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SYNTHESIS OF 1,2-PROPANEDIOL FORMATES FROM CARBON DIOXIDE, HYDROGEN, AND METHYLOXIRANE CATALYZED BY TRANSITION METAL COMPLEX

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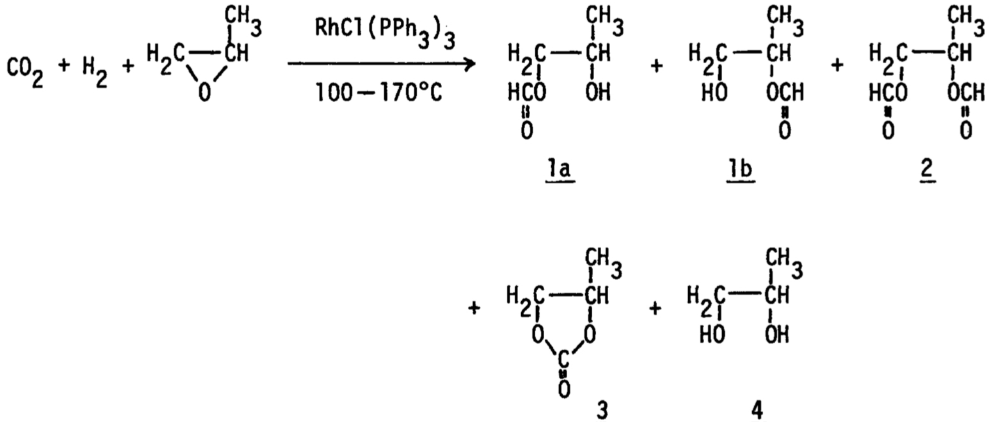
Glycol formates were prepared in a new type of catalytic reaction using carbon dioxide, hydrogen, and an oxirane as direct starting materials, and a transition metal complex like tris(triphenylphosphine)chlororhodium as catalyst.

Despite increasing interests in a catalytic fixation of carbon dioxide with the use of transition metal complexes, only a few successful reactions have been reported so far. In the preceding study, we revealed that chlorocarbonylbis(triphenylphosphine)rhodium can be prepared by the reaction of tris(triphenylphosphine)chlororhodium with carbon dioxide and molecular hydrogen and suggested the possibility of catalytic synthesis of formic acid from carbon dioxide and hydrogen.1)

The present communication deals with our recent finding of a novel reaction in which carbon dioxide was catalytically fixed with hydrogen and methyloxirane to form 1,2-propanediol formates (1a, 1b, and 2) as main products. Tris(triphenylphosphine)chlororhodium and some other complexes of group VIII transition metals worked as catalysts for this reaction. Propylene carbonate (4-methyl-1,3-dioxolane-2-one) (3) and 1,2-propanediol (4) were also produced as by-products. A typical reaction and the product identification were conducted as described below.



A suspension of $RhCl(PPh_3)_3$ (0.3g:0.32mmol) in methyloxirane (20ml:300mmol) was placed in a 100 ml stainless steel autoclave and constantly stirred at 100°C under pressure of CO_2 (40 atm) and H_2 (40 atm). After reacting for 40hr, the reaction mixture was separated into two fractions by distillation. The first volatile fraction (bp 34°C) was unreacted methyloxirane. The second fraction which was distilled at 170-200°C was found to contain three main products (1-3). These products were

Table I IR and ^{1}H-NMR data of products in the reaction of CO_2, H_2, and Methyloxirane catalyzed by $RhCl(PPh_3)_3$

	1a	1b	2	3	4
IR (cm^{-1})	3400(νOH)	3400(νOH)			3400(νOH)
	1718(νC=O)	1718(νC=O)	1718(νC=O)	1800(νC=O)	
	1190(νCO-O)	1190(νCO-O)	1190(νCO-O)	1190(νCO-O)	
^{1}H-NMR$^{a)}$ (ppm)	8.10(HC=O)	8.10(HC=O)	8.05(HC=O)		4.70(OH)
	4.10(CH_2+CH)	5.10(CH)	5.30(CH)		3.80(CH)
	2.85(OH)	3.70(CH_2)	4.20(CH_2)		3.50(CH_2)
	1.25(CH_3)	2.85(OH)	1.30(CH_3)		1.10(CH_3)
		1.25(CH_3)			

a) Chemical shift from TMS

separated by GLPC and examined by means of IR, NMR and GC-MS. The analytical data of the products are summarized in Table I.

