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Rhodium-Catalyzed Hydroformylation of Allyl Alcohol. A Potential Route to 1,4-Butanediol

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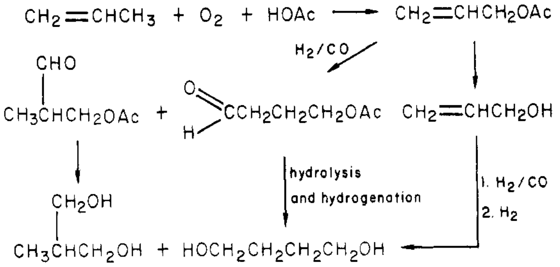
A detailed study of the rhodium-catalyzed hydroformylation of allyl alcohol to 4-hydroxybutanal (1) and 3-hydroxy-2-methylpropanal (2) was carried out, using $RhH(CO)(PPh_3)_3$ and its polymer-bound analogues. The reaction is complicated by isomerization of allyl alcohol to propanal, hydrogenation to propanol, and the production of higher boiling products. The product distribution and normal/branched selectivity were studied as a function of the P/Rh ratio, pressure, temperature, H_2/CO ratio, and phosphine ligand. Ligands employed included triphenylphosphine, tributylphosphine, triphenyl phosphite, tris(*p*-chlorophenyl) phosphite, 1,2-bis(diphenylphosphino)ethane, $(Ph_2PCH_2CH_2)_2PPh$ (triphos), and 1,1′-bis(diphenylphosphino)ferrocene. The highest n/b selectivities at high conversions were achieved with 1,1′-bis(diphenylphosphino)ferrocene where yields of 1 in excess of 80% could be routinely achieved at 60 °C and 800 psi, H_2/CO = 1:1. The variation in selectivity with respect to reaction variables was compared to the behavior of olefins in hydroformylations.

Introduction

Widespread interest exists in 1,4-butanediol as an intermediate in the synthesis of high-performance engineering plastics.[1,2] One route to 1,4-butanediol could be via hydroformylation of allyl acetate or allyl alcohol[3,4] as shown in Scheme I. This route is attractive because allyl acetate is available by vapor-phase reaction of propene with oxygen and acetic acid,[5,6] and allyl alcohol may be obtained by hydrolysis of allyl acetate.[7] Although not yet in commercial practice, a single large (>100 000 000 lb/yr) plant could drop the price of allyl acetate significantly. In view of the importance of the hydroformylation (of allyl acetate or allyl alcohol) steps in this proposed route, we conducted a study of the rhodium-catalyzed hydroformylation of allyl alcohol after a brief examination of allyl acetate hydroformylation.

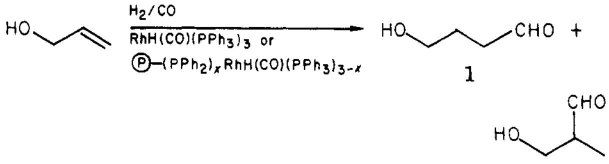
Unsaturated alcohols of the allyl alcohol type are hydroformylated in poor yields according to numerous literature reports.[8-12] Yields do not rise over 30% in these reports due to the formation of many byproducts, especially propanal.[12] Wilkinson[13] briefly mentioned the use of $RhH(CO)(PPh_3)_3$ for allyl alcohol hydroformylations at lower temperatures than previous studies using $Co_2(CO)_8$ as the catalyst. A recent patent also reported rhodium catalysis.[14] Previous studies demonstrated that the normal/branched product ratio is greater in hydroformylations of terminal olefins using $RhH(CO)(PPh_3)_3$ than in those using $Co_2(CO)_8$ as the catalyst, and this ratio is dependent on temperature, pressure, P/Rh(Co) ratio, and H_2/CO ratio.[13,15-17] However, the influence of these factors in allyl alcohol hydroformylations is not well-discussed in the literature. Thus, we undertook a study of these variables in the $RhH(CO)(PPh_3)_3$-catalyzed hydroformylation of allyl alcohol. Furthermore, since it is desirable to have the highest possible normal/branched ratio in this reaction (to maximize the production of 4-hydroxybutanal and subsequently 1,4-butanediol), we examined the use of polymer-attached $RhH(CO)(PPh_3)_3$. This was prompted by our recent discovery of some exceptionally high normal/branched ratios in the hydroformylation of 1-pentene using polymer-bound rhodium complexes.[18-20]

Scheme I



Results and Discussion

Allyl alcohol was hydroformylated by using both homogeneous and polymer-attached analogues of $RhH(CO)(PPh_3)_3$ according to eq 1. 4-Hydroxybutanal (1) has been prepared by a number of routes and is well-characterized.[8,9,14,21-26] It undergoes a ring-closure equilibrium



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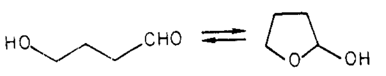
to 2-hydroxytetrahydrofuran (**3**, eq 2).[24] In contrast, the



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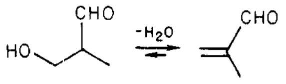
physical properties of 3-hydroxy-2-methylpropanal (**2**) have not appeared, and it has only been characterized as its diethyl acetal.[27] The reaction mixture of **1** and **2** was reported to be difficult to work up.[27] The isolation of **2** is particularly troublesome, presumably due to the relative ease with which it dehydrates to methacrolein (**4**, eq 3).



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At equilibrium in basic aqueous solutions at 25 °C, **4** was reported to predominate 98.8/1.2.[28]

For identification purposes, we found **1** and **2** could be analyzed by analytical GLC and isolated by preparative GLC. **1** (presumably in equilibrium with **3**) could be converted to its 2,4-dinitrophenylhydrazone, but a mixture of products was obtained from **2**. Reaction mixtures containing **1** and **2** were quantitatively reduced to their corresponding diols with $LiAlH_4$. This further confirms the indentification.

