violanthrene—electron donor— or whether the VEA-I_2 complex is essential for the isomerization.

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Hydrogenation of Conjugated Diolefins with Cobalt(II) Complexes

It has been already shown (*1*) that a number of transition metal compounds, for example, Ti(O-iso-$C_3H_7)_4$, VO(O-*n*-$C_4H_9)_3$, and Cr(acac)$_3$, combined with organometallic derivatives, are soluble catalysts for the hydrogenation of olefins such as cyclohexene, 1-octene, *trans*-stilbene, 2-methyl-2-butene, *trans*-2-pentene, tetramethylethylene, and 1-hexene. Transition metals in Groups IV–VIII, mostly as acetylacetonates or as alkoxides, have been found to be active when combined with, preferably, a trialkylaluminum compound.

In this paper, hydrogenation of butadiene or isoprene by binary catalyst systems of cobalt(II) complexes and aluminum triethyl is reported. Cobalt(II) complexes tried were bis(triphenylphosphine)cobalt(II) dichloride, $[(C_6H_5)_3P]_2CoCl_2$; bis(triphenylphosphine oxide)cobalt dinitrate, $[(C_6H_5)_3PO]_2Co(NO_3)_2$; and tris(pyridine)cobalt dinitrate, $Py_3Co(NO_3)_2$. Cobalt(II) acetylacetonate, Co(acac)$_2$; and bis(salicylaldehyde)cobalt (II), $Co(C_6H_4OCHO)_2$, were also tried.

Cobalt(II) acetylacetonete, Co(acac)$_2$, was prepared (*2*) by heating bis(acetylacetonate)cobalt(II) dihydrate in vacuo for 6 hr at 58°C. The dihydrate was prepared according to the method (*3*) of Charles and Pawlikowski. Bis(salicylaldehyde)cobalt(II), $Co(C_6H_4OCHO)_2$, was prepared (*2*) by heating bis(salcylaldehyde)cobalt dihydrate in vacuo for 12 hr at 58°C. The dihydrate was prepared according to the method (*4*) of Tyson and Adams. Bis(triphenylphosphine) cobalt(II) dichloride, $Co(PPh_3)_2Cl_2$, was prepared (*5*) by reaction of a hot absolute ethanol solution of the anhydrous cobaltous chloride and triphenylphosphine. Bis(triphenylphosphine oxide)cobalt(II) dinitrate $Co(PPh_3O)_2(NO_3)_2$ was prepared (*6*) by the reaction of cobalt(II) nitrate and excess of the triphenylphosphine oxide. Tris(pyridine)cobalt(II) dinitrate, $Co(Py)_3(NO_3)_2$, was prepared (*7*) by the reaction of the methanol solution of cobalt(II) nitrate and pyridine.

The hydrogenation reactions were carried out in an autoclave (100 ml), and all operations were carried out in a nitrogen atmosphere. In general, 2 mmole of cobalt complex, (4 mmole of triphenylphosphine), 10 mmole of aluminum triethyl, 50 ml of benzene as a solvent, and 5.6 g of butadiene (or 6.2 g

TABLE 1

Hydrogenation of Butadiene by Cobalt Complex–AlEt$_3$ Catalyst Systems[a]

Catalyst Systems[b]	Conversion (%)	Content (%)			
		1-Butene	*cis*-2-Butene	*trans*-2-Butene	Butane
1	80.7	7.1	12.6	5.0	75.3
2	72.1	13.8	28.4	7.7	50.1
3	59.7	19.7	35.5	6.6	38.2
4	44.5	32.1	46.2	10.5	11.2
5	36.4	30.2	51.8	8.2	9.8
6	28.0	21.1	61.5	14.6	2.8
7	16.9	27.7	63.8	7.6	0.9
8	9.1	27.3	57.2	15.2	0.3

[a] The hydrogenation reactions were carried out at 90°C for 1 hr under a hydrogen pressure of 40 kg/cm^2. With Catalyst Systems 1–3, butadiene oligomers were also produced in 3–5% yield (see Table 2, footnote *c*); 5.6 g of butadiene was used in each experiment.

