19 14α isomer, 54780-63-1; **19** 14β isomer, 54809-24-4; **20aA,** 61046-87-5; **20aB,** 61116-61-8; **20bA,** 61046-88-6; **20bB,** 61091-77-8; **21,** 61091-78-9; **24,** 19884-98-1; **25,** 61046-89-7; **26,** 61046-90-0; **28,** 61046-91-1; **29** 14α epimer, 61091-79-0; **29** 14β epimer, 61091-80-3; **32,** 61046-92-2; **33a,** 61046-93-3; **33b,** 61046-94-4; **34,** 18102-90-4; **35,** 61046-95-5; **36a** 15α epimer, 61046-96-6; **36a** 15β epimer, 61046-97-7; **36b,** 61046-98-8; **37,** 61046-99-9; **38,** 61047-00-5; *cis*-2-bromo-2-butene, 3017-71-8.

References and Notes

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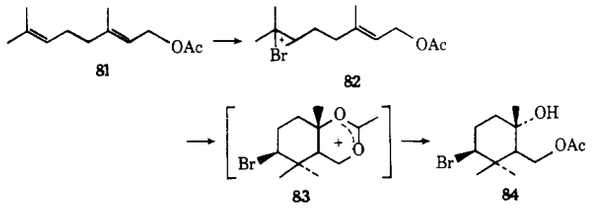

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Oxidative Rearrangements of Tertiary and Some Secondary Allylic Alcohols with Chromium(VI) Reagents. A New Method for 1,3-Functional Group Transposition and Forming Mixed Aldol Products[1]

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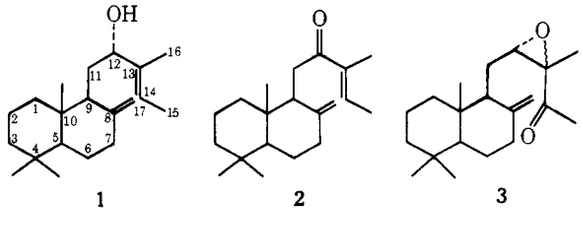
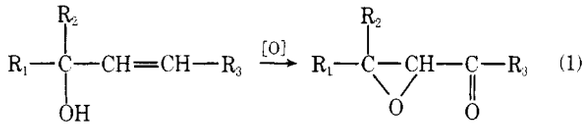
Oxidation of tertiary allylic and some secondary allylic alcohols with Collins reagent results in oxidative rearrangement to α-epoxy aldehydes or ketones. Oxidation of tertiary allylic alcohols and some secondary alcohols with pyridinium chlorochromate results in oxidative rearrangement to α,β-unsaturated aldehydes or ketones. These reactions are useful for effecting the 1,3-transposition of oxygen and for carrying out mixed aldol condensations. A detailed study of the reaction of labda-8(17),12-dien-14-ol with Cr(VI) reagents was carried out. Possible mechanisms for the oxidative rearrangements are discussed.

In connection with work on a biogenetic-type synthesis of the strobanes, we had occasion to attempt the oxidation of the allylic alcohol **1** to the α,β-unsaturated ketone **2**.[2] Oxidation with active manganese dioxide failed; oxidation with Collins reagent[3] furnished as sole product and in good yield the epoxy ketone **3**.

The formation of an epoxy ketone from an allylic alcohol with Collins reagent was unprecedented, although there are



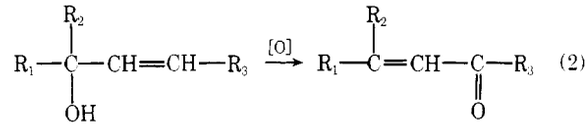
several reports of the formation of epoxy ketones from steroidal allylic alcohols with Jones and Sarett reagent.[4-6] These reactions, however, are not synthetically useful whereas the conversion of 1 to 3 is. The success of the reaction in the case of 1 seemed to be due to the difficulty encountered by the reagent in abstracting hydrogen from the carbon atom carrying the hydroxyl group, as suggested by the resistance of 1 toward oxidation by MnO_2.[7] If this were so, the oxidation of tertiary allylic alcohols with Collins reagent might provide a general and useful means of synthesizing rearranged α-epoxy aldehydes and ketones (eq 1). The verification of this hy-



(1)

pothesis is reported in this communication; the result of the observed oxidative rearrangement shown in eq 1 is a reversal of the Wharton reaction.[8,32]

We have also observed that oxidation of tertiary allylic alcohols with pyridinium chlorochromate is a general and useful method for carrying out the oxidative rearrangement depicted in eq 2. Since the allylic alcohols serving as substrates can be



(2)

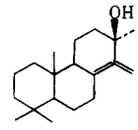
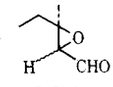
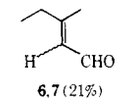
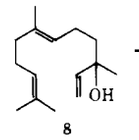
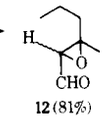
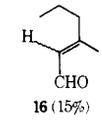
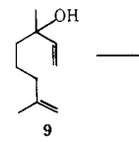
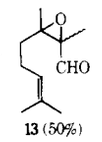
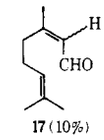
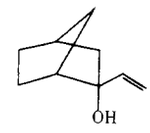
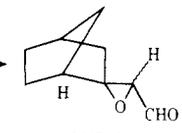
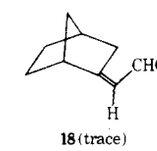
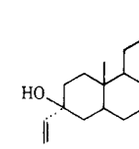
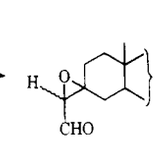
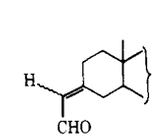
made by reaction of vinyllithiums with ketones, this two-step sequence provides a simple and efficient method for carrying out mixed aldol condensations.

