selectivity occur with an increasing pressure, while increasing temperature causes small selectivity decreases for both **1** and **2**. A selectivity of 56% terminal product, using **2** at 900 psi and 130 °C, is quite high when compared to recent patent claims using rhenium catalysts.[21]

Hydroformylations catalyzed by **1** and **2** are encouraging, not only because they are fairly selective but also because they are easily prepared,[7,8] relatively cheap, and air stable even in solution. Air-sensitive mononuclear cobalt[15,16,22-24] and rhodium[18,19,25-27] catalysts have now been widely studied.

In general, selectivity and reactivity may be varied greatly by the addition of phosphine or other ligands. Studies of the effect of added phosphine and cluster concentration on selectivity, reactivity, and cluster stability are underway.[28] Most importantly, these studies may shed light on possible catalytic mechanisms involving clusters that are not easily dissociated.[29] While it is not yet possible to provide definitive mechanistic information, the formation of intermediates such as **6**, **7**, and **8** is suggested.

Acknowledgments. The authors thank the National Science Foundation for generous support. We acknowledge the interest of Professor L. F. Dahl at the University of Wisconsin where the clusters **1** and **2** were prepared; a cooperative effort with his group will be the basis for future efforts in this area.

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(9) Yields are based on pentene consumed. The major products were the linear aldehyde, **3**, hexanal, and two branched aldehydes, **4**, 2-methylpentanal, and **5**, 2-ethylbutanal. Only small amounts of pentane ($\leq 3\%$) were formed during the reactions. The corresponding linear and branched alcohols were formed at higher temperatures but in small yields ($\leq 8\%$) and only in trace amounts if the reaction was stopped before 100% of the pentene was consumed. The formation of high molecular weight compounds, presumably due to aldehyde condensation reactions, becomes noticeable at higher reaction temperatures and long reaction times.

(10) The ratio of hexanal, **3**, to 2-methylpentanal, **4**, and 2-ethylbutyral, **5**, was determined by analytical GLC on a 10 ft × ⅛ in. 20% Carbowax 20M/Chromosorb W column (programmed from 100 °C for 4 min to 130 °C at 16°/min) using electronic integration and normalization techniques.

(11) Both 1- and 2-pentyne are reduced at 90 °C and 400 psi hydrogen to a mixture of pentene and pentane with **2**. For example, 1-pentyne gave pentane (14%), 1-pentene (72%), and 2-pentene (14%) after 21 h at these conditions. The reduction of both 1- and 2-pentene is slow even at 140 °C and 400 psi where pentane was obtained in 89% (90 h) and 27% (40 h) from the 1- and 2-isomers, respectively. Fairly selective reduction of enzynes to dienes is thus possible.

(12) The melting point and IR spectra were identical.

(13) These reactions were carried out at constant volume. Thus, the pressure dropped during the reaction (see Table I).

(14) The pressure given refers to the average between the starting and final pressures observed.

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(29) Cluster catalysis has never been definitively proved. Clusters, generally, could reversibly dissociate, under catalytic conditions, to smaller fragments which, in turn, could catalyze the observed reaction. One method to prove catalysis by a cluster would be to synthesize a cluster which itself is optically active (e.g., $FeCoNi(CO)_9(\mu_3\text{-}CR)$ where R = alkyl or aryl group. Here there are four different groups attached to the carbon bridging the cluster), then use the chiral cluster to carry out asymmetric catalytic reactions. If the product is optically active, then cluster catalysis is established.

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Received November 9, 1976

(Acetylacetonato)[(−)-*N*-alkylephedrinato]dioxomolybdenum, a New Class of Chiral Chelate Complexes Which Catalyze Asymmetric Epoxidation of Allylic Alcohol

Sir:

In asymmetric synthesis,[1] the use of an asymmetric catalyst is considered the most efficient way to minimize a loss of a precious chiral source. Although Wynberg et al.[2] have recently succeeded in asymmetric epoxidation of α,β-unsaturated ketones by employing chiral phase transfer agents as oxidation catalysts, no attempts have been made in the area of asymmetric epoxidations which can be catalyzed by chiral transition metal complexes.

