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CODIMERIZATION OF BUTADIENE AND ETHYLENE

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SUMMARY

The catalytic system $CoCl_2$/1,2-bis(diphenylphosphino)ethane/Et_3Al, in 1,2-dichloroethane, shows high activity and selectivity for the production of *cis*-1,4-hexadiene from butadiene and ethylene. The temperature of reaction appears to be critical; between 80° and 110° *cis*-1,4-hexadiene is formed in high yield whereas below 80° more ethylene than butadiene is consumed, with the result that C_8 compounds are produced. Above 110° 1,4-hexadiene is isomerized to 2,4-hexadiene.

A yield of 8×10^4 moles of 1,4-hexadiene per mole of $CoCl_2$ has been obtained at a rate of formation of the diene of 8 $mol \cdot l^{-1} \cdot h^{-1}$.

The catalytically active species is probably an octahedral complex of a cobalt-(I) hydride with Et_3Al. A reaction scheme is proposed.

1. INTRODUCTION

The codimerization of butadiene and ethylene to obtain 1,4-hexadiene has been frequently reported in the literature (see Table 1). Of the catalytic systems cited the one used by Iwamoto *et al.* appeared to be the most promising; it was therefore chosen for the present mechanistic study.

TABLE 1

CODIMERIZATION OF BUTADIENE AND ETHYLENE

Authors	Catalyst	Conditions	Conversion[a] (%)	Yield 1,4-hexadiene[b] (%)
Lindsey *et al.*[1]	$RhCl_3$	Alcohol 50° $C_4/C_2 = 1$ (batch)	80	67
Miller *et al.*[2]	$NiCl_2$, Bu_3P i-Bu_2AlCl	Toluene 20° 70 atm	33	65
Iwamoto *et al.*[3,4]	$CoCl_2$, Diphos Et_3Al	Toluene 80° 50 atm	99.4	90

[a] Referred to butadiene. [b] Referred to total products.

The Japanese authors used toluene as solvent for the system $CoCl_2$/Diphos/Et_3Al [Diphos = 1,2-bis(diphenylphosphino)ethane]. It is, however, known that alkylation reactions of transition metal salts with aluminum alkyls are faster and more complete in halogenated solvents than in aromatics[5]. Moreover the catalyst precursor, *i.e.* the complex $CoCl_2 \cdot$Diphos, is insoluble in toluene. Both these facts favour the use of 1,2-dichloroethane as solvent.

The Japanese authors also recently used 1,2-dichloroethane as solvent for the codimerization, but emphasizing its disadvantages[4]. Since our results show that these difficulties can be overcome, and the yields obtained are by far higher than those reported for toluene, data and considerations given in the present paper refer exclusively to runs carried out in this halogenated solvent.

2. THE CODIMERIZATION REACTION

The mixture of catalyst solution and butadiene is heated in an autoclave. At temperature T_1, some 30–50° below the reaction temperature T_2, ethylene is introduced under pressure. The temperature of the autoclave is then raised to T_2. The reaction is always preceded by a short induction period. After this period (3–5 min), reaction sets in, and the ethylene pressure drops rapidly. The latter has therefore to be adjusted continuously.

Some results are given in Table 2. For comparative purposes, run No. 1 may be taken as a standard. The ethylene was introduced at an autoclave temperature $T_1 = 50°$. At the end of the induction period the mixture had reached the reaction temperature, $T_2 = 100°$.

A decrease in the Et_3Al concentration results in an increase in selectivity, but at the cost of total conversion (runs 2 and 3). An increase in cobalt concentration by a factor of 10 does not improve the results at all (run 4). An increase in butadiene concentration, however, has a favorable effect on the selectivity (run 5). A considerable improvement in selectivity can also be obtained if the reaction mixture is heated to

TABLE 2

THE CODIMERIZATION OF BUTADIENE AND ETHYLENE, CATALYZED BY $CoCl_2 \cdot 2$Diphos-Et_3Al IN 1,2-DICHLOROETHANE

Ethylene: 30 kg/cm^2; reaction time: 1 h; $T_2 = 100°$.

