Kugelrohr apparatus, giving pure product (1.00 g, 10.1 mmol, 85%) as a colorless liquid.

Glycyl-DL-aspartic Acid. Glycyl-DL-asparagine (100 mg, 0.53 mmol) and Amberlyst XN-1010 resin (1.5 g) were combined with water (4 mL), and the mixture was heated in a closed flask (100 °C) for 72 h. The resin was collected in a small column and washed once with water. Elution with aqueous ammonia (0.5 N) and concentration provided glycyl-DL-aspartic acid (95.5 mg, 0.50 mmol, 95%) as a white foam.

Dimethyl DL-Aspartate. DL-Asparagine monohydrate (100 mg, 0.67 mmol) and Amberlyst 15 resin (1.5 g) were combined with methanol (4 mL), and the mixture was heated in a closed flask (60 °C) for 4 days. The resin was collected in a small column and the product eluted with a solution of methanolic ammonia (a saturated solution diluted with six volumes of methanol). Evaporation and purification of the residue on silica gel (1-mm plate, 20:1 CH_2Cl_2–CH_3OH) afforded dimethyl DL-aspartate (82.3 mg, 0.51 mmol, 77%) as a colorless oil.

***N*-Benzoylglycine Methyl Ester.** *N*-Benzoylglycinohydrazide (99.1 mg) and Amberlyst 15 resin (1.5 g) were combined with methanol (4 mL), and the mixture was heated in a closed flask (60 °C) for 20 h. After filtration and evaporation, the residue was purified by silica gel chromatography (1-mm plate, EtOAc), giving *N*-benzoylglycine methyl ester (77.7 mg, 0.40 mmol, 78%) as a colorless oil.

L-*N*-Phthaloylphenylalanine methyl ester was prepared by the general procedure and purified by chromatography on silica gel: NMR ($CDCl_3$) δ 3.50 (1 H, d, J = 9 Hz), 3.52 (1 H, d, J = 8 Hz), 3.72 (3 H, s), 5.08 (1 H, dd, J = 8, 9 Hz), 7.05 (5 H, s), 7.8 (4 H, m); IR ($CHCl_3$) 1770, 1735, 1710 cm^{-1}; mass spectrum, m/e 309 (M^+). Anal. Calcd for $C_{18}H_{15}NO_4$: C, 69.89; H, 4.89; N, 4.53. Found: C, 69.57; H, 5.08; N, 4.22.

L-*N*-Phthaloylphenylalanine ethyl ester was prepared by the general procedure and purified by chromatography on silica gel: NMR ($CDCl_3$) δ 1.22 (3 H, t, J = 7 Hz), 3.50 (1 H, d, J = 9 Hz), 3.53 (1 H, d, J = 7 Hz), 4.18 (2 H, q, J = 7 Hz), 5.07 (1 H, dd, J = 7, 9 Hz), 7.1 (5 H, s), 7.7 (4 H, m); IR ($CHCl_3$) 1770, 1735, 1710 cm^{-1}; mass spectrum, m/e 323 (M^+). Anal. Calcd for $C_{19}H_{17}NO_4$: C, 70.57; H, 5.30; N, 4.33. Found: C, 70.60; H, 5.32; N, 4.22.

DL-*N*-Benzoylalaninamide. A solution of DL-*N*-benzoylalanine methyl ester (1.0 g, 4.83 mmol) in ammonia-saturated methanol (20 mL) was allowed to stand for 48 h. The resulting crystalline product was collected (0.79 g, 85%) and washed with methanol: mp 231–233 °C; NMR (Me_2SO-d_6) δ 1.33 (3 H, d, J = 7 Hz), 4.42 (1 H, quintet, J = 7 Hz), 7.0 (1 H, br), 7.3–7.6 (4 H, m), 7.8–8.0 (2 H, m), 8.2–8.4 (1 H, br); IR (KBr) 3250, 3150, 1620, 1540 cm^{-1}; mass spectrum m/e 148 (P – $CONH_2$). Anal. Calcd for $C_{10}H_{12}N_2O_2$: C, 62.48; H, 6.29; N, 14.58. Found: C, 62.51; H, 6.23; N, 14.58.

10-Undecenamide. A solution of methyl 10-undecenoate (2.0 g, 10.0 mmol) in ammonia-saturated methanol (40 mL) was allowed to stand for 5 days. Recrystallization from ethyl acetate gave pure amide: mp 85–86 °C; 0.90 g (48%); NMR ($CDCl_3$) δ 1.2–1.9 (12 H, br s), 1.9–2.4 (4 H, m), 4.7–5.1 (2 H, m), 5.1–6.0 (3 H, m); IR ($CHCl_3$) 2940, 2860, 1660, 995, 915 cm^{-1}; mass spectrum, m/e 183 (M^+). Anal. Calcd for $C_{11}H_{21}NO$: C, 72.18; H, 11.55; N, 7.64. Found: C, 72.14; H, 11.79; N, 7.47.

