Hydroperoxide Oxidations Catalyzed by Metals. III. Epoxidation of Dienes and Olefins with Functional Groups

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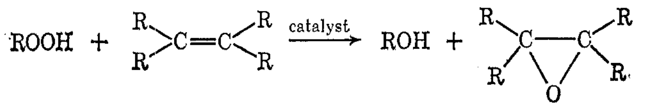
The molybdenum hexacarbonyl and the vanadyl acetylacetonate catalyzed epoxidations of olefins by organic hydroperoxides have been tried on a series of diolefins and olefins with functional groups. Molybdenum hexacarbonyl was a better catalyst for the epoxidation of all the olefinic compounds except allylic alcohols. Only with allylic alcohols did vanadyl acetylacetonate give higher yields of epoxide. A mechanism has been proposed for the allylic alcohol–vanadium catalyzed reaction.

In the first paper[1] of this series, the epoxidation of monoolefins with organic hydroperoxides catalyzed by group Vb and VIb transition metals was reported, and a mechanism for the reaction was proposed. The reaction has now been extended to a series of diolefins and olefins with functional groups.



Results

Nonconjugated Dienes.—To test the reactivity of double bonds in nonconjugated dienes, the epoxidation of 4-vinylcyclohexene and 1,4-hexadiene was carried out. It was found that these compounds were similar in reactivity to monoolefins.[1] As more alkyl substituents are bonded to the carbon atoms of the double bond, the reactivity of the double bond increases. Thus, with 4-vinylcyclohexene, only the ring olefin was epoxidized, and, with 1,4-hexadiene, the internal epoxide was the predominant product. When the pure *cis*- and *trans*-1,4-hexadienes were allowed to react separately, the *cis* isomer showed an 11 to 1 preference for internal epoxidation, and the *trans* isomer showed a 6 to 1 preference. The greater ratio of internal to terminal epoxide for the *cis* olefin is probably due primarily to the steric effect, although the energy difference between the *cis* and *trans* isomer may also be important.

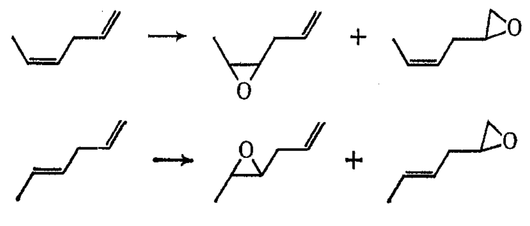
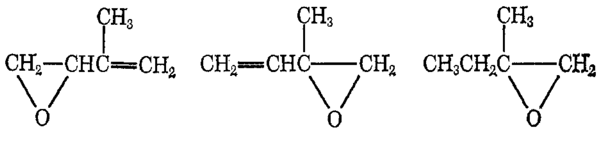


Table I summarizes the experimental conditions and the yields of monoepoxides obtained with various dienes using a 2:1 molar ratio of diene to hydroperoxide. Previous work[1] has shown that this ratio assures a high yield of epoxide. Some diepoxide also formed in these reactions. The yield of diepoxide varied from less than 1% for 4-vinylcyclohexene to 13% for dicyclopentadiene. The amount of diepoxide can be decreased further by using a higher ratio of diene to hydroperoxide.

The synthesis of diepoxide from nonconjugated dienes was also investigated. First, the monoepoxide was made and isolated. It was then allowed to react with more hydroperoxide using a ratio of unsaturated epoxide to hydroperoxide of 2:1 or higher. The experimental conditions and results are shown in Table II.

endo-Dicyclopentadiene was unique among the dienes since the double bonds are very reactive and the epoxides are very stable. Steric effects would be expected to prevent *trans* nucleophilic attack on both epoxide rings, and *cis* nucleophilic ring opening should be a slow reaction. Since both double bonds are easily epoxidized, the diepoxide can be made in high yield in one step with molar quantities of reagents. To obtain the diepoxide with no monoepoxide contaminant, at atmospheric pressure, the *t*-butyl alcohol must be removed as it forms. These data are shown in Table III.

