

## Catalytic Hydrogenation of 3,4-Epoxybut-1-ene with Cationic Rhodium Complexes

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Catalytic hydrogenation of 3,4-epoxybut-1-ene with cationic rhodium complexes has been investigated under 1 atmosphere of hydrogen at 30 °C. But-2-enal, the main product, but-2-en-1-ol, and but-3-en-1-ol were produced by isomerization *via* selective abnormal fission of the epoxide ring.

The catalytic activity for hydrogenation of the epoxide depended on the nature of the phosphorus ligands of the catalyst. The order of activity of the ligands for the formation of alcohols ( $\text{PEt}_3 \gg \text{diphos} \gg \text{PPh}_3 > \text{PMe}_3$ ) [diphos = 1,2-bis(diphenylphosphino)ethane] was different from that observed for hydrogenation of 1,2-epoxy-1-phenylethane. It should be noted that the diphos- and  $\text{PPh}_3$ -catalysts, which showed quite limited activity for both carbonyl compounds and 1,2-epoxy-1-phenylethane, exhibited considerable activity for the title compound. The epoxide ring may be activated by the adjacent olefinic bond to a considerable extent. A mechanism is proposed to explain the high reactivity of the epoxide and the ligand effects on the catalytic activity which differed in the hydrogenation of 1,2-epoxy-1-phenylethane and 1,2-epoxybutane.

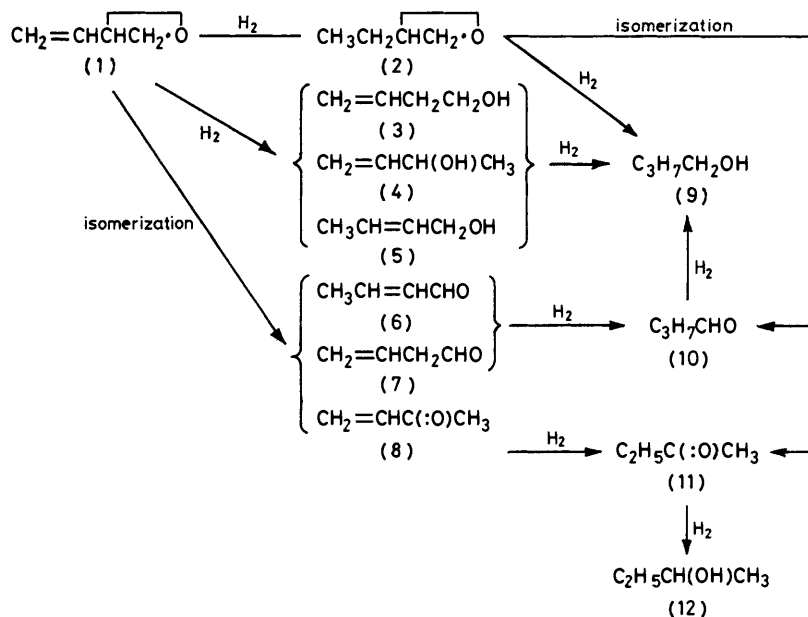
THE use of rhodium complexes as catalysts for hydrogenation is well established,<sup>1</sup> cationic ones in particular being reported as active for the hydrogenation of carbonyl groups<sup>2-4</sup> as well as olefinic bonds.<sup>5</sup> We have previously reported that cationic rhodium complexes hydrogenated 1,2-epoxy-1-phenylethane to 2-phenylethanol selectively and that the catalytic activity depended very much on the phosphorus ligand in the catalyst.<sup>6</sup> The ring-opening reaction of asymmetric epoxides, especially unsaturated conjugated epoxides, has been studied extensively using metal catalysts,<sup>7</sup> aluminium- or boron-hydrides,<sup>8</sup> and organocopper reagents;<sup>9</sup> however, their homogeneous hydrogenation has been scarcely investigated except for our previous study with the Wilkinson complex,  $\text{RhCl}(\text{PPh}_3)_3$ .<sup>10</sup>

Here the catalytic activities of cationic rhodium complexes containing phosphorus ligands are discussed

in terms of the influences of the ligand on the reaction rate and the selectivity in the hydrogenation of 3,4-epoxybut-1-ene (1) which contains two reactive and co-ordinative functions, *i.e.* an olefinic double bond and an epoxide ring. The olefinic group may alter the reactivity of the epoxide ring not only through the electronic substituent effect, but also by its ability to co-ordinate to the catalyst. The possible reactions of the epoxide (1) in the presence of the rhodium catalyst are summarized in Scheme 1.