Results

Oxidations with Collins Reagent. Oxidation of manool (4), a diterpene alcohol possessing the required functionality, with Collins reagent gave three fractions in 69, 10, and 11% yield, respectively, which were separated by high-pressure liquid chromatography. The NMR spectrum of the major fraction, $C_{20}H_{32}O_2$, showed that it was a 1:1 mixture of two epimers, since in addition to the presence of three methyl singlets at 0.60, 0.78, and 0.80 ppm each integrating for three protons (methyls on C-4 and C-10), it exhibited two methyl singlets at 1.33 and 1.36 ppm, together integrating for three protons, and two doublets at 3.08 and 3.10 ppm (J = 8 Hz), the sum of which integrated for one proton. The chemical shifts of these signals were appropriate for a methyl resonance attached to carbon bearing an oxygen atom and a proton attached to epoxidic carbon. In addition there were two doublets at 9.46 and 9.53 ppm (J = 8 Hz), together equivalent to 1 H, showing the presence of an aldehyde. Consequently, the major product was a 1:1 mixture of the epimeric aldehydes **5**. The other two compounds had very similar NMR spectra, both exhibiting the presence of a vinyl methyl group at 1.90 and 2.13 ppm, respectively, and an aldehydic proton at 9.8 (or 10.00) ppm coupled to a vinylic hydrogen at 5.83 ppm. The IR spectra displayed a band at 1690 cm^{-1} showing the presence of a conjugated carbonyl group. Hence the two minor products were **6** and **7**, the E isomer **6** being identified with the substance exhibiting the vinyl methyl resonance at lower field.[10]

The oxidative rearrangement depicted in eq 1 had thus been found applicable to manool. A series of other tertiary alcohols **8** (nerolidol), **9** (linalool), **10**, and **11** were also studied; in each case, a 1:1 mixture of epimeric epoxy aldehydes **11–14** represented the major, if not the exclusive, products. The results are presented in Table I. Structure assignments were based on NMR spectra, the epoxy aldehydes exhibiting the relevant resonances near 1.3 (methyl), 3 (proton under epoxide), and

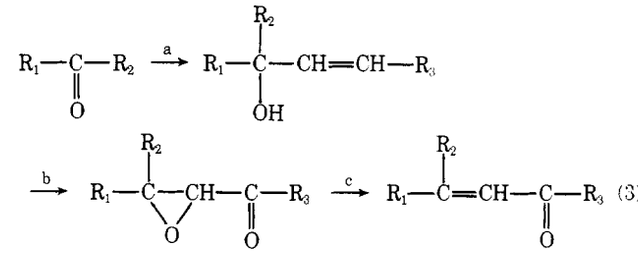
Table I. Oxidation of Allylic Alcohols with Collins Reagent[a]

Compd	Epoxy aldehydes[b]	Olefinic aldehydes[c]
 4	 5 (69%)	 6,7 (21%)
 8	 12 (81%)	 16 (15%)
 9	 13 (50%)	 17 (10%)
 10	 14 (50%)	 18 (trace)
 11	 15 (70%)	 19 (trace)

[a] All yields are isolated yields. [b] 1:1 mixture of epimers. [c] 1:1 mixture of geometrical isomers.

9 ppm (aldehyde). Compounds **10** and **11** were prepared by reaction of vinyllithium with norbornanone and 3-cholestanone, respectively. The stereochemistry assigned to **10** and **11** is based on the assumption that the vinyllithium reagent approaches the substrate from the least hindered side (exo in the case of **10**, α in the case of **11**). The stereochemistry at C-2 of **14** and at C-3 of **15** is based on the finding that configuration is retained at the site of the tertiary hydroxyl in the oxidation of manool (vide infra).

This interesting oxidative rearrangement appears to be an excellent method of converting a ketone to the bishomologous epoxy aldehyde since the tertiary allylic alcohols used as substrates can be prepared by reaction of a ketone with vinyllithium. The product α-epoxy aldehyde (or ketone in the case of **3**) may or may not be convertible to the α,β-unsaturated carbonyl compounds obtained as by-products in the case of **4**, **8**, and **9** by reagents such as chromous chloride (depending on the degree of steric hindrance); if so, the overall result is the product expected of a mixed aldol condensation and eq 1 can be expanded to eq 3. Thus, chromous chloride



(3)

reduction of the epoxy aldehyde mixture **12** from nerolidol afforded a 1:1 mixture of (E)- and (Z)-farnesals (**16**) in quantitative yield.

Oxidations with Pyridinium Chlorochromate. Forma-

Table II. Oxidation of Allylic Alcohols with Pyridinium Chlorochromate[a]

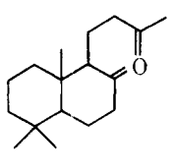
Compd	Product[b]	Yield, %
4	6, 7	98
8	16	98
9	17	80
10	18	79
11	19	72

[a] All yields are isolated yields. [b] 1:1 mixture of geometrical isomers.

tion of α-epoxy aldehydes and ketones by oxidation of tertiary allylic alcohols with Collins reagent prompted an investigation into the possible use of other Cr(VI) oxidizing agents. One of these is pyridinium chlorochromate, whose use for oxidation of alcohols to aldehydes and ketones has been demonstrated by Corey and Suggs.[9]

Oxidation of manool (4) with this reagent gave a quantitative yield of the *E* and *Z* aldehydes **6** and **7** in a 1:1 ratio, i.e., use of the reagent seems to obviate the need for carrying out steps b and c in eq 3 above. The generality of the reaction was shown by carrying out the oxidation on the same series of tertiary allylic alcohols, as before; the results are summarized in Table II. In each case the mixture of unsaturated aldehydes was obtained in very good yield. Apparently, the addition of a vinyllithium reagent to a ketone followed by oxidation with pyridinium chlorochromate is a very efficient method for synthesizing the product of a mixed aldol reaction. The development of techniques for carrying out directed aldol condensations with ketones has received considerable attention in recent years;[11-19] the simple two-step process presented here, while not stereoselective, will undoubtedly be useful in a number of situations.