While Sharpless et al.[3] have reported highly stereo- and regioselective epoxidation of allylic alcohols (**1**) by using achiral vanadium and molybdenum complexes as catalysts, we have now found, as shown in Scheme I, that **1** can be asymmetrically oxidized with cumene hydroperoxide, giving optically active epoxy alcohols (**2**), in the presence of chiral molybdenum catalyst, MoO_2 (acac)[(−)-*N*-alkylephedrinate] (**3**).[4]

Since the high stereo- and regioselectivity achieved by Sharpless et al.[3] are seemingly due to the coordination of **1** to the metal catalysts in the transition state, complexes such as **3**, which can fulfill the following two postulates, are expected to act as catalysts for asymmetric epoxidation of **1**: (a) the catalyst should contain the chiral ligand which behaves as a fixed ligand and does not dissociate from a central metal atom during a reaction; (b) the catalyst should contain two labile ligands both of which can be readily replaced by reactants under an influence of the fixed chiral ligand. We selected (−)-*N*-alkylephedrine (**4**) as ligands which fulfilled the former criterion because amine complexes of Mo had been known to be catalytically less active for epoxidation of olefins.[5] Acetylacetone was chosen as a replaceable ligand because MoO_2 $(acac)_2$ was catalytically active for epoxidation of olefins.[6]

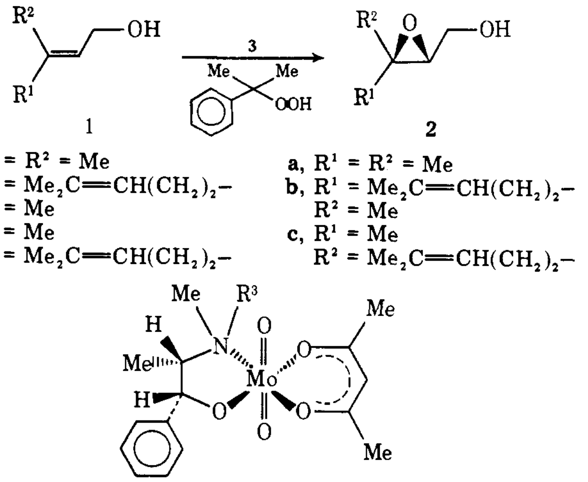
By employing our novel chiral complexes (**3**), it has become possible for the first time to produce **2** whose optical yields

Table I. Catalytic Asymmetric Epoxidation of Allylic Alcohols (1) with Cumene Hydroperoxide in the Presence of 3

Allylic alcohols (1)	Mo complexes (3)		Epoxy alcohols (**2**)[a]					
	Nature	Mole equiv to 1	Nature	Bp (mmHg), °C	Chem yield (%)[b]	$[\alpha]^{20}{}_{\text{D}}$ (*c*, $CHCl_3$)	Opt yield (%)[c]	Confign
1a	**3a**	0.01	**2a**[d]	71 (10)	50	+3.18 (6.91)	17	2(*R*)
		0.05		66–67 (8)	46	+5.39 (6.42)	29	2(*R*)
	3b	0.01		69–70 (9)	48	+4.67 (7.47)	25	2(*R*)
		0.05		64–65 (7)	33	+6.04 (4.65)	33	2(*R*)
1b	3a	0.01	**2b**[e]	89 (0.05)	57	+0.72 (14.56)	10	2(*R*), 3(*R*)
		0.05		81–83 (0.02)	43	+1.31 (11.81)	18	2(*R*), 3(*R*)
	3b	0.01		86–87 (0.03)	42	+1.18 (12.55)	16	2(*R*), 3(*R*)
		0.05		90–91 (0.05)	36	+1.75 (9.49)	24	2(*R*), 3(*R*)
1c	3a	0.01	**2c**[f]	83–84 (0.035)	56	+2.42 (15.63)	13	2(*R*), 3(*S*)
		0.05		87 (0.04)	52	+3.49 (13.98)	18	2(*R*), 3(*S*)
	3b	0.01		83 (0.03)	54	+3.95 (14.48)	21	2(*R*), 3(*S*)
		0.05		87–88 (0.045)	48	+6.25 (12.40)	33	2(*R*), 3(*S*)

