**30**) had ν_{max} 3475, 1740, 1370, and 1350 cm^{-1}; nmr δ 4.55 (m, $J_{6,F} \cong 49$, $J_{6,7}$ = 6, $J_{6,5}$ = 4 Hz, C^6 H), 4.08 (apparent t, $J_{1,2}$ = 6 Hz, CH_2OAc), 3.93–3.50 (m, C^5 H), 2.03 ($OCOCH_3$), 1.83–1.22 (C^2 H_2, C^3 H_2, C^4 H_2), 1.30 (m, $J_{7,F}$ = 25, $J_{7,6}$ = 6 Hz, C^7 H_3).

Anal. Calcd for $C_9H_{17}FO_3$: C, 56.2; H, 8.9; F, 9.9. Found: C, 56.2; H, 8.9, F, 10.6.

erythro-1-Acetoxy-5-fluoroheptan-6-ol (**31**) had ν_{max} 3475, 1740, 1370, and 1350 cm^{-1}; nmr δ 4.33 (m, $J_{5,F}$ = 49, $J_{5,6} \cong 5$, $J_{5,4} \cong 6$ Hz, C^5 H), 4.07 (apparent t, $J_{1,2}$ = 6 Hz, CH_2OAc), 3.87 (m, $J_{6,F} \cong 22$, $J_{6,7}$ = 6, $J_{6,5} \cong 4$ Hz, C^6 H), 2.03 ($OCOCH_3$), 2.10–1.00 (C^2 H_2, C^3 H_2, C^4 H_2), 1.20 (m, $J_{7,6}$ = 6, $J_{7,F}$ = 1.2 Hz, C^7 H_3).

Anal. Calcd for $C_9H_{17}FO_3$: C, 56.2; H, 8.9; F, 9.9. Found: C, 55.9; H, 8.8; F, 10.3.

Synthesis and Rearrangement of C=^{18}O *trans*-1-Acetoxy-3,4-epoxypentane (15). To a solution of *trans*-1-hydroxy-3,4-epoxypentane in 2 ml of pyridine was added 230 mg of acetyl chloride containing 21% ^{18}O label. The mixture was kept at room temperature for 16 hr. The product was isolated by means of ether and the pyridine was removed by washing with dilute acid. The solvent was removed by careful distillation and the crude acetoxy olefin was treated with 20 ml of 0.35 *M* monoperoxyphthalic acid at 5° for 9 days. Anhydrous potassium carbonate was added and the mixture was stirred overnight. The organic phase was removed by filtration and the ether was removed by careful distillation. The product, C=^{18}O *trans*-1-acetoxy-3,4-epoxypentane (**15**), was allowed to react with boron trifluoride etherate in ether in the usual manner and the product *cis*-3-acetoxy-2-methyltetrahydrofuran (**16**) was purified by preparative glc. The percentage of oxygen label was determined from the ratio of M/(M + 2) and (M − M)/ (M + 2 − Me) peaks in the mass spectrum to be 21.5%. Reaction of *cis*-3-acetoxy-2-methyltetrahydrofuran (**16**) with $LiAlH_4$ in ether gave *cis*-2-methyltetrahydrofuran-3-ol. The mass spectra showed 20% incorporation of ^{18}O label in this furanol.

Synthesis and Rearrangement of C=^{18}O *trans*-1-Acetoxy-4,5-epoxyhexane (21). Synthesis of *trans*-1-acetoxy-4,5-epoxyhexane (**21**) from *trans*-4,5-epoxyhexan-1-ol was carried out in a similar manner to above.

Rearrangement of C=^{18}O labeled *trans*-1-acetoxy-4,5-epoxyhexane with boron trifluoride etherate in ether gave *threo*-2-(1-acetoxyethyl)tetrahydrofuran (**22**) containing 21% ^{18}O label. Reduction of *threo*-2-(1-acetoxyethyl)tetrahydrofuran (**22**) with $LiAlH_4$ in ether gave *threo*-2-(1-hydroxyethyl)tetrahydrofuran containing no detectable ^{18}O label.