Oxidation of Manool with Other Reagents. As a matter of interest, the reaction of manool as a typical tertiary allylic alcohol with two other Cr(VI) reagents was examined. Oxidation of manool with chromium trioxide–3,5-dimethylpyrazole[20] yielded **6, 7,** and **20,** whereas oxidation with Jones reagent and extensive chromatography gave **6, 7,** and **21**



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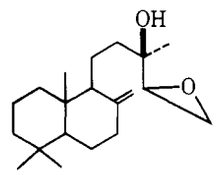


21

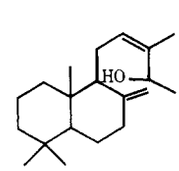
(mixture of epimers at carbon 14), as well as a mixture of highly polar substances, probably acids, which were not identified.

Oxidations of Labda-8(20),12-dien-14-ol (22). The formation of different products from tertiary allylic alcohols with different Cr(VI) reagents raised the question of mechanism. Now it had been observed, incidental to our work on strobane synthesis,[2] that oxidation of the epimeric mixture **22** with Collins reagent gave a mixture of keto epoxides **25** as well as the expected "normal" product **23.** Formation of the rearranged keto epoxides **25** suggested that **22** might be somewhat hindered, thus reducing the rate of the "normal" process (which involves abstraction of H-14 in the chromate ester of **22**) and permitting the observation of competing reactions. Since **22** was relatively accessible, a more detailed study of the oxidation of mixture **22** (~1:1 mixture of epimers) and the epimer **22A,** whose syntheses are described elsewhere,[2] was undertaken in the hope of shedding light on the mechanism of the oxidative rearrangements.

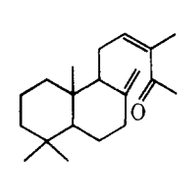
Table III. Oxidation of 22

Reagents	Yields, %[a] 23	24	25
Jones[b]	14.5	25	9.6
Modified Collins[c]	38	17.3	31[d]
Pyridinium chlorochromate[e]	30	11	11
CrO_3–3,5-dimethylpyrazole	22	18.8	26

[a] Yields are isolated yields. [b] Overall yield low owing to formation of highly polar substances which were not identified. [c] R. Ratliff and R. Rodehorst, *J. Org. Chem.*, **35,** 4000 (1970). [d] Not detected in run using Collins reagent (ref 2). [e] Compounds **26** and **27** were also isolated from this run.



22, OH α and β
22A, OH, β



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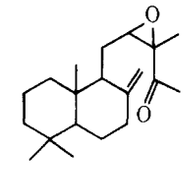
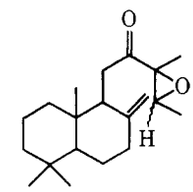
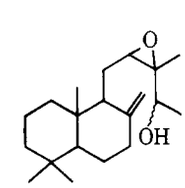


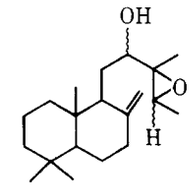
24, 24A



25, H-14 α and β
25A, H-14, β



26, OH α and β
26A, OH β



27, H-14 α and β
27A, H-14, β

Oxidation of **22** with the four Cr(VI) reagents employed previously gave the three products **23**[2] and **25,**[2] but also the new keto epoxide mixture **24** in the proportions detailed in Table III. Ketone **2** was not detected. During the earlier stages, TLC showed the presence of two polar constituents **26** and **27** which were isolated from the runs with pyridinium chlorochromate.

As might have been expected, **24, 26,** and **27,** like **25** reported previously,[2] were inseparable mixtures of at least one epimer pair as shown by NMR spectrometry at 270 MHz. The IR spectra showed that **24** was a ketone and that **26** and **27** were alcohols. The NMR spectrum of **24** exhibited methyl singlets at 1.43 and 2.00 ppm characteristic of methyl on carbon carrying oxygen and $CH_3C{=}O$, respectively; but H-12 appeared as a multiplet at 3.02 ppm. The NMR spectrum of **26** resembled that of **24**[2] with the exception that the methyl ketone singlet was replaced by a somewhat broadened methyl doublet (H-16) and a pair of slightly overlapping quartets (H-14), while the spectrum of **27** was similar to that of **25** except for a multiplet near 3.4 ppm representing H-12.[21]

The simultaneous formation of the normal keto epoxide **24** and the rearranged keto epoxide **25** led to the surmise that one

Table IV. Oxidation of 22A

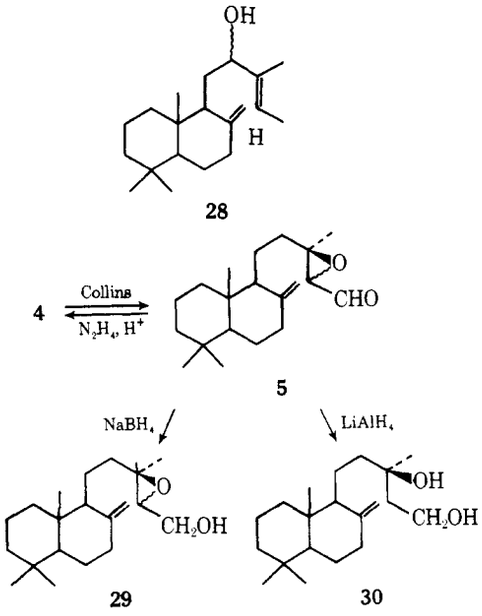
Reagent	Yields, %[a] 23	24A	25A
Jones[b]	15	24	7.2
Modified Collins	40	15.3	30
Pyridinium chlorochromate[c]	39	11	11
CrO_3–3,5-dimethylpyrazole	35	13.8	25

[a] Yields are isolated yields. [b] Yields low owing to formation of unidentified polar products. [c] Yields relatively low owing to formation of **26A** and **27A.**

of them might arise from one epimer of alcohol **22**, whereas the other might be produced by the second epimer. To check this hypothesis, alcohol **22A** was prepared;[2] however, oxidation of **22A** provided both keto epoxides **24A** and **25A**, this time as individual compounds, in approximately the same proportions as previously (Table IV). The stereochemistry assigned to C-14 of **25A** is based on the finding that the configuration at C-13 of manool was retained during the oxidation; the stereochemistry of **25A** at C-13 and that of **24A** at C-12 and C-13 is unknown.[22]