Run No.	[Co] × 10^3 (mol/l)	[Et_3Al] × 10^3 (mol/l)	Butadiene (mol/l)	Conversion (%)[a]	1,4-Hexadiene (%)[b]	Other C_6 + C_8 (%)[b]	Polymer + oligomer. (%)[b]
1[c]	0.1	35	6.2	98	84	15	1.0
2[c]	0.1	7	6.2	83	91	4	5.0
3[c]	0.1	3.5	6.2	6	100	–	–
4[c]	1.0	45	6.2	94	84	14	2.0
5[c]	0.1	35	8.3	98	94.5	5	0.5
6[d]	0.1	35	6.2	95	98	2	<0.5
7[e]	0.1	35	6.2	98	48	50	2.0
8[c,f]	0.1	35	6.2	98	91	9	<0.5
9[c,f]	0.1	35	6.2	98	87	9	4.0

[a] Referred to the charged butadiene. [b] Referred to total yield. [c] $T_1 = 50°$. [d] $T_1 = 70°$. [e] $T_1 = 30°$. [f] See text.

70° before the ethylene is introduced (run 6). If, however, ethylene is introduced at 100°, the reaction temperature cannot be controlled, and undesired side products are formed in prohibitive amounts.

A negative influence is observed if the ethylene is introduced at 30°, since reaction following the induction period sets in at 70° (run 7). Product analysis showed that the ethylene consumption was 1.5 times the quantity required by stoichiometry based upon a 1/1 reaction with butadiene. Mass spectra of the products are consistent with a ratio of C_6/C_8 of about 1/1, *i.e.* the fraction cited in column 7 of Table 3 is predominantly C_8 in this case.

Finally the isomerization potential of the system was checked in runs 8 and 9. After one hour under standard conditions (*cf.* run 1) the autoclave was vented to eliminate the ethylene, and the reaction mixture was heated in the autoclave for one more hour at 60° (run 8) and at 100° (run 9). Evidently 1,4-hexadiene is not isomerised under these conditions. At $T \geqslant 120°$, however, isomerization is observed.

For comparative purposes, the results obtained by the Japanese workers with the same catalytic system, but in toluene[4], are given in Table 3. (The Japanese data have been converted to the same units as used in Table 2.) In the most favorable case (Table 3, run 3) a yield of 225 kg of 1,4-hexadiene per mol of $CoCl_2 \cdot 2$ Diphos per hour was obtained for the toluene system, whereas in the 1,2-dichloroethane system reported here, up to 6300 kg of 1,4-hexadiene per mol $CoCl_2 \cdot 2$ Diphos per hour was obtained (Table 2, run 5).

TABLE 3

RESULTS OF IWAMOTO AND YUGUCHI[4]

Solvent: toluene. $T = 80–90°$.

$[Co] \times 10^3$ (mol/l)	$[Et_3Al] \times 10^3$ (mol/l)	Time (h)	Butadiene (mol/l)	P(Et) (kg/cm^2)	Conversion (%)	1,4-Hexadiene (%)
0.98	41	2	10.0	25	61.4	97
0.70	28	5	10.8	50	44.5	90.5
0.98	70	2	6.2	55	99.4	90.2

3. THE ACTIVE SPECIES

$CoCl_2$ is insoluble in 1,2-dichloroethane. On addition of two moles of Diphos per mole $CoCl_2$, however, a bright green, homogeneous solution is obtained in a relatively slow reaction (20–30 minutes at room temperature is required to produce concentrations of the order of 10^{-3} mol/l). The complex is air-stable, and decomposes on addition of strong electron donors (alcohols, ethers, amines, etc.). $CoCl_2 \cdot 2$ Diphos has been previously described in the literature[6], and is paramagnetic.

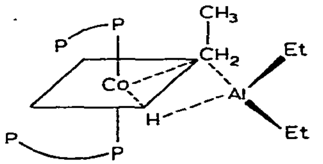
As a Ziegler type catalyst, the active species is formed only when a solution of the transition metal component is brought into contact with a Group III metal-organic compound. If a Grignard reagent is added (alkyl/Co>3), a paramagnetic cobalt(II) hydride is formed, as detected by its EPR signal[7]. At higher alkyl/Co ratios, the solution becomes diamagnetic, *i.e.* the cobalt is reduced. A red colored cobalt(I) hydride species is then observed, as described by Ugo *et al.*[8].

This substance alone does not catalyse the codimerization of butadiene and ethylene. It can, however, be "activated" by aluminum alkyls[8]. If, on the other hand, Et_3Al is used as reducing agent, the solution turns brown, as observed previously[9] during the formation of bridging Ti–Al complexes. This brown solution possesses high catalytic activity.