Hydroformylations of allyl alcohol were carried out over the temperature range of 40–120 °C, a pressure range of 50–800 psi, and at H_2/CO ratios of 0.1 to 10. In homogeneous reactions employing $RhH(CO)L_3$, the following ligands, in addition to triphenylphosphine, were also used: tributylphosphine, triphenyl phosphite, tris(*p*-chlorophenyl) phosphite, 1,1′-bis(diphenylphosphino)ferrocene, 1,2-bis(diphenylphosphino)ethane, and bis(2-phenylphosphinoethyl)phenylphosphine. The resin-anchored catalysts were prepared from styrene–divinylbenzene resins with divinylbenzene contents of 1 or 2%. The resins were brominated by Friedel-Crafts techniques (Br_2, $FeBr_3$, 0 °C, dark), and then phosphinated by treating the brominated resin with excess $LiPPh_2$ in THF as described previously.[29,30] The phosphinated resins were then heated in benzene with $RhH(CO)(PPh_3)_3$ to effect ligand exchange and rhodium incorporation.[18,19,29–30] The analyses, P/Rh ratio, and phosphine loadings (percentage of the polymer's benzene rings derivatized with phosphine) of these resins are summarized in Table I. Two levels of phosphine loading (PL) 29–30% and 61% were employed. At 29% PL, P/Rh ratios of 3 and 20 were used. At 61% PL, a P/Rh ratio of 31 was employed. These resins were prepared in order to examine the sensitivity of the normal/branched (n/b) product selectivity on variations in P/Rh and phosphine loading in the resins. This point was important in view of the extremely high n/b selectivities we previously observed in rhodium-catalyzed hydroformylations of 1-pentene using resin catalysts with high phosphine content and high P/Rh ratios.[18,19]

Table I. Resin-Attached Rhodium Catalysts Employed in Allyl Alcohol Hydroformylations

resin	% divinylbenzene	% P	% Rh	P/Rh	phosphine loading[a]
5A	1	4.53	5.06	3	29
5B	1	5.38	0.90	20	29
5C	1	8.13	0.87	31	61
5D	2	6.52	1.20	18	30

[a] The percentage of the polymer's phenyl rings which have been substituted with PPh_2 groups.

Dependence of Selectivity on P/Rh Ratio. Previous studies demonstrated that an increase in P/Rh caused increases in the n/b ratio in hydroformylation of normal olefins.[10,12–15] Mechanistic studies by Wilkinson et al.[15] implicated $RhH(CO)_2(PPh_3)_2$ and $RhH(CO)_2(PPh_3)$ as the active hydroformylation intermediates which underwent rhodium hydride addition to olefins. Regiospecific terminal addition of rhodium was significantly favored for $RhH(CO)_2(PPh_3)_2$ due to the presence of two bulky phosphine ligands.[15] Thus, the addition of excess phosphine resulted in higher n/b ratios because the equilibrium $RhH(CO)_2(PPh_3) + PPh_3 \rightleftharpoons RhH(CO)_2(PPh_3)_2$ was shifted to the right. Although *trans*-$RhH(CO)(PPh_3)_2$ was active (and very selective) in olefin hydrogenations,[5] evidence was presented that it was not an active intermediate in hydroformylations at low temperatures.[15] That evidence, however, does not rule out the involvement of either *cis*- or *trans*-$RhH(CO)(PPh_3)_2$ addition to the olefin at temperatures above 40–60 °C. Steric requirements dictate that the trans isomer would be more selective than the cis.[31] To evaluate the effect of excess ligand in allyl alcohol hydroformylations, the P/Rh ratio was varied and example results are shown in Table II.

With homogeneous $RhH(CO)(PPh_3)_3$, the variation in n/b with changes in P/Rh was strikingly small. For example, n/b increased from 1.7 to only 2.5 as P/Rh increased from 3 to 40 (at 60 °C, 100 psi). The polymer catalyst behaved in the same fashion. The n/b selectivity was relatively insensitive to the P/Rh ratio in the resin. At 60 °C and 100 psi, the n/b ratio remained the same (1.93–1.94) as the P/Rh ratio in the resin went from 3 to 20. Increasing P/Rh further to 30 and increasing the phosphine loading to 61% resulted in only a small increase (to 2.33) in n/b. At 100 °C and 400 psi, the n/b ratio varied from 2.51 to 2.03 as the P/Rh ratio went from 3 to 20. When the PL is raised to 60 at P/Rh = 30, n/b = 2.09. Over the entire range of variables studied, the n/b ratio varied between 1.5 and 2.5 (see Supplementary Material). Furthermore, variations in the phosphine loading within the resin did not produce marked changes in the n/b ratio. Thus, the response of selectivity in allyl alcohol hydroformylations to variations in phosphine loading and P/Rh stands in marked contrast to the results previously observed in terminal olefin hydroformylations.

Unlike allyl alcohol, large increases in selectivity were often observed with polymer-anchored catalysts in 1-pentene hydrofromylations (vs. the corresponding homogeneous catalyst). For example, using resin **5D** (P/Rh = 18, PL = 30, 2% DVB) as the catalyst at 60 °C and 100 psi gave a n/b selectivity of 10.5 with 1-pentene compared to only 3.6 when $RhH(CO)(PPh_3)_3$ was used homoge-

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Table II. Effect of Varying the P/Rh Ratio in Allyl Alcohol Hydroformylations Catalyzed by $RhH(CO)(PPh_3)_3$[a]

					product distribution				
P/Rh	temp, °C	pressure, psig	time, h	% conversion	% propanal	% propanol	% 1	% 2	n/b
3	60	100	7.1	97.5	0.9		62.3	36.8	1.70
10	60	100	4.0	98.8	0.2		65.2	34.6	1.89
20	60	100	5.7	100			62.1	32.9	2.04
40	60	100	7.0	94.7	1.1	0.1	70.4	28.4	2.48
3	40	100	7.1	96.2			62.8	37.2	1.69
20	40	100	7.0	98.4			67.1	32.9	1.60
3	40	400	19.7	99.4		0.4	61.7	37.2	1.66
20	40	400	6.7	97.6			64.6	35.4	1.82
3	120	400	1.2	98.6	27.1	0.1	36.9	19.8	1.87[b]
20	120	400	0.8	99.3	16.4	1.3	44.2	20.8	2.13[c]

[a] All runs performed at [Rh] = 5.54×10^{-3} M in benzene. [b] Higher boiling condensation products made up 16.1% of the product. [c] Higher boiling condensation products made up 17.3% of the product.

