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Asymmetric Carbon Dioxide Fixation into Optically Active Propylene Carbonate by the Reactions of Propylene Bromohydrins

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Asymmetric carbon dioxide fixation was achievd by the cyclization of propylene bromohydrins into chiral propylene carbonate of 38% enantiomeric excess in the presence of a chiral cobalt salen type complex.

Fixation of carbon dioxide, which has attracted much attention in connection with the photosynthesis, has been extensively studied from the point of the cultivation of new chemical resources.[1] As the extension of our studies on the asymmetric cyclization of halohydrins into oxiranes[2,3] using a chiral cobalt salen type complex, N,N'-disalicylidene-1(R),2(R)-1,2-cyclohexanediaminatocobalt(II),[4] Co*,(Fig.1), we report here our new findings of catalytical asymmetric carbon dioxide fixation under very mild conditions, as a novel asymmetric reaction of bromohydrins. As to the asymmetric carbon dioxide fixation, only one case has been known so far.[5]

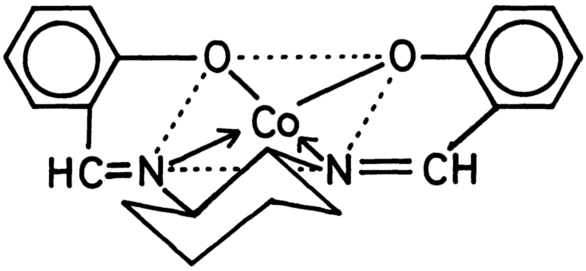


Fig.1. Structure of Co*.

Typical reaction procedure is as follows. Catalytic amount of Co* (0.5 mmol, 0.1895 g) and K_2CO_3 (60 mmol, 8.292 g) were dried at 150 °C for 3 h. After cooling the flask to room temperature, 40 ml of dioxane (solvent) and 120 mmol of 2-bromo-1-propanol (1a) were added and stirred at 25 °C under the CO_2 atmosphere. Formation of propylene carbonate (2) was confirmed by GC analysis as shown in Table 1. Small amount of methyloxirane (3), which

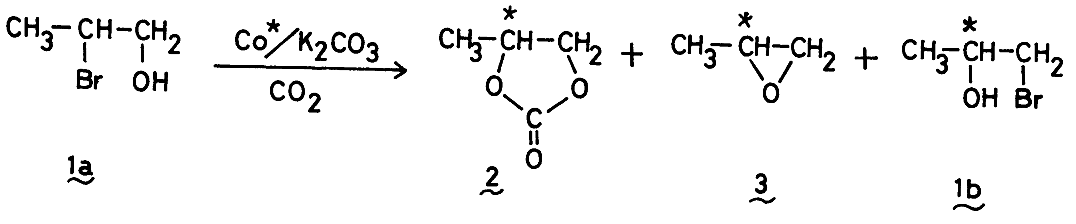


Table 1. Reaction of 2-bromo-1-propanol in the presence of CO_2 catalyzed by optically active cobalt complex[a)]

Run	Co* (mmol)	K_2CO_3 (mmol)	CO_2	Time d	Conv/% of 1a	Yield/%[b)] 2	3	1b
1	0.5	60	yes	6	90	22	7	40
2	0.5	60	yes	11	93	46	4	33
3	0	60	yes	6	2	0	trace	0
4	0.5	0	yes	5	1	0	0	0
5	0.5	60	no	5	26	trace	20	trace

a) Solvent (dioxane) 40 ml, 1a 120 mmol, 25 °C.

b) GC yield, based on the starting 1a.

was the sole product when 1a was reacted in the absence of CO_2, was also confirmed. It is notable that 1-bromo-2-propanol (1b), the isomer of the substrate, was obtained in 40% yield. Propylene carbonate and other cyclic carbonates are known to be synthesized from oxiranes and CO_2 by many catalysts.[6)] Interestingly, methyloxirane was not transformed into propylene carbonate in our reaction system, and propylene carbonate was synthesized in one step from propylene bromohydrins, a new type of CO_2 fixation.