### RESULTS AND DISCUSSION

Conversions, product distributions, and reaction profiles in the hydrogenation of the epoxide (1) with cationic rhodium complexes derived from the catalyst precursors  $[\text{Rh}(\text{nbd})(\text{PR}_3)_n]$   $[\text{ClO}_4]$  (nbd = norbornadiene;  $n = 2,3$ ) are shown in Table I and the Figure.



SCHEME 1

TABLE 1  
Catalytic hydrogenation of (1) with several cationic rhodium catalysts.<sup>a</sup> Yields (selectivities)/%<sup>b</sup>

Conversion (%) <sup>b</sup>	Ligand (L) in [Rh(nbd)L][ClO <sub>4</sub> ]				RhCl(PPh <sub>3</sub> ) <sub>3</sub> <sup>c</sup> (%)
	(PEt <sub>3</sub> ) <sub>2</sub> 68.6/100	(PMe <sub>3</sub> ) <sub>3</sub> 12.8 / 14.0	(PPh <sub>3</sub> ) <sub>2</sub> 73.2 / 100	diphos 68.6 / 100	
Product					
(2)	9.3 / 8.9 (13.6) (8.9)	4.1 / 4.0 (32.0) (28.6)	2.4 / 2.1 (3.3) (2.1)	0 / 0	24.0 (40.0)
(6)	29.6 / 34.9 (43.1) (34.9)	5.9 / 7.6 (46.1) (54.3)	30.2 / 44.3 (41.3) (44.3)	36.8 / 38.6 (41.8) (38.6)	—
(10)	5.1 / 15.1 (7.4) (15.1)	— / —	1.8 / 4.4 (2.5) (4.4)	2.3 / 8.0 (2.6) (8.0)	28.8 (48.0)
(5)	10.2 / 20.7 (14.9) (20.7)	1.5 / 0.9 (11.7) (6.4)	8.6 / 11.7 (11.7) (11.7)	15.5 / 19.7 (17.6) (19.7)	—
(3)	7.2 / 10.8 (10.5) (10.8)	0.9 / 1.2 (7.0) (8.6)	11.9 / 16.5 (16.3) (16.5)	16.0 / 12.2 (18.2) (12.2)	—
(9)	2.1 / 5.2 (3.1) (5.2)	0.4 / 0.3 (3.1) (2.1)	0.2 / 1.7 (0.3) (1.7)	trace / 4.2 (—) (4.2)	7.2 (12.0)
Oligomers	5.1 / 4.9 (7.4) (4.9)	— / —	18.1 / 19.3 (24.7) (19.3)	17.4 / 17.3 (19.8) (17.3)	—

<sup>a</sup> Catalyst: 0.1 mmol in 50 ml 1% aq. diglyme; substrate: 10 mmol;  $P(H_2)$ : 1 atm; reaction temp: 30 °C. <sup>b</sup> Conversion and yield after 3 h/8 h reaction. <sup>c</sup> RhCl(PPh<sub>3</sub>)<sub>3</sub>: 5 mmol in 50 ml benzene, 10 h reaction.

The reaction of the epoxide in the presence of the rhodium catalysts, except that with PMe<sub>3</sub> ligands, was fairly fast, achieving 100% conversion within 8 h. The comparable reaction with 1,2-epoxy-1-phenylethane<sup>6</sup> was much faster than that with 1,2-epoxybutane (2), of which conversion was only 0.65% after 100 h.<sup>6</sup> The low activity of the PMe<sub>3</sub>-catalyst may be due to the steric hindrance of its three-co-ordination state. The consumption rate of the epoxide was only slightly dependent on the phosphorus ligand, except with the PMe<sub>3</sub> catalyst (Tables 1–4). Good first-order kinetic plots were obtained until 50–80% conversion had been achieved with all catalysts examined.

TABLE 2

Hydrogenation of (1) with [Rh(nbd)(PEt<sub>3</sub>)<sub>2</sub>][ClO<sub>4</sub>].  
Yields (%)

Curve <sup>a</sup>	Product	Reaction time (h)				
		0.5	1	3	4.5	8
1	(1)	79.1	47.5	31.4	11.1	—
2	(2)	5.5	8.1	<i>b</i>	9.8	<i>b</i>
3	(6)	8.7	21.2	<i>b</i>	34.4	<i>b</i>
4	(10)	0.3	2.9	<i>b</i>	11.2	<i>b</i>
5	(5)	2.6	7.7	<i>b</i>	15.7	<i>b</i>
6	(3)	2.3	6.2	<i>b</i>	8.6	<i>b</i>
7	(9)	0.3	1.3	<i>b</i>	3.9	<i>b</i>
8	Oligomers	1.1	5.1	<i>b</i>	5.3	<i>b</i>

<sup>a</sup> Curves refer to Figure a. <sup>b</sup> Yields for 3 h/8 h given in Table 1.