Table III. Dependence of n/b Selectivity on Pressure in Allyl Alcohol Hydroformylations in Benzene

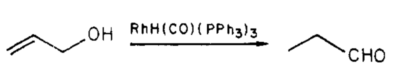
catalyst	temp, °C	pressure, psig	time, h	% conversion	% 1	% 2	n/b
$RhH(CO)(PPh_3)_3$, P/Rh = 3	60	50	19.2	99.9	64.8	31.6	2.05
	60	100	7.1	97.5	62.3	36.8	1.70
	60	200	5.4	98.2	64.0	35.7	1.79
	60	400	7.5	100	62.9	37.1	1.70
	60	800	4.3	100	63.4	36.6	1.73
$RhH(CO)(PPh_3)_3$, P/Rh = 20	60	50	17.7	99.6	65.9	33.8	1.95
	60	100	5.7	100	67.1	32.9	2.04
	60	200	7.0	98.1	67.0	33.1	2.03
	60	400	7.3	100	63.4	36.7	1.75
	60	800	2.3	99.5	62.7	37.3	1.68
resin 5A, P/Rh = 3, PL = 29	60	50	23.8	99.2	66.8	30.7	2.17
	60	100	10.2	46.2	64.8	33.5	1.94
	60	200	10.9	98.1	66.3	33.6	1.97
	60	400	13.1	85.7	65.5	33.4	1.96
	60	800	22.0	99.2	63.4	36.6	1.73

neously under identical conditions. In contrast, when resin **5D** was used to catalyze allyl alcohol hydroformylations under the same conditions, the n/b selectivity was 2.20 vs. 2.04 for the homogeneous analogue.

Dependence of Selectivity on Pressure. The selectivity in allyl alcohol hydroformylations was not highly sensitive to pressure (Table III). This was true when either $RhH(CO)(PPh_3)_3$ or its resin-attached analogues were used. For example, n/b varied only from 2.05 to 1.73 as pressure increased from 50 to 800 psi at 60 °C with $RhH(CO)(PPh_3)_3$ and P/Rh = 3. At P/Rh = 20, a similar small variation in selectivity occurred over the same pressure range. With resin catalyst **5A** there was also a small decrease in n/b selectivity with an increase in pressure from 50 to 800 psi at 60 °C. Little change in n/b occurred over this pressure range for any of the resins employed at 60 °C. Similar results were observed at other temperatures (see Supplementary Material).

In contrast to allyl alcohol, the hydroformylation of 1-pentene using polymer-anchored $PhH(CO)(PPh_3)_3$ exhibited a strong pressure dependence on selectivity.[19] For example, raising the pressure from 100 to 800 psi resulted in a drop from 14 to 4 in the n/b ratio in 1-pentene hydroformylations at 100 °C using a resin where P/Rh = 19.[19]

Dependence of Selectivity on Temperature. At 40–60 °C, the normal and branched aldehydes ($\mathbf{1} \rightleftharpoons \mathbf{3}$ and **2**) were the only products formed. However, as the temperature increased the product distribution became more complex. First, allyl alcohol isomerizes to propanal in competition with hydroformylation (eq 4). This isomerization becomes progressively more serious as the temperature increases.



(4)

For example, at P/Rh = 3 and 100 psi, the percent propanal in the product increases from less than 1% at 60 °C to 34% at 120 °C. Similarly, at P/Rh = 3 and 400 psi, propanal increases from 0 to 27% as the temperature increases from 60 to 120 °C. The same trend is observed at higher P/Rh ratios and when polymer-anchored catalysts are used. Detailed product distributions are listed in Table IV for the homogeneous catalyst at P/Rh = 20 and resin **5A**. The Supplementary Material details similar results for resins **5B** and **5C**.

The isomerization of olefins during hydroformylation is strongly inhibited both by excess phosphine and higher carbon monoxide pressures when rhodium catalysts are employed.[13,15] However, excess phosphine does not prevent isomerization of allyl alcohol to propanal under hydroformylation conditions except, perhaps, when resin **5C** (P/Rh = 30 and PL = 60) was used.

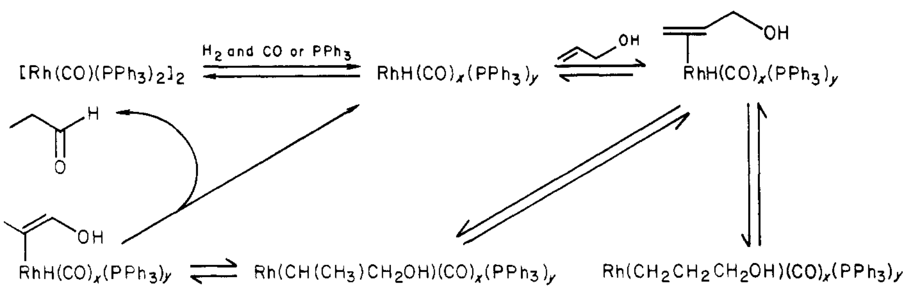
Propanal formation, in the presence of $RhH(CO)(PPh_3)_3$, was studied independent of hydroformylation at 120 °C. The formation of propanal was faster under 200 psi of carbon monoxide than under nitrogen. Under 200 psi of carbon monoxide, the initial isomerization rate was faster when P/Rh = 20 than when P/Rh = 3. These studies are shown in Figure 1 as plots of ln (C_0/C_t) vs. time. When P/Rh = 3, the plot of ln C_0/C_t vs. time was linear in the presence of carbon monoxide. The plots were curved when isomerizations were run in the presence of excess phosphine or when run under nitrogen.

