CHEMISTRY LETTERS, pp. 1323-1326, 1986.

Nickel-catalyzed Ring-opening Reactions of Epoxides and Their Regioselectivities

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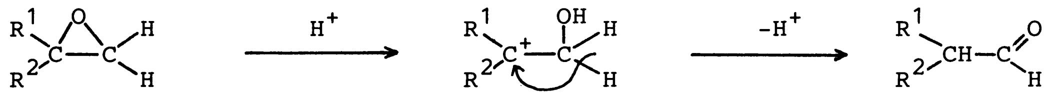
$NiBr_2(PPh_3)_2$ catalyzed ring-opening isomerization of epoxides to yield the corresponding aldehydes exclusively, while $Ni(PPh_3)_3$ and $NiBr_2L_2$ (L= PMe_2Ph, PEt_3 and PCy_3) were found to afford ketones, alcohols and olefins. Regioselectivity for a C-O bond cleavage of epoxides is determined by the nature of the ligand coordinated to the metal center.

Syntheses of aldehydes and ketones by ring-opening isomerization of epoxides are known as one of the important industrial process. Of particular, a sort of Lewis acid such as magnesium, zinc, boron or silver salt is effective catalyst. These reactions are well explained by taking account of a mechanism based on the formation of more stable carbonium ion intermediates as in Eq.1.$^{1)}$ Consequently, regioselectivity of the C-O bond cleavage is mainly dependent on the substitution pattern of epoxides.



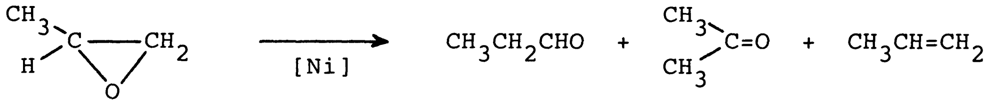
(1)

Although transition metal-catalyzed isomerization of epoxides currently attracts much attention,$^{2)}$ a detailed reaction mechanism remains unexplored. In this paper, we report Ni-catalyzed ring-opening reactions of epoxides. Regioselectivity and reaction mode are largely affected by the electronic state of the metal center. Isomerization mechanism via oxanickellacyclobutane intermediates$^{3)}$ is suggested for the reaction catalyzed by low valent Ni complexes.

Into a THF or toluene solution of Ni complex (0.5 mmol) was added epoxides

(10 mmol) at 20 °C under N_2. The solution was, then, placed in a constant temperature bath for the prescribed time and the product yields were directly analyzed by GLC. The structures of the products were identified by NMR, Mass and IR spectroscopies after isolation using preparative GLC.

$NiBr_2(PPh_3)_2$ was found to catalyze ring-opening isomerization of 1,2-epoxypropane to propionaldehyde under mild conditions, while $NiBr_2(PMe_2Ph)_2$ gave a mixture of acetone, propylene and aldehyde as in Table 1. $Ni(0)(PPh_3)_3$ facilitated to afford a mixture of acetone and olefin as major components. PPh_3 was inactive for deoxygenation[1)] of the epoxide under the same conditions in Table 1.



(2)

Table 1. Ni-catalyzed ring-opening reaction of 1,2-epoxypropane[a)]

Catalyst	Products/mol%			Conv./%
	CH_3CH_2CHO	CH_3COCH_3	$CH_3CH=CH_2$	
$NiBr_2(PPh_3)_2$	97	2	1	100
$NiBr_2(PMe_2Ph)_2$	49	33	18	58
$NiBr_2(PPh_3)_2/Zn/PPh_3$	16	63	21	62
PPh_3[b)]	-	-	-	0

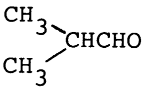
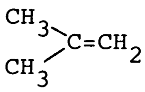
a) $NiBr_2L_2$ 5 mol%, 18 °C, THF, 25 h. b) 50 mol%.

Deoxygenation reaction of 1,2-epoxy-2-methylpropane or 1,2-epoxy-2-phenylpropane giving the corresponding olefin such as isobutylene or α-methylstyrene became more predominant with increasing σ-basicity of phosphines coordinated to Ni. $NiBr_2$ and $NiBr_2(PPh_3)_2$ catalyzed the conversion of epoxides to the corresponding aldehydes as in Tables 2 and 3. It was observed that the net conversion of epoxide was largely decreased as the relative amount of olefin production was increased.

$NiBr_2$ and $NiBr_2(PPh_3)_2$ apparently catalyzed ring-opening isomerization of epoxides giving the corresponding aldehydes under mild conditions, presumably by a similar manner by Lewis acids which attack on epoxide oxygen as electrophile, followed by a C-O bond scission to form more stable carbonium ion as in Eq.1.