With the aim of determining the nature of the active species, we investigated the optical spectra of the catalyst solutions. Whereas the cobalt(I) hydride species does not present any special absorption in the range of 10000–26000 cm^{-1}, two broad absorption peaks at 14100 and 17900 cm^{-1} appear in the presence of Et_3Al. These peaks have very low extinction coefficients ($\varepsilon \simeq 50$–100), strongly suggesting the presence of an octahedral complex. On addition of a small amount of THF the absorption disappears and the red color of the cobalt(I) hydride is observed. Further addition of Et_3Al restores the optical absorption. This reaction may be repeated and can be represented as:

$$\text{Cobalt(I) hydride} \underset{\text{THF}}{\overset{Et_3Al}{\rightleftharpoons}} \text{Catalytic complex}$$

These observations are strongly reminiscent of the behaviour of the Ti–Al complexes already mentioned. We therefore suggest that the catalytically active species is an octahedral complex formed from the cobalt(I) hydride and Et_3Al. A possible structure would be (with P–P = Diphos):



(I)

4. THE NATURE OF THE REACTION PATH

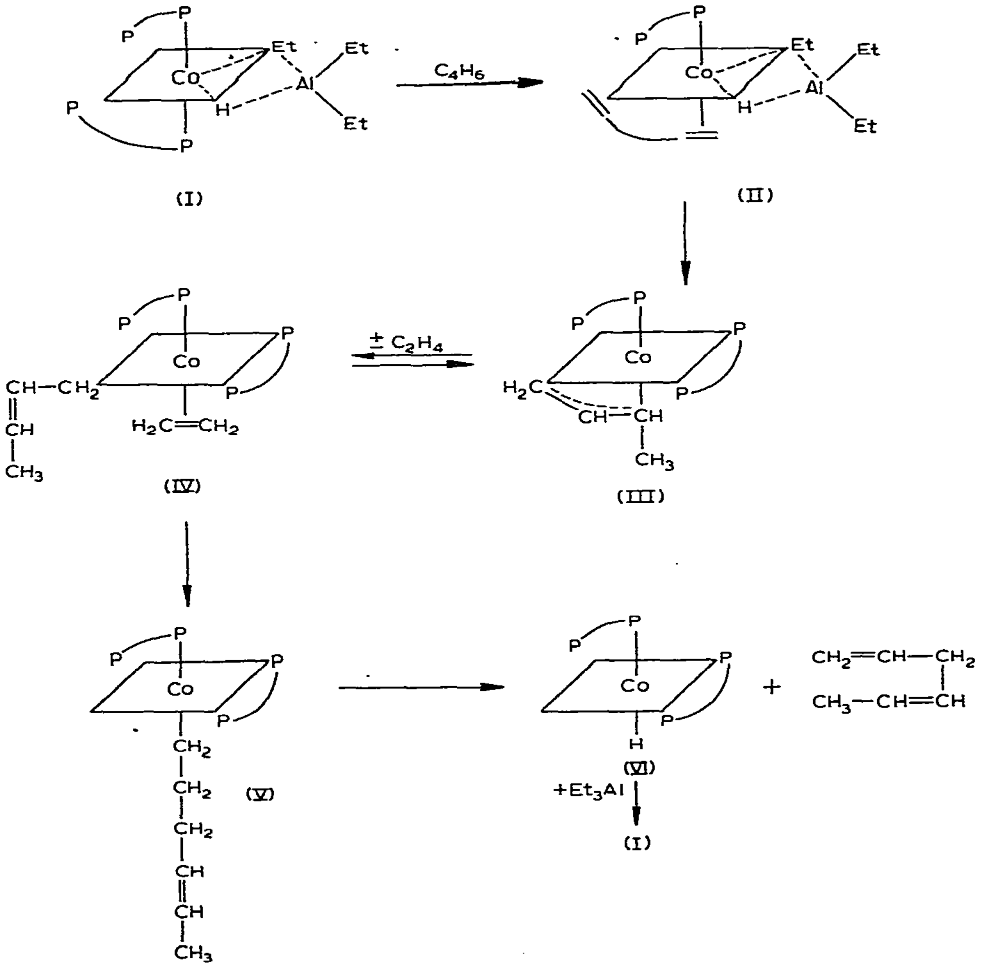
Based on the catalytic complex (I), postulated in the preceding section, the reaction sequence given in Scheme 1 is suggested in order to account for the butadiene-ethylene addition. On mixing butadiene and (I), one Diphos molecule is displaced by butadiene (II). The hydride hydrogen then adds to the butadiene molecule, giving the probably more stable π-allyl ligand, which, according to current ideas, occupies two coordination sites[10] [see (III)]. Since this step leaves the cobalt without a ligand able to form a bridge bond, the Et_3Al is probably displaced from the complex by Diphos. The π-bonded allylic ligand is thus in equilibrium with the σ-bonded 2-butenyl group (IV). Such a σ–π equilibrium has been reported for other allylic transition metal complexes[11,12] and, in the absence of other π-donors is probably displaced to the side of the π-allylic complex. If, however, ethylene is present, the equilibrium is probably shifted to (IV). The two subsequent steps are identical to those postulated for every soluble Ziegler–Natta system[5,9]: Ethylene becomes incorporated, probably via *cis*-migration of the alkenyl group (V). Since the Co–alkyl bond is known to be very unstable, 1,4-hexadiene is released after the abstraction of a β-hydrogen. In this way the hydride (VI) is regenerated and reaction with Et_3Al again gives the catalyst unit (I).