Conjugated Dienes.—Conjugated dienes can also be epoxidized by this method. The reactivity of the individual double bonds in the diene again depends on the alkyl group substituents. Overall, the reactivity of the dienes studied is less than compounds containing isolated double bonds. This was shown in a competitive experiment using equimolar quantities of isoprene and 2-methyl-1-butene. At partial hydroperoxide conversion, the yield of the epoxide based on the hydroperoxide converted was quantitative, and the ratio of the three epoxides, 2-methyl-3,4-epoxy-1-butene, 3-methyl-3,4-epoxy-1-butene, and 2-methyl-1,2-epoxybutane, was 1:3.7:4.7. Typical experimental results with other conjugated dienes are shown in Table I.



With butadiene, the formation of polymeric materials was observed. This could be prevented by the addition of free-radical inhibitors. The butadiene monoepoxide yield, based on the hydroperoxide conversion, did not change in the presence or absence of a free-radical inhibitor. It changed, however, based on the diene, indicating that only the diene is involved in the polymer formation.

The hydroperoxide epoxidation of isoprene gives both 3,4-epoxy-3-methyl-1-butene and 3,4-epoxy-2-methyl-1-butene in a 4:1 molar ratio. The epoxidation of

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(1) N. N. Sheng and J. G. Zajacek, *Advan. Chem. Ser.*, **76**, 418 (1968).

TABLE I

EPOXIDATION OF DIENES

Olefin (mol)	Hydroperoxide (mol)	$Mo(CO)_6$, g	Temp, °C	Time, min	Conversion,[a] %	Yield,[b] %	Product[c] (ratio)
			Nonconjugated Dienes				
cis-1,4-Hexadiene (a) (0.18)	Cumene (0.07)	0.03	85	50	100	90	A:B (11:1)
trans-1,4-Hexadiene (b) (0.18)	Cumene (0.07)	0.03	85	75	94	93	C:D (6:1)
1,7-Octadiene (c) (0.10)	*t*-Butyl (0.05)	0.02	90	240	88	86	
4-Vinylcyclohexene (d) (0.10)	*t*-Butyl (0.05)	0.02	85	75	75	95	E
1,4-Cyclohexadiene (e) (0.10)	*t*-Butyl (0.05)	0.02	90	30	92	78	
1,5-Cyclooctadiene (f) (1.0)	*t*-Butyl (0.50)	0.10	80	60	100	82	
Dicyclopentadiene[d] (g) (0.05)	*t*-Butyl (0.025)	0.02	85	60	97	87	F:G (1.1:1)
			Conjugated Dienes				
Butadiene[e] (h) (0.58)	*t*-Butyl (0.17)	0.04	100	40	97	85	
1,3-Pentadiene (i) (0.03)	Cumene (0.007)	0.003	80	60	71	91	H:I (2:1)
Isoprene (j) (0.03)	*t*-Butyl (0.01)	0.003	90	64	97	84	J:K (4:1)

[a] Conversion of the hydroperoxide. [b] Yield of monoxide based on hydroperoxide converted. [c] A, *cis*-4,5-epoxy-1-hexene; B, *cis*-1,2-epoxy-4-hexene; C, *trans*-4,5-epoxy-1-hexene; D, *trans*-1,2-epoxy-4-hexene; E, 1,2-epoxy-4-vinylcyclohexane; F, 8,9-epoxy-*endo*-tricyclo[5.2.1.$0^{2,6}$]dec-4-ene; G, 4,5-epoxy-*endo*-tricyclo[5.2.1.$0^{2,6}$]dec-8-ene; H, 3,4-epoxy-1-pentene; I, 1,2-epoxy-3-pentene; J, 3-methyl-3,4-epoxy-1-butene; K, 2-methyl-3,4-epoxy-1-butene. [d] Benzene (12 ml) was used as solvent. [e] Benzene (60 ml) was used as solvent and hydroquinone (0.03 g) was added as inhibitor.

