BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 50 (3), 769—770 (1977)

A Study of the Asymmetric Reaction of Methyloxirane with Acetic Acid Catalyzed by an Optically-Active Cobalt Complex

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(Received July 14, 1976)

Synopsis. A novel asymmetric reaction of methyloxirane with acetic acid catalyzed by an optically-active Co(salen)-type complex was explored. The products were identified to be propylene diacetate, 2-hydroxypropyl acetate, and 2-hydroxy-1-methylethyl acetate. The mechanistic features of this resolution-type reaction were characterized by the optical activities of the products and of the unchanged methyloxirane.

It has been reported that *N*,*N*′-disalicylidene-(1*R*,-2*R*)- 1,2-cyclohexanediaminatocobalt(II), $Co^{II}(sal)_2(R$-CHXDA), is a low-spin square-planar complex with a λ-conformation of the central chelate ring. Highly asymmetric selectivity was observed in a kinetic resolution of DL-methyloxirane using the $Co^{II}(sal)_2(R$-CHXDA)/$LiAlH_4$ system,[1] however, the isomerization of the selected methyloxirane to acetone was observed to occur by hydride shift involving electron transfer from the oxygen to the cobalt atom.[2]

It would be of interest and preparatively useful to explore a reaction in which an asymmetric center is maintained throughout the reaction. In the present series of our studies, the $Co^{II}(sal)_2(R$-CHXDA)/butyllithium/methyloxirane/acetic acid system has been found to give optically-active products. In this paper we would like to report the identification of the products and the mechanistic features of the reaction system.

Results and Discussion

Optically-active products I, II, and III, were found to be formed when a reaction was carried out at a mole ratio for Co^{II}: BuLi: methyloxirane: CH_3COOH of 1: 1: 150: 40 at 20 °C (the reaction conditions were as described in Table 1). The optical purity of the reacted methyloxirane calculated from the optical rotation of the unchanged methyloxirane, (L−D/L+D)rm, was 31% (conv. 11.8%). When $MgEt_2$, $ZnEt_2$, $LiAlH_4$, and $AlEt_3$ were used instead of BuLi, the (L−D/L+D)rm values were observed to be 18 (conv. 27.6%), 14 (2.9%), 8 (6.8%), and 0% (27.6%), respectively.

Products I, II, and III were isolated and respectively determined to be propylene diacetate, 2-hydroxypropyl acetate, and 2-hydroxy-1-methylethyl acetate, by mass spectral, elemental, and NMR analyses. Further confirmation of the products was obtained by comparison with authentic samples (see Experimental).

In order to clarify the features of the Co^{II}/BuLi/methyloxirane/CH_3COOH system, was carried out a series of experiments given in Tables 1 and 2. The ratio of the amount of product II $CH_3COOCH_2CH(CH_3)CH_2OH$ to the amounts of products II and III $CH_3COOCH(CH_3)CH_2OH$ was found to be 68—78% in the systems in Tables 1 and 2, indicating that the ring openings take place by acid-catalyzed reactions.[3] In accord with this observation, the systems involving little or no free acetic acid (Nos. 6 and 7 in Table 1) exhibit little or low reactivity for the ring opening reactions. The reaction of acetic acid with methyloxirane was catalyzed by the Co-complex, and presumably also by lithium acetate (formed by a rapid reaction of the Li moiety with CH_3COOH) as shown in Nos. 4, 5, and 9.

In Table 2, products I, II, and III were combined and hydrolyzed to 1,2-propanediol, their optical purities (L−D/L+D)mp* being about 11%. Assuming that III was formed by a complete inversion mechanism (CH–O opening),[3,5] the expected optical purity of 1,2-propanediol (L−D/L+D)cp was calculated from that of reacted methyloxirane (L−D/L+D)rm and the product ratio of III to II (see Table 2). Concerning the data at 25 °C (No. 2-1), the measured optical purity (L−D/L+D)mp is higher than the calculated value (L−D/L+D)cp, suggesting that another type of reaction such as oligomerization involving non-asymmetric selection [see the equations in d) of Table 1 and in e) of Table 2] may take place in parallel with the product(I/II/III)-forming reaction, a suggestion of which is supported by low material balance, (I+II+III)/reacted methyloxirane=78%. On the other hand, in Exp No. 2-2 of high material balance (98%) at 18 °C, the measured value (L−D/L+D)mp is lower than the calculated value; racemization is considered to take place to some extent during hydrolyzing of the products to 1,2-propanediol. The optical activity of pure D(+)-methyloxirane(neat) was assumed to be 15°, which, however, may be a higher value estimated to be 18.3°, using the highest $[\alpha]^{25}_{589}$ value (in $CHCl_3$) so far reported [14.05 (neat) × 8.9 ($CHCl_3$)/7.0 ($CHCl_3$)];[6,7] the value of (L−D/L+D) cp (No. 2-2) would be 12.6% if this [α] value were used for $[\alpha_0]$.