TABLE 3

Hydrogenation of (1) with [Rh(nbd)(PPh<sub>3</sub>)<sub>2</sub>][ClO<sub>4</sub>].  
Yields (%)

Curve <sup>a</sup>	Product	Reaction time (h)				
		0.5	1	3	5	8
1	(1)	69.7	64.8	26.8	—	—
2	(2)	2.5	2.8	<i>b</i>	2.6	<i>b</i>
3	(6)	14.0	15.5	<i>b</i>	43.9	<i>b</i>
4	(10)	1.3	1.3	<i>b</i>	2.0	<i>b</i>
5	(5)	1.8	2.8	<i>b</i>	11.5	<i>b</i>
6	(3)	1.6	3.0	<i>b</i>	16.1	<i>b</i>
7	(9)	—	—	<i>b</i>	0.5	<i>b</i>
8	Oligomers	9.1	9.8	<i>b</i>	23.4	<i>b</i>

<sup>a</sup> Curves refer to Figure b. <sup>b</sup> Yields for 3 h/8 h given in Table 1.

The product distributions were very similar regardless of the phosphorus ligand used, as shown in Table 1. The main product was but-2-enal (6), an isomerization product; but-2-en-1-ol (5), but-3-en-1-ol (3), n-butanol (9), and (2) were minor products, *via* hydrogenation. Some oligomers were also found with all catalysts.

TABLE 4

Hydrogenation of (1) with [Rh(nbd)(diphos)][ClO<sub>4</sub>].  
Yields (%)

Curve <sup>a</sup>	Product	Reaction time (h)				
		0.5	1	3	5	8
1	(1)	73.5	53.0	12.0	—	—
2	(2)	—	—	—	—	—
3	(6)	17.3	20.5	<i>b</i>	43.4	<i>b</i>
4	(10)	—	—	<i>b</i>	5.5	<i>b</i>
5	(5)	3.8	6.3	<i>b</i>	19.6	<i>b</i>
6	(3)	5.4	7.1	<i>b</i>	15.4	<i>b</i>
7	(9)	—	—	<i>b</i>	3.6	<i>b</i>
7	(9)	—	—	<i>b</i>	3.6	<i>b</i>
8	Oligomers	—	13.1	<i>b</i>	12.5	<i>b</i>

<sup>a</sup> Curves refer to Figure c. <sup>b</sup> Yields for 3 h/8 h given in Table 1.

The total yields of alcohols with the PEt<sub>3</sub>- and diphos-catalysts reached 36% after 8 h reaction, comparable to the yield of the aldehyde (6). Thus, a selective abnormal fission of the epoxide ring occurred regardless of isomerization and hydrogenation, neither ketones nor secondary alcohols being detected. As shown in the Figure, unsaturated products were formed competitively from the epoxide. But-3-en-1-ol (3) was further hydrogenated to n-butanol (9). The yield of the epoxide (2), which was the product by exclusive hydrogenation of the double bond, was very low. It is interesting that the diphos- and PPh<sub>3</sub>-catalysts, which showed no hydrogenation activity with 1,2-epoxy-1-phenylethane,<sup>6</sup> ketones,<sup>2,4</sup> or aldehydes (except for phenylacetaldehyde),<sup>2,3</sup> produced alcohols rather more rapidly than did the PEt<sub>3</sub>-catalyst. The latter catalyst showed the highest hydrogenation activity for these compounds.<sup>3,4,6</sup> Although the total yield of alcohols after 8 h reaction also depended on the phosphorus