5. SIDE REACTIONS

Traces of 2,4-hexadiene were found in most runs (detected and identified by gas chromatography and NMR, and included in the numbers given in column 7, Table 2). Since the catalyst has been shown not to subsequently isomerize the 1,4-hexadiene already formed at this temperature, one must conclude that isomerization occurs to a small extent before the hexadiene leaves the catalytic complex. The reaction path (V) → (VI) in Scheme 1 probably includes an intermediate state (VII), with the newly formed double bond still π-complexed to the cobalt (see Scheme 2; for the sake of simplicity, only the relevant ligands to Co are written).

SCHEME 1

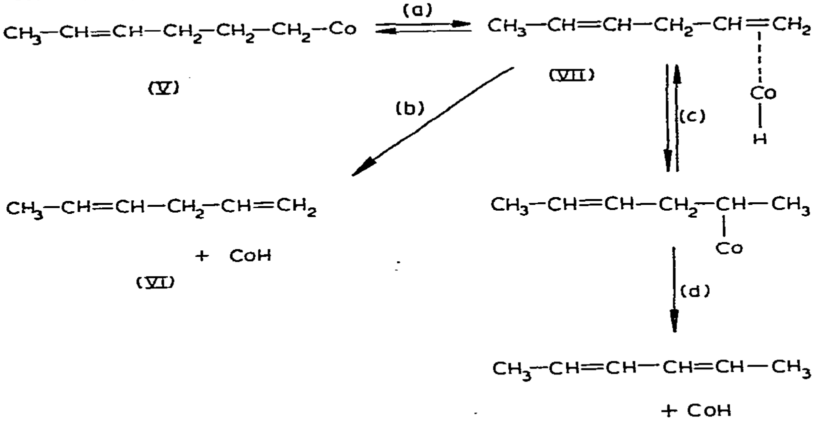
REACTION SEQUENCE



Complex VII is thought to be highly unstable at 100°, so that at this temperature predominantly 1,4-hexadiene is obtained by reaction path (b). At lower temper-

SCHEME 2

ISOMERIZATION



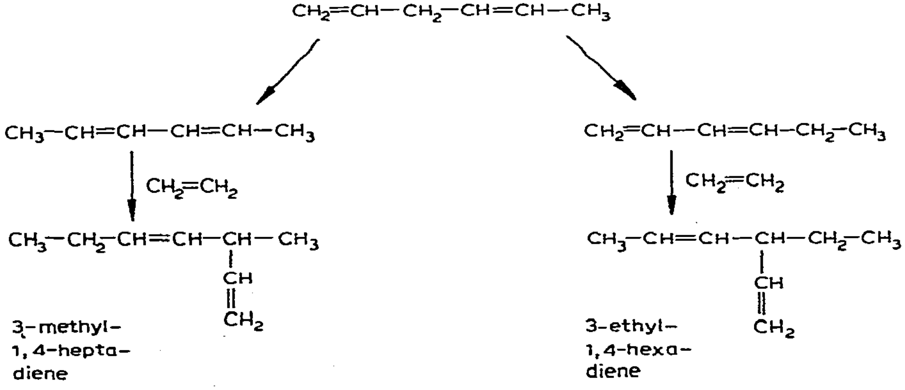
ature, however, intermediate (VII) may be more stable, and isomerization via equilibrium (c) and reaction (d) becomes more important. It should be borne in mind that $\sigma \rightleftarrows \pi$ coordination equilibria like (a) and (c) are well established in other transition metal olefin systems[5,13,14] and are thus also plausible in the present case.

