the intermediate.¹⁶ Clearly, ascorbate is an unusually effective nucleophile despite being an oxyanion with a rather low basicity. Our results raise the question of the involvement of ascorbate anion in biological acyl-transfer reactions.

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Registry No. Ascorbate anion, 299-36-5; p-nitrophenyl acetate, 830-03-5; 2,4-dinitrophenyl acetate, 4232-27-3; p-nitrophenyl diphenylphosphinate, 10259-20-8.

(16) See also the related structure of a 3-ester; J. Jernow, J. Blount, E. Oliveto, A. Perrotta, P. Rosen, and V. Toome, *Tetrahedron*, **35**, 1483 (1979). Unfortunately the 2-OH hydrogen is not shown but the structure suggests hydrogen bonding between the 2-OH and the P=O groups.

Molybdenum-Catalyzed Oxidation of Allylic Alcohols Using t-BuOOH. Regioselective Cleavages of the Double Bond and the Adjacent Single Bond with a Hydroxyl Group

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There have been many procedures for oxidative cleavage of olefinic double bonds to produce carbonyl compounds,¹ e.g.: (a) ozonolysis;² (b) oxo-metal reagents, such as permanganate^{3,4} and ruthenium tetraoxide;⁵ (c) for certain nucleophilic olefins, the O₂-copper system⁶ and singlet molecular oxygen.⁷ The transition metal-alkyl peroxide systems have attracted much interest because of the useful reagents for selective oxidations.⁸ In the metal-catalyzed epoxidation of olefins, the hydroxyl group at the allylic position accelerates the regio-, stereo-, and enantioselectivity.⁸⁻¹⁰ However, there are few reports concerning the olefinic double bond cleavage reaction using these transition metal-alkyl peroxide systems. Recently, we have found that the double bond of silyl enol ethers undergoes

Scheme I. Oxidative Cleavage of 2-Ethyl-2-hexen-1-ol



Scheme II. Possible Mechanism of the Cleavage Reaction



oxidative cleavage with the $MoO_2(acac)_2$ -t-BuOOH system.¹¹ Here, we show that molybdenum complexes can be used to catalyze the oxidative cleavage of olefinic double bonds by use of excess t-BuOOH and that the allylic hydroxyl group exerts the directing effect for the regioselectivity. Molybdenum compounds appear specific in the present cleavage reaction.¹²

In the molybdenum-catalyzed oxidation of allylic alcohol, the effects of metal valency and ligands on the catalytic activity were examined. These results are shown in Table I. Profound differences in both catalytic activity and the product selectivity were not observed among the homogeneous molybdenum complexes; 1-octen-3-òl gave hexanoic acid of two less carbons as a major product accompanying a small amount of valeric acid from a loss of three carbons. The heterogeneous MoO₃ catalyst showed low activity (run 4). Probably it takes a long time for MoO_3 to dissolve in the reaction medium. $MoO_2(acac)_2$ complex is used as a representative catalyst because of its availability and facility in handling as well as activity.

The reaction of 2-ethyl-2-hexen-1-ol gave butyric acid and propionic acid as major products (Scheme I). The cleavage at the α -position leads to the formation of butyric acid, and both α and β cleavages give propionic acid. Formic acid is derived from the β cleavage. A small amount of acetic acid was also observed. It is notable that the cleavage occurs selectively at the two positions of the double bond and adjacent single bond with the hydroxyl group in the allylic alcohol oxidation. The results of allylic alcohol and isolated olefin oxidations using the MoO₂-(acac)₂-t-BuOOH system are summarized in Table II. 2-Octen-1-ol (internal olefin) gave hexanoic acid formed from the cleavage of the double bond. The regioisomers of 1-phenyl-2-propen-1-ol and cinnamyl alcohol produced the same product, benzoic acid, in good yields. Acyclic and aromatic allylic alcohols showed high reactivity for the present reaction, whereas cyclic allylic alcohols afforded dicarboxylic acids in poor yields. In the case of isolated olefins without hydroxyl groups, aromatic olefins gave the double bond cleavage products in moderate yields. Aliphatic olefins with allylic hydrogens showed low reactivity for the cleavage reaction, and the lower carboxylic acids were formed as overoxidation products.¹³ It is clear that the allylic hydroxyl group can accelerate the molybde-

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⁽¹²⁾ By use of the epoxidizing catalyst $VO(acac)_2$ in place of MoO_2 -(acac)₂, a small amount of cleavage products was observed, and an epoxy alcohol was the major product.