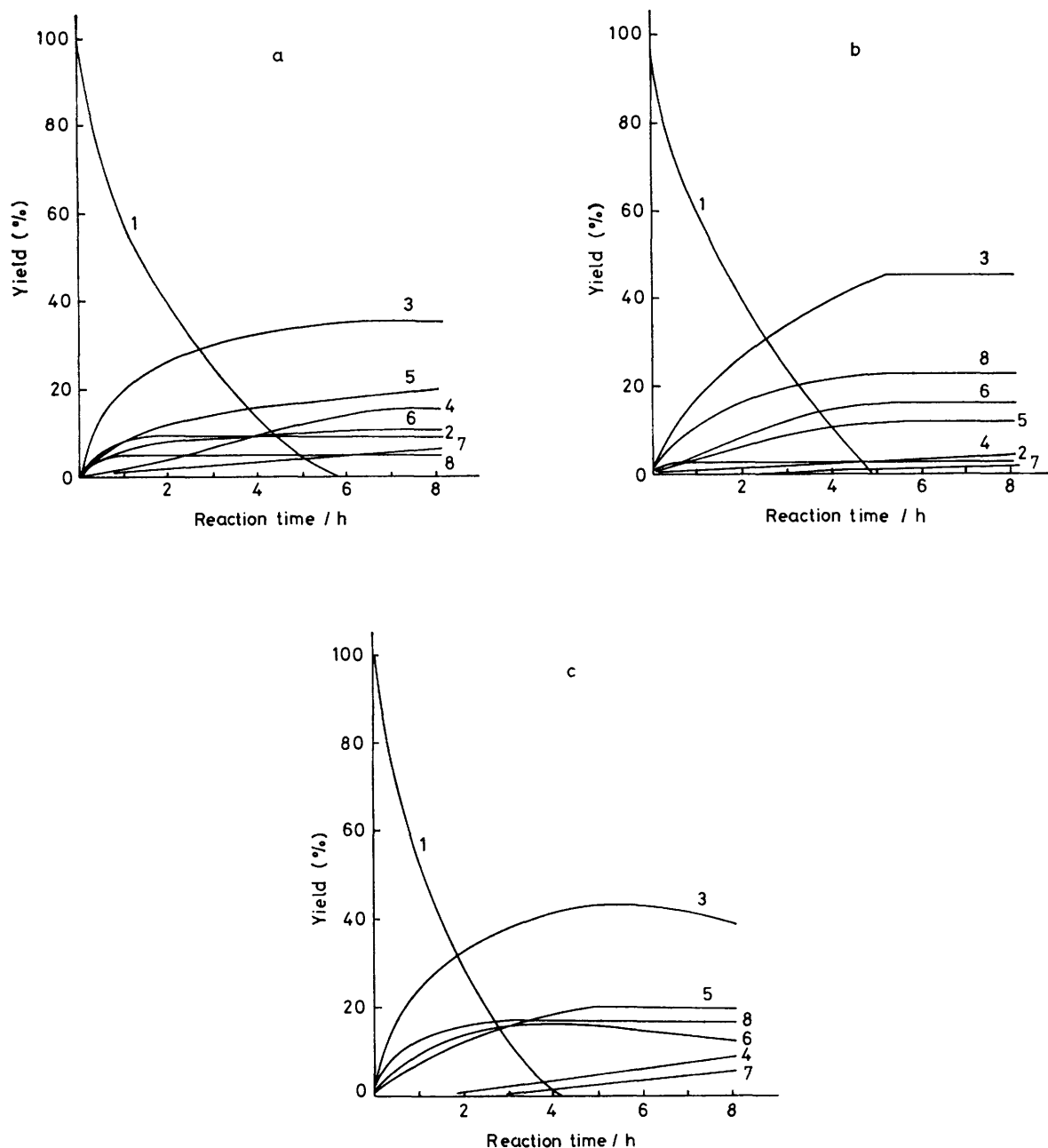
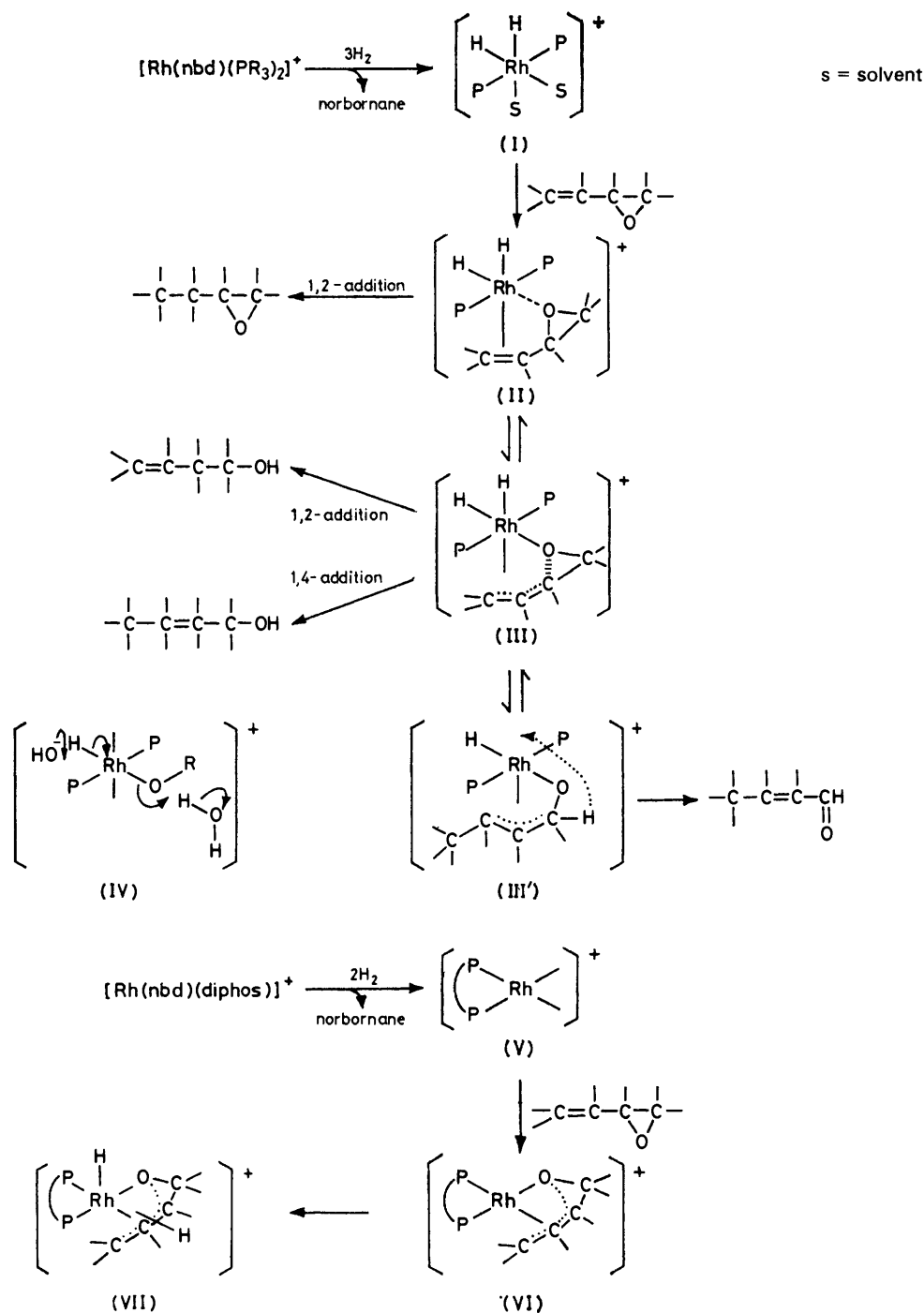