TABLE II

EPOXIDATION OF NONCONJUGATED DIENE MONOXIDES

Olefin (mol)	*t*-Butyl hydroperoxide, mol	Solvent (ml)	$Mo(CO)_6$, g	Temp, °C	Time, min	Conversion,[a] %	Yield,[b] %
1,2-Epoxy-4-vinylcyclohexene (a) (0.12)	0.06		0.03	85	60	96	83
1,2-Epoxy-5-cyclooctene (b) (2.0)	1.0	Toluene (300)	0.15	100	300	100	54
Dicyclopentadiene monoxides[c] (c and c′) (0.05)	0.025	Benzene (12)	0.02	85	120	89	89
cis-1,4-Hexadiene monoxides[d] (d[e] and d′[f]) (0.02)	0.01	Benzene (2)	0.01	100	120	65	77

[a] Conversion of hydroperoxide. [b] Based on the hydroperoxide converted. [c] A 1.1:1 molar mixture of the two monoxides. [d] A 15:1 molar mixture of the internal and terminal epoxides. [e] Internal epoxide. [f] Terminal epoxide.

isoprene by the bromohydrin method[2] or by perbenzoic acid[3] gave only the 3,4-epoxy-3-methyl-1-butene. The 3,4-epoxy-2-methyl-1-butene was isolated and identified by nmr, elemental analysis, and oxirane titration. To obtain high yields of the isoprene epoxides, all the reactants must be anhydrous. It was found that 3,4-epoxy-3-methyl-1-butene reacts very rapidly with water even at room temperature to give the diol. This proves to be a convenient method for isolating the 3,4-epoxy-2-methyl-1-butene from 3,4-epoxy-3-methyl-1-butene. If the epoxidation mixture was washed with water, the 3,4-epoxy-3-methyl-1-butene was converted to the diol and dissolved in the water layer while 3,4-epoxy-2-methyl-1-butene remained in the organic layer from which it was isolated by fractional distillation.

Allylic Compounds.—This epoxidation technique was tried on a variety of allylic compounds. The results are shown in Table IV. The epoxidation of these compounds was more difficult than compounds with isolated double bonds. This would be expected based on the electrophilic mechanism proposed for this reaction. Allylic compounds which have weaker electron-withdrawing groups such as chlorides and ethers give a faster reaction and a higher yield of epoxide than those which have stronger electron-withdrawing groups such as esters and nitriles. Substitution of an alkyl group on the double bond again increased the reaction rate and the yield of the epoxide. With these compounds, a molar ratio of olefin to hydroperoxide higher than 2:1 increased the yield of the epoxides. For some of the more reactive compounds, the addition of free-radical inhibitors also increased the epoxide yield.

TABLE III

EPOXIDATION OF DICYCLOPENTADIENE[a]

Expt no.	*t*-Butyl hydroperoxide, mol	Time, hr	Conversion,[b] %	Yield, %[c]	
				Monoxide	Dioxide
1	0.025	1	97	87	13
2	0.050	1	84	73	27
3	0.050	1.5	95	66	32
4	0.075	1.5	82	53	47
5	0.075	2	88	48	50
6	0.075	3	94	35	65
7	0.100	2	77	33	66
8	0.100	3	86	17	80
9	0.113	2.5	100	0	86

[a] In expt 1–8 reagents were *t*-butyl hydroperoxide (as indicated), 0.05 mol of dicyclopentadiene, 0.02 g of $Mo(CO)_6$, and 10 g of benzene; reflux temperature for this mixture is 85°. In expt 9 reagents were the same except 30 g of toluene was used as solvent and *t*-butyl alcohol was removed as it formed to keep the temperature at 100°. [b] Conversion of hydroperoxide. [c] The epoxide yield is based on hydroperoxide converted.

Allylic Alcohols.—The epoxidation of allylic alcohols gave unexpected results. With other olefinic compounds, molybdenum-catalyzed reactions, in general, gave a higher yield of epoxide than the reaction catalyzed by vanadium. Vanadium catalysts, however, gave faster reactions and higher epoxide yields in the case of allyl alcohol. With allyl alcohol and vanadium catalyst, a stoichiometric amount of olefin and hydroperoxide or an excess of hydroperoxide can be used, and high yields of the epoxide are still obtained. For other

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[2] E. J. Reist, J. G. Junge, and B. R. Baker, *J. Org. Chem.*, **25**, 1674 (1960).