[a] Satisfactory spectral (IR and NMR) data have been obtained for this compound. [b] Calculated on the distilled sample. [c] Expressed by percent enantiomeric excess. [d] The absolute configuration and optical rotation of the optically pure sample were determined by the chemical correlation with (*R*)-(+)-3-methylbutan-1,2,3-triol ((*R*)-(+)-i). Tosylation (91%) of **2a**, $[\alpha]^{20}{}_{\text{D}}$ +3.16° (*c* 7.29, $CHCl_3$), with tosyl chloride (1.2 equiv) in pyridine, followed by substitution of the tosyloxy group (88%) with sodium benzylate (1.2 eq) in dimethoxyethane, acid catalyzed epoxide opening (73%) with 0.1 *N* sulfuric acid in tetrahydrofuran (THF), and reductive cleavage of benzyl group (99%) with 5% Pd-C and hydrogen (1 atm) in THF, gave (*R*)-(+)-i, $[\alpha]^{20}{}_{\text{D}}$ +3.79° (*c* 5.25, MeOH). Since optically pure (*R*)-(+)-i was reported to show $[\alpha]^{20}{}_{\text{D}}$ +22° (MeOH) (B. E. Nelson and J. Lemmich, *Acta Chem. Scand.*, **23**, 967(1969)), it was established that 2a had 2(*R*) configuration and the optical rotation of the optically pure **2a** was $[\alpha]^{20}{}_{\text{D}}$ +18.4° ($CHCl_3$). [e] The absolute configuration and optical rotation of the optically pure sample were determined by the chemical correlation with (*R*)-(−)-linalool ((*R*)-(−)-ii). Tosylation (79%) of **2b**, $[\alpha]^{20}{}_{\text{D}}$ +1.07° (*c* 13.29, $CHCl_3$), with tosyl chloride (1.05 equiv) in pyridine, followed by substitution of the tosyloxy group (86%) with sodium iodide (1.32 equiv) in acetone, and deiodinative epoxide opening (71%) with zinc (10 equiv) and acetic acid in ether, gave (*R*)-(−)-ii, $[\alpha]^{20}{}_{\text{D}}$ −2.83° (*c* 6.19, $CHCl_3$). Since optically pure (*R*)-(−)-ii was reported to show $[\alpha]^{20}{}_{\text{D}}$ −19.42° ($CHCl_3$) (G. Ohloff and E. Klein, *Tetrahedron*, 18, 37(1962)), the absolute configuration and optical rotation of optically pure **2b** were determined as 2(*R*), 3(*R*) and $[\alpha]^{20}{}_{\text{D}}$ +7.33° ($CHCl_3$), respectively. [f] Determination of the absolute configuration and optical rotation of optically pure **2c** was carried out by the chemical correlation with (*S*)-(+)-ii. Similar successive treatments of **2c**, $[\alpha]^{20}{}_{\text{D}}$ +3.95° (*c* 14.48, $CHCl_3$), to the case for **2b**, afforded (*S*)-(+)-ii, $[\alpha]^{20}{}_{\text{D}}$ +4.00° (*c* 5.81, $CHCl_3$). Therefore, it was established that **2c** had 2(*R*),3(*S*)-configuration and optically pure **2c** showed $[\alpha]^{20}{}_{\text{D}}$ +19.2° ($CHCl_3$).

Scheme I



1

a, R¹ = R² = Me
b, R¹ = Me₂C═CH(CH₂)₂–
R² = Me
c, R¹ = Me
R² = Me₂C═CH(CH₂)₂–

2

a, R¹ = R² = Me
b, R¹ = Me₂C═CH(CH₂)₂–
R² = Me
c, R¹ = Me
R² = Me₂C═CH(CH₂)₂–

3

a, R³ = Me
b, R³ = Et

(max. 33%) are clearly superior to those of hitherto examined asymmetric oxirane formations.[2,7]

Preparation of **3a,b** was achieved by stirring a mixture of commercially available $MoO_2(acac)_2$ (1.0 mmol) and optically active (−)-*N*-methyl-[8] or (−)-*N*-ethylephedrine[9] (**4a** or **4b**) (1.2 mmol) in cyclohexane (15 mL) (for **4a**) or in a mixture of cyclohexane and hexane (1:1) (15 mL) (for **4b**) at 70–75 °C for 1 h. Structures of **3a** and **3b** obtained as a white mossy powder, respectively, were assigned as shown in Scheme I, based on their spectral and analytical data.[10]

Results for the asymmetric epoxidation attempted are summarized in Table I.