Registry No. Methyl benzoate, 93-58-3; phenylacetic acid, 103-82-2; methyl cinnamate, 103-26-4; PhCO-DL-Ala-OMe, 38767-73-6; Pht-L-Phe-OMe, 14380-85-9; Pht-L-Phe-OEt, 50468-37-6; Methyl 10-undecenoate, 111-81-9; dimethyl malonate, 108-59-8; methyl cyanoacetate, 105-34-0; H-L-Pro-OH, 147-85-3; H-DL-Asp dimethyl ester, 40149-67-5; DL-Gly-Asp-OH, 79731-35-4; methyl 1-hydroxycyclohexanecarboxylate, 6149-50-4; diethyl 1,4-bicyclo[2.2.2]octanecarboxylate, 1659-75-2; *N*-benzoylglycine methyl ester, 1205-08-9; Cbz-L-Val-L-Tyr-OMe, 15149-72-1; benzamide, 55-21-0; phenylacetamide, 103-81-1; cinnamamide, 621-79-4; PhCO-DL-Ala-NH_2, 24250-70-2; Pht-L-Phe-NH_2, 21946-94-1; 10-undecenamide, 5332-51-4; malonamide, 108-13-4; 2-cyanoacetamide, 107-91-5; H-LPro-NH_2·HCl, 42429-27-6; H-DL-Asn-OH, 3130-87-8; DL-Gly-Asn-OH, 32729-21-8; 1-hydroxycyclohexanecarboxamide, 7500-69-8; ethyl 1-(aminocarbonylbicyclo[2.2.2]octane-4-carboxylate, 79663-72-2; *N*-methylbenzamide, 613-93-4; benzoic acid hydrazide, 613-94-5; 2-(benzoylamino)acetic acid hydrazide, 2443-68-7; Cbz-L-Val-L-Tyr-$NHNH_2$, 5992-90-5.

Reactivities of Aldehydes in Homogeneous Catalytic Hydrogenation with Cationic Rhodium Complexes

Hiroshi Fujitsu,* Eiichi Matsumura, Kenjiro Takeshita, and Isao Mochida

Research Institute of Industrial Science, Kyushu University 86, Fukuoka 812, Japan

Received April 6, 1981

Catalytic hydrogenation of several aldehydes with cationic rhodium complexes was investigated at 30 °C under atmospheric and 50-atm pressures of hydrogen. The catalytic activity was found to depend very much on the structure of the phosphorus ligands, PEt_3 exhibiting the highest activity among the ligands examined. The PPh_3 catalyst showed essentially no activity for aldehydes except for phenylacetaldehyde. The diphos catalyst was completely inactive for all the aldehydes examined. Although catalyst deactivation occurred in the early stages of the reactions under 1 atm of hydrogen for almost all the aldehydes examined, its extent depended very much on the substrate. Decarbonylation products were detected under the reaction conditions, suggesting the formation of carbonyl complexes as the reason for catalyst deactivation. A higher pressure of hydrogen, 50 atm, reduced to a great extent such catalyst deactivation. Selective hydrogenation of the unsaturated aldehyde, crotonaldehyde, yielding the corresponding unsaturated alcohol, was partially achieved, the yields being 4% and 13% under hydrogen pressures of 1 and 50 atm, respectively. The reactivities of aldehydes are discussed from the point of view of their coordination and hydrogenation mechanisms, in comparison with those of ketones and olefins.

Introduction

Hydrogenation of aldehydes with homogeneous catalysts has been extensively studied.[1,2] Although simultaneous decarbonylation often takes place even under mild reaction conditions,[3] a few catalysts have been reported to show the high catalytic activity at room temperature under atmospheric pressure of hydrogen.[2] It must be noted that $RuCl_2(PPh_3)_3$ was reported to hydrogenate aldehydes without decarbonylation at 50~70 °C under hydrogen

(1) Birch, A. J.; Williamson, D. H. *Org. React.* **1976**, *24*, 1.
(2) James, B. R. "Homogeneous Hydrogenation"; Wiley: New York, 1973; pp 157, 224, 258, 271, 282, 302.
(3) Baird, M. C.; Nyman, C. J.; Wilkinson, G. *J. Chem. Soc. A 1968*, 348. Ohno, K.; Tsuji, J. *J. Am. Chem. Soc.* **1968**, *90*, 99.