[3] R. Pummerer and W. Reindel, *Ber.*, **66**, 335 (1933).

TABLE IV

EPOXIDATION OF ALLYL COMPOUNDS

Olefin (mol)	*t*-Butyl hydroperoxide, mol	Benzene, ml	Mo(CO)$_6$, g	Temp, °C	Time, min	Conversion,[a] %	Yield,[b] %
Allyl ethyl ether (a) (0.023)	0.005	2	0.01	95	30	73	77
Diallyl ether (b) (0.15)	0.050		0.02	95	120	89	85
Dimethallyl ether (c) (0.25)	0.125	50	0.10	93	60	84	70
Allyl glycidyl ether (d) (0.20)	0.070	12	0.03	100	180	88	58
Dimethallyl ether monoxide[c] (e) (0.05)	0.016	10	0.008	95	90	65	68
Ethyl methacrylate[d] (f) (0.08)	0.006	5	0.006	80	180	61	72
1-Cyclohexenyl acetonitrile (g) (0.41)	0.280	30	0.15	110	60	100	41
Allyl chloride (h) (0.08)	0.005		0.01	85	120	63	75
Methallyl chloride (i) (0.08)	0.010		0.01	85	120	100	89
1,4-Dichlorobutene-2 (j) (0.10)	0.030		0.01	90	90	84	21

[a] Conversion of hydroperoxide. [b] The epoxide yield is based on the conversion of hydroperoxide. [c] 2-Methyl-2,3-epoxypropyl 2-methyl-2-propenyl ether. [d] Diphenylamine (0.03 g) was added as free-radical inhibitor.

TABLE V

EPOXIDATION OF ALLYLIC ALCOHOLS

Olefin (mol)	*t*-Butyl hydroperoxide, mol	Catalyst (g)	Temp, °C	Time, min	Hydroperoxide conversion, %	Epoxide[a] yield, %
Allyl alcohol (a) (0.07)	0.01	Mo(CO)$_6$ (0.01)	100	60	100	10
(0.07)	0.01	VO(acac)$_2$ (0.01)	100	25	92	83
(0.01)[b]	0.01	VO(acac)^2 (0.01)	100	120	88	78
(0.01)[b]	0.015	VO(acac)^2 (0.01)	100	180	89	64
Methallyl alcohol (b) (0.06)	0.004	VO(acac)^2 (0.01)	80	30	97	100
(0.06)	0.004	Mo(CO)$_6$ (0.01)	80	30	82	69
2-Methyl-1-penten-3-ol (c) (0.04)	0.004	VO(acac)$_2$ (0.01)	80	30	94	100[c]
(0.04)	0.004	Mo(CO)$_6$ (0.01)	80	30	94	100[c]
4-Methyl-4-penten-2-ol (d) (0.04)	0.004	VO(acac)$_2$ (0.01)	80	30	88	100[c]
(0.04)	0.004	Mo(CO)$_6$ (0.01)	80	30	90	83[c]
5-Hexen-2-ol (e) (0.04)	0.004	VO(acac)$_2$ (0.01)	80	30	7	51[d]
(0.04)	0.004	Mo(CO)$_6$ (0.01)	80	30	69	86[d]
2-Cyclohexen-1-ol (f) (0.02)	0.002	VO(acac)$_2$ (0.01)	80	30	85	51[d]
(0.02)	0.002	Mo(CO)$_6$ (0.01)	80	30	62	95[d]
1,5-Hexadien-3-ol (g) (0.04)	0.004	VO(acac)$_2$ (0.01)	80	30	77	92[e]
(0.04)	0.004	Mo(CO)$_6$ (0.01)	80	30	91	75[e]
3,4-Dihydroxylbutene-1 (h) (0.03)	0.01	VO(acac)$_2$ (0.005)	80	60	87	60
3-Methyl-3,4-dihydroxylbutene-1 (i) (0.05)	0.01	VO(acac)$_2$ (0.01)	80	60	84	91