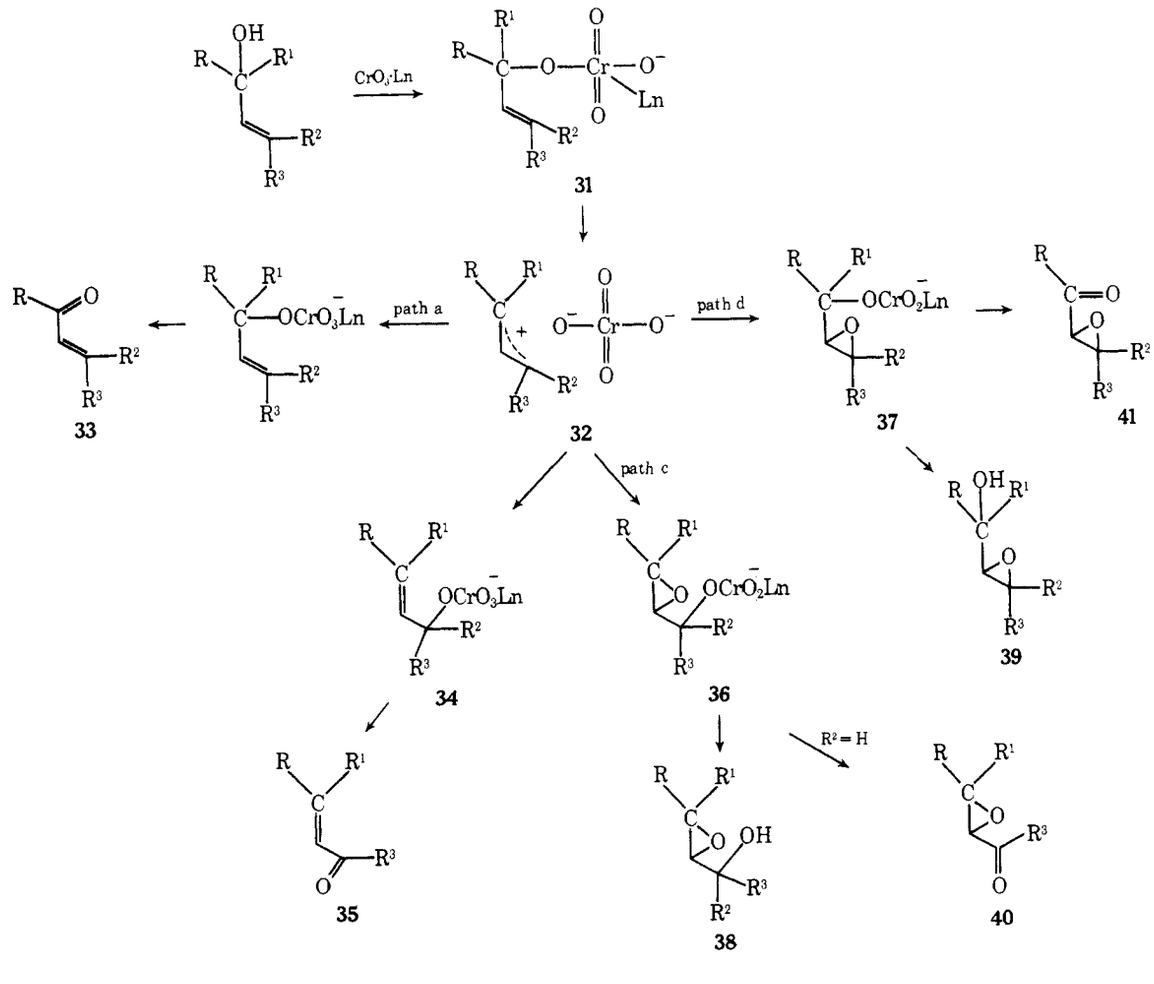
Possible Oxidation Mechanisms. Prior to discussing possible oxidation mechanisms, two additional results must be noted. (1) Alcohol **22** was recovered quantitatively on exposure to 8 N H_2SO_4 in acetone. Since rearrangement to alcohol **28** did not occur in the acid environment, **28** cannot be a precursor of **27** and **25** when **22** is oxidized with Jones reagent. (2) Manool (**4**) was the only product when **5**, which is a mixture of epimers as shown by the doubling of the H-16 resonance, was subjected to the Wharton reaction.[23] This shows that the C-13 stereochemistry of **5** is that of manool; hence the origin of diastereoisomerism must be C-14. Reduction of **5** with $NaBH_4$ gave the epoxy alcohol **29** whose NMR spectrum showed that it was a mixture of C-14 epimers, the H-16 resonance appearing as two singlets at 1.26 and 1.38 ppm. On other other hand, reduction of **5** with $LiAlH_4$ gave the diol **30** whose NMR spectrum indicated that it was a pure substance, the H-16 resonance appearing as a sharp singlet at 1.31 ppm which integrated for three protons. These observations taken together indicate that the configuration at C-13 is retained in the oxidation of manool (**4**) with Collins reagent.

Three possible mechanisms can be advanced for the oxidative rearrangements of allylic alcohols exemplified by eq 1 and 2.