FIGURE Hydrogenation of (1) with cationic rhodium complexes (a)  $\text{PEt}_3$ -catalyst. (b)  $\text{PPh}_3$ -catalyst. (c) diphos-catalyst. Reaction conditions: see Table 1. Curve 1, compound (1); 2, (2); 3, (6); 4, (10); 5, (5); 6, (3); 7, (9); 8, oligomers

ligand, decreasing in the order  $\text{PEt}_3 \gg \text{diphos} > \text{PPh}_3 \gg \text{PMe}_3$  (Table 1), the consumption rate of the substrate in the early stages showed a different order ( $\text{diphos} > \text{PPh}_3 \sim \text{PEt}_3 \gg \text{PMe}_3$ ) (Figure; Tables 2–4). This contradiction can be ascribed to the ability of the  $\text{PEt}_3$ -catalyst to hydrogenate compounds (2) and (6) to their corresponding alcohols.<sup>3,6</sup> Such an activity order for the epoxide (1) suggests that the coordination abilities of cationic rhodium complexes for both olefinic double bonds and epoxide oxygens, but

not the reactivity of the hydrogen co-ordinated to the complex,<sup>3</sup> may govern the catalytic activity.

The effects of hydrogen pressure on the activity of the  $\text{PEt}_3$ -catalyst are shown in Table 5. The conversion was almost independent of the hydrogen pressure; however, the yields of compounds (2) and (3) increased with a marked decrease of (6) under higher pressure of hydrogen. This last fact suggests that the co-ordinated substrate which may isomerize to the aldehyde is effectively hydrogenated *via* 1,2-addition by the in-



SCHEME 2

creased hydrogen pressure. The initial rate of the hydrogenation in diglyme containing 1%  $D_2O$  (v/v) under deuterium gas is identical with that in the same solvent containing 1%  $H_2O$  (v/v) under hydrogen gas, which suggests that the hydride-transfer step is not rate-determining for hydrogenation and isomerization.