0022-3263/81/1946-5353$01.25/0

Table I. Hydrogenation of Aldehydes at Room Temperature under an Atmospheric Pressure of Hydrogen[a]

compnd	% conv (1 h/20 h)			
	PEt_3	PMe_3	PPh_3	diphos
n-butyraldehyde	30.7/41.4[b]	15.8/	0	0
benzaldehyde	40.8/97.4	5.2/29.1[c]	0/tr	0
phenylacetaldehyde	67.5/79.8	15.2/47.8	12.7/45.7	0/<1.0
acetone	8.2/73.4	7.7/	0	0
methyl *n*-propyl ketone	3.0/47.6		0	0
acetophenone	5.5/69.8	1.3/19.3	0	0
phenylacetone	6.3/81.9	0.5/66.0	0	0

[a] Catalyst, 0.1 mmol in 50 mL of 1% aqueous diglyme; aldehyde, 10 mmol at 30 °C; P_{H_2} = 1 atm. [b] 24 h. [c] 15 h.

pressure of 10~20 atm.[4] Schrock and Osborn[5] reported some activity of a cationic rhodium complex of dimethylphenylphosphine, although it rapidly became almost inactive after several turnovers. The complex showed high and stable activity for the hydrogenation of ketone[5] as well as olefinic double bonds.[6] We synthesized a catalyst precursor of a cationic triethylphosphine complex, $(Rh(NBD)(PEt_3)_2)^+ClO_4^-$, and found much stabler and higher activity of its dihydride complex for the hydrogenation of several ketones at room temperature.[7]

In the present study, similar complexes of variable phosphorus ligands are applied to the hydrogenation of several aldehydes.

Results

Hydrogenation of Saturated Aldehydes. Catalytic activities of the cationic complexes carrying variable phosphine ligands and the reactivities of some saturated aldehydes are summarized in Table I where the conversions by 1- and 20-h reactions are described. Catalytic activity of the complex depended strongly on the ligand, the PEt_3 ligand showing the greatest activity for the aldehydes, as has been reported for acetone.[7,9] In contrast, the triphenylphosphine (PPh_3) complex showed essentially no activity for the hydrogenation of aldehydes except for phenylacetaldehyde. The 1,2-bis(diphenylphosphino)ethane (diphos) complex showed no activity at all for any aldehyde examined.

In the hydrogenation reaction catalyzed by the PEt_3 and PMe_3 complexes, all the aldehydes used displayed a reactivity greater by a factor of 10 in the initial stage of the reaction than their corresponding methyl-substituted ketones.[7]

The profiles of the reaction catalyzed by the PEt_3 catalyst are shown in Figure 1. Although all aldehydes examined were hydrogenated quickly in the early stages, with some aldehydes the catalyst lost its activity after several turnovers, as has been reported previously.[5] The extent of catalyst deactivation was found to depend very much on the substrate. The catalyst could complete the hydrogenation of benzaldehyde within 24 h, whereas it could hydrogenate only 80% of the phenylacetaldehyde and only 41.4% of the *n*-butyraldehyde under the same conditions. Propane and propylene were detected dissolved in the reaction mixture of *n*-butyraldehyde in amounts reaching up to 0.2 mol (propane/propylene = 5/1) to 1 mol of catalyst after 1 h. For phenylacetaldehyde, 1 mol of toluene for 1 mol of catalyst was detected after the reaction. These facts suggest that decarbonylation took place along with the hydrogenation catalyzed by the complex.

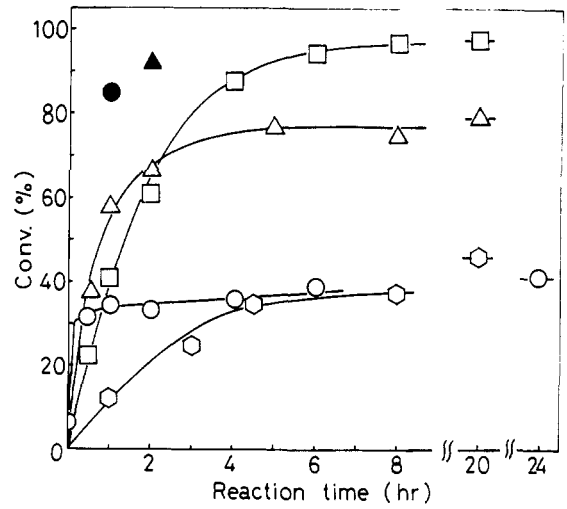


Figure 1. Hydrogenation of some aldehydes with the PEt_3 catalyst (for reaction conditions, see Table I): (○, ●) *n*-butyraldehyde with the PEt_3 catalyst, (△, ▲) phenylacetaldehyde with the PEt_3 catalyst, (□) benzaldehyde with the PEt_3 catalyst, (⬡) phenylacetaldehyde with the PPh_3 catalyst, (open) P_{H_2} = 1 atm, and (closed) P_{H_2} = 50 atm.