$RhH(CO)(PPh_3)_3$ reacts to give the dimer $[Rh(CO)(PPh_3)_2]_2$ even at room temperature.[15] This dimer is inactive in olefin isomerizations. Carbon monoxide or excess phosphine may retard the formation of dimer to give a higher concentration of the actual active catalyst, thereby increasing the rate of allyl alcohol isomerization. The

Table IV. Product Distributions in Allyl Alcohol Hydroformylations Catalyzed by $RhH(CO)(PPh_3)_3$ and Its Resin-Anchored Analogues[a]

					product distribution					
catalyst (P/Rh)	temp, °C	pressure, psig	time, h	% conversion	% propanal	% propanol	% 1	% 2	% unidentified	n/b
$RhH(CO)(PPh_3)_3$, P/Rh = 3	40	100	7.1	96.2			62.8	37.2		1.69
	60	100	7.1	97.5	0.9		62.3	36.8		1.70
	80	100	7.3	98.1	10.9		57.0	30.1	2.0	1.89
	100	100	7.3	94.2	31.7	0.1	34.8	16.9	16.5	2.06
	120	100	5.8	88.1	34.1	0.7	27.3	8.7	29.2	3.12
	40	400	19.7	99.3		0.4	61.7	37.2		1.66
	60	400	7.5	100			62.9	37.1		1.70
	80	400	4.7	100	1.1	0.6	60.8	37.5		1.62
	100	400	3.3	100	3.1	0.1	62.6	34.3		1.82
	120	400	1.2	98.6	27.1	0.1	36.9	19.8	16.1	1.87
	60	50	19.2	99.9	3.6		64.8	31.6		2.05
	60	100	7.1	97.5	0.9		62.3	36.8		1.70
	60	200	5.4	98.2	0.3		64.0	35.7		1.79
	60	400	7.5	100			62.9	37.1		1.70
	60	800	4.3	100			63.4	36.6		1.73
$RhH(CO)(PPh_3)_3$, P/Rh = 20	40	100	7.0	98.4			61.6	38.5		1.60
	60	100	5.7	100			67.1	32.9		2.04
	80	100	4.2	93.9	9.1		59.1	23.8	8.0	2.48
	100	100	3.0	99.3	16.6	0.1	33.3	11.2	38.9	2.98
	120	100	3.7	94.3	22.6	2.3	16.2	2.8	56.0	5.73
	40	400	6.7	97.6			64.6	35.4		1.82
	60	400	7.3	100			63.4	36.7		1.75
	80	400	1.4	100	0.18		64.5	30.6	4.7	2.11
	100	400	0.9	100	4.03	0.1	61.6	28.9	5.4	2.13
	120	400	0.8	99.3	16.4	1.3	44.2	20.8	17.3	2.13
	60	50	17.7	99.6	0.4		65.9	33.8		1.95
	60	100	5.7	100			67.1	32.9		2.04
	60	200	7.0	98.7			67.0	33.1		2.03
	60	400	7.3	100			63.4	36.7		1.75
	60	800	2.3	99.5			62.7	37.3		1.68
resin 5A, P/Rh = 3, PL = 29	40	100	45.7	74.3			67.8	32.2		2.11
	60	100	10.2	46.2	0.8	0.9	64.8	33.5		1.94
	80	100	8.6	94.1	1.4		58.2	23.2	17.2	2.51
	100	100	3.4	94.8	1.1	0.1	67.1	23.2	8.6	2.89
	120	100	1.8	95.2	11.2	0.3	49.2	10.5	28.8	4.72
	40	400	75.8	85.4			66.0	34.0		1.94
	60	400	13.1	85.7	1.0	0.1	65.5	33.4		1.96
	80	400	7.8	88.7	1.8	0.1	65.8	32.3		2.04
	100	400	10.0	79.1	4.6	0.1	66.6	26.6	2.2	2.51
	120	400	7.2	98.7	2.1	0.1	60.9	21.8	15.1	2.79
	60	50	23.8	99.2	1.6		66.8	30.7		2.17
	60	100	10.2	46.2	0.8	0.9	64.8	33.5		1.94
	60	200	10.9	98.1		0.1	66.3	33.6		1.97
	60	400	13.1	85.7	0.9	0.1	65.5	33.4		1.96
	60	800	22.0	99.2			63.4	36.6		1.73

[a] All reactions were carried out in benzene.



(5)

isomerization of allyl alcohol to propanal is known to be catalyzed by $Fe(CO)_5$[32,33] and $HCo(CO)_4$.[34] $Fe(CO)_5$ has been proposed to catalyze isomerization via formation of a π-allyl complex,[32,33] while $HCo(CO)_4$ isomerizations are thought to occur through an alkyl cobalt intermediate.[34]

We suggest that a general scheme such as eq 5 may operate for the rhodium complex to explain the fast isomerization of allyl alcohol to propanal in the presence of excess phosphine or carbon monoxide.

As the temperature increases, the yields of **1** and **2** decrease markedly. Many examples of this can be seen in Table IV. For example, at both 40 and 60 °C (100 and 400 psi) the only products observed are **1** and **2** when $RhH(CO)(PPh_3)_3$ is used homogeneously. When resins **5A**, **5B**, or **5C** are used at 40 or 60 °C, the combined yield of **1** and

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Table V. Effect of H_2/CO Ratio on Product Distribution in the Hydroformylation of Allyl Alcohol Catalyzed by $RhH(CO)(PPh_3)_3$ and Its Polymer-Anchored Analogue

						product distribution					
catalyst	H_2/CO	temp, °C	pressure, psig	time, h	% conversion	% propanal	% propanol	% 1	% 2	% higher-boiling products	n/b
$RhH(CO)(PPh_3)_3$,	0.1	60	200	20.5	41.3			62.0	38.1		1.63
P/Rh = 3	1	60	100	7.1	97.5	0.9		62.3	36.8		1.70
	2	60	100	3.4	100		0.5	64.7	34.8		1.86
	4	60	100	1.7	99.8	11.8	2.8	60.2	25.3		2.38
	10	60	100	8.4	78.7	5.8	33.7	53.0	8.1		6.54
$RhH(CO)(PPh_3)_3$,	1	60	100	5.7	100			67.1	32.9		2.04
P/Rh = 20	2	60	100	1.8	96.9		0.1	68.8	31.2		2.21
	4	60	100	3.9	98.2	23.2	10.5	55.4	11.0		5.06
	10	60	100	19.0	100	17.4	25.5	51.0	6.1		8.33
resin 5B	1	60	100	21.8	100	0.1	0.1	65.7	34.0		1.93
PL = 29, P/Rh = 20	10	60	100	2.9	97.5	3.5	3.5	74.5	18.5		4.02
	1	100	400	8.8	100	11.6		26.7	13.2	48.5	1.58
	10	100	400	3.9	96.4	33.0	8.6	30.4	10.6	17.4	2.94