The presence of peak at mass number of 44 in the mass spectra indicates that both (1) and (2) have carboxyl group(s). The reference reaction of methyloxirane with formic acid resulted in the formation of products which gave the same retention times in GLPC and the same IR and NMR spectra as those of (1) and (2). This reaction is known to afford 1,2-propanediol monoformate and 1,2-propanediol diformate.$^{2)}$ From all these results, (1) and (2) were identified as 1,2-propanediol monoformate and 1,2-propanediol diformate, respectively. NMR spectrum of (1) clearly indicated that (1) is actually a mixture of two isomers, (1a) and (1b), with a molar ratio of 3 : 2, suggesting the regioselectivity of the oxirane-ring opening in this reaction is rather low. Propylene carbonate (3) and 1,2-propanediol (4) were identified by referring to the spectral data also given in Table I. It can be considered that transesterifications between 1a('s) and/or 1b('s) provided (2) and (4).

Table II lists the results of reactions carried out under various conditions. The data of Runs 1 through 4 show that all of CO_2, H_2 and $RhCl(PPh_3)_3$ are necessary for this reaction. Tris(triphenylphosphine)dichlororuthenium is a catalyst as effective as $RhCl(PPh_3)_3$ for the syntheses of glycol formates, (1) and (2), while it is a far better catalyst for producing (3). Although tris(triphenylphosphine)chlorocobalt is inactive as catalyst for the preparation of (1) and (2) under the conditions employed in this study, it exhibits a high selectivity to form (3) in a good yield.$^{3)}$

The maximum yields of (1) and (2) in the reaction using tris(triphenylphosphine)chlororhodium as catalyst are obtained at about 150°C, whereas the yield of (3) increases monotonously. This result as well as the fact that (3) can be obtained even in the absence of $RhCl(PPh_3)_3$ indicates that the rhodium complex catalyzes only the formation of 1,2-propanediol formates, (1) and (2), or that it has two active sites; one for the reaction to give (1) and (2) and the other for (3).

Reactions of some other oxiranes with carbon dioxide and hydrogen also yielded glycol formates as represented by Runs 9 through 11 in Table II.

Table II The reaction of an oxirane with CO_2 and H_2 in the presence of a group VIII transition metal complex[a)]

Run	Oxirane	Complex	Temp. °C	CO_2 atm	H_2 atm	Products (mol/mol complex)		
						1	2	3
1	Methyloxirane	$RhCl(PPh_3)_3$	100	40	40	12	4	5
2	"	"	"	0	40	0	0	0
3	"	"	"	40	0	0	0	3
4	"	none	"	40	40	0	0	5
5[a)]	"	$RhCl(PPh_3)_3$	"	"	"	220[a)]	48[a)]	270[a)]
6	"	$RuCl_2(PPh_3)_3$	"	"	"	45	12	1300
7	"	$CoCl(PPh_3)_3$	"	"	"	0	0	680
8	"	$RhCl(CO)(PPh_3)_2$	"	"	"	0	0	0
9	Oxirane	$RhCl(PPh_3)_3$	"	"	"	169[b)]	41	97
10	Chloromethyloxirane	"	"	"	"	13	n.d.	72
11	1,2-Epoxycyclohexane	"	"	"	"	9	n.d.	0
12	Methyloxirane	"	50	"	"	2	1	1
13	"	"	120	"	"	20	4	10
14	"	"	150	"	"	72	14	34
15	"	"	170	"	"	44	5	676