Table II. Hydrogenation of Crotonaldehyde[a]

compnd	% yield (1 h/20 h)		
	PEt_3		PPh_3,
	1 atm	50 atm	1 atm
$CH_3CH_2CH_2CHO$	4.2/4.9	9.0	8.9/52.8[b]
$H_3CCH{=}CHCH_2OH$	4.0/5.3	13.4	
$CH_3CH_2CH_2CH_2OH$	0.5/0.6	5.7	
$H_2C{=}CHCH_2CH_2OH$	0.8/2.7	0.3	0/2.6[b]
unident prod	4.0/5.3	13.1	
% total conv	9.5/13.6	41.5	8.9/55.4

[a] For the reaction conditions, see Table I. [b] 21 h.

The PPh_3 catalyst can hydrogenate only phenylacetaldehyde among the aldehydes described above. The reaction profile is shown in Figure 1. The reaction became very slow after 5 h and the yield of alcohol was less than 40%. Thus, the deactivation of the catalyst was much more severe than that of the PEt_3 catalyst.

Reactivity of α,β-Unsaturated Aldehydes. The products of the hydrogenation of crotonaldehyde with PEt_3 and PPh_3 catalysts are summarized in Table II. The PEt_3 catalyst produced crotyl alcohol (4.0% of its yield) together with butyraldehyde (4.2%) after 1 h under atmospheric pressure, indicating the partially selective hydrogenation of the aldehyde group. Such a selective hydrogenation of the carbonyl groups in α,β-unsaturated carbonyl com-

(4) Tsuji, J.; Suzuki, H. *Chem. Lett. 1977*, 1085.
(5) Schrock, R. R.; Osborn, J. A. *J. Chem. Soc., Chem. Commun., 1970*, 567.
(6) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 2134, 2143, 4450.
(7) Fujitsu, H.; Matsumura, E.; Takeshita, K.; Mochida, I. *J. Chem. Soc., Perkin Trans. 1*, in press.
(8) Mizoroki, T.; Seki, K.; Meguro, S.; Ozaki, A. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2148.
(9) Törös, S.; Heil, B.; Marko, L. *J. Organometal. Chem.* **1978**, *159*, 401.

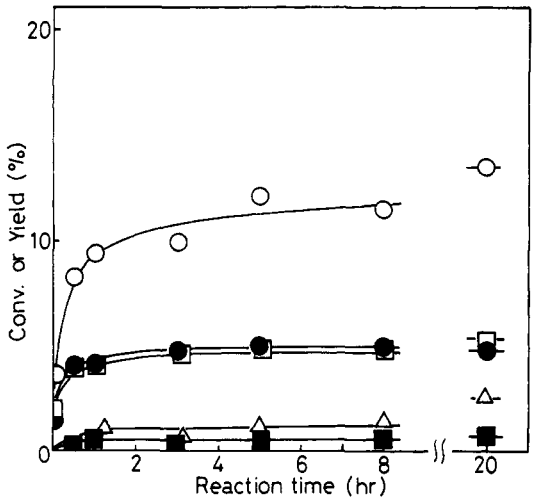


Figure 2. Hydrogenation of crotonaldehyde with the PEt_3 catalyst (for reaction conditions, see Table I): (○) conversion, (●) $CH_3CH_2CH_2CHO$, (□) $CH_3CH{=}CHCH_2OH$, (■) $CH_3CH_2CH_2CH_2OH$, and (△) $CH_2{=}CHCH_2CH_2OH$.

Table III. Hydrogenation of Cinnamaldehyde with the PEt_3 and PMe_3 Catalyst

	% yield				
	P_{H_2}, atm				
	PMe_3			PEt_3	
compnd	1[a]	10[b]	50[b]	1[a]	50[b]
$PhCH_2CH_2CHO$	4.9	60.9	65.3	3.9	18.0
$PhCH{=}CHCH_2OH$	tr	tr	1.2	1.2	6.7
$PhCH_2CH_2CH_2OH$	0	0	4.0	0	
unident prod	3.4	2.2	22.5		
% conv	8.3	63.1	93.0	5.1	24.7

[a] At 30 °C, 20 h. [b] At 25 °C, 3 h.

pounds[8] has never been achieved for α,β-unsaturated ketones with the PEt_3 catalyst.[7] This suggests that the coordinating ability and reactivity of the aldehydes are greater than those of the ketones. Because of this coordinating ability, the aldehyde can compete for the active site with the olefinic bond. In contrast, the PPh_3 catalyst hydrogenated the olefinic double bond almost exclusively. The reaction profile with the PEt_3 catalyst is illustrated in Figure 2. The reaction was fast for the first hour but then was quite slow without any essential change in product distribution, indicating the deactivation of the catalyst. Although the activities were low, the PEt_3 and PMe_3 catalysts hydrogenated the olefinic double bond of cinnamaldehyde under an atmospheric pressure of hydrogen, producing phenylpropionaldehyde with a trace amount of cinnamyl alcohol (Table III).