[a] Epoxide yield is based on the hydroperoxide conversion. [b] Tetrahydrofuran (2 g) was used as solvent in these experiments. [c] The epoxide for 2-methyl-1-penten-3-ol is a 10:1 (vanadium catalyst) and a 4:1 (molybdenum catalyst) ratio of the two possible optical racemic pairs based on vpc retention times; for 4-methyl-4-penten-2-ol, the epoxide is a 1:2 (vanadium catalyst) and a 1:1 (molybdenum catalyst) mixture based on vpc retention times. [d] The two optical racemic pairs were not separated by vpc. [e] The epoxide is a 4:1 mixture of 1,2-epoxy-3-hydroxyl-5-hexene and 1,2-epoxy-4-hydroxyl-5-hexene for the vanadium-catalyzed reaction; for the molybdenum-catalyzed reaction, the epoxide is a 1:1 mixture.

olefins a 2:1 molar ratio of the olefin to hydroperoxide is best for maximum epoxide yields. The experimental results on the epoxidation of various allylic and unsaturated alcohols are summarized in Table V. These data show that there are three variables which determine whether vanadium or molybdenum compounds give a higher yield of epoxide. These variables are the presence or absence of an alkyl group on the double bond of the unsaturated alcohol and on the carbinol carbon, and the position of the hydroxyl group relative to the double bond. Substitution of an alkyl group on the double bond, as in methallyl alcohol, allows the reaction to be run at a lower temperature, and the molybdenum catalyst gives only a slightly lower yield of epoxide than the vanadium catalyst. With substitution of an alkyl group on the double bond and the carbinol carbon in 2-methyl-1-penten-3-ol and 4-methyl-4-penten-2-ol, the molybdenum- and vanadium-catalyzed reactions gave comparable epoxide yields. As the position of the hydroxyl group relative to the double bond changes as in 5-hexen-2-ol, the olefin becomes more like an unsubstituted olefin, and the molybdenum-catalyzed reaction gives both a higher conversion of the hydroperoxide and a higher yield of the epoxide.

If optically active unsaturated alcohols had been used, the epoxidation reaction would give two optically active epoxides. In the case of 2-methyl-1-penten-3-ol and 4-methyl-4-penten-2-ol, starting with the racemic mixture of the unsaturated alcohol, the gas chromatograph separated the two optical racemic pairs of epoxides. The ratio of the racemic pairs varied with the hydroxyl position and whether the catalyst was molybdenum or vanadium. The racemic pairs were separated by preparative gas chromatography and were shown to be epoxides by nmr and ir. Unambiguous identification of the stereochemistry of the two isomeric pairs was not possible by nmr.

1,5-Hexadien-3-ol was epoxidized with molybdenum and vanadium catalysts to see which double bond would be epoxidized. In the vanadium-catalyzed reaction, vpc analysis showed that the epoxide was a 4:1 mixture of 1,2-epoxy-3-hydroxyl-5-hexene (I) and 1,2-epoxy-4-hydroxyl-5-hexene (II) and, in the molybdenum-catalyzed reaction, was a 1:1 mixture of these epoxides. Compound I had the shorter retention time on the vpc. These epoxides were separated by preparative vpc and identified by nmr and mass spectrometry.

Discussion

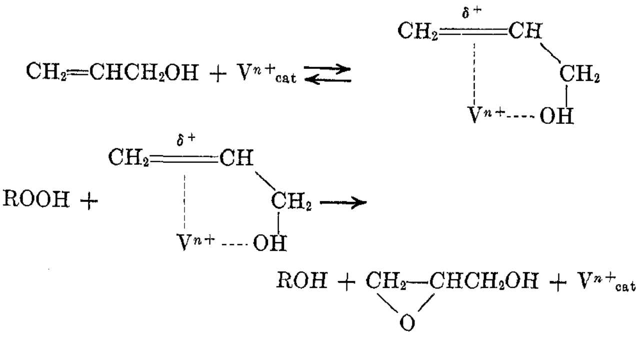
From previous studies on the epoxidation of olefins,[1] the results obtained in the vanadium-catalyzed epoxidation reactions of allylic alcohols, especially allyl alcohol and 1,5-hexadien-3-ol, were unexpected. In the epoxidation of simple olefins, molybdenum catalysts always gave higher yields of epoxides.