[b] Catalyst systems (Tables 1–4): 1, CoCl$_2$–AlEt$_3$; 2, Co(acac)$_2$–AlEt$_3$; 3, Co(C$_6$H$_4$OCHO)$_2$–AlEt$_3$; 4, CoCl$_2$–PPh$_3$–AlEt$_3$; 5, Co(acac)$_2$–PPh$_3$–AlEt$_3$; 6, Co(PPh$_3$)$_2$Cl–AlEt$_3$; 7, Co(PPh$_3$O)$_2$(NO$_3$)$_2$–AlEt$_3$; 8, Co(Py)$_3$(NO$_3$)$_2$–AlEt$_3$. In each catalyst system, 2 mmole of cobalt compound, (4 mmole of PPh$_3$), and 10 mmole of AlEt$_3$ were used. As a solvent 50 ml of benzene was used.

of isoprene) were taken in the autoclave under the nitrogen atmosphere. Then, hydrogen was introduced up to 40 kg/cm^2. The reactions were carried out at 90°C for 1 hr, (or at 110°C for 3 hr) under vigorous agitation. The products were analyzed by isolation and identification or determined by gas chromatography.

The results are shown in Tables 1–4. In Table 1, the results of hydrogenation reactions of butadiene are shown. The reactions were carried out at 90°C for 1 hr. For Catalyst Systems 6, 7, and 8, hydrogenation was much retarded, and lower conversion (9.1–28.0%) and smaller content (0.3–2.8%) of the saturated hydrocarbon (butane) in the reaction products were obtained, than with the CoCl$_2$-AlEt$_3$ or Co(acac)$_2$-AlEt$_3$ catalyst systems (*1*, *2*), for which 72.1–80.7% conversion and 50.1–75.3% of butane content were obtained. When the reaction was carried out at higher temperature (110°C) for a longer time (3 hr), as shown in Table 2, conversion of butadiene was almost equal with all catalyst systems (1–8), but the content of butane in the reaction products was much decreased with Catalysts Systems 6–8, as compared with Catalysts Systems 1

TABLE 2

Hydrogenation of Butadiene by Cobalt Complex–AlEt$_3$ Catalyst Systems[a]

Catalyst Systems[b]	Conversion (%)	Content (%)			
		1-Butene	*cis*-2-Butene	*trans*-2-Butene	Butane
1	81.4[c]	0.2	6.3	0.2	93.3
2	82.3[c]	2.8	6.8	0.5	89.9
3	86.2[c]	1.7	12.3	0.4	85.6
4	89.1	1.8	12.4	1.3	84.5
5	85.1	8.4	27.8	7.6	56.2
6	84.0	29.2	57.4	11.2	8.2
7	78.9	41.3	42.9	11.2	4.6
8	79.4	41.7	42.4	9.5	6.4

[a] The hydrogenation reactions were carried out at 110°C for 3 hr under a hydrogen pressure of 40 kg/cm^2.

[b] Catalyst Systems 1–8 and solvent used were the same as in Table 1; see footnote *b*.

[c] Oligomerigation also occurred. In Tables 1 and 2, 75–85% of cyclododecatriene, 12–20% of vinylcyclohexene, and 3–5% of cyclooctadiene were included in oligomers.

TABLE 3
HYDROGENATION OF ISOPRENE BY COBALT COMPLEX–$AlEt_3$ CATALYST SYSTEMS[a]

Catalyst Systems[b]	Conversion (%)	Content (%)			
		3-Methyl-1-butene	2-Methyl-2-butene	2-Methyl-1-butene	2-Methylbutane
1	88.9	10.3	15.2	9.8	64.7
2	79.8	3.6	31.7	21.4	43.3
3	63.5	0.1	40.7	21.0	38.2
4	42.6	11.2	60.7	21.8	6.1
5	35.7	10.4	59.5	26.5	3.6
6	25.9	16.2	64.6	17.8	1.4
7	18.4	26.2	66.8	6.5	0.5
8	16.9	18.1	68.4	13.2	0.3

[a] The hydrogenation reactions were carried out at 90°C for 1 hr under the hydrogen pressure of 40 kg/cm^2; 6.2 g of isoprene was used in each experiment.