Hydrogenation of Aldehydes under the Higher Hydrogen Pressure. The hydrogenation of *n*-butyraldehyde, crotonaldehyde, and cinnamaldehyde with the PEt_3 and PMe_3 catalysts was studied under the increased hydrogen pressure to improve the conversion levels which were rather limited under atmospheric pressure because of the catalyst deactivation.

Hydrogenation of *n*-butyraldehyde with the PEt_3 catalyst under 50 atm of hydrogen achieved an 84% conversion after 1 h, although the reaction rate was similar to the initial reaction rate under 1 atm (Figure 1). Hydrogenation of phenylacetaldehyde reached 92% conversion after 2 h under the same reaction condition. The catalyst deactivation can be reduced to a great extent under the high hydrogen pressure.

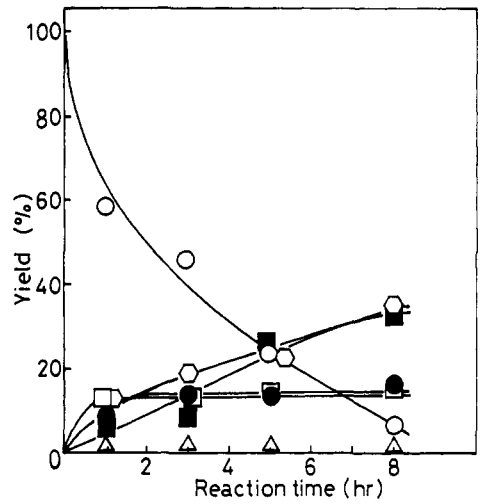


Figure 3. Hydrogenation of crotonaldehyde with the PEt_3 catalyst under 50 atm of hydrogen pressure: catalyst, 0.1 mmol in 50 mL of 1% aqueous diglyme; aldehyde, 10 mmol; reaction temperature, 25 °C; (○) $CH_3CH{=}CHCHO$, (●) $CH_3CH_2CH_2CHO$, (□) $CH_3CH{=}CHCH_2OH$, (■) $CH_3CH_2CH_2CH_2OH$, (△) $CH{=}CHCH_2CH_2OH$, and (○) unidentified products.

Table IV. ^{13}C NMR Chemical Shift and IR Spectral Data of Several Aldehydes and Ketones

	RCH=O		$RC(O)CH_3$	
R	^{13}C, ppm	$\nu_{C=O}$[a]	^{13}C, ppm	$\nu_{C=O}$[a]
C_3H_7	201.9	1724	208.7	1709
Ph	192.7	1704	197.7	1684
$PhCH_2$	199.2	1716	206.1	1712
$CH_3CH{=}CH$	194.0	1692	198.1	1669
$PhCH{=}CH$	193.5	1678		
$PhCH_2CH_2$	201.3	1727	207.5	1701

[a] C. J. Pouchert, Ed. "The Aldrich Library of Infrared Spectra"; 1975.

The reaction profile of the hydrogenation of crotonaldehyde with the PEt_3 catalyst under 50 atm of hydrogen is shown in Figure 3. The conversion increased monotonously with the reaction time to 100%. The yields of both the unsaturated alcohol and *n*-butyraldehyde reached up to 13% (selectivity, 32%) after 1 h, although no increase in their yields was observed in spite of a steady increase in the conversion. Instead, the yield of saturated alcohol increased monotonously up to 30.9% in contrast to the reaction under 1 atm where a yield of only ca. 1% was achieved. Again the catalyst deactivation was reduced by the higher hydrogen pressure.

In the reaction of cinnamaldehyde with the PEt_3 and PMe_3 catalysts, both rates of hydrogenation depended very much on the hydrogen pressure, the principal product being hydrocinnamaldehyde with both catalysts (Table III). The yield of cinnamyl alcohol reached 1.2% and 6.7% with the PMe_3 and PEt_3 catalysts, respectively, under a hydrogen pressure of 50 atm. The activity of the PEt_3 catalyst for the olefinic bond in the unsaturated aldehyde was much smaller than that of the PMe_3 catalyst, as has been observed for olefins such as styrene.[7]

Reactivity of the Carbonyl Group in Aldehydes and Ketones. ^{13}C NMR chemical shifts of the carbon atom of the carbonyl in aldehydes are generally located higher in the magnetic field by 5 ppm than those of the corresponding ketones[10] as summarized in Table IV. The inductive effect of the methyl group in the ketone may