Furthermore, a considerable amount of C_8 compounds was found at lower temperature (see run 7, Table 2), and were shown to be made up of one butadiene and two ethylene molecules. In order to be able to add a second ethylene molecule, the hexadiene must form an allylic ligand, according to the reaction scheme outlined in the preceding section (Scheme 1). In other words, the formation of C_8 compounds has to be preceded by isomerization of the 1,4-hexadiene to conjugated dienes. Addition of a second ethylene molecule would then give 3-methyl-1,4-heptadiene (starting from the 2,4-isomer), and 3-ethyl-1,4-hexadiene (starting from the 1,3-isomer, which may proceed from reactions similar to those given in Scheme 2) (see also ref. 15).

The C_8 fraction of run 7 has not been investigated in detail, but the formation

SCHEME 3

FORMATION OF C_8 DERIVATIVES



of the two C_8 isomers from butadiene and ethylene has been reported in the literature, although in this case a rhodium catalyst was used[1].

From Schemes 2 and 3 it follows then, that in order to mininise the formation of 2,4-hexadiene and C_8 derivatives: two factors are important:

(1). High temperature in order to rapidly remove the 1,4-hexadiene from the complex and thus avoid further reaction. The optimum is around 100° since at $T \geqslant 120°$, subsequent isomerization to 2,4-hexadiene becomes important.

(2). High butadiene concentration, so that the butadiene competes successfully with the hexadienes for the coordination sites.

Consistent with these expectations, highest yield and selectivity have been found in runs 5 and 6 in Table 2.

6. EXPERIMENTAL

(a). *Equipment*

An autoclave "Magne Drive" supplied by Autoclave Engineers, Pa, of 0.3 l capacity and provided with a dismountable heating jacket was used. Ethylene glycol from a thermostatted bath was used as a circulating heating fluid.

(*b*). *Reagents*

Butadiene (Research grade, Phillips Petroleum, Bartlesville Oklahoma), ethylene (Polymerization grade, Monsanto Chemicals Ltd., Fawley Works, England), Et_3Al (Schering AG., Werke Bergkamen, Germany) and Diphos (Strem Chemicals Inc., St. Danvers, Mass., U.S.A.) were used without further purification. $CoCl_2$ (Fluka AG, Buchs, Switzerland) was dried under vacuum for 2 h at 120° before use. 1,2-Dichloroethane (Fluka AG, Buchs, Switzerland) was boiled under reflux with CaH_2 and distilled in *vacuo* just prior to use.

(*c*). *Mode of operation*

The autoclave was connected to the vacuum line, evacuated, and cooled to −80°. Butadiene was then distilled in from a graduated container at about −20°. The complex solution, $CoCl_2 \cdot 2$ Diphos in 1,2-dichloroethane was prepared separately in a flask by distilling the necessary amount of solvent onto an aliquot of a mother complex solution. The corresponding amount of Et_3Al was then added under argon with a medical syringe. The liquid (yellow at this dilution) was injected under argon into the autoclave. The latter was then introduced into a jacket and heated rapidly to the desired temperature. Ethylene was then introduced (T_1) and the autoclave was brought to the reaction temperature (T_2). The ethylene pressure was maintained between 30 and 25 kg/cm^2 during the reaction. After one hour the autoclave was cooled down to 5° and vented through a trap cooled with methanol and CO_2, and the volume of the condensed liquid was measured. After opening, the volume and weight of the reaction solution were determined. The appearance of the liquid had not changed, but both volume and weight had increased. The liquid was washed with water to remove salts, and then distilled to separate oligomers and polymers. Distillates were qualitatively and quantitatively analysed by VPC, IR, NMR and MS. Authentic samples of 1,4-hexadiene and *cis,cis*-2,4-hexadiene were supplied by "Chemical Samples Co." Columbus, Ohio (U.S.A.).

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