Since allylic olefins should be less reactive than simple olefins, vanadium compounds should not have been good catalysts for any epoxidation reactions under the experimental conditions reported in this paper. Since the vanadium compounds were good catalysts for the epoxidation of allylic alcohols, the original mechanism proposed for this epoxidation reaction[1,4] must be modified slightly to fit these new data. Alcohols have been observed to retard the rate of the epoxidation reaction, and a metal compound–alcohol complex has been postulated to explain these results. The kinetic studies[1] with molybdenum hexacarbonyl have been made to over 70% hydroperoxide conversion and showed no deviation due to molybdenum–alcohol complexing. Only when alcohols are used as solvents is the retardation observed with molybdenum catalyst. However, kinetic studies[4] under comparable conditions with vanadyl acetylacetonate showed a very marked retardation by alcohol. These two studies indicate that the alcohol formed in the epoxidation reaction complexes better with the vanadium than the molybdenum catalyst. This evidence would indicate that an allylic alcohol–vanadium catalyst complex should form quite readily. Three mechanisms can be postulated to explain the epoxidation of the allylic alcohols.

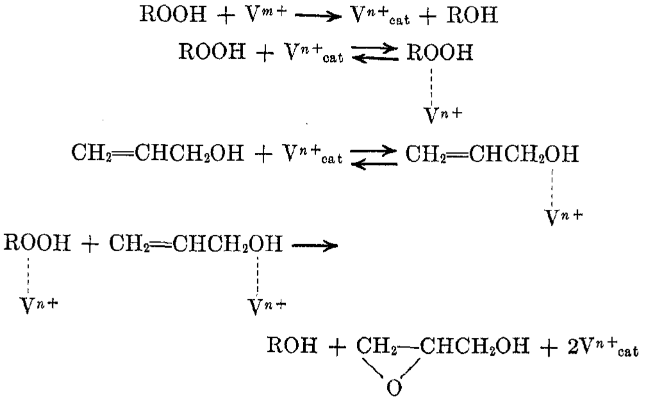
In mechanism 1, both the hydroxyl group and the double bond of the allyl alcohol complex with the vanadium catalyst. In this complex the double bond would have a partial positive charge and then could be epoxidized by a nucleophilic hydroperoxide. This mechanism is similar to the base-catalyzed epoxidation of α,β-unsaturated ketone by the hydroperoxide.[5] If this were the mechanism for the reaction, methallyl alcohol for electronic and steric effects should be less reactive than allyl alcohol. The results show that the opposite is true. Methallyl alcohol is epoxidized at a lower temperature than allyl alcohol.

Mechanism 2 shows that the hydroxyl group of the allyl alcohol first complexes with the vanadium. This complex is then epoxidized by the hydroperoxide–vanadium intermediate. This mechanism would not explain why vanadium complexing with the hydroxyl group of the allyl alcohol should give a high epoxide yield compared with molybdenum. Also it would not explain why the allylic double bond was preferentially epoxidized in 1,5-hexadien-3-ol.