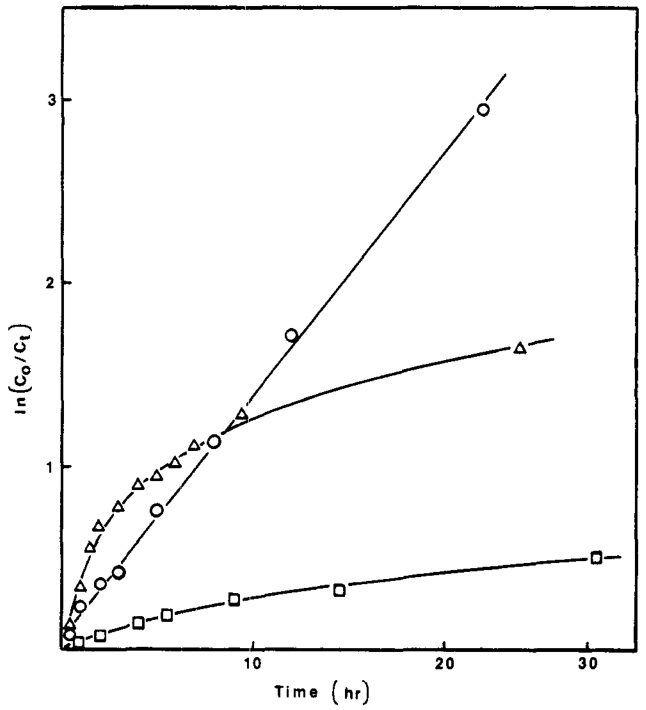

Figure 1. Plot of ln (C_0/C_t) vs. time for the isomerization of allyl alcohol to propanal catalyzed by $RhH(CO)(PPh_3)_3$ in benzene at 120 °C and [Rh] = 5.54×10^{-3} M: (□) under nitrogen atmosphere, P/Rh = 3; (○) under 200 psig of carbon monoxide, P/Rh = 3; (△) under 200 psig of carbon monoxide, P/Rh = 20.

2 exceeds 98% of the total product produced. However, at 120 °C, the combined yield of 1 and 2 drops to only 36% and 56.7% of the total product using homogeneous $RhH(CO)(PPh_3)_3$ (P/Rh = 3) at 100 and 400 psi, respectively. Increasing P/Rh to 20 did not affect this trend. At 120 °C the combined yield of 1 and 2 was only 19% and 65% at 100 and 400 psi, respectively. Reductions in the yields of 1 and 2 were also severe with resins **5B** (PL = 29, P/Rh = 20) and **5C** (PL = 60, P/Rh = 30) at both 100 and 400 psi. Only resin **5A** (PL = 29, P/Rh = 3) gave a reasonable combined yield of 1 and 2 (82%) when used at 120 °C (400 psi).

The decreasing yields of 1 and 2 result only partially from the competing isomerization to propanal. Propanol is also formed, but only in very small amounts (i.e., <1%). More important, some 3-hydroxy-2-methylpropanal (2) dehydrates at higher temperatures to methacrolein (4). However, 4 was never detected, presumably because it oligomerizes or polymerizes. The destruction of 2 in reactions carried out at 80 °C, or above, certainly masks the true value of the n/b selectivity. If 2 disappears faster then 1, then the n/b ratio would increase at higher temperatures. This is in accord with results in Table IV. As the temperature increases from 60 to 120 °C with resin catalysts **5A**, **5B**, or **5C**, the n/b selectivity does appear to increase at both 100 and 400 psi. These increases were larger at 100 psi. A similar pattern was observed with $RhH(CO)(PPh_3)_3$ with P/Rh = 20. For example, the apparent n/b ratio increased from 2.04 at 60 °C to 5.73 at 120 °C at 100 psi. However, the combined yield of 1 + 2 decreased from 100% to 19%.

The hemiacetal form of 1 (i.e., 3) was also found to be thermally unstable. Heating a pure sample of 3 in benzene at 120 °C in a sealed ampule resulted in the formation of several new products with longer GLC retention times. These experiments demonstrated that 3 would react without adding acid or base catalysis. As the temperature was increased in hydroformylations, other products were formed. These unknown compounds result from decomposition of 3 and 2.

The amount of unknown or polymeric materials formed, when either the homogeneous or polymer-attached complex is used, tends to be greater at higher P/Rh ratios and at higher phosphine concentrations. The amount of unknown products formed is also dependent on the rate of hydroformylation and the reaction time.

The unidentified products did not yield any 1,4-butanediol upon $LiAlH_4$ reduction. This was confirmed by carrying out $LiAlH_4$ reductions of product mixtures containing 1, 2, and the unidentified peaks. No enhancement of the 1,4-butanediol yield over that expected (based on the amount of 1 originally present) was observed. The same was true regarding the production of 2-methyl-1,3-propanediol from 2. Thus, C_4-diols do not form on $LiAlH_4$ reduction of the unknown products.

Dependence of Selectivity on H_2/CO Ratio. It is now known that by increasing the H_2/CO ratio, the n/b selectivity may be increased sharply in rhodium-catalyzed hydroformylations of terminal olefins.[19] For example, at 200 psi with a polymer-anchored rhodium catalyst (PL = 40%, P/Rh = 19), we achieved a n/b selectivity of 64 in 1-pentene hydroformylations at 100 °C with H_2/CO = 20.[19] In general, however, the use of higher H_2/CO ratios leads to increasing yields of hydrogenation products. By analogy with terminal olefin hydroformylations, allyl alcohol hydroformylations were carried out at higher H_2/CO ratios in order to seek an increase in the n/b selectivity. Rep-

Table VI. Effect of Phosphine Ligand Structure on Rhodium-Catalyzed Hydroformylation of Allyl Alcohol[a]

						product distribution					
ligand	P/Rh	temp, °C	pressure, psig	time, h	% conversion	% proanal	% proanol	% 1	% 2	% higher boiling products	n/b
PPh_3	3	60	400	19.7	99.3			62.9	37.1		1.70
PPh_3	20	60	400	7.3	100			63.4	36.7		1.75
PPh_3	3	100	400	4.7	100	3.1		62.6	34.3		1.82
PPh_3	20	60	100	5.7	100			67.1	32.9		2.04
$P(OPh)_3$	20	60	100	3.0	95.9	0.2		61.0	38.8		1.57
$P(OC_6H_4Cl)_3$	20[b]	60	100	11.8	99.5	3.8		6.7	11.2	78.3	0.6
$P(OC_6H_4Cl)_3$	20[c]	60	100	7.1	97.5			38.6	25.4	36.0	1.52
n-Bu_3P[c,d]	20	60	100	11.9	73.3	12.4		39.7	1.42	46.4	27.95
$Ph_2PCH_2CH_2PPh_2$	3	60	400	20.2	100	3.9		5.0	17.4	73.7	0.29
$Ph_2PCH_2CH_2PPh_2$	3	100	400	5.5	99.7	50.4		4.2	8.3	37.1	0.50
$Ph_2PCH_2CH_2PPh_2$	20	60	100	26.5	1	50		50			
$(Ph_2PCH_2CH_2)_2PPh$	20	60	100	46.9							
$(Ph_2PC_5H_4)_2Fe$	20	60	100	22.6	99.3	0.6	1.9	74.6	22.9		3.26

