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Letter

Formation of 1,6-hexanedial via hydroformylation of 1,3-butadiene

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Abstract

Rhodium catalyst promoted by bidentate phosphine with natural bite angle being 102–113°, particularly DIOP, is effective for 1,6-hexanedial formation in the hydroformylation of butadiene.

Keywords: Hydroformylation; Rhodium catalyst; DIOP

Hexamethylenediamine (HMDA), an important precursor for Nylon66, is now mainly manufactured by two-step hydrocyanation of butadiene, followed by hydrogenation of the resulting 1,4-dicyanobutane [1,2]. On the other hand, 1,6-hexanedial, possibly obtainable by one-step hydroformylation of butadiene, is an immediate precursor of HMDA. Since not only the latter method is presumably the simplest method to prepare HMDA and the use of highly toxic hydrogen cyanide can also be avoided, this method will be economically most advantageous than any other ones. Rhodium-catalyzed hydroformylation reaction of butadiene has been already known for two decades. However, selectivity to the desired 1,6-hexanedial is very poor, and large amounts of pentanal and 3-pentenal are obtained as by-products. For example, up to 31% selectivity to C_6-dialdehydes were previously reported with catalysts composed of Rh and monophosphine PR_3, but selectivity to 1,6-hexanedial did not exceed 20% in the C_6-dialdehydes obtained [3,4].

We describe here that novel catalysts composed of rhodium and certain bidentate phosphine, particularly DIOP, produce considerable amounts of the desired 1,6-hexanedial in the hydroformylation of butadiene. Van Leeuwen and Roobeck [5] described that the Rh-DIOP system gave C_6-dialdehydes up to 30% selectivity, but still no further information even on the product composition has been available.

A mixture of butadiene, $Rh_4(CO)_{12}$ ([Rh] = 0.1 mol%), and DIOP (see Scheme 2; DIOP/Rh = 5 equivalent ratio) were exposed to

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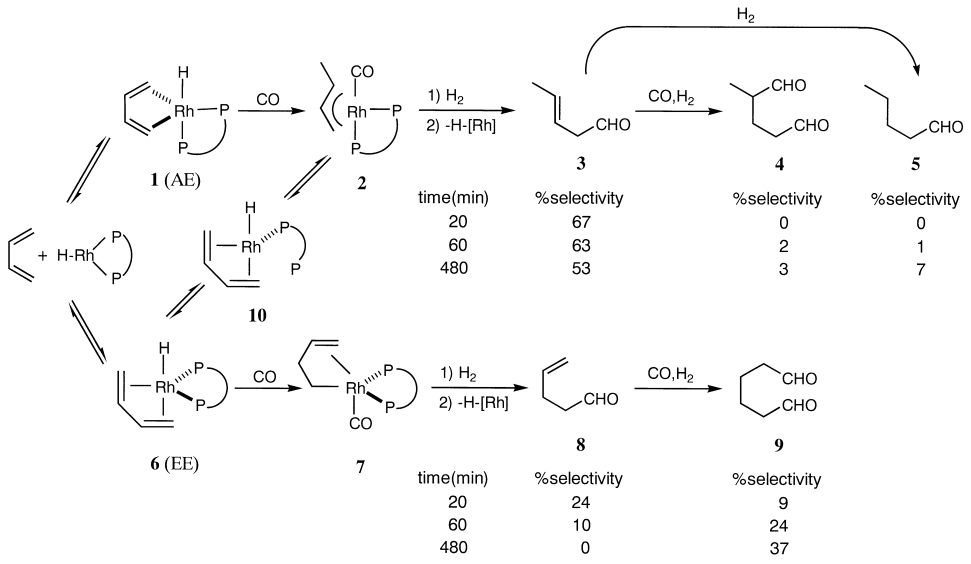
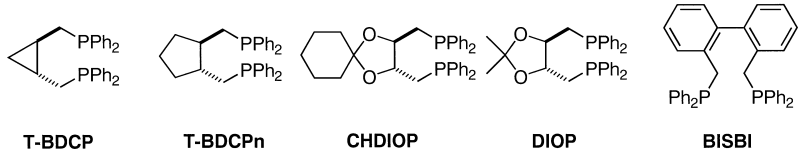


Scheme 1. Proposed reaction pathway.