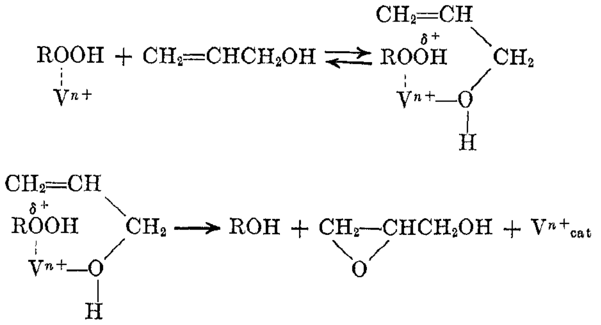
Mechanism 1



Mechanism 2



Mechanism 3



Mechanism 3 shows that the hydroperoxide (or the allyl alcohol)–vanadium intermediate, which forms first, has to further complex with the allyl alcohol (or the hydroperoxide), before the double bond is epoxidized. This mechanism is most consistant with the experimental observation. The allyl alcohol–hydroperoxide–vanadium complex should be more stable than the hydroperoxide–vanadium complex. The geometry of the intermediate complex would place the electron-deficient oxygen of the hydroperoxide in the vicinity of the double bond. This makes the epoxidation reaction favored over the decomposition of the hydroperoxide. Inserting additional carbon atoms between the double bond and the hydroxyl group destroys this favorable geometry for the epoxidation reaction. Thus, 1,5-hexadien-3-ol gave 1,2-epoxy-3-hydroxy-5-hexene as the major product, and 5-hexen-2-ol gave only a poor yield of the epoxide.

Further studies on the kinetics and the stereochemistry of the vanadium-catalyzed epoxidation of allylic alcohols are in progress in order to learn more about this reaction.

Experimental Section

General Procedure.—Infrared spectra data were obtained with a Perkin-Elmer infracord; nmr data, with a Varian A-60; and

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(4) E. S. Gould, R. R. Hiatt, and K. C. Irwin, *J. Amer. Chem. Soc.*, **90**, 4573 (1968).

(5) N. C. Yang and R. A. Finnegan, *ibid.*, **80**, 5845 (1958).

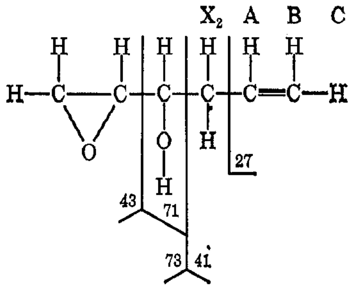
the mass spectra data, on a Consolidated Electrodynamics Corp. Model 104 at 70 eV. Gas–liquid partition chromatography was done using either a Varian Aerograph Model 90-P or a Perkin-Elmer Model 226. The column used in the Aerograph was 10 ft × .25 in. packed with 20% Carbowax 20M on 30–60 mesh acid-washed firebrick. The stainless steel capillary column used in the Perkin-Elmer chromatograph was 100 ft × 0.02 in. coated with Carbowax 15–40M. Hydroperoxide concentration was analyzed by standard titration procedure.[6] Epoxide concentration was analyzed by vpc. All epoxides were identified by comparison (vpc retention and ir and nmr spectra) with authentic samples. Reagent grade chemicals were used when available without further purification. Commercially available cumene hydroperoxide was purified according to Davies.[7] *t*-Butyl hydroperoxide (94% purity) was obtained from the Lucidol Division, Wallace and Tiernan, Inc., and purified to 97% by drying over anhydrous magnesium sulfate. Olefins were purified by distillation.

Isoprene.—A solution of 45 g of cumene hydroperoxide (99+% purity), 110 g of isoprene, and 0.1 g of $Mo(CO)_6$ was charged into a 500 ml Magnedrive autoclave (Pressure Product Co.) and heated to 80–82° for 35 min. The reactor was cooled to room temperature. The products were collected and were analyzed for hydroperoxide by standard iodometric titration and epoxides by vpc. There was a 97% conversion of the hydroperoxide and 92% yield of two isomeric epoxides based on the conversion of hydroperoxide. The two epoxides were 3,4-epoxy-3-methyl-1-butene and 3,4-epoxy-2-methyl-1-butene in a ratio of 4:1. Spinning-band distillation gave two fractions with bp 79–80 and 80–84°.

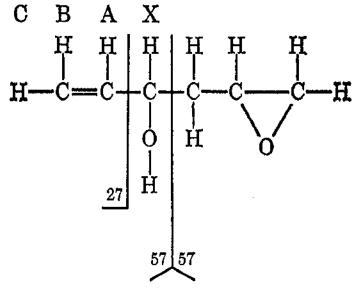
The ratio of 3,4-epoxy-3-methyl-1-butene and 3,4-epoxy-2-methyl-1-butene was 7.9:1 in the fraction of bp 79–80°, 2.4:1 in the one of bp 80–84°. With the first fraction, 3,4-epoxy-3-methyl-1-butene was identified by comparison (vpc retention and ir and nmr spectra) with an authentic sample prepared by the bromohydrin method.[2] With the second fraction, the pure 3,4-epoxy-2-methyl-1-butene was isolated by preparative vpc. It was identified by nmr (τ 4.83, 5, 6.65, 7.25, 8.37), elemental analysis (Calcd: C, 71.50; H, 9.50; O, 19.05. Found: C, 71.58; H, 9.37; O, 19.08.), and oxirane titration.[8]