Mechanism I (Scheme I). The first step in this mechanism is the formation of chromate ester **31**, the same as the first step in the oxidation of alcohols with chromium(VI),[24] which undergoes ionization to ion pair **32**. The ion pair can undergo recombination and oxidation (path a) to give the normal ketone **33**, or recombination with rearrangement (path b) to **34** which is oxidized to **35**. Since **32** has a chromate moiety, it can also transfer oxygen to the double bond to give the epoxy es-

Scheme I

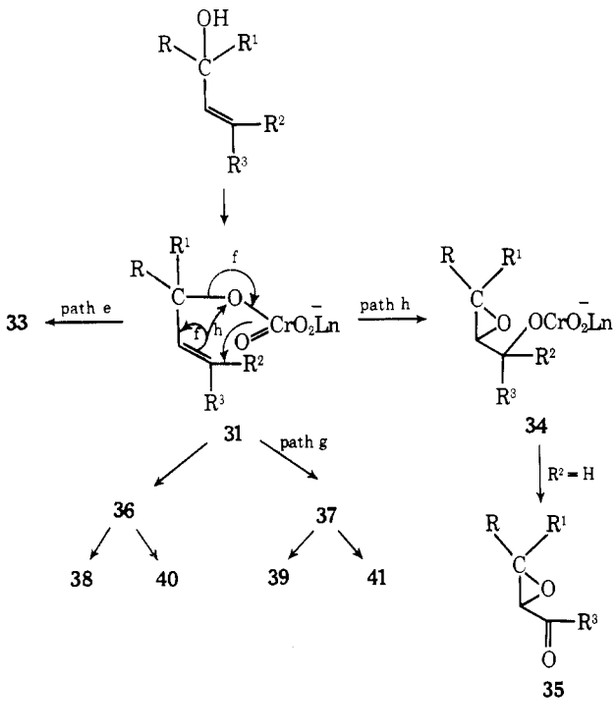


ters **36** (path c) or **37** (path d). The latter are subject to hydrolysis to give **38** or **39**, or can undergo oxidation to give epoxy aldehydes or ketones **40** or **41**.

Although this scheme accounts for all products, it does not explain the dramatic contrast between the results of oxidation with Collins reagent (Table I) and pyridinium chlorochromate (Table II) nor the following observations. Formation of ion pair **32** implies that configuration at the starting point is lost. This is not in accordance with the observation that **4** and **5** have the same configuration at C-14. The difficulty could be overcome if we assume that **32** is a tight ion pair and that the chromate moiety travels on the surface of the carbonium ion. Another objection to this mechanism is that in the oxidation of manool, rearranged epoxy aldehyde was obtained only when Collins reagent was used. If **32** is a reality, the chromate moiety should be formed regardless of reagent, thus leading at least partially to **40** and **41**. Finally, in the oxidation of **22**, there was no evidence for the formation of the rearranged α,β-unsaturated ketone, whereas oxidation of manool led to the rearranged conjugated compounds **6** and **7**.

Mechanism II (Scheme II). Chromate ester **31** undergoes normal oxidation to ketone **33** (path e) or rearrangement via a six-membered transition state (path f) to rearranged ester **34** which is oxidized to rearranged ketone **35**. Alternatively, oxygen transfer to the double bond of **31** (path g) could provide **37** which undergoes hydrolysis to **39** or oxidation to **41**. Finally **31** could undergo rearrangement (path h) to **36** which undergoes hydrolysis to **38** or oxidation to **40**.

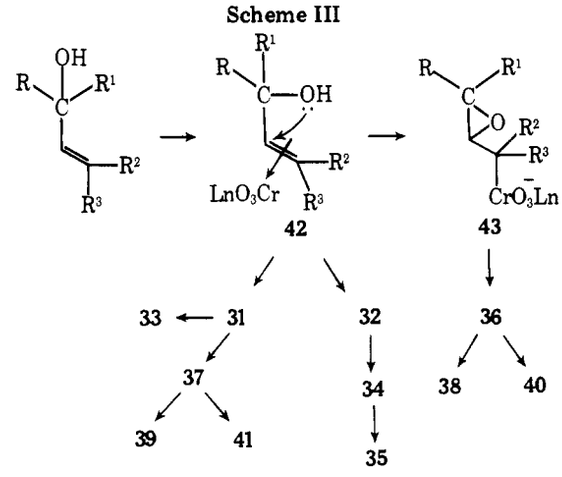
Scheme II



This mechanism explains the retention of configuration, since the C–O bond is not broken in the transition state. In other respects, however, it suffers from the same deficiencies as mechanism I, i.e., it does not explain the difference in the nature of the products depending on the oxidizing agent employed and that in the oxidations of manool, **5** was obtained only with Collins reagent and that **2** is not formed from **22**.

Mechanism III (Scheme III). The first step in this mechanism is the formation of π complex **42** which can rearrange to chromate ester **31** which as mentioned earlier can undergo oxidation to **33** or oxygen transfer to **37**. Alternatively, π complex **42** may undergo rearrangement to intermediate **43** with a C–Cr σ bond which can further rearrange to ester **36**, the precursor of **38** and **40**.[25]

Scheme III



Rearrangement of π complex **42** to chromate ester **31** is favored in those instances where the chromium complex possesses a ligand suitable for ester formation. Such ligands are present in pyridinium chlorochromate (Cl^-, eliminates HCl to form ester), Jones reagent, and CrO_3–3,5-dimethylpyrazole complex ($-OH^-$, eliminates water to form ester). No such ligand is present in Collins reagent, hence formation of ester **31** is not particularly favored. Ester **31** transfers oxygen to the double bond to give **37** which undergoes hydrolysis to **39**. This explains the formation of **21** from manool on oxidation with Jones reagent and the formation of **26** and **27** on oxidation of alcohol **22**. On the other hand, ester **37** can undergo oxidation to give **41** which explains the formation of **24** from **22**. Ester **31** can undergo ionization to the ion pair **32**. Such ion pair formation is facilitated by crowding in **31**, hence tertiary alcohol **4** can follow this route, whereas secondary alcohol **22** does not. This explains why ketone **2** is not formed from **22**. Ion pair formation is also highly favored in the case of bulky complexes such as pyridinium chlorochromate, Collins reagent, and 3,5-dimethylpyrazole complex, which explains why epoxy alcohol **21** was not obtained from manool except with Jones reagent. The postulated neighboring group participation in the rearrangement of **42** to **43** satisfies the requirement that the configuration of the C–O bond be maintained in the conversion of manool to **5**. Lastly, since ester formation is repressed in the case of Collins reagent, rearranged epoxide is formed to a larger extent than with the other three reagents.

Although mechanism III thus accounts for most of our observations, neither it nor mechanisms I and II explain the formation of ketone **20** from manool on oxidation with the pyrazole complex. We surmise that it arises from **5**, since oxidation of **5** with pyrazole complex yielded **20**, albeit in poor yield. Hence we conclude that mechanism III accommodates the facts more satisfactorily than the other proposals, although there is no conclusive evidence in its favor.