The catalytic activities of cationic rhodium complexes mentioned above appear to contrast that of the Wilkinson

catalyst,  $RhCl(PPh_3)_3$ , which yielded principally (2) and butanal (10), with a little (9) (Table 1).<sup>10</sup> Such a difference may be due to the comparable affinity of the cationic catalyst for both olefinic double bonds and the oxygen in epoxides and carbonyl groups.

A tentative mechanism consistent with the above observations is illustrated in Scheme 2, being based essentially on the hydrogenation mechanism of ketones

proposed by Schrock and Osborn.<sup>2</sup> The  $\text{PEt}_3$ - and  $\text{PPh}_3$ -catalysts absorb molecular hydrogen very quickly to form the dihydrido-complex (I), to which (I) coordinates in a bidentate manner to form the intermediate (II) or (III). Within the intermediates (II) and (III), 1,2-addition of hydrogen takes place to yield (2) and (3), respectively. 1,4-Addition of hydrogen gives (5). But-2-enal (6) is formed as an isomerization

TABLE 5  
Hydrogenation of (1) with  $[\text{Rh}(\text{nbd})(\text{PEt}_3)_2][\text{ClO}_4]_x$ <sup>a</sup>  
Yields (%)

$P(\text{H}_2)/\text{atm}$	1.0	50.0
Conversion (%)	47.5	41.8
Product		
(2)	8.1	12.6
(6)	21.2	7.8
(10)	2.9	1.4
(5)	7.7	6.4
(3)	6.2	10.6
(9)	1.3	3.0
Oligomers	5.1	—

<sup>a</sup> Catalyst 0.1 mmol, reaction time 1 h.

product from (III)' by the  $\beta$ -elimination of a hydrogen atom from the terminal carbon of the epoxide group. In contrast to the  $\text{PEt}_3$ - and  $\text{PPh}_3$ -catalysts, the diphos-catalyst is reported not to form a hydrido-complex, but instead gives complex (V) which has been shown to hydrogenate *N*-acetylphenylalanine.<sup>11</sup> In the present case (1) may co-ordinate to (V) forming the intermediate (VI). The existence of chelating intermediates is supported by the fact that the colours of all the catalyst solutions changed on injection of (1) from very light yellow to red, the same colours as the chelating catalyst precursors.<sup>5,11,12</sup>

The rate-determining step of the hydrogenation must be the co-ordination of the epoxide, *i.e.* (I) or (V)  $\rightarrow$  (II), (III), or (VI), because of the lack of isotopic effect, the activity order of the catalysts in the initial stages of the reaction and the zero-order kinetic effect of hydrogen pressure.

#### EXPERIMENTAL

The catalyst precursors,  $[\text{Rh}(\text{nbd})(\text{PR}_3)_n][\text{ClO}_4]$ , were prepared under nitrogen according to literature methods.<sup>13</sup> Because the catalyst precursors, especially that with  $\text{PEt}_3$  ligands, were very unstable in the presence of oxygen and

moisture, they were dried *in vacuo* and stored in sealed glass tubes saturated with pure, dry nitrogen. 'Butadiene monoxide' (1) (Aldrich) was used without further purification. Diglyme (Wako Junyaku Co.) solvent was dried by refluxing with sodium metal, then distilled and stored in a sealed glass tube.

Reactions under hydrogen (1 atm) were carried out in a glass reactor equipped with greaseless valves, as described elsewhere.<sup>6</sup> After the catalyst precursor (0.1 mmol) was dissolved in 1% aqueous diglyme (50 ml) under nitrogen, the nitrogen was replaced with hydrogen, the solution being aged for 5 min strictly under atmospheric pressure of hydrogen to yield the active complex. Epoxide (1) (10 mmol) was then injected with a syringe through a silicone rubber stopper to start the reaction. The reaction was followed by g.l.c. (Yanako G 180; column: polyethylene glycol 4 000, 2 m) of 0.2 ml aliquots of the reaction mixture which was sampled by the equipment<sup>6</sup> at appropriate intervals without any contact of the reaction system with air. The reaction under 50 atm of hydrogen was carried out in an autoclave (200 ml capacity, Taiatsu Garasu Kogyo Co.).

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