⁽¹³⁾ This phenomenon was reported on the potassium permanganate oxidation of terminal olefins (see ref 4c).

Table I. Effect of Metal Valency and Ligands on Molybdenum-Catalyzed Oxidation of 1-Octen-3-ol^a

	run	catalyst	metal valency	reaction time	product yield, ⁰ %		
					C _s COOH ^c	C₄COOH ^d	
	1	MoO ₂ (acac) ₂	+ 6	48 h	79	6	
	2	Mo(CO)	0	48 h	65	9	
	3	MoO(TPP)OH ^e	+ 5	48 h	61	8	
		· · ·		72 h	74	9	
	4	MoO	+ 6	48 h	18	trace	
		3		10 days	77	4	

^a Reaction conditions: 1-octen-3-ol, 3 mmol; catalyst, 0.06 mmol; t-BuOOH, 30 mmol; dry benzene, 15 mL; 70 °C. ^b Yield was based on substrate and determined by GLC. ^c Hexanoic acid of two less carbons. ^d Valeric acid of three less carbons. ^e TPP = tetraphenylporphyrin.

Table II.	Oxidation	of Various	Olefinic	Compounds
Usin	g the MoO	$(acac)_2 - t - B$	uOOH S	ystem ^a

			yield,
run	substrate	products ^b	%
1	1-octen-3-ol	hexanoic acid	79
		valeric acid	6
5	2-octen-1-ol	hexanoic acid	73
		valeric acid	11
6	2-ethyl-2-hexen-1-ol	butyric acid	70
	·	propionic acid	77
		acetic acid	6
7	4-methyl-3-penten-2-ol	acetic acid	96
8	1-cyclohexyl-2-	cyclohexane-	72
	propen-1-ol	carboxylic acid	
9	1-phenyl-2-propen-1-ol	benzoic acid	92
10	cinnamyl alcohol	benzoic acid	84
11	2-cyclohexen-1-ol	glutaric acid	8
12	2-methylene-	adipic acid	11
	cyclohexan-1-ol		
13	1-octene ^c	heptanoic acid	22
		hexanoic acid	7
		valeric acid	3
14	2-octene ^c	hexanoic acid	34
		valeric acid	11
15	styrene ^c	benzoic acid	57
16	α -methylstyrene ^d	acetophenone	63

^a Reaction conditions: substrate, 3 mmol;

 $MoO_2(acac)_2$, 0.06 mmol; t-BuOOH, 30 mmol; dry benzene, 15 mL; 70 °C; 48 h. ^b Formic acid was also detected in all runs. ^c t-BuOOH (24 mmol), 24 h. Although the reaction was prolonged further, the yields of carboxylic acids did not increase. ^d t-BuOOH (24 mmol).

num-catalyzed cleavage reaction and control the regioselectivity.

This cleavage reaction involves epoxidation at an early stage;¹⁴ the initially formed epoxides disappeared as the oxidation of allylic alcohols or isolated olefins proceeded. The reaction of 1,2-epoxyoctan-3-ol gave hexanolic acid under similar conditions as those in the above oxidations. Also, oxidation of 1,2-epoxyoctane exhibited a result similar to that of 1-octene.¹⁵ Presumably the cleavage of an epoxide might occur via a five-membered metallacyclic

(C-O-Mo-O-C) species which is formed from the attack of a Mo=O species on the oxirane ring. An allylic alcohol which can bind to the Mo=O species as an allylic alkoxide affords a double five-membered metallacyclic species (Scheme II).

The metallacyclic species immediately decomposes to give carbon-carbon bond cleavage products of aldehydes

or ketones. The coordination of the allylic hydroxyl to molybdenum causes the high reactivity for the cleavage reaction and prevents the overoxidation. The low reactivity of the cyclic allylic alcohols is due to the rigid metallacyclic intermediate. Aldehyde is further oxidized to the corresponding carboxylic acid under the reaction conditions.¹⁶

It should be noted that the regioisomers of allylic alcohols lead to the same carboxylic acids in the present system (runs 1 and 5; 9 and 10). When a successive procedure of allylic oxidation and the molybdenum-catalyzed cleavage reaction is carried out, terminal olefins can be transformed into carboxylic acids of two less carbons.