(10) Stothers, J. B., "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972; p 279.

decrease the polarization of the carbonyl bond. The

(1)

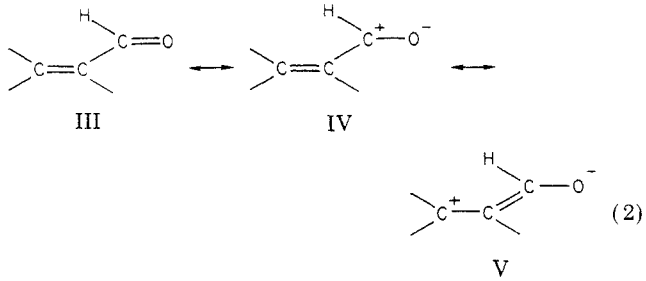
I II

higher wavenumbers of the carbonyl stretching of aldehydes compared with those of the corresponding ketones can be explained by the extent of this resonance. Such a polarization may enhance both the coordinating ability of anionic oxygen and the susceptibility to hydride attack of the carbon atom of carbonyl groups in aldehydes compared with those of ketones.

Steric hindrance around the carbonyl group in aldehydes should be much smaller than that in ketones, since one of the substitutents in the former is always hydrogen. Such steric hindrance may influence the first step of the catalysis where the π coordination of the carbonyl bond may take place in advance to its σ coordination. Thus, the significantly higher reactivity of aldehydes compared with ketones[9] may be due both to such larger polarization and smaller steric factors in the former.

The reactivity order of aldehydes studied, *n*-butyraldehyde > phenylacetaldehyde > benzaldehyde > crotonaldehyde > cinnamaldehyde, may be also explained in terms of polarization and steric hindrances.

It is of value to note that crotyl alcohol and butyl alcohol were produced at comparable yields in the hydrogenation of crotonaldehyde by the PEt_3 catalyst. Similar coordination abilities of carbonyl and olefinic groups with this catalyst are suggested by the results. It seems quite possible that both C=C and C=O coordinate, either inter- or intramolecularly. This dual binding could compete with H_2 for coordination sites on the metal, lowering the reactivity of unsaturated aldehydes compared with saturated ones. The lower reactivity of aldehydes could be explained also by the resonance between IV and V[10] in eq 2 as supported by ^{13}C NMR and IR spectral data (Table IV).

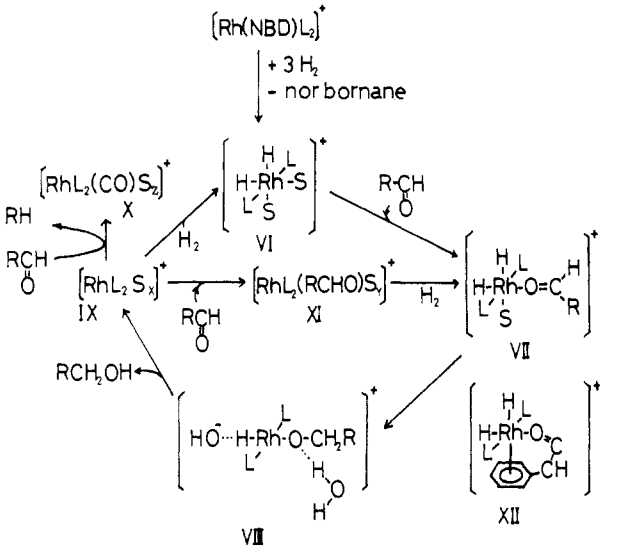


III IV V (2)

Mechanistic Explanation of the Activity Order and Deactivation of the Catalyst. The extent of catalyst deactivation in the hydrogenation of the aldehydes studied was decreased in the order of *n*-butyraldehyde > phenylacetaldehyde > benzaldehyde, which is identical with that of reactivity for hydrogenation. The deactivation may be due to the decarbonylation which is well-known for the Wilkinson catalyst with aldehydes.[3]

A possible mechanism for the hydrogenation of aldehydes is proposed in Scheme I, in which some details proposed by Schrock and Osborn[5,6] are added. The carbonyl group, with strong coordination ability, may compete the coordination site of the active intermediate (IX) with hydrogen. When aldehyde reacts with IX to produce olefin or alkane, leaving carbon monoxide in the catalyst, the resulting carbonyl complex (X) may not be regenerated into the hydrogenation active species (VI) under atmospheric pressure of hydrogen.[11] A higher pressure of hydrogen, however, can regenerate the dihydride species (VI) from IX, reducing the catalyst deactivation to a great extent. Thus, the varying extent of deactivation of aldehydes may be attributed principally to their susceptibility to decarbonylation.