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Registry No.—**13**, 41763-95-5; **14**, 41763-96-6; **15**, 41763-93-3; **16**, 41763-94-4; **17**, 41763-97-7; **18**, 33964-67-9; **19**, 50273-74-0; **20**, 50273-75-1; **21**, 41763-98-8; **22**, 33964-66-8; **24**, 50273-78-4; **25**, 50273-79-5; **28**, 50273-80-8; **29**, 50273-81-9; **30**, 50273-82-0; **31**, 50273-83-1; *cis*-1-bromopent-3-ene, 50273-84-2; *trans*-1-bromopent-3-ene, 7515-62-0; *cis*-1-acetoxypent-3-ene, 42125-19-9; *trans*-1-acetoxypent-3-ene, 42125-35-9; *trans*-pent-3-en-5-ol, 1576-96-1; pent-3-yn-1-ol, 10229-10-4; *cis*-pent-3-en-1-ol, 764-38-5; *cis*-3-chloro-2-methyltetrahydropyran, 50273-91-1; *trans*-3-chloro-2-methyltetrahydropyran, 50273-92-2; *cis*-hex-4-en-1-ol, 928-91-6; *trans*-hex-4-en-1-ol, 928-92-7; *cis*-hept-5-en-1-ol, 50273-95-5; *trans*-hept-5-en-1-ol, 25143-94-6; *erythro*-2-(1-hydroxyethyl)tetrahydrofuran, 16765-39-2; 1-acetoxyhexan-4-one, 13777-63-4; 1-acetoxyhexan-5-one, 4305-26-4; *threo*-2-(1-hydroxyethyl)tetrahydrofuran, 16765-41-6; 1-acetoxyheptan-5-one, 50274-01-6; 1-acetoxyheptan-6-one, 5070-61-1; *threo*-1,5-diacetoxy-6-fluoroheptane, 50274-03-8; *threo*-1,6-diacetoxy-5-fluoroheptane, 50546-28-6.

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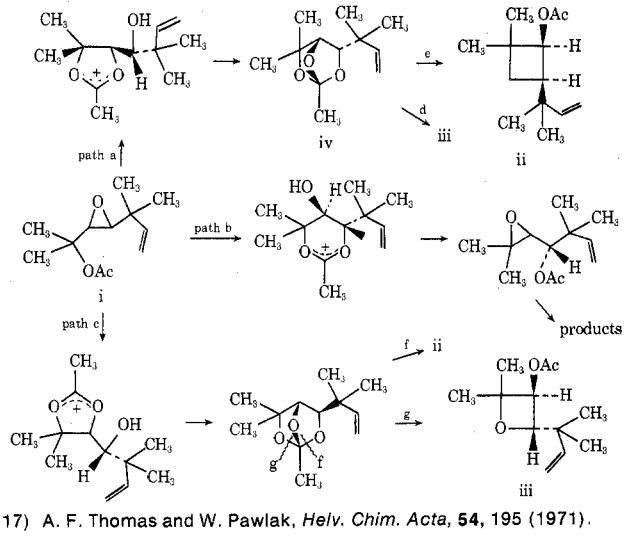
(16) The only other report[17] where such a rearrangement may have been observed was the conversion of yomogi acetate epoxide i to oxetane ii or iii which occurs in Dowex 50 resin. The stereochemistry of the oxetane is unknown, but the authors suggested it to be cis oxetane ii. The ortho ester iv (path a) was considered an unlikely intermediate because of the steric compression of the methyl and dimethylallyl groups in endo positions. Two other reaction mechanisms were considered: path b, involving acetate participation not on the adjacent position to the epoxide ring, but at one carbon atom further away; and path c, involving acetate attack at the adjacent epoxide carbon with retention of configuration at that atom.



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