Experimental Section[26]

Oxidations of Manool. A. With Collins Reagent. A solution of 0.5 g of manool in 5 ml of CH_2Cl_2 was added in one portion to a suspension of 5 g of CrO_3·2Py in 100 ml of CH_2Cl_2. After 15 min the reaction mixture was filtered through a column of Florisil; the solid residue was washed several times with CH_2Cl_2. The combined filtrate and filtered washings were evaporated at reduced pressure. The residue was taken up in ether. The washed and dried ether extracts were evaporated; the residue was separated into three fractions by pressure liquid chromatography using a 12-ft Porasil column and hexane–1% ether as solvent. Fraction 1 (0.36 g, 69%) was a 1:1 mixture of the epimers **5**: IR band at 1705 cm^{-1}, NMR signals (270 MHz) at 0.60, 0.78, 0.80 (C-4 and C-10 methyls), 1.33 and 1.36 (together three protons, C-13 methyl), 3.08 d, 3.10 d (together 1 proton, H-14), 4.43 br and 4.80 br (H-17), and 9.46 d, 9.53 ppm d (J = 8 Hz, together one proton, H-15).

Anal. Calcd for $C_{20}H_{32}O_2$: C, 78.90; H, 10.59; O, 10.51. Found: C, 78.89; H, 10.70; O, 10.41.

Fraction 2, a 1:1 mixture[30] of **6** and **7** (0.11 g, 21%), exhibited an IR band at 1690 cm^{-1} and had NMR signals (60 MHz) at 0.66, 0.80, 0.86 (C-4 and C-10 methyls), 1.90 and 2.13 ppm (together three protons, C-13 methyl).

B. Oxidation with Pyridinium Chlorochromate. A solution of 0.5 g of manool in 5 ml of CH_2Cl_2 was added in one portion to a suspension of 1 g of pyridinium chlorochromate in 20 ml of CH_2Cl_2. The reaction was followed by TLC. At the end of the reaction, the mixture was diluted with an equal amount of ether and filtered and the residual solid was washed thoroughly with ether. The combined filtrate and washings were evaporated; the residue (0.5 g, 98%) was a 1:1 mixture of **6** and **7**.

C. Oxidation with Jones Reagent. To an ice-cold solution of 0.4 g of manool in 10 ml of acetone was added Jones reagent dropwise until the reaction was complete (~20 min). The solvent was evaporated and the residue was taken up in ether. The washed and dried extract was evaporated and the residue was separated by preparative TLC into two fractions. IR and NMR spectra of the first fraction (80 mg, 20%) demonstrated that it was a 1:1 mixture of **6** and **7**. Fraction 2 (**21**,[2] 105 mg, 36%) had an IR band at 3500 cm^{-1} and NMR signals (270 MHz) at 0.70, 0.80, 0.90 (C-4 and C-10 methyls), 1.20, 1.30 (together three protons, C-13 methyl), 2.86 m (three protons, H-14, H-15), 4.53 br and 4.83 ppm br (H-17).

Anal. Calcd for $C_{20}H_{34}O_2$: C, 78.38; H, 11.19; O, 10.44. Found: C, 78.33; H, 11.04; O, 10.53.

D. Oxidation with Chromium Trioxide–3,5-Dimethylpyrazole Complex. A solution of 0.5 g of manool in 5 ml of CH_2Cl_2 was added in one portion to a solution of the reagent prepared by addition of 1.5 g of 3,5-dimethylpyrazole to a suspension of 1.5 g of anhydrous CrO_3 in 20 ml of CH_2Cl_2. The reaction was followed by TLC. After the reaction was complete, the mixture was diluted with anhydrous ether and filtered. Evaporation of the filtrate gave a gum which was separated by preparative TLC into two fractions. Fraction 1 was the known ketone **20**, which had an IR band at 1705 cm^{-1} and NMR signals (60 MHz) at 0.70, 0.80, 0.87 (C-4 and C-10 methyls), 2.08 (C-14 methyl), 4.45 br and 4.70 ppm br (H-17). Fraction 2 was a 1:1 mixture of **6** and **7**.

Conversion of 5 to Manool. To a solution of 280 mg of **5** in 10 ml of methanol was added 120 mg of hydrazine hydrate and then 1 drop of acetic acid. The mixture was stirred at room temperature for 1 h, diluted with water, and extracted with ether. Evaporation of the washed and dried extract followed by preparative TLC gave 60 mg of manool.

Oxidations of Nerolidol. The crude product mixture obtained by oxidation of 0.5 g of nerolidol with Collins reagent was separated by pressure liquid chromatography (Porasil column, solvent hexane–1% Et_2O). The major fraction (0.39 g, 81%) was **12**: IR band at 1705 cm^{-1}, NMR signals (60 MHz) at 1.40, 1.43 (together three protons, C-3 methyl), 1.63 and 1.68 (three vinyl methyls), 3.16 d, 3.20 d (J = 6 Hz, together one proton, H-2), 5.15 br (two protons, H-6 and H-10), 9.40 d and 9.45 ppm d (J = 6 Hz, together one proton, H-1).

Anal. Calcd for $C_{15}H_{24}O_2$: mol wt, 236.1772. Found: mol wt (MS), 236.1793.

The minor fraction, 33 mg (15%), was a 1:1 mixture of farnesals (**16**) as evidenced by the NMR spectrum.

Application of procedure B to 0.5 g of nerolidol gave a 1:1 mixture of farnesals (98%).

Reduction of 12. To a solution of 0.15 g of **12** in 5 ml of acetic acid was added a solution of chromous chloride until the blue color persisted. The reaction was carried out in a CO_2 atmosphere. After dilution with water and neutralization with solid Na_2CO_3, the mixture was extracted with ether. Evaporation of the washed and dried ether extract furnished 0.125 g (90%) of the isomeric farnesals **16**.