Scheme I



Influence of the Ligand on Catalytic Activity. The activity order of the catalyst for the hydrogenation of aldehydes was $PEt_3 > PMe_3 \gg PPh_3 >$ diphos~O, which is the same order as that observed for ketone hydrogenation.[7] This order can be explained in terms of the anionic character of the hydride as suggested by the fact that the PEt_3 catalyst, the most active catalyst among the phosphine complexes, showed highest chemical shift of hydride in ^1H NMR.[7]

The PPh_3 catalyst exhibited a catalytic activity only for phenylacetaldehyde. Since the phenyl group is generally reported to coordinate to cationic rhodium complexes,[9] phenylacetaldehyde may form an intermediate (XII in Scheme I, which replaces VII in Scheme I) which is endowed with extra reactivity to be hydrogenated even by weakly activated hydrogen (moderately anionic),[7] whereas other aldehydes could not form such an intermediate and would thus be inactive with this catalyst.

The diphos catalyst is known to fail to form dihydride species under hydrogen pressure, although it can hydrogenate the olefinic double bond (eq 3).[12] It may be of

$$(Rh(NBD)(diphos))^+ \xrightarrow{2H_2} (Rh(diphos))^+ + \text{norbornane} \quad (3)$$

value to distinguish the reaction mechanism of aldehyde and olefin hydrogenation by this catalyst. According to the reaction steps proposed[12] for the olefin hydrogenation catalyzed by this catalyst, molecular hydrogen can never produce a partially hydrogenated intermediate, because of the steric difficulty due to the σ coordination of the carbonyl group.

Experimental Section

The catalyst precursors, $(Rh(NBD)(PR_3)_{2or3})^+ClO_4^-$ (NBD = norbornadiene; PR_3 = tertiary phosphine), were prepared under a nitrogen atmosphere according to the methods described in the literature.[11] Because the catalyst precursors, especially PEt_3, were very vulnerable to oxygen and moisture, they were dried in a

(11) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 2397.

(12) Chan, A. S. C.; Halpern, J. *J. Am. Chem. Soc.* **1980**, *102*, 838.

vacuum and stored in sealed tubes saturated with pure, dry nitrogen. The aldehydes were commercially available reagents of the highest grade. They were used without further purification. Diglyme (Wako Junyaku Co.), used as a reaction solvent, was dried by being refluxed with sodium, distilled, and stored in a sealed glass tube.

The reaction was carried out under an atmospheric pressure of hydrogen in a glass reactor equipped with greaseless valves, which is described elsewhere.[13] After the catalyst precursor (0.1 mmol) was dissolved in 1% aqueous diglyme (50 mL) in a nitrogen atmosphere, nitrogen was replaced with hydrogen, the solution being aged for exactly 5 min under an atmospheric pressure of hydrogen, to yield the active hydrido complex. The aldehyde (10 mmol) was injected with a syringe through a silicon rubber stopper to start the reaction. The reaction was followed by gas chromatographic analysis (Yanako G180, column: polyethylene glycol (20 M), 2 m, polyethylene glycol 4000, 2 m) of a small portion of the reaction mixture (0.2 mL) which was sampled by the equipment[13] at appropriate intervals without any contact of the reaction system with air. The reaction under the higher pressure of hydrogen was carried out in an autoclave (200cc, Taiatsu Garasu Kogyo Co.).

^{13}C NMR of the aldehydes was measured with an FT NMR spectrometer (JEOL, FX-100).

Registry No. *n*-Butraldehyde, 123-72-8; benzaldehyde, 100-52-7; phenylacetaldehyde, 122-78-1; acetone, 67-64-1; methyl *n*-propyl ketone, 107-87-9; acetophenone, 98-86-2; phenylacetone, 103-79-7; crotonaldehyde, 4170-30-3; cinnamaldehyde, 104-55-2; hydrocinnamaldehyde, 104-53-0; methyl propenyl ketone, 625-33-2; methyl phenethyl ketone, 2550-26-7; PEt_3, 554-70-1; PMe_3, 594-09-2; PPh_3, 603-35-0; diphos, 1663-45-2; Rh, 7440-16-6.

(13) Fujitsu, H.; Matsumura, E.; Takeshita, K.; Mochida, I. *J. Org. Chem.* **1981**, *46*, 2287.