The general procedure for the epoxidation is given as follows; to a stirred solution of **1** (10 mmol) in benzene (10 mL), was added **3a** or **3b** (0.01–0.05 equiv), and the whole mixture was stirred at 40–45 °C for several minutes. Then, a solution of cumene hydroperoxide (commercially available, 75% pure) (12.5 mmol) in benzene (5 mL) was added dropwise to the stirred mixture over a period of 10 min at the same temperature. After stirring was continued at 40–45 °C[12] for 40 h, a yellow solution which was obtained, was concentrated in vacuo, giving a yellow oily residue, from which **2** was separated by column chromatography(alumina, solvent ether for **2a** or a mixture of ether and petroleum ether (ca. 1:1) for **2a** and **2c**). Short path vacuum distillation afforded pure **2** as a colorless oil, which showed reasonable behavior on spectral (IR and NMR) and chromatographic analyses.

Whether or not the catalytic asymmetric epoxidation exploited here actually proceeds through the assumed reaction process is still ambiguous and is being studied in these laboratories; applications of these chiral catalysts to asymmetric epoxidations of homo- and bishomoallylic alcohols, and further improvements of the catalysts are also under progress.

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(9) This sample (**4b**), mp 36–37 °C, $[\alpha]^{20}{}_{\text{D}}$ −15.2° (c 2.00, MeOH), was prepared according to the reported method (O. Červinka and O. Bělovský,

Collect. Czech. Chem. Commun., **32,** 3897 (1967)).

(10) **3a**: Ir ν_{max}^{Nujol} cm^{-1}: 1595, 1275 (MeCOCHCOMe); 930, 910 (O═Mo═O).[11] NMR (in $CDCl_3$–CD_3OD (1 drop)–Me_4Si): δ 1.05 (3 H, d, *J* = 6.5 Hz, NCH–C*H*$_3$), 2.03 (6 H, s, C*H*$_3$COCHCOC*H*$_3$), 2.83 (6 H, s, N(C*H*$_3$)$_2$), 2.8–3.4 (2 H, m, OC*H*–C*H*N), 5.3–5.5 (1 H, broad s, COC*H*CO), 7.32 (5 H, s, C_6H_5). Anal. Calcd for $C_{16}H_{23}O_5NMo$: C, 47.42; H, 5.72; N, 3.46. Found C, 47.44; H, 5.74; N, 3.62. **3b**: IR ν_{max}^{Nujol} cm^{-1}: 1595, 1280(MeCOCHCOMe); 930, 910 (O═Mo═O).[11] NMR (in $CDCl_3$–CD_3OD (1 drop)–Me_4Si): δ 0.96 (3 H, d, *J* = 7 Hz, NCH–C*H*$_3$), 1.23 (3 H, t, *J* = 7 Hz, NCH$_2$C*H*$_3$), 2.01 (6 H, s, C*H*$_3$COCHCOC*H*$_3$), 2.68 (3 H, s, C*H*$_3$), 4.0–4.5 (4 H, broad m, OC*H*–C*H*N and NC*H*$_2$CH$_3$), 5.2–5.6 (1 H, broad s, COC*H*CO), 7.25 (5 H, s, C_6H_5).

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(12) When the reaction temperature is lowered, the optical yield of **2** is clearly increased with a remarkable delay of the epoxidation speed. This tendency, which is frequently observed in usual asymmetric synthesis, can be visualized in the following data for the epoxidation of **1b** in the presence of **3a**: reaction temperature, reaction time, chemical yield, optical yield; 30–35 °C, 8 days, 43%, 15%; 40–45 °C, 60 h, 39%, 10%; 70–75 °C, 20 h, 47%, 4.5%. Therefore, the reaction temperature was kept in a range of 40–45 °C to complete the epoxidation within a moderate period.

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Received July 6, 1976

Chiral Hydroxamic Acids as Ligands in the Vanadium Catalyzed Asymmetric Epoxidation of Allylic Alcohols by *tert*-Butyl Hydroperoxide

Sir:

In spite of great current interest in asymmetric synthesis[1] little has been achieved in the area of asymmetric oxidations. By contrast asymmetric reductions have been quite successful, and, in the case of hydrogenation of certain olefins,[2] remarkably so. Of all organic oxidations, the epoxidation of olefins would be the most useful to accomplish in an asymmetric manner. The best induction to date with simple olefins is 10% enantiomeric excess (ee) realized using percamphoric acid.[3,18] Recently Wynberg and co-workers have reported substantial (25%) inductions in the epoxidation of α,β-unsaturated ketones by alkaline hydrogen peroxide employing chiral phase transfer agents.[4] We felt that the transition metal catalyzed epoxidations of olefins by alkyl hydroperoxides[5,15d] offered a special opportunity to achieve asymmetric epoxidations. Therefore we have, for the past few years,[9a] been investigating the effects of chiral ligands on these systems and report here our initial successes.