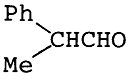
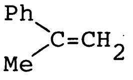
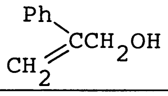
By contrast, as increasing σ-donor character of the coordinated phosphines, the reaction mode was considerably affected so as to decrease the relative amount of aldehydes. Compared with Ni(II) complexes, Ni(0) complexes were found to show completely different reaction mode leading to olefins. In order to get better

Table 2. Ni-catalyzed ring-opening reaction of 1,2-epoxy-2-methylpropane[a]

Catalyst	Products / mol%		Conv./%
	 $(CH_3)_2CHCHO$	 $(CH_3)_2C{=}CH_2$	
$NiBr_2$	97	3	23
$NiBr_2(PPh_3)_2$	98	2	82
$NiBr_2(PMe_2Ph)_2$	68	32	41
$NiBr_2(PCy_3)_2$	43	57	19
$NiBr_2(PPh_3)_2/Zn/PPh_3$	19	81	15
PPh_3[b]	-	100	1

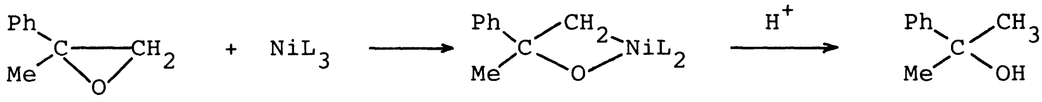
a) $NiBr_2(PPh_3)_2$ 5 mol%, 50 °C, THF, 48 h. b) 50 mol%.

Table 3. Ni-catalyzed ring-opening reaction of 1,2-epoxy-2-phenylpropane[a]

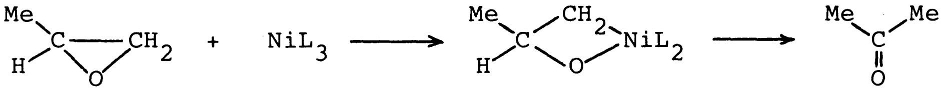
Catalyst	Time/h	Products / mol%			Conv./%
		 $Ph(Me)CHCHO$	 $Ph(Me)C{=}CH_2$	 $Ph(CH_2{=})CCH_2OH$	
$NiBr_2$	25	99	1	-	100
$NiBr_2(PPh_3)_2$	6	98	2	-	100
$NiBr_2(PMe_2Ph)_2$	47	60	12	28	65
$NiBr_2(PEt_3)_2$	115	42	37	21	31
$Ni(PPh_3)_4$	23	7	93	-	18
PPh_3[b]	78	88	12	-	7
-	118	100	-	-	7

a) Ni complexes 5 mol%, 50 °C, toluene. b) 50 mol%, 55 °C.

defined mechanisms of Ni(0) catalyzed reaction with epoxides, we have attempted the reaction of 1,2-epoxy-2-phenylpropane with $Ni(PPh_3)_3$ in toluene at 21 °C until the initial deep red solution turned to yellow orange color. Although attempted isolation of the complex was unsuccessful,[5] 2-phenyl-2-propanol was obtained in 34% yield (per Ni) after protonolysis with dry HCl. This result may be associated with the nucleophilic attack of the complexes to less hindered carbon leading to the formation of oxanickellacyclobutane intermediate **1**[3] during the course of the reaction. Then, the complex 1 could be subjected to a metathesis type bond cleavage to afford α-methylstyrene. In Table 1, the major formation of acetone, when 1,2-epoxypropane was treated with $Ni(0)(PPh_3)_3$ indicates the possible formation of oxanickellacyclobutane intermediate 2 in which the removable β-hydrogen exists to effect the conversion to acetone. Attempted isolation of disubstituted oxanickellacyclobutane complexes are now in progress.



1 34%



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We believe these findings may offer us fundamental information for understanding not only the factors governing the multifarious reaction modes of epoxides with transition metals, but also the mechanism of carbon-oxygen bond activation by transition metal complexes.

References

1) R. C. Elderfield, S. Winstein, and R. B. Henderson, "Heterocyclic Compounds," John Wiley (1950), Vol. 1, p. 48; G. Wittig and R. Haag, Chem. Ber., 88, 1654 (1955).

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3) A. Miyashita, J. Ishida, and H. Nohira, Tetrahedron Lett., 27, 2127 (1986).

4) $Ni(0)(PPh_3)_3$ was obtained in-situ by the treatment of $NiBr_2(PPh_3)_2$ with Zn (10 molar excess) in the presence of PPh_3 (equimolar to Ni).

5) ^1H-NMR (-12 °C, CD_2Cl_2) of the yellow complex 1 obtained by removing unreacted epoxide and solvent; δ 1.6 ppm (s, $C\underline{H}_3$, 3H), 1.1 (m, $-C\underline{H}_2$-Ni, 2H), 7.5 (m, Ph, 35H).

(Received May 22, 1986)