Oxidations of Linalool. Oxidation of 0.5 g of linalool with 3 g of Collins reagent (procedure A) gave a mixture which was separated by pressure liquid chromatography. The first fraction (0.2 g) was a 1:1 mixture of isomeric 2,3-epoxy-3,6-dimethyloct-2-en-1-als (**13**)[27] which had an IR band at 1705 cm^{-1} and NMR signals (60 MHz) at 1.41, 1.44 (together three protons, C-3 methyl), 1.63 br and 1.68 br (three vinyl methyls), 3.18 d, 3.20 d (J = 6 Hz, together one proton, H-2), 5.15 br (vinyl proton), and 9.45 d, 9.50 ppm d (J = 6 Hz, together one proton, H-1).

The second fraction was a 1:1 mixture of geranial and neral (**17**) as evidenced by the NMR spectrum.

Oxidation of 0.5 g of linalool by procedure B gave 0.4 g (80%) of mixture **17**.

***exo*-2-Vinylbicyclo[2.2.1]heptan-2-ol (10).** A solution of 1 g of vinyllithium in THF was added dropwise with stirring to 2 g of norbornanone in THF. After 2 h, the mixture was poured onto crushed ice, neutralized with NH_4Cl, and extracted with ether. The washed and dried ether extract was evaporated and the residual gum was chromatographed over a Florisil column. Hexane–ether (9:1) eluted 2 g (95%) of gummy **10**, whose NMR spectrum (60 MHz) exhibited the typical ABC pattern of the vinyl group. This substance decomposed on standing and gave an unsatisfactory elemental analysis. For similar reasons, the high-resolution mass spectrum did not have the required accuracy in the second decimal place.

Anal. Calcd for $C_9H_{14}O$: mol wt, 138. Found: mol wt, 138.

Oxidations of 10. A. Oxidation of 0.64 g of **10** with 5 g of Collins reagent by procedure A followed by preparative TLC gave 0.343 g (50%) of mixture **14** which had an IR band at 1720 cm^{-1} and NMR signals (60 MHz) at 3.2 d, 3.36 d (J = 6 Hz, together 1 H), and 9.25 d, 9.40 d (J = 6 Hz, together 1 H).

Anal. Calcd for $C_9H_{12}O_2$: mol wt, 152.0836. Found: mol wt (MS), 152.0838.

B. Oxidation of 0.25 g of **10** by procedure B with 0.5 g of the reagent gave 0.2 g (79%) of the aldehyde mixture which had an IR band at 1690 cm^{-1} and NMR signals (60 MHz) at 5.70 d, 5.90 d (J = 6 Hz), together 1 H), and 9.70 d, 9.80 ppm d (J = 6 Hz, together 1 H). This mixture decomposed on standing and gave an unsatisfactory elemental analysis. The high-resolution mass spectrum also did not give the molecular ion within the required accuracy in the second decimal place.

Anal. Calcd for $C_9H_{12}O$: mol wt, 136. Found: mol wt (MS), 136.

3α-Vinylcholestan-3β-ol (11). Reaction of 1 g of vinyllithium with 2 g of choestan-3-one in the manner described above followed by chromatography over Florisil gave in the 19:1 hexane–ether fraction 1.0 g of recovered cholestanone and in the 9:1 hexane–ether fraction 0.9 g (84%) of **11**: after recrystallization from hexane it had mp 110 °C, and exhibited a hydroxyl band in the infrared at 3400 cm^{-1} and the typical ABC pattern of the vinyl group in the NMR spectrum.[26]

Anal. Calcd for $C_{29}H_{50}O$: mol wt, 414.3860. Found: mol wt (MS), 414.3876.

Oxidations of 11. A. Oxidation of 0.385 g of **11** by procedure A followed by high-pressure liquid chromatography on a Porasil column yielded 0.275 g of solid **15**, mp 107–109 °C after recrystallization from hexane, which had an IR band at 1705 cm^{-1} and significant NMR signals at 3.13 d (J = 5 Hz) and 9.55 ppm d (J = 5 Hz). On the basis of the NMR spectrum, the substance appeared to be homogeneous.[29]

Anal. Calcd for $C_{29}H_{48}O_2$: mol wt, 428.3653. Found: mol wt (MS), 428.3643.

B. Oxidation of 0.250 g of **11** with 0.5 g of pyridinium chlorochromate and chromatography of the crude product by preparative TLC yielded 72% of solid, mp 118–120 °C after recrystallization from hexane–chloroform, which had IR bands at 1672 and 1620 cm^{-1}, significant NMR signals at 5.83 d (J = 7 Hz) and 10.08 ppm d (J = 7 Hz).

Anal. Calcd for $C_{29}H_{48}O$: mol wt, 412.3703. Found: mol wt (MS), 412.3695.

Oxidation of the Labda-8(17),12-dien-14-ol Mixture (22). A. Oxidation of 0.2 g of mixture **22**[2] with Jones reagent by procedure C and chromatography gave 20 mg (10%) of **25**,[2] 53 mg (25%) of **24**, and 29 mg (15%) of **23**.[2] The previously unreported mixture of epimers **24** had IR bands similar to those previously[2] reported for **24A** (compound **15** of ref 2).

Oxidation of 0.2 g of **22** by procedure B and chromatography gave 61 mg (30%) of **23**, 21 mg (11%) of **24**, and 23 mg (11%) of **25**. Oxidation of 0.25 g of **22** by procedure A gave 95 mg (30%) of **23**, 45 mg (14%) of **24**, and 80 mg (31%) of **25**. Oxidation of 0.25 g of **22** by procedure D gave 65 mg (22%) of **23**, 49 mg (19%) of **24**, and 68 mg (26%) of **25**.