It would be of interest to discuss some plausible mechanism for this asymmetric reaction, the mechanism of which is much different from the Co^{I}-catalyzed process observed for the systems $Co^{II}/LiAlH_4$/methyloxirane (L-selectivity, max. ee. 90%)[1] and Co^{II}/BuLi/methyloxirane (D-selectivity, 10%)[8] in dioxane/benzene solvents, where CH_2–O opening predominantly takes place, giving acetone by isomerization.

Comparing the data of No. 5 in Table 1 with those of Nos. 1, 2, 3, and 2-1, the chiral structure of the active species is suggested to be established by the Co^{II} species and acetic acid. In the reaction systems of Nos. 1, 2, 2-1, and 2-2 (addition order: Co^{II}/BuLi/methyloxirane/CH_3COOH), and of No. 3 (Co^{II}/BuLi/CH_3COOH/methyloxirane), there should be Co^{II} species produced

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* (L−D/L+D)mp, (L−D/L+D)cp and (L−D/L+D)rm: optical purities measured for 1,2-propanediol, calculated for 1,2-propanediol, and measured for the reacted methyloxirane.

Table 1. Asymmetric reactions in the $\mathrm{Co^{II}(sal)_2}$(*R*-CHXDA)/BuLi/methyloxirane(MO)/acetic acid system and related systems

Exp No.	Li Compd	$\mathrm{Co^{II}}$	Li[a]	Conv (%)	$[\alpha]^{20}_{589}$[c] (°)	$\left(\frac{\text{L}-\text{D}}{\text{L}+\text{D}}\right)_{\text{rm}}$[d] (%)	I	II	III
							(rel. mol %)		
1	*n*-BuLi	1	1	29.8	+0.856	13.4	6	68	26
2	*n*-BuLi	1	1	27.0	+0.872	15.7	—	—	—
3	*n*-BuLi	1	1[b]	12.5	+0.406	18.9	4	72	24
4	*n*-BuLi	0	1	5.5	—	—		trace	
5	—	1	0	8.1	+0.176	13.3	1	74	25
6	*n*-BuLi	1	40	0.0	+0.001	—		nil	
7	$\mathrm{CH_3COOLi}$	1	40	4.0	+0.011	1.7		nil	
8	$\mathrm{LiAlH_4}$	1	1	13.0	+0.015	0.6		trace	
9	—	0	0	0.0	0.000	—	—	—	1.5

a) Moles relative to $\mathrm{Co^{II}}$ (0.35 mmol). $\mathrm{AcOH/Co^{II}}=40$, but for No. 7 (AcOH, not added). Addition order, $\mathrm{Co^{II}}$/Li/MO/AcOH; [MO 70 mmol, benzene (10 ml)/dioxane (5 ml), 25 °C, 8 days]. b) Addition order, $\mathrm{Co^{II}}$/Li/AcOH/MO. c) [α] (neat) for non-reacted MO recovered, error ±0.005°. d) Optical purity of the reacted MO, evaluated by Eq. $[\alpha]/[\alpha_0]\times\{100-(\text{conv})\}/(\text{conv})$, where $[\alpha]/[\alpha_0]$ is the optical purity of the non-reacted MO. $[\alpha_0]^{21}_{589}=+15°$ for pure (*R*)-(*D*)-(+)-MO (Ref. 4).

Table 2. Asymmetric reactions in the $\mathrm{Co^{II}(sal)_2}$(*R*-CHXDA)/BuLi/methyloxirane(MO)/acetic acid system[a]

Exp No.	Temp (°C)	Conv (%)	$[\alpha]^{20}_{589}$[b] (°)	$\left(\frac{\text{L}-\text{D}}{\text{L}+\text{D}}\right)_{\text{rm}}$[b] (%)	I	II	III	1,2-Propanediol $[\alpha]^{20}_{589}$[c] (°)	1,2-Propanediol $\left(\frac{\text{L}-\text{D}}{\text{L}+\text{D}}\right)_{\text{mp}}$[d] (%)	1,2-Propanediol $\left(\frac{\text{L}-\text{D}}{\text{L}+\text{D}}\right)_{\text{ep}}$[e] (%)
					(rel. mol %)					
2—1	25	23.0	+0.724	16.2	5	71	24	+1.60	10.8	8.0
2—2	18	9.5	+0.451	28.7	5	73	22	+1.61	10.8	15.4

a) $\mathrm{Co^{II}/BuLi/AcOH}=1/1/100$ (mole ratio). $\mathrm{Co^{II}}$ 0.70 mmol, MO 140 mmol, benzene (20 ml)/dioxane (10 ml), 7 days. b) Described as in Table 1. c) [α] (neat) for 1,2-propanediol obtained by hydrolysis of I, II, and III. d) Measured optical purity. $[\alpha_0]^{25}_{589}=15.9°$ for pure (*S*)-(*L*)-(+)-1,2-propanediol (Ref. 4). e) Expected optical purity calcd from (L—D/L+D)rm × [(II—III)/(II+III)].