From our earlier results on the vanadium and molybdenum catalyzed epoxidations of allylic alcohols,[5b,5c] we had good evidence that the alcohol function was coordinated to the metal during the oxygen atom transfer step. This attachment of the allylic alcohol substrate to the metal was expected to enhance any asymmetric selection process. All that seemed necessary was to find a chiral ligand which was stable to the conditions and did not block coordination sites essential to the epoxidation process. We first investigated chiral β-diketone[6] complexes of vanadium and molybdenum; these gave poor results and we have since found that β-diketones are rapidly destroyed under the conditions of these oxidations.[7] After trying a variety of other chiral ligands, hydroxamic acids were found to be especially attractive.[9a] They are very resistant to oxidation and seem to bind well to molybdenum and vanadium. Well characterized, chiral molybdenyl bishydroxymates [O_2Mo(hydroxymate)$_2$] were easily prepared from chiral hydroxamic acids such as **1a.**[9a] However, these molybdenum complexes[8] have so far given poor (<2%) asymmetric inductions. On the other hand, although we have not yet managed to prepare a characterizable chiral hydroxymate complex of vanadium,[9b] asymmetric epoxidations with in situ generated vanadium hydroxymates have been encouraging. The results using vanadium catalysis with three related chiral hydroxamic acids (**1a**–**1c**)[10] and three allylic alcohols (geraniol (**2**), *E*-α-phen-

Table I. Asymmetric Epoxidations of Allylic Alcohols[a]

Hydroxamic acid (equiv)[b]	Allylic alcohol	°C	% ee[c]	% conversion[d]
1 **1a** (5)	**2**	−78 → 25	17	83
2 **1a** (3)	**3**	−78 → 25	10	100
3 **1a** (5)	**3**	−78 → 25	21	80
4 **1a** (10)	**3**	−78 → 25	18	22
5 **1b** (4)	**2**	−78 → 25	19	100
6 **1b** (4)	**2**	25	17.5	100
7 **1b** (5)	**2**	25	30	86
8 **1b** (5)	**2**	−78	—	0
9 **1b** (7)	**2**	−78 → 25	10	10
10 **1b** (1)	**3**	−78 → 25	<8	100
11 **1b** (2)	**3**	−78 → 25	8	100
12 **1b** (3)	**3**	−78 → 25	22.5	100
13 **1b** (5)	**3**	−78 → 25	50	30
14 **1b** (5)	**3**	25	40	84
15 **1b** (5)	**4**	25	40	87
16 **1b** (5)	**4**	−10	44	75
17 **1c** (3)	**2**	0	5	70
18 **1c** (4)	**2**	0	19	55
19 **1c** (5)	**2**	0	—	0

[a] All reactions were performed with 1 mmol of allylic alcohol and 2.5 mg (1%) of $VO(acac)_2$ catalyst in 20 mL of toluene under a nitrogen atmosphere. When the appropriate amount of hydroxamic acid was added to these solutions they immediately turned from green to reddish brown in color. Stirring was continued at room temperature for 15 min then, after cooling, 2 equiv of *tert*-butyl hydroperoxide (90+%, Lucidol) was added dropwise. During addition of the hydroperoxide the solution turned ruby red and this color persisted even after warming to room temperature. Reactions were monitored by TLC and acetylation was accomplished in situ by addition of pyridine and acetic anhydride. Acetylation was allowed to proceed for 2 h at room temperature and workup (see ref 5b) afforded the crude epoxyacetates which were purified by PLC and or microdistillation. [b] The figure in parentheses refers to the equivalents of hydroxamic acid added based on the amount of $VO(acac)_2$ catalyst. [c] The enantiomeric excess (ee) was determined by ^1H NMR using Eu-OPTISHIFT II [Eu(hfbc)$_3$] chiral shift reagent on the epoxyacetates (see ref 13 for estimated rotations of the three epoxyacetates). [d] The percent of epoxy alcohol product plus the percent of unreacted allylic alcohol equals 100%. In cases of 100% conversion the isolated yields of epoxy acetates ranged from 70 to 90%.