Experimental Section

Infrared spectra were recorded on a Hitachi EPI-G spectrophotometer. NMR spectra were obtained on a Hitachi R-600 spectrometer with tetramethylsilane as an internal standard. Gas chromatography (GLC) was performed on Yanaco G-8 and G-180 instruments with a 3 m \times 2.6 mm i.d. or 0.5 m \times 2.6 mm i.d. column packed with 3% silicone OV-17 on Celite, 15% polyester FF on Neosorb, and 10% Unisole 30T on Uniport.

Metal compounds were commercial grade and used without further purification. The MoO(TPP)OH complex was prepared according to the method of Fleischer.¹⁷ 2-Octen-1-ol, 2-ethyl-2-hexen-1-ol, and 4-methyl-3-penten-2-ol were prepared by the LiAlH₄ reduction of the corresponding carbonyl compounds. 1-Phenyl-2-propen-1-ol and 1-cyclohexyl-2-propen-1-ol were synthesized by the Grignard method. 2-Cyclohexen-1-ol was obtained by the following reaction sequence, i.e., bromination of cyclohexene with N-bromosuccinimide followed by hydrolysis with NaHCO₃ in acetone-water (3:2). 2-Methylenecyclohexan-1-ol was prepared by the SeO₂-H₂O₂ oxidation of methylenecyclohexan-8¹⁸ Other allylic alcohols and olefins were commercially available.

General Method for Oxidation of Olefinic Compounds with Metal Catalyst. Metal catalyst (0.06 mmol) was placed into a 50-mL round-bottom flask, and the atmosphere was replaced with a nitrogen stream. The olefinic compound (3.0 mmol) in 8 mL of benzene was introduced through the side arm. To this solution was added 24-30 mmol of t-BuOOH in 7 mL of benzene dropwise during 30 min at room temperature. Then the reaction solution was stirred at 70 °C for 24-48 h and quenched by addition of saturated Na₂SO₃ and NaHCO₃ solution. To the resulting aqueous layer was added concentrated HCl followed by extraction with ether. The ethereal solution was dried over anhydrous

⁽¹⁴⁾ In the oxidative cleavage of dihydropyran with a peroxomolybdenum complex, a pyran epoxide has been reported as an intermediate. See: Frimer, A. A. J. Chem. Soc., Chem. Commun. 1977, 205.

⁽¹⁵⁾ One may imagine that the cleavage reaction involves a diol intermediate formed from hydrolysis of the epoxide. However, the participation of a diol should be ruled out, because the best solvent was absolute benzene and diol could not be detected in the present reaction.

⁽¹⁶⁾ During the course of the cleavage reaction, the amount of the intermediate aldehyde increased with decreasing epoxy alcohol in GLC analysis.

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MgSO₄ without neutralization. Concentration on a rotary evaporator gave crude products. The crude oxidation products were analyzed by GLC to determine the product yields. Exceptionally, the produced dicarboxylic acids were directly analyzed by GLC without the treatment as above.

Preparation and Oxidation of Epoxy Alcohol. 1,2-Epoxyoctan-3-ol was prepared according to the our previous method.⁹ Fractional distillation under reduced pressure gave the epoxy alcohol. For 1,2-epoxyoctan-3-ol: bp 132-138 °C (13 mm); NMR (CDCl₃) δ 0.8–1.7 (m, 11 H, CH₃ and CH₂), 1.97 (br s, 1 H, OH), 2.7-3.1 (m, 3 H, CHO), 3.7-4.0 (m, 1 H, CHO).

Oxidation of 1,2-epoxyoctan-3-ol (430 mg, 3 mmol) and t-BuOOH (3.3 g, 30 mmol) in the presence of $MoO_2(acac)_2$ (19.6 mg, 0.06 mmol) was carried out under the same conditions as those described in allylic alcohol oxidations. Hexanoic acid (254 mg, 73% yield) was obtained as the major oxidation product.