General Synthesis of ω-Acetylenic Vinyl Esters and Ethers

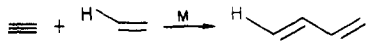
Michael C. Croudace and Neil E. Schore*

Department of Chemistry, University of California, Davis, California 95616

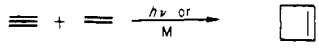
Received December 17, 1980

Vinyl ethers of the general structure $CH_2{=}CHO(CH_2)_nC{\equiv}CH$ and vinyl esters of the general structure $CH_2{=}CHOC(O)(CH_2)_nC{\equiv}CH$ have been prepared by mild elimination methods from the corresponding ω-acetylenic alcohols and acids. A two-step procedure involving addition of alcohol to (trimethylsilyl)oxirane followed by silanol elimination, and only slightly modified from the one developed by Hudrlik, provides the vinyl ethers in average overall yields of 45%. The vinyl esters must be prepared in three steps due to the unexpected lack of reactivity of the acid–oxirane adducts toward elimination. Vinyl 3-butynoate is not accessible at all via this route. Other vinyl esters are realized in overall yields of 40% or better. Several of these compounds exhibit high reactivity toward $Co_2(CO)_8$ in preliminary studies of possible cyclization reactions.

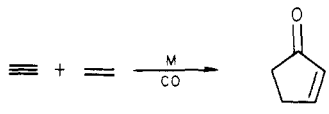
The versatility of the alkyne functional group makes its incorporation an important part of the design of many synthetic intermediates. In recent years a number of useful techniques for the linkage of alkyne and alkene groups have been developed, among these several that allow the direct construction of such important intermediates as 1,3-dienes,[1] cyclobutenes,[2] and cyclopentenones[3] (eq 1–3).



(1)



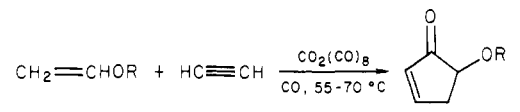
(2)

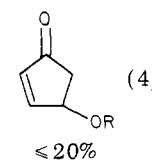


(3)

We are especially intrigued by the as yet unrealized potential of the cyclopentenone synthesis (eq 3) in the natural products field. The best conditions under which cocyclization of an alkene, an alkyne, and CO can be effected are those developed by Pauson and co-workers, who used $Co_2(CO)_8$ as a catalyst. Only strained alkenes (e.g., norbornene) are reactive under mild conditions (60–80 °C),[3] while simple alkenes participate only at much higher temperature (e.g., 140–150 °C) and usually produce only very low yields of cyclopentenones.[1b]

In a series of pilot experiments we have examined a variety of alkenes and discovered that the presence of electron-donor groups and intramolecularity are two key factors that can contribute to cyclization reactivity under mild conditions (eq 4 and 5).[4] These results have

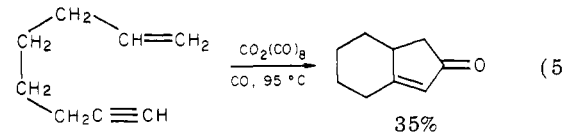




(4)

≤20%

R = CH_3CO, $(CH_3)_3C$



(5)

35%

(1) For M = Co: (a) Khand, I. U.; Pauson, P. L. *J. Chem. Soc., Chem. Commun.* **1974**, 379. (b) Khand, I. U.; Pauson, P. L. *J. Chem. Res. (Miniprint)* **1977**, 0168. Moderate yields (e.g., 20%) are obtainable if the alkyne is aryl substituted. Unfortunately, the products obtained are not generally useful in natural product synthesis.

(2) For UV review: Coyle, J. D. In "The Chemistry of the Carbon–Carbon Triple Bond"; Patai, S., Ed., Wiley-Interscience: New York, 1978. For M = Al: Snider, B. B.; Hrib, N. J. *Tetrahedron Lett.* **1977**, 1725. Fienemann, H.; Hoffmann, H. M. R. *J. Org. Chem.* **1979**, *44*, 2802. Snider, B. B.; Roush, D. M. *J. Am. Chem. Soc.* **1979**, *101*, 1906. For M = Ti: Clark, R. D.; Untch, K. G. *J. Org. Chem.* **1979**, *44*, 248. For M = Ru: Mitsudo, T.; Kokuryo, K.; Takegami, Y. *J. Chem. Soc., Chem. Commun.* **1976**, 722. For M = Zn: Snider, B. B.; Brown, L. A.; Conn, R. S. E.; Killinger, T. A. *Tetrahedron Lett.* **1977**, 283.

(3) For M = Co: Khand, I. U.; Knox, G. R.; Pauson, P. L.; Watts, W. E.; Foreman, M. I. *J. Chem. Soc., Perkin Trans. 1* **1973**, 977. Khand, I. U.; Pauson, P. L. *Ibid.* **1976**, 30. Khand, I. U.; Pauson, P. L. *J. Chem. Res. (Miniprint)* **1977**, 0153. Schore, N. E. *Synth. Commun.* **1979**, *9*, 41.

0022-3263/81/1946-5357$01.25/0