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CATALYTIC ACTIVITIES OF CATIONIC RHODIUM COMPLEXES FOR THE HYDROGENATION OF STYRENE OXIDE

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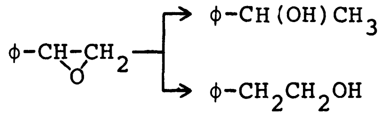
Cationic rhodium complexes were found to show catalytic activity for the hydrogenation of styrene oxide under atmospheric hydrogen at 30°. The identified products were β-phenylethyl alcohol and phenylacetaldehyde, both of which were formed by the cleavage of the same carbon-oxygen bond. The yield of the alcohol reached up to 59% after 20 hrs' reaction. However, neither secondary alcohol nor ketone was detected.

Hydrogenation of epoxides is one of interesting reactions from the view points of the reactivities of three-membered heterocyclic compounds and the selectivities among isomeric alcohols produced as shown in Eq. (1). Although some metal catalysts were reported to show excellent activities for this reaction[1)], the homogeneous catalyst has been scarcely investigated except for pentacyanocobaltate[2)]. The present authors found the interesting activities of cationic rhodium complexes which were recently reported to have catalytic activity for the hydrogenation of ketones by Schrock and Osborn[3)].



(1)

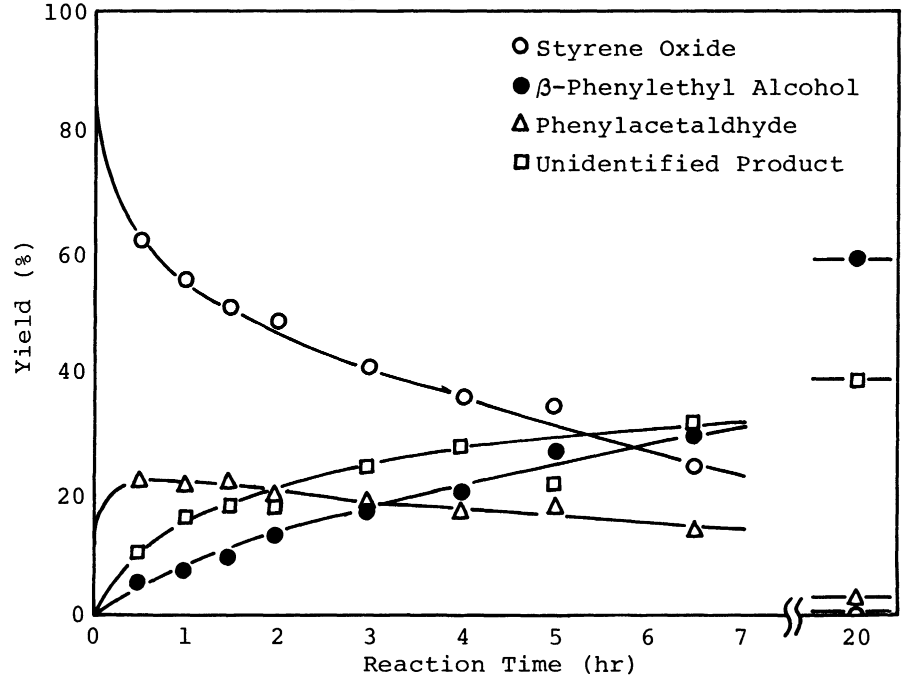
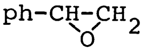
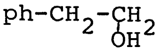


Figure. Hydrogenation of Styrene Oxide with $[Rh(NBD)\{PEt_3\}_2]^+ClO_4^-$.
Experimental conditions : see Table.

Table. Hydrogenation of Styrene Oxide

Catalyst Precursor	 $ph\text{-}CH\text{-}CH_2$ (O bridge) (%)	$ph\text{-}CH_2\text{-}CHO$ (%)	 $ph\text{-}CH_2\text{-}CH_2OH$ (%)	Unidentified Product (%)
$[Rh(NBD)(PMe_3)_3]^+A$	82.5	13.9	trace	3.6
$[Rh(NBD)(PEt_3)_2]^+A^-$	24.8	13.7	30.3	31.2
$[Rh(NBD)(PBu_3)_2]^+A^-$	-	3.6	28.5	67.9
$[Rh(NBD)(PPh_3)_2]^+A^-$	-	31.8	23.2	45.0
$[Rh(NBD)(diphos)]^+A^-$	-	56.2	1.0	42.8

A^- : ClO_4^-, catalyst precursor : 1.0×10^{-4} mol in 1% aqueous diglyme 50 ml, styrene oxide : 9.5×10^{-3} mol, hydrogen pressure : 1 atm, reaction temp. : 30°C, reaction time : 8.0 hr.

The complexes of $[Rh(NBD)\{PR_3\}_n]^+ClO^-_4$ were prepared under a nitrogen atmosphere according to the method described in the literature$^{4)}$. All commercial reagents were used without further purification. The reaction was carried out under atmospheric pressure of hydrogen. After the complex(0.1 mmole) dissolved in 1% aqueous diglyme (50 ml) was aged for 2 hr under hydrogen, the epoxide was introduced with a syringe through a silicon rubber stopper to start the reaction. The addition of 1% water by volume was found to give the maximum activity as observed in the hydrogenation of ketones^{3}.

Figure shows a typical reaction profile with $[Rh(NBD)\{PEt_3\}_2]^+ClO^-_4$ as the catalyst precursor. β-Phenylethyl alcohol and phenylacetaldehyde were identified in the products, however neither secondary alcohol nor ketone was detected although a considerable amount of the products was unidentified yet. They may be oligomers of the epoxide. The yield of β-phenylethyl alcohol increased linearly with the reaction time, reaching 59% after 20 hrs' reactions. It should be noted that only the primary alcohol without the secondary alcohol was produced whereas the same amounts of both alcohols were produced when pentacyanocobaltate was used$^{5)}$. Selective synthesis of the primary alcohol is of value to be surveyed$^{6)}$.

The yield of phenylacetaldehyde reached 30% at the early stage of the reaction and did not increase later, indicating that some portion of β-phenylethy alcohol is formed via this aldehyde.

The catalytic activities of some other cationic rhodium complexes for this reaction are summarized in the Table. The activity and product distribution depended very much on the kind of phosphine ligands. Further mechanistic study including the identification of oligomeric products is now in progress.

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