Registry No. t-BuOOH, 75-91-2; MoO₂(acac)₂, 17524-05-9; Mo(CO)₆, 13939-06-5; MoO(TPP)OH, 28780-74-7; MoO₃, 1313-27-5; 1-octen-3-ol, 3391-86-4; 2-octen-1-ol, 22104-78-5; 2-ethyl-2hexen-1-ol, 50639-00-4; 4-methyl-3-penten-2-ol, 4325-82-0; 1cyclohexyl-2-propen-1-ol, 4352-44-7; 1-phenyl-2-propen-1-ol, 4393-06-0; cinnamyl alcohol, 104-54-1; 2-cyclohexen-1-ol, 822-67-3; 2-methylenecyclohexan-1-ol, 4065-80-9; 1-octene, 111-66-0; 2octene, 111-67-1; styrene, 100-42-5; α-methylstyrene, 98-83-9.

Synthesis of Substituted Cyclopentadienes: Intramolecular Diels-Alder Precursors¹

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In the course of developing a versatile synthetic route to natural products containing more than one five-membered carbocyclic ring (polyquinanes) we needed a general route to cyclopentadienes substituted with functionalized alkenyl chains. These compounds can serve as precursors for intramolecular Diels-Alder reactions.¹

Two complementary routes to substituted cyclopentadienes may be envisioned (eq 1). Route A represents

$$\textcircled{D} \xrightarrow{\chi \xrightarrow{R^{2}}_{R^{3}}}_{\textcircled{A}} \qquad \textcircled{D} \xrightarrow{R^{1}}_{R^{3}} \xrightarrow{R^{3}}_{\textcircled{B}} \textcircled{D} \xrightarrow{R^{4}}_{R} \xrightarrow{0 \xrightarrow{R^{4}}}_{\textcircled{R}} \textcircled{D} (1)$$

the well-precedented alkylation of cyclopentadiene anion. This method works well for primary and secondary tosylates (or mesylates)³ but not for tertiary halides (Brieger⁴ has reported alkylation with a tertiary halide but in poor yield). Method B outlines a less explored two-step approach that requires the formation of a fulvene followed by addition of a nucleophile to the polarized exocyclic double bond. A few examples of this type of reaction have been reported.5-7 In the majority of these examples, the

reaction was used to prepare substituted metallocenes by addition of simple alkyllithiums to 6,6-dialkylfulvenes and trapping of the intermediate anions with a metal salt.^{5,6} Only in one instance⁷ was the reaction used specifically for the preparation of a functionalized cyclopentadiene.

For many of our target molecules, application of method A would require the alkylation of cyclopentadiene with a secondary neopentyllic halide. Since the outlook for such an alkylation was poor, we decided to further explore the use of method B for the preparation of functionalized cyclopentadienes. Herein we report the synthesis of several Diels-Alder precursors by this method.

The fulvenes may be formed by condensation of cyclopentadiene with an aldehyde in the presence of base. For relatively unhindered aldehydes (i.e., aldehydes with α protons), a dialkylamine may be used as the base⁸ (eq 2) while for α, α -disubstituted aldehydes preformation of sodium cyclopentadienide is necessary to obtain good yields of fulvenes (eq 3).



Conversion of the resulting fulvenes into substituted cyclopentadienes has been carried out in two different ways. When no additional substituent is desired, reduction of the exocyclic fulvene double bond with LiAlH₄ affords fair to good yields of substituted cyclopentadienes (eq 2 and Table I, entry a). Attempts at selectively reducing a fulvene in the presence of an α , β -unsaturated ester (i.e., 2) failed. Either the reagent had no effect on the fulvene (NaBH₄ or DIBAl-H at -78 °C) or complex mixtures resulted (LiAlH₄ or CuI/Vitride), presumably by subsequent reactions of the cyclopentadiene anion with the α,β -unsaturated ester. Finally, we found that when the ester functionality was intentionally reduced first with diisobutylaluminum hydride at room temperature, subsequent reduction of the fulvene with $LiAlH_4$ to 3 occurred in good yield (65%). Reduction of the ester might be circumvented by the use of method A (requiring alkylation with a primary halide). However, attempts at suitable alkylations did not result in the formation of the desired product.⁹

The addition of alkyllithiums was generally carried out by addition of the fulvene to a solution of the desired lithium compound at 0-25 °C. In all examples mixtures of double bond isomers in the cyclopentadiene ring were formed. In addition, when the fulvene contained a chiral center, a mixture of epimers at the newly formed chiral center was obtained (Table I, entries c-e).

In all cases the fulvenes were characterized by ¹H and ¹³C NMR and IR. The substituted cyclopentadiene

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