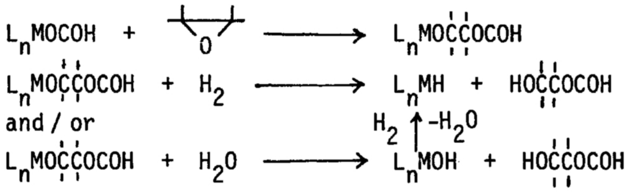
a) Reaction time : 40hr except Run 5 (160hr)

b) $HCOOCH_2CH_2OCH_2CH_2OH$

There are some known reactions of the same kind; the syntheses of formamides,[4)] alkyl formates,[5,6)] and formic acid[7)] by the reactions of secondary amines, alcohols, and water, respectively, with carbon dioxide and hydrogen. In all these reactions, active-hydrogen compounds, i.e. amines, alcohols, and water, were used. The active-hydrogen compounds were considered to react with the formato ligand in the intermediate complex, M-O-CO-H, which might be formed by the reaction of a transition metal complex used as catalyst with hydrogen and carbon dioxide.[8)] This reaction was presumed to yield the products and another intermediate complex with a metal-hydroxo bond. Thus, an active-hydrogen compound should play an important part in these catalytic reactions.

$$L_nMH + CO_2 \longrightarrow L_nMOCOH$$
$$L_nMOCOH + BH \longrightarrow L_nMOH + HCOB \qquad (B : NR_2, OR, OH)$$
$$L_nMOH + H_2 \longrightarrow L_nMH + H_2O$$

Therefore, our reaction has a signigicant novelty compared to the reactions cited above, since no active-hydrogen compound is used. Instead of an active-hydrogen compound, an oxirane was employed in our case. Oxiranes were expected to have a reactivity high enough to insert into the transition metal-formato bond to give an intermediate complex with metal-alkoxo bond.[9) The reaction of this intermediate with a catalytic amount of water or with hydrogen would provide a glycol monoformate and another intermediate complex which is substantially the same as the one obtained in the above mentioned reactions using active-hydrogen compounds. A trace of water, even if it is necessary, would be sufficient for this reaction, since it could be reproduced in the subsequent reaction.



Furthermore, the formation of formic acid should be noted here briefly.[10) The presence of formic acid in this reaction products was detected from the analyses by ^{1}H-NMR, TLC, and chromotropic acid-sulfuric acid test. Its yield in the reaction using $RhCl(PPh_3)_3$ at 100°C for 40hr was determined to be 5(mol/Rh atom) from the difference between the total amount of formyl groups (1, 2, and formic acid) measured by ^{1}H-NMR and amount of formyl groups in the glycol formates measured by GLPC. This fact suggests us the possibility of another reaction path: the reaction between hydrogen and carbon dioxide affords formic acid, which then reacts with an oxirane directly. This reaction path, however, is hard to consider as the main route to the products, since the yields of glycol formates varied appreciably depending on the kind of oxiranes used in the reaction (cf. Runs 1 and 9 in Table II). In view of a high reactivity of formic acid with oxiranes to give glycol formates, the yields were expected to be rather insensitive to the oxirane species, if the rhodium catalyst worked only to produce formic acid. Stereochemistry of the reaction is being studied to get further informations on the reaction mechanism.

References and Notes

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9) A key step of the alternating copolymerization of carbon dioxide and oxiranes by diethylzinc-water system found by one of the authors (H.K.) et al., is the insertion of an oxirane into zinc-carbonate bond, which is analogous to this reaction step; S.Inoue, H.Koinuma, and T.Tsuruta, Makromol. Chem., 130, 210 (1969).
10) Although the presence of a strong base such as triethylamine was considered indispensable for the formation of formic acid from CO_2 and H_2 in Ref.6, no such base was used in our reaction.

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