9 MPa of CO/H_2 (1/1) in mesitylene solvent for 1.5 h at 100°C. The following products were obtained at 99% conversion of butadiene (percent yields are shown in the parentheses): 1,6-hexanedial (31), 3-pentenal (52), 2-methyl-1,5-pentanedial (8), 1-pentanal (1), and 2-methyl butanal (0.2). In the next step, we examined dependency of product distribution on reaction time (reaction conditions: [Rh], 0.1 mol%; [butadiene], 5.8 M; DIOP/Rh, 5 mol/g-at.; solvent, mesitylene; CO/H_2 (1/1), 2 MPa; 80°C). Scheme 1 represents selectivities to the products and a possible reaction pathway. Conformation of **1** and **6** is proposed to be trigonal bipyramid in the hydroformylation of alkenes catalyzed by the Rh–phosphine system [6]. The sum of the yields of products **3**–**5** (1,4-addition products) varies in small extent between 63–67% over the course of reaction, and the rest 33–37% is for sum of the products **8**–**9** (1,2-addition products). Products **3** and **8** are major products at an early stage of reaction. 4-Pentenal **8** can be obtained through intermediate **7**, which is the 1,2-addition product of H–Rh bond to butadiene. Since **8** is very reactive, it is converted to **9** through the second hydroformylation. In contrast with our catalysts, **3** has been known to be obtained in over 94% selectivity using the other phosphorus ligands [7–9]. In that reported system, a stable η^3-butenyl complex of Rh may be formed by coordination of butadiene to catalytically active H–Rh species, followed by subsequent insertion of the butadiene ligand into the H–Rh bond of resulting (η^4-butadiene)(H)Rh intermediate **1**. The 1,2-addition reaction indicated above has not been observed. The η^3-butenyl complex exclusively leads to **3** formation [10].



Scheme 2. Structure and abbreviations of phosphine ligands.

Table 1
Effect of ligand in the hydroformylation of butadiene catalyzed by Rh[a]

Ligand	Natural bite angle (°)[b]	Selectivity (%)		Relative rate
		3	**8+9**	
PPh_3		100	–	0.01
$Ph_2P(CH_2)_2PPh_2$ DPPE	85 (70–95)	94	6	1.15
$Ph_2P(CH_2)_3PPh_2$ DPPP		89	11	0.71
$Ph_2P(CH_2)_4PPh_2$ DPPB		76	24	1.49
$Ph_2P(CH_2)_5PPh_2$ DPPPn		84	16	0.49
T-BDCP	107 (93–131)	74	26	1.34
T-BDCPn		68	32	1.36
CHDIOP		68	32	1.31
DIOP	102 (90–120)	65	35	1.00
BISBI	113 (92–155)	87	13	–[c]

[a] Reaction conditions: [Rh], 0.01 mol%; [butadiene], 5.38 M; ligand/Rh, 10 mol/g-at.; solvent (toluene), 5 cm^3; CO/H_2 (1/1), 2 MPa; 100°C, 3 h.
[b] Data taken from Ref. [10]; bite angle with less than 3 kcal/mol additional strain energy are shown in parentheses.
[c] Not measured.

We have examined some bidentate phosphines, structures of which are illustrated in Scheme 2. Table 1 shows natural bite angles of the phosphines used, and results for hydroformylation of butadiene. Since the reaction was conducted with low catalyst concentration and at low CO/H_2 pressure, the reaction solutions were substantially composed of **3**, **8** and **9**. In the series of bis(diphenylphosphino) alkanes, the best initial rate and selectivity to **8** and **9** were observed for DPPB. Diphosphine with natural bite angle of 102–113° provides moderate selectivity to 1,2-addition products. This diphosphine has been shown to be coordinated to Rh with diequatorial (EE) geometry [11]. Butadiene should be coordinated to the above complex at apical–equatorial (AE) position to form intermediate **6**, which eventually produces 1,2-addition products. As noted by Casey et al. [11], the flexibility of ligand increases in the following order: DIOP < T-BDCP < BISBI, that is suggested by the bite angle with less than 3 kcal/mol strain energy shown in Table 1. Selectivity to 1,2-addition products decreases in the same order. In the case of the flexible ligands, e.g., BISBI, these are able to coordinate to Rh not only at EE position, but also at AE position. η^3-Butenyl complexes are thermodynamically more stable than η^4-butadiene complexes. As a result, equilibrium between **2** and **6** may be shifted to **2** direction with increase in the flexibility of ligand. The order of selectivity described above may be explained in this context. DPPE, with natural bite angle being 85°, is coordinated to Rh with AE geometry [11]. Therefore, butadiene is coordinated to the above complex at EE position to form intermediate **1**. This intermediate exclusively produces 3-pentenal through π-allyl complex **2**. Thus, ratio of 1,2-addition/1,4-addition may be determined by equilibrium constant between **1** and **6**.

To conclude: (1) Rh complexes, in which diphosphine ligand is coordinated at EE position, allow butadiene to be coordinated at AE position around Rh; (2) {η^4-(AE)-butadiene}{(EE)-diphosphine}(H)Rh species obtained above produces 4-pentenal, which in turn leads to 1,6-hexanedial formation.

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