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CATALYTIC HYDROGENATION OF EPOXIDE WITH TRISTRIPHENYLPHOSPHINERHODIUM CHLORIDE

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$RhCl(PPh_3)_3$ was found to hydrogenate catalytically butadienemonooxide, which has a double bond adjacent to the epoxide group, whereas it could not alkyl nor aryl epoxide at all. The catalyst also hydrogenated phenylcyclopropane which may have significant π-character in its three-membered ring. The substrate may have to have π-coordination ability to be hydrogenated with $RhCl(PPh_3)_3$.

Although $RhCl(PPh_3)_3$[1] is one of the most active homogeneous catalysts for the hydrogenation of the carbon-carbon double bond, it has no activity for the reaction of ketone nor aldehyde. Cationic rhodium complexes were recently reported to be active for the hydrogenation of ketones.[2] In the present study the catalytic activity of $RhCl(PPh_3)_3$ for the hydrogenation of epoxides was investigated expecting the catalytic reactions because of high reactivity of the epoxide. A patent[3] claims the catalytic activity of the complex for the isomerization of butadienemonooxide into crotonaldehyde suggesting the interaction of the catalyst with the substrate.

$RhCl(PPh_3)_3$ was prepared under a nitrogen atmosphere according to the method described in the literature.[1b] Commercial phenylcyclopropane and epoxides of butene, butadiene, and styrene were used without further purification. The reaction was carried out in a constant volume apparatus, using benzene as the solvent. The reactant and products were analyzed by means of a gas-chromatograph with columns of 2m PEG and 4m DOS.

The reactivities of three epoxides and cyclopropane are shown in Table. Neither alkyl- nor aryl-epoxide was reactive at all with the catalyst, whereas they were easily hydrogenated into corresponding alcohols with cyanocobaltate[4] or its amine complexes.[5]

In contrast, the epoxide group of butadienemonooxide was certainly hydrogenated into alcohol with the rhodium catalyst, although the rate was slow. The products were found to be 1,2-buteneoxide, n-butylaldehyde, and n-butylalcohol after 10 hr reaction, however no secondary alcohol nor ketone was detected. The reaction was the consecutive one, where crotylalcohol and crotonaldehyde were produced at the first step of the reaction and then further hydrogenated into n-butylalcohol and n-butylaldehyde, respectively.

Phenylcyclopropane was found to be hydrogenated with the rhodium catalyst in spite of its analogous structure of the three-membered ring to styreneoxide. Product distribution in the hydrogenation and isomerization of the three-membered ring

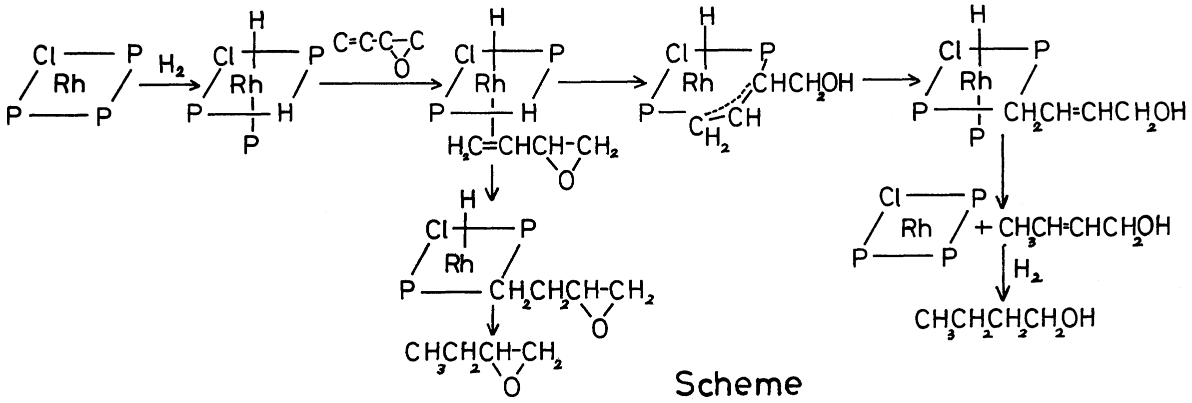
Table. Reactivity and Product Selectivity of Epoxides for Hydrogenation with $RhCl(PPh_3)_3$

substrate	conv. %	products & selectivity
$CH_2=CH-CH\underset{O}{-}CH_2$	60%/10hr	$CH_3-CH_2-CH\underset{O}{-}CH_2$ 40% $CH_3-CH_2-CH_2-CH_2OH$ 12% $CH_3-CH_2-CH_2-CHO$ 48%
$CH_3-CH_2-CH\underset{O}{-}CH_2$	0 /72hr	
$Ph-CH\underset{O}{-}CH_2$	0 /72hr	
$Ph-CH\underset{CH_2}{-}CH_2$	4.6%/14hr	$Ph-CH_2-CH_2-CH_3$ 100%
$Ph-CH=CH_2$	100%/20min.	$Ph-CH_2-CH_3$ 100%

$RhCl(PPh_3)_3$; 0.5×10^{-3} mole in Benzene 50 ml,
hydrogen initial pressure; 1 atm, reaction temp.; 30°C.
substrate; 1.3×10^{-2} mole

indicates the exclusive fission of the C-C or C-O bond of the ring to form the normal skeletal form.

The supreme activity of the catalyst for the styrene hydrogenation in addition to the above results may indicate that π-coordination of the substrate seems necessary for the substrate to be activated by the rhodium catalyst for hydrogeantion as well as isomerization, and that the epoxide ring has not sufficient π-donation ability as the cyclopropane ring has. Taking account of the intermediate products as well as product structures, the following schemes may be assumed based on the mechanism as for olefin hydrogenation.[1a]



Scheme

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