Oxidation of Labda-8(17),12-dien-14(*S*)-ol (22A). Oxidation of 200 mg of **22A**[2] by procedure C gave 15 mg (7%) of **25A**, mp 91–93 °C from hexane, in whose NMR spectrum H-14 appeared as a sharp quartet (J = 7 Hz) at 3.20 ppm, 50 mg (24%) of gummy **24A**, where the H-12 resonance was a sharp doublet of doublets (J = 8, 3 Hz), and 30 mg (15%) of **23**. Oxidation of 0.25 g of **22A** by procedure A gave **23** (102 mg, 40%), **24A** (40 mg, 15%), and **25A** (78 mg, 30%). Oxidation of 0.2 g of **22A** by procedure B gave **23** (78 mg, 39%), **24A** (23 mg, 11%), and **25A** (19 mg, 10%). Procedure D yielded **23** (85 mg, 35%), **24A** (36 mg, 14%), and **25A** (65 mg, 35%) from 0.25 g of **22A**.

Anal. for **25A**. Calcd for $C_{20}H_{32}O_2$: C, 78.90; H, 10.59. Found: C, 79.00; H, 10.40.

Isolation of 26 and 27. Oxidation of mixture **22** with pyridinium chlorochromate and TLC of the crude product revealed, in addition to **23**, **24**, and **25**, two spots corresponding to substances **26** and **27**. Substance **26** was a gum which had IR signals at 3480 and 1640 cm^{-1};

NMR signals at 0.66, 0.80, 0.86 (C-4 and C-10 methyls), 1.26 (C-13 methyl), 1.16 d (J = 7 Hz, C-14 methyl), 3.00 (H-12), 3.4 q (J = 7 Hz, H-14), 4.43 br and 4.83 ppm br (H-17).

Anal. Calcd for $C_{20}H_{34}O_2$: mol wt, 306.2559. Found: mol wt (MS), 306.2558.

Substance **27** melted at 134 °C after recrystallization from $CHCl_3$–hexane and had IR bands at 3490 and 1640 cm^{-1}; NMR signals at 0.66, 0.80, 0.86 (C-4 and C-10 methyls), 1.23 (C-13 methyl), 1.28 d (J = 6 Hz, C-14 methyl), 3.00 q (J = 6 Hz, H-14), 3.2 m (H-12), 4.33 br and 4.00 ppm br (H-17).

Anal. Calcd for $C_{20}H_{34}O_2$: C, 78.38; H, 11.18; O, 10.44. Found: C, 78.59, H, 10.99; O, 10.42.

Hydride Reductions of 5. A solution of 1.25 g of **5** in 10 ml of methanol was added to 200 mg of $NaBH_4$ in 25 ml of methanol at room temperature. The reaction mixture was stirred at room temperature, excess reducing agent was destroyed by adding dilute hydrochloric acid, solvent was evaporated, and the residue was taken up in ether and washed with water. Evaporation of the dried ether extract gave a gum which upon chromatography gave 1.00 g (80%) of epimeric mixture of epoxy alcohols[31] **29:** NMR signals at 0.70, 0.80, 0.86 (C-4 and C-10 methyl), 1.30 and 1.33 (together three protons, C-13 methyl), 2.96 t br (H-14), 3.76 m (two protons, H-15), 4.50 br (H-17), and 4.83 ppm br (H-17); IR signals at 3350 and 1640 cm^{-1}.

Anal. Calcd for $C_{20}H_{34}O_2$: C, 78.38; H, 11.18. Found: C, 77.89; H, 11.49.

A solution of 0.31 g of **5** in 2 ml of THF was added dropwise with stirring to a slurry of 0.09 g of $LiAlH_4$ in 10 ml of THF (nitrogen atmosphere). Stirring was continued for 1 h, excess reducing agent was destroyed by addition of wet ethyl acetate, and the complex was destroyed by addition of water. The mixture was filtered and the residue was thoroughly washed with ethyl acetate. The combined filtrate and washings were evaporated to yield a gum which upon chromatography over Florisil gave 0.30 g (>90%) of diol: NMR signals at 0.77, 0.88, 0.95 (C-4 and C-10 methyls), 1.31 (C-13 methyl), 3.94 m (H-15), 4.62 br (H-17), and 4.91 ppm br (H-17) and IR signals at 3400 and 1640 cm^{-1}.

Registry No.—**4,** 596-85-0; *cis*-**5,** 61063-26-1; *trans*-**5,** 61116-89-0; **6,** 17633-79-3; **7,** 38237-44-4; **8,** 142-50-7; **9,** 78-70-6; **10,** 61063-16-9; **11,** 61116-81-2; *cis*-**12,** 61063-27-2; *trans*-**12,** 61116-90-3; *cis*-**13,** 61063-17-0; *trans*-**13,** 61063-18-1; *cis*-**14,** 61063-19-2; *trans*-**14,** 61116-82-3; *cis*-**15,** 61063-20-5; *trans*-**15,** 61116-83-4; *E*-**18,** 61063-21-6; *Z*-**18,** 61063-22-7; *E*-**19,** 61116-84-5; *Z*-**19,** 61116-85-6; **20,** 10266-75-8; **21,** 61116-86-7; **22**-OHα, 61045-84-2; **22A,** 61091-75-6; **24A,** 61046-83-1; **25A,** 61046-86-4; **26,** 61063-23-8; **27,** 61063-24-9; **29** α isomer, 61116-87-8; **29** β isomer, 61116-88-9; **30,** 61063-25-0; norbornanone, 497-38-1; cholestan-3-one, 15600-08-5.

References and Notes

(1) Supported in part by a grant from the National Science Foundation (GP-12582).

(2) P. Sundararaman and W. Herz, *J. Org. Chem.*, preceding paper in this issue. The configuration of **3** at C-12 is based on the work described in the present paper. The configuration at C-13 is unknown.

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(32) **Note Added in Proof.** After acceptance of this manuscript, we became aware of a recent report that oxidation of 13β*H*,14α,18-dihydroxyabiet-7-ene with Collins reagent furnished, in addition to the expected oxidation products, some 13β*H*-7-oxo-8α,14α-epoxyabietan-18-al as the result of an oxidative rearrangement similar to the one reported here: A. G. Gonzalez, J. L. Breton, C. R. Fagundo, and J-M. Trujillo, *Anal. Quim.*, **72,** 65 (1976).