[a] The solvent was benzene unless otherwise stated. [b] Phase separation occurred. [c] THF was solvent. [d] When n-Bu_3P is used in benzene at 60 °C and either 100 or 400 psi (1:1 H_2/CO), three new products were observed in the GLC analysis. These constitute the majority of all products formed and they phase separate from benzene. These products have different retention times than the (two) unknowns formed in other runs at higher temperatures. They are not yet identified.

resentative results are summarized in Table V.

When H_2/CO was increased from 1 to 10, there was a substantial increase in the n/b ratio. For example, at 60 °C and 100 psi, n/b increased from 1.70 to 6.54 with $RhH(CO)(PPh_3)_3$ at P/Rh = 3. Unfortunately, hydrogenation became competitive with hydroformylation as attested to by the 33.7% yield of propanol with H_2/CO = 10 under these conditions. When a large excess of phosphine was present (P/Rh = 20), the selectivity again increased from 2.04 to 8.33 as H_2/CO was increased from 1 to 10 at 60 °C. Again, a substantial amount of propanal (25.5%) was observed when H_2/CO = 10. In these homogeneously catalyzed reactions no high-boiling secondary products were produced.

The most promising results were observed with polymer-anchored catalysts. For example, using resin **5B** (PL = 29, P/Rh = 20) led to high yields of **1** and **2** (combined yield of **1** and **2** = 92.6% at 97.5% conversion) and only small amounts of propanol (3.5%) and propanal (3.5%) at 60 °C, 100 psi, and H_2/CO = 10. Under these conditions n/b = 4. This selectivity, while substantially lower than the n/b values of 6.54 and 8.33 found with the homogeneous catalyst (at P/Rh = 3 and 20, respectively) under the same conditions, ultimately gives more of the desired 4-hydroxybutanal because less propanal and propanol are formed. It appears as if the resin catalyst supresses the propensity toward hydrogenation (relative to the homogeneous catalyst) at high H_2/CO ratios and 60 or 100 °C. This reduction of hydrogenation relative to hydroformylation at high H_2/CO ratios was recently demonstrated with some polymer-anchored catalysts in terminal olefin hydroformylation.[20]

As expected, higher temperatures led to more propanal and higher-boiling products. Isomerization to propanal becomes increasingly competitive with hydroformylation as the H_2/CO ratio is raised while holding the temperature constant at 100 °C.

Dependence of Selectivity on Phosphine Ligand. The addition of phosphines to rhodium-catalyzed hydroformylations of olefins significantly increases the n/b ratio. Pruett and Smith showed that phosphites are more effective than phosphines in giving high n/b ratios.[16] The effect of ligands on rhodium-catalyzed allyl alcohol hydroformylations has not been previously reported. Thus, we have examined, in addition to PPh_3, the following monodentate ligands: PBu_3, $P(OPh)_3$, and $P(OC_6H_4Cl)_3$. The effect of ligand structure on the product distribution is summarized in Table VI. Slightly lower n/b selectivities are obtained with $P(OPh)_3$ relative to PPh_3. No higher-boiling products are produced at 60 °C with either PPh_3 or $P(OPh)_3$. Using tris(p-chlorophenyl) phosphite gave a large increase of higher-boiling products when either benzene or THF was the solvent. Similarly, the use of Bu_3P led to large yields of higher-boiling products. The n/b ratio was very high, but the overall combined yield of **1** and **2** was too low. A significant amount of propanal also resulted from the use of nBu_3P.

Intermediate bis(phosphine)rhodium complexes with a cis arrangement of the bulky phosphines are expected to be less selective than when the phosphines are trans.[31] We previously demonstrated[35] that use of the cis chelating ligand 1,2-bis(diphenylphosphino)ethane (diphos) does, indeed, give very low n/b selectivities in terminal olefin hydroformylations. Either *cis*-RhH(CO)(diphos) or *cis*-$RhH(CO)_2$(diphos) could have been the key intermediate.[35] Chelating ligands have not previously been employed in allyl alcohol hydroformylations. Thus, diphos, 1,1′-bis(diphenylphosphino)ferrocene, and $(Ph_2PCH_2CH_2)_2PPh$ (triphos) were studied. The results are summarized in Table VI.

The n/b ratio decreased sharply when $RhH(CO)(PPh_3)$(diphos) was used. For example, at 60 °C, 400 psi, and P/Rh = 3, the n/b ratio was only 0.29. Under the same conditions $RhH(CO)(PPh_3)_3$ gave n/b = 1.70. Strikingly, the diphos complex gave 74% of the high-boiling byproducts under these conditions whereas $RhH(CO)(PPh_3)_3$ gave none. When the temperature was raised to 100 °C, the major product (50.4%) was propanal when the diphos complex was used. Under the same conditions, $RhH(CO)(PPh_3)_3$ gave only 3.1% propanal. No hydroformylation occurred after 47 h when triphos (P/Rh = 20) was used at 60 °C. The use of 1,1′-bis(diphenylphosphino)ferrocene (BDPF) gave the most promising results. A n/b ratio of 3.26 was achieved at high conversions at 60 °C, P/Rh = 20. Furthermore, no high-boiling products and only very small amounts of propanal and propanol were produced. These results led to a more detailed investigation of the use of this ligand (see Table VII).