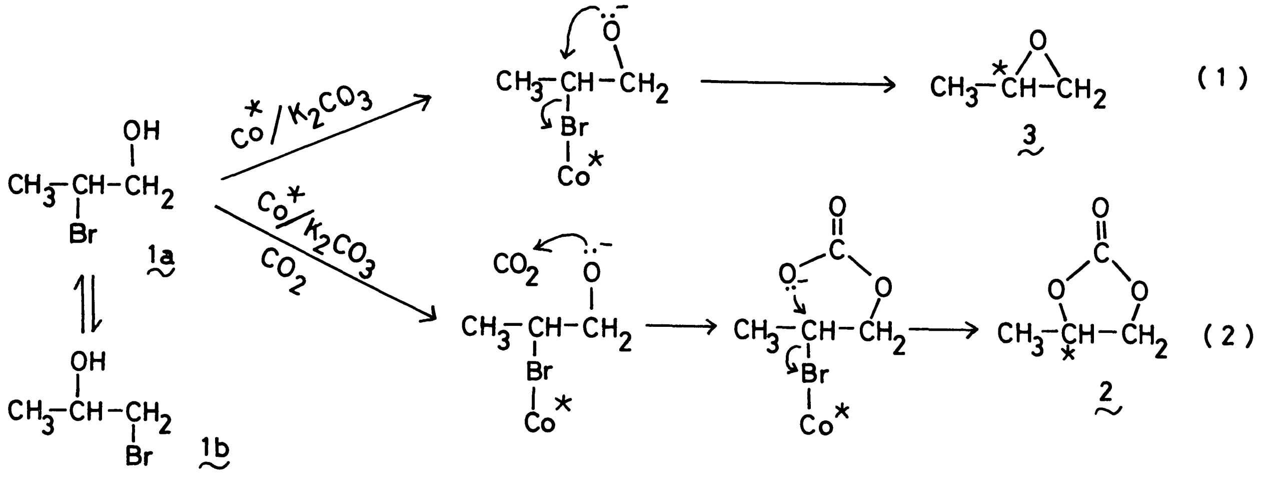
Products were isolated by distillation and the optical properties are shown in Table 2. The enantiomeric excess of 2 was 38%. The moderately high asymmetric induction at above 90% of the conversion of 1a looks strange for this kinetic resolution type asymmetric reaction, but the result can be explained by taking into account the isomerization of 1a to 1b. Chiral cyclic carbonates were prepared from chiral oxiranes and CO_2,[6g)] and this is the first case that chiral cyclic carbonate was prepared by the asymmetric reaction with CO_2.

Table 2. Optical properties of the products of run 1 in Table 1

		$[\alpha]_D$ /°	e.e.[a)] (%)	config.
Recovered	1a	5.4 (neat)	38	S
Products	2	-0.65(c 0.92, ethanol)	38	S
	3	-0.91(neat)	7.3	S
	1b	-0.98(neat)	20	R

a) Enantiomeric excess was calculated based on the reported optical rotations : 2, Ref.7; 3, Ref.8; 1a and 1b, Ref.9.

The cyclization of various chlorohydrins occurs by the nucleophilic attack of alcoholate anion on the carbon bearing halogen as described previously.[2,3] In the presence of CO_2, the formation of 2 can be explained reasonably by considering the attack of alcoholate anion on CO_2 prior to the intramolecular cyclization, as shown in Scheme below. The fact that the configuration of 2 was S, same as that of 3, is consistent with the mechanism. The fact that 1a and 1b gave almost the same product distribution suggest that an equilibrium between 1a and 1b exists.



The ratio of the reactions (1) and (2) in the above Scheme depends on the concentration of CO_2 in the reaction system. The reaction was carried out similarly under 8 Pa CO_2 pressure using an autoclave. As expected, the yield of 2 increased to 54% based on the substrate and the formation of 3 decreased.(Table 3) The e.e. of 2 was 30%, which is almost the same as that from atomospheric pressure of CO_2.

Table 3. Reaction of 2-bromo-1-propanol under 8 Pa CO_2 pressure at 25 °C[a)]

Co* (mmol)	Time d	Conv/% of 1a	Yield/% 2	Yield/% 3	Yield/% 1b
0.25	8	87.3	54.2	0.7	26.5
0	7	23.4	14.4	0.1	0.0

a) K_2CO_3 30 mmol, 1a 60 mmol, dioxane 20 ml.

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