Allyl Alcohol.—A solution of 4.1 g of allyl alcohol, 0.95 g of *t*-butyl hydroperoxide (95%), and 0.01 g of vanadyl acetylacetonate was sealed in a pressure tube and allowed to react for 25 min in a constant-temperature bath at 100°. The tube was removed and cooled. Hydroperoxide and epoxide were analyzed by iodometric titration and vpc. There was a 92% conversion of the hydroperoxide and an 83% yield of the epoxide based on the hydroperoxide conversion.

1,5-Hexadien-3-ol.—A solution of 19.6 g of 1,5-hexadien-3-ol, 9.0 g of *t*-butyl hydroperoxide (97% purity), and 0.01 g of vanadyl acetylacetonate was heated for 30 min at 80° in a three-necked flask equipped with a condensor, magnetic stirrer, and a thermometer. Fractional distillation on a Nester–Faust spinning-band gave 1,2-epoxy-3-hydroxyl-5-hexene [bp 45° (1 mm)] in 93% purity. The remainder of the cut was 1,2-epoxy-4-hydroxyl-5-hexene. An identical run with 0.01 g of molybdenyl acetylacetonate as catalyst followed by fractional distillation gave 1,2-epoxy-4-hydroxyl-5-hexene [bp 53° (1 mm)] in 85% purity. The remainder of the cut was 1,2-epoxy-3-hydroxyl-5-hexene. The nmr spectra of these epoxides exhibit resonances corresponding to a terminal olefin, a terminal epoxide, and a $-CH_2\overset{|}{C}HOH$ group. In both cases, the position of the hydroxyl group is clearly indicated by the splitting patterns of the epoxide and olefinic protons. For compound I, the olefinic proton appears as the ABC part of an $ABCX_2$ system with J_{AX} = 6.8 Hz, while compound II appears as the ABC part of an ABCX system



I



II

with J_{AX} = 5.6 Hz. The mass spectra (70 eV) showed a large ion intensity at *m/e* 43 ($C_2H_3O^+$) and 57 ($C_3H_5O^+$) for compounds I and II, respectively. Some basic characteristic peaks of these two compounds are listed in Table VI.

TABLE VI

CHARACTERISTIC MASS SPECTRA OF COMPOUNDS I AND II

m/e	Intensity of I	Intensity of II
43[a]	100	24
57[a]	10	100
27	68	86
31	22	47
55	54	34
69	15	4
73	11	3
71	8	3
96	7	3

[a] Base peak for compounds I and II, respectively.

Registry No.—I, 24058-61-5; II, 24058-62-6; molybdenum hexacarbonyl, 13939-06-5; vanadyl acetylacetonate, 13930-95-5; Table I—a, 7318-67-4; b, 7319-00-8; c, 3710-30-3; d, 100-40-3; e, 628-41-1; f, 111-78-4; g, 77-73-6; h, 106-99-0; i, 504-60-9 j, 78-79-5; Table II—a, 106-86-5; b, 637-90-1; c, 4387-46-6; c′, 4387-45-5; d, 14031-68-6; d′, 24578-16-3; Table IV—a, 557-31-3; b, 557-40-4; c, 628-56-8; d, 106-92-3; e, 24058-76-2; f, 97-63-2; g, 6975-71-9; h, 107-05-1; i, 563-47-3; j, 764-41-0; Table V—a, 107-18-6; b, 513-42-8; c, 2088-07-5; d, 2004-67-3; e, 626-94-8; f, 822-67-3; g, 924-41-4; h, 497-06-3; i, 24058-88-6.

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