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Table VII. Effect of P/Rh, H_2/CO, and Pressure on Selectivity of Allyl Alcohol Hydroformylations Catalyzed by Rhodium in the Presence of 1,1′-Bis(diphenylphosphino)ferrocene (BDPF) at 60 °C

BDPF/Rh	total P/Rh	H_2/CO	pressure, psig	time, h	% conversion	% propanal	% propanol	n	b	n/b
1	5	1	100	3.0	89.8	1.6		71.6	26.8	2.67
8.5	20	1	100	22.6	99.3	0.6	1.9	74.6	22.9	3.26
8.5	20	1	400	23.0	90.4	1.3	1.2	85.4	12.1	7.07
8.5	20	1	800	22.0	70.2		1.5	87.4	11.1	7.88
a	3	1	100	7.1	97.5	0.9		62.3	36.8	1.70
a	20	1	100	5.7	100			67.1	32.9	2.04
a	20	1	400	7.3	100			63.4	36.6	1.75
a	20	1	800	2.3	99.5			62.7	37.3	1.68
a	3	1	800	4.3	100			63.4	36.6	1.73
8.5	20	1	100	22.6	99.3	0.6	1.9	74.6	22.9	3.26
8.5	20	2	100	23.5	100	45.3	8.5	25.5	7.2	3.56
8.5	20	10	100	23.0	100	72.9	15.8	9.1	2.2	4.08
8.5	20	1	400	23.0	90.4	1.3	1.2	85.4	12.1	7.07
8.5	20	2	400	23.0	96.3	0.9	2.5	83.2	13.4	6.20
8.5	20	10	400	23.0	100		22.1	36.6	6.7	5.48
1	5	1	800	5.0	86.9	9.0		72.2	18.8	3.85
1	5	2	800	5.0	100	9.5	2.6	63.7	24.1	2.64

[a] PPh_3 = ligand.

The use of BDPF gave higher n/b selectivities than the use of PPh_3 under equivalent conditions. At P/Rh = 20, 60 °C, and 400 psi, the n/b ratio was 7.07 with BDPF vs. 1.75 with PPh_3 (compare entries 3 and 7 in Table VII). The use of BDPF led to an increase in the n/b ratio as the pressure increased. At a BDPF/Rh ratio of 8.5:1 at 60 °C, n/b increased from 3.26 at 100 psi to 7.88 at 800 psi. This behavior is the opposite of that observed in allyl alcohol hydroformylations using $RhH(CO)(PPh_3)_3 + PPh_3$. Apparently, higher partial pressures of carbon monoxide can favor larger n/b ratios when BDPF is used because lowering the H_2/CO ratio, at constant pressure, produced higher values of n/b. For example, at 60 °C, 400 psi, and BDPF/Rh = 8.5, the n/b ratio increased from 5.48 to 7.07 as the H_2/CO ratio decreased from 10 to 1. However, the opposite effect was noted at 100 psi.

The use of higher H_2/CO ratios with BDPF resulted in considerable amounts of isomerization to propanal and hydrogenation to propanol (Table VII). At 60 °C, 100 psi, H_2/CO = 10, and P/Rh = 20, the use of BDPF led to 15.8% propanol, 72.9% propanal, and only 11.3% of the desired hydroxy aldehydes. Under the same conditions, 17.4% propanol and 25.5% propanal were obtained with PPh_3.

Higher P/Rh ratios increase the n/b ratio with BDPF. For example, n/b increased from 2.67 to 3.26 as the BDPF/Rh ratio was increased from 1 to 8.5 at 60 °C and 100 psi. At 800 psi, a corresponding increase in n/b from 3.85 to 7.88 occurred.

Conclusions

The search for a highly selective high-yield route to terminally hydroformylated allyl alcohol has been frustrated by competing hydrogenation and isomerization as the temperature is raised to 100 °C or above. Variation of selectivity with pressure or P/Rh ratio is small and does not appear to be promising to effect a breakthrough. With the homogeneous rhodium catalyst, varying the H_2/CO ratio gave higher n/b ratios but only at the expense of greater competition from hydrogenation and isomerization. The best results were obtained at 60 °C with resin catalyst **5B** (PL = 29, P/Rh = 20) by increasing the H_2/CO ratio to 10. Under these conditions the combined yield of 1 and 2 was 90.3% with n/b = 4. Thus, 72.2% of 1 was realized based on allyl alcohol charged. Improved results probably could be obtained by further optimizing the phosphine loading and P/Rh ratio of the resin catalyst. Of all the phosphines studied, only 1,1′-bis(diphenylphosphino)ferrocene gave better yields of 1 than PPh_3. At 60 °C, 800 psi and P/Rh = 20, yields of 1 greater than 80% were readily achieved. Thus, high selectivities to 1,4-butanediol are now possible from allyl alcohol.

Experimental Section

Benzene was distilled from CaH_2 and THF was distilled from potassium/benzophenone under nitrogen prior to use. Allyl alcohol was dried over and distilled from anhydrous magnesium sulfate. Styrene–divinylbenzene resins containing 1 and 2% divinylbenzene were purchased from Bio-Rad Laboratories (SX-1 and SX-2, 200–400 mesh). $RhCl_3 \cdot xH_2O$ was purchased from Strem, Inc. Microanalytical analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, NY.

Styrene-divinylbenzene resins were brominated (Br_2, $FeBr_3$, dark) and then phosphinated (excess $LiPPh_2$, THF) as previously described.[19,29,30] $RhH(CO)(PPh_3)_3$ was prepared from $RhCl_3 \cdot xH_2O$ by published methods[36] and was attached to the phosphinated resins by thermal exchange followed by extensive benzene extraction (Soxhlet)[19,29,30] and drying in vacuo at 80 °C.

Hydroformylation Reactions. Hydroformylations were carried out in small stainless-steel autoclaves which were rapidly shaken at constant temperature after careful deoxygenation. All reactions were held at constant pressure with pressure-regulating valves. In each experiment the catalyst charge was 5.54×10^{-2} mmol of rhodium complex. Excess allyl alcohol (22.16 mmol; allyl alcohol:Rh 400) was used in each experiment in addition to *o*-xylene (internal standard, 2.5–3.0 mmol) and benzene to give a total volume of 10 mL. The reaction solutions were analyzed by analytical GLC (Hewlett-Packard Model 5710A) equipped with a 4 ft × $^1/_8$ in. Carbowax 20M/Chromosorb W column, using electronic-integration and internal-standard techniques (Hewlett-Packard model 3380A electronic integrator). In experiments using catalyst resins, the reaction solutions were filtered from the catalyst resins before analysis. The recovered resins were dried in vacuo at room temperature prior to reuse.