[b] Catalyst systems 1–8 and solvent were same as in Table 1; see footnote *b*.

and 2, indicating that the hydrogenation of butane to butane was conspicuously retarded by the coordination from the ligands to the cobalt(II) metal orbital. In Tables 3 and 4, the results of hydrogenation of isoprene by the same catalyst systems (1–8) as above, are shown. The same tendency was observed as in the hydrogenation of butadiene, also indicating that the hydrogenation of methyl-1-butene or methyl-2-butene to methylbutane was much retarded by the coordination from the ligands. In both hydrogenation reactions, by the addition of PPh_3 to the binary catalyst system of $CoCl_2$–$AlEt_3$ or $Co(acac)_2$–$AlEt_3$, the reactions were retarded to some extent, but not so much as that in Catalyst Systems 6–8. No distinguishable change was observed in the product distributions when triphenylphosphine was added.

The reaction mechanism of the hydrogenation was postulated as described (*1*) by Sloan, Matlack, and Breslow, as follows. The reaction is initiated by alkylation of the cobalt metal derivative by aluminum triethyl (1). This step is followed by hydrogenolysis of the cobalt–alkyl bond formed to yield a cobalt hydride (2), which then adds to butadiene (isoprene) or butene (methylbutene) forming a new cobalt–carbon bond (3). Hydrogenolysis of the latter yields butene (methylbutene) or butane (methylbutane) with regeneration of the cobalt hydride (4).

$$Et_3Al + CoX_n \rightarrow Et_2AlX + EtCoX_{n-1} \qquad (1)$$

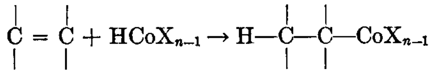
TABLE 4
HYDROGENATION OF ISOPRENE BY COBALT COMPLEX–$AlEt_3$ CATALYST SYSTEMS[a]

Catalyst Systems	Conversion (%)	Content (%)			
		3-Methyl-1-butene	2-Methyl-2-butene	2-Methyl-1-butene	2-Methylbutane
1	94.8	—	0.7	0.2	99.1
2	96.5	1.2	7.1	2.1	89.6
3	95.0	1.5	6.8	3.4	88.3
4	93.8	1.6	55.3	3.1	40.0
5	84.9	8.8	47.3	11.2	32.7
6	76.3	2.7	64.3	26.8	6.2
7	61.5	2.1	74.8	19.1	4.0
8	66.6	2.1	76.7	18.1	3.1

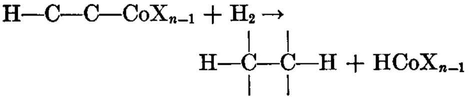
[a] The hydrogenation reactions were carried out at 110°C for 3 hr under a hydrogen pressure of 40 kg/cm^2; 6.2 g of isoprene was used in each experiment.

[b] Catalyst Systems 1–8 and the solvent used were same as in Table 1; see footnote *b*.

$$\mathrm{EtCoX}_{n-1} + \mathrm{H}_2 \rightarrow \mathrm{C}_2\mathrm{H}_6 + \mathrm{HCoX}_{n-1} \qquad (2)$$



$$\mathrm{C{=}C} + \mathrm{HCoX}_{n-1} \rightarrow \mathrm{H{-}C{-}C{-}CoX}_{n-1} \qquad (3)$$



$$\mathrm{H{-}C{-}C{-}CoX}_{n-1} + \mathrm{H}_2 \rightarrow \mathrm{H{-}C{-}C{-}H} + \mathrm{HCoX}_{n-1} \qquad (4)$$

On the other hand, selective hydrogenation of butadiene to butene by pentacyanocobaltate(II) was studied by Kwiatek (*5*). He postulated a reaction intermediate of isomeric α-butenyl complex in equilibrium with the π-allylic structures shown below.

From the above experimental results, the following were presumed: In cobalt(II) complex–$\mathrm{AlEt_3}$ catalyst systems (6, 7, 8), the coordination of olefins to cobalt metal [which was considered as the prereaction step of reaction (3)] was hindered by the ligands ($\mathrm{PPh_3}$, $\mathrm{POPh_3}$, or Py) already coordinated, and the cobalt–carbon bonds once formed [in step (3)] were stabilized to the same extent. Therefore, reactions (3) and (4) were much retarded; hydrogenation of monoolefins to the saturated derivatives was hindered the most. When the reactions were continued at higher temperature for longer times, the ligands were released from the element, making olefin coordination easy, and the reactions proceeded as shown in Table 2 and Table 4.

The results would suggest the possibility of selective hydrogenation of diolefins to monoolefins with Ziegler type catalyst systems by proper coordination from ligands to transition metals and by proper reaction conditions.

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