by radical decompositions of the $\mathrm{CH_3COOCo^{III}}$-[8,9] and $\mathrm{HCo^{I}}$-complexes formed,[10] respectively. However, the (L—D/L+D)rm value of run No. 5, in spite of the low conversion, is similar to those of Nos. 1, 2, and 2—1, which suggests that a Li compound may also play an important role in this asymmetric reaction, since (L—D/L+D)rm usually decreases with conversion in kinetic resolution.

As to the reaction of cobalt complexes with acetic acid, Clifford and Waters have reported the following equilibrium:[9,11]

$$\mathrm{RCOOH + Co^{III}(H_2O)_6 \rightleftarrows RCOO\text{-}Co^{III}(OH_2)_5 + H_3O^+}$$

It seems reasonable to consider the enhancement of acidity of the acetic acid interacting with the $\mathrm{Co^{II}(sal)_2}$-(*R*-CHXDA) complex in the present study using an aprotic solvent, $[\mathrm{Co^{II}\cdots RCO\overset{\delta-}{O}\text{–}\overset{\delta+}{H}}]$. The selective ring opening of L(—)-methyloxirane with the acetic acid interacting with the chiral $\mathrm{Co^{II}}$-complex leads to the resolution of DL-methyloxirane and formation of the optically-active products in this $\mathrm{Co^{II}}$/BuLi/methyloxirane/acetic acid system.

Experimental

Measurements. The NMR spectra were taken on a JEOL PS-100 spectrometer. The mass spectra were measured by electron impact method using a Hitachi RMU-6E instrument and by the chemical ionization method with a Jasco/Finnigan 3100 instrument. Optical rotations were observed by means of a Perkin-Elmer model 241 polarimeter.

Reagents. The $\mathrm{Co^{II}}$-complex, BuLi, and other reagents were prepared and/or purified by the usual methods described elsewhere.[1,8]

Procedure. To a benzene/dioxane solution of $\mathrm{Co^{II}(sal)_2}$(*R*-CHXDA) and BuLi, methyloxirane and acetic acid were added. The mixture was sealed in an ampule under dry nitrogen and reacted with stirring at an appropriate temperature. After a given reaction time, the non-reacted methyloxirane and products were analyzed by GLC. The methyloxirane was recovered by distillation and the products were isolated using the preparative GLC technique. The NMR analyses for the products were satisfactory; $\mathrm{-CH(CH_3)CH_2-}$ parts: $\mathrm{ABMX_3}$(I), $\mathrm{A_2BX_3}$(II), and $\mathrm{A_2MX_3}$(III) spin systems.

Authentic Samples. Propylene diacetate(I) was prepared by the reaction between 1,2-propanediol (60 ml) and acetic anhydride (300 ml) with a few drops of sulfuric acid at 170—180 °C for 4.5 h,[12] bp 81 °C/14 mmHg; n_{D}^{20} 1.4110; MW 160 (mass). Found: C, 52.41; H, 7.47%. Calcd for $\mathrm{C_7H_{12}O_4}$: C, 52.49; H, 7.55%. 2-Hydroxypropyl acetate(II) and 2-hydroxy-1-methylethyl acetate(III) were prepared by the reaction of methyloxirane (8 ml) with acetic acid (80 ml) at 35 °C for 8 days.[13] The products (II and III) were isolated as a mixture from the distillate at 86—88 °C/16 mmHg, by preparative GLC. MW 118 (mass). Found: C, 50.85; H, 8.55%. Calcd for $\mathrm{C_5H_{10}O_3}$: C, 50.84; H, 8.53%.

Hydrolysis. Products I, II, and III (in Table 2) were combined and hydrolyzed with a 5-M KOH aq solution to give 1,2-propanediol, which was extracted with ethyl acetate.

The authors are grateful to Prof. M. Tsuchiya of the University of Tokyo for the mass spectral measurements and analysis and to Dr. N. Akimori of Hitachi Ltd. (Naka) for his technical advice on GLC analysis. We also thank Mr. T. Takeichi for performing some of the experiments and other assistance.

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