The two hydroformylation products, 4-hydroxybutanal and 3-hydroxy-2-methylpropanal, were collected as pure compounds by preparative-scale gas chromatography. 4-Hydroxybutanal was identified by comparison of its infrared spectrum with that reported[25] and by conversion to its 2,4-dinitrophenylhydrazone, mp 115–116 °C (uncorrected) (lit.[21] mp 116–117 °C). 3-Hydroxy-2-methylpropanal was also converted to its 2,4-dinitrophenylhydrazone derivative, mp 156–158 °C (lit.[27,28] mp 165–167 °C). The mass spectrum of 2 was that expected, exhibiting prominant ions at *m/e* 87 (M − 1), 71, 70, 58, and 57.

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J. Org. Chem. **1980**, *45*, 2139–2145

LiAlH$_4$ Reductions. Allyl alcohol (5.0 mL) was hydroformylated in dry THF at 60 °C and 400 psi in the presence of RhH(CO)(PPh$_3$)$_3$ as described above. A portion (1.0 mL) of the resulting solution was analyzed by GLC, using *o*-xylene as an external standard, demonstrating the presence of the following known products: allyl alcohol (1.69 mmol), aldehyde **1** (2.09 mmol), and aldehyde **2** (1.22 mmol). An aliquot (1.0 mL) of the product solution was added to dry THF (10 mL) and LiAlH$_4$ was slowly added until no further reaction occurred and a small excess of LiAlH$_4$ was present. After the solution was refluxed for 3 h, cooled, and hydrolyzed with water, the organic layer was analyzed by GLC (*o*-xylene external standard). The products were 1,4-butanediol (2.08 mmol) and 2-methyl-1,3-propanediol (1.26 mmol), demonstrating that no increase in desired products could be achieved by reducing the unknown products.

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Registry No. 1, 25714-71-0; **2**, 38433-80-6; allyl alcohol, 107-18-6; RhH(CO)(PPh$_3$)$_3$, 17185-29-4; RhH(CO)(P(OPh)$_3$)$_3$, 18346-73-1; RhH(CO)(P(OC$_6$H$_4$Cl)$_3$)$_3$, 22829-75-0; RhH(CO)(P(*n*-Bu)$_3$)$_3$, 22829-69-2; RhH(CO)(PPh$_3$)(Ph$_2$PCH$_2$CH$_2$PPh$_2$), 64611-33-2; RhH(CO)(triphos), 73347-65-6; BDPF, 12150-46-8; Rh, 7440-16-6.

Supplementary Material Available: The dependence of selectivity on P/Rh using polymer-anchored catalysts; the dependence of selectivity on pressure for several systems not shown in Table III of this manuscript; and a summary of product distribution data not given in Table IV of this manuscript (3 pages). Ordering information is given on any current masthead page.

Isomerization of *N*-Allylamides and -imides to Aliphatic Enamides by Iron, Rhodium, and Ruthenium Complexes

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Substituted aliphatic *N*-propenylamides and -imides are readily synthesized from *N*-allylamides by double bond migration induced by rhodium or ruthenium hydrides. *N*-Propenylimides can be prepared from allylimides only in the presence of iron pentacarbonyl.

The available methods of synthesis of enamides are rather limited, allowing neither a wide variety of reactants nor reaction conditions. The most widely used method consists of the acylation of an imine with an acid chloride or an anhydride.[2]

In this paper, we report the catalytic isomerization of allylamide derivatives to a series of enamide derivatives. These compounds are potential precursors for catalytic asymmetric hydroformylation to afford amino acid intermediates, as described in the following paper.

Double-bond migration catalyzed by soluble transition-metal compounds has found few useful applications in organic synthesis. The Rh(I)-catalyzed isomerization of an allyl ether to the corresponding enol ether is used in a relatively new method for the selective removal of a protecting group from an alcohol.[3] This type of isomerization can also be effected by Fe(0)[4] complexes. The isomerization of 3-pentenonitrile to the thermodynamically unfavorable 4-isomer by a Ni(0) catalyst is an important step in the synthesis of adiponitrile from butadiene and HCN.[5]

After the work described in this paper had been completed, the enantioselective isomerization of prochiral allylamines to the corresponding optically active enamines was reported.[6] This process, effected by an optically active Co(I) catalyst, provides a new route to optically active aldehyde precursors. The iron(0)-catalyzed photoisomerization of unsubstituted *N*-allylamides[7] or the iron(0)-catalyzed thermal isomerization of *N*-allylimides affords the 2-propenyl enamides or enimides.[8]

Results and Discussion

The isomerization of *N*-allylamides to *N*-propenylamides is best effected by heating toluene or xylene solutions of the substrates with a catalytic amount (5×10^{-3} mol) of (triphenylphosphine)hydridorhodium or -ruthenium complexes. The reaction must be conducted under an inert atmosphere, and usually several hours are required for complete conversion (Table I). Unfortunately, a general catalyst could not be found, and it was necessary to match the transition-metal complex, temperature, and time with a particular substrate in order to reach optimum conditions.

The isomerization of *N*-allylacetamide (**1**) by HRuCl(PPh$_3$)$_3$ (**2**) or HRh(PPh$_3$)$_4$ (**3**) affords a cis–trans mixture of isomers (**1a,b**); the cis isomer predominates. The same isomeric composition is obtained by using a polymer-supported rhodium catalyst bearing DIOP as the phosphine ligand.[9] With the polymer-attached catalyst, the product is readily recovered simply by filtration of the catalyst and evaporation of the solvent. The catalyst may be reused for further isomerization, although a decrease in its activity was observed. A much more reactive catalyst toward substrates **1** and **5** bearing an NH group was the ruthenium hydride catalyst **2**. The isomerization of these substrates in the presence of **2** is almost completed (TLC) after 3 h in refluxing toluene. Much longer reaction times are required to achieve the same conversion with **3** (Table I). If traces of oxygen are present, the purple solutions of **2** in aromatic hydrocarbons turn green immediately, and the catalytic activity disappears. However, under an inert

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