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Enhanced Catalytic Activity of a Nickel Complex for the Dimerization of Isoprene by the Addition of Cyclic Amines

ISAO MOCHIDA, KAZUNORI KITAGAWA, HIROSHI FUJITSU, AND KENJIRO TAKESHITIA

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

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Catalytic dimerization of isoprene with a nickel complex is re-investigated in the presence of cyclic amines. These enhance the formation of cyclic dimers such as dipentene and dimethylcyclootadiene. Small amounts of water as a co-catalyst cause the system to show high activity. Structure of the amine influences the activity and selectivity of the dimer formation, via electronic and steric effects. The mechanism of enhanced activity by the cyclic amines is discussed.

INTRODUCTION

Catalytic dimerization reactions of conjugated dienes have been intensively studied (*1*). Nickel ion, in as phosphine complexes, shows interesting features (*2*). Addition of certain amines significantly accelerates the reaction rate with selectivity between linear and cyclic dimers being controlled by using alkyl or conjugated amines (*3*). Further, a requisite amount of water as co-catalyst causes the catalyst system to show a high activity (*4*). The co-catalyst considerably modified the catalytic process with the amines, enhancing the dimerization activity of the nickel complex.

This present study re-investigates the enhanced catalytic activity by cyclic amines in the presence of requisite quantities of water and correlates the catalytic enhancement with the structure of cyclic amines.

EXPERIMENTAL

$Ni(PPh_3)_2Cl_2$ was prepared (*5*). Isoprene was dried over anhydrous calcium chloride and a molecular sieve and distilled under nitrogen, both distillations being made immediately prior to experimentation to control water content. The dimerization reaction was carried out in a sealed glass tube that was kept in an oil bath at a constant temperature of 80 ± 0.1°C for 1 or 24 hr. Typically, the glass tube flushed with nitrogen was charged with 0.5 mmol of $Ni(PPh_3)_2Cl_2$, 1.5 mmol of $NaBH_4$, 1 ml of isoprene, 1 ml of amine, 5 ml of benzene as a solvent, and 1 ml of *n*-pentane (internal standard). Controlled amounts of water were injected with a microsyringe, and the contents were frozen in liquid nitrogen and then outgased before sealing the tube. After reaction, the contents were washed with 1 *N* HCl to remove the amine from the products. A mixture of resultant isoprene oligomers was analyzed by a gas chromotograph using a column packed with Apiezon Grease L. Identification of the dimeric products was based on previous results (*3*).

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TABLE 1

Effects of the Co-catalysts[a]

Co-catalyst	Yield(%)					DMCOD/DP	Conversion (%)
	DMOD	DMOT	DP	DMCOD	Others		
None	0.3	0.4	0.6	0.1	0.1	0.16	1.5
H_2O	25.9	2.2	12.2	31.5	21.9	2.10	93.7
CH_3OH	0.4	1.2	6.5	0.2	2.5	0.03	11.0
C_2H_5OH	0.9	3.3	14.4	4.3	1.5	0.3	24.5
iso-C_3H_7OH	0.5	0.3	1.1	—	—	~0	1.9
n-$C_3H_7NH_2$	0.1	0.4	1.3	0.1	0.1	0.07	1.5
CH_3COOH	7.7	0.1	5.4	0.6	11.2	0.1	25.0
C_6H_5OH	0.3	0.1	3.2	—	0.8	~0	4.9
$C_6H_5NH_2$	—	1.2	2.0	—	Trace	~0	3.8

[a] $Ni(PPH_3)_2Cl_2$, 0.5 mmol; $NaBH_4$, 1.5 mmol; co-catalyst, 1.5 mmol; isoprene, 1 ml; *n*-pentane, 1 ml; benzene, 5 ml; 3-methylpyridine, 1 ml; reaction temperature, 80°C; reaction time, 24 hr.

RESULTS AND DISCUSSION

Enhanced Activity of $NiCl_2(PPh_3)_2$–$NaBH_4$ by 3-Methylpyridine in the Presence of Co-Catalyst

The enhanced catalytic activity of $NiCl_2(PPh_3)_2$–$NaBH_4$ for dimerization reactions of isoprene by cyclic amines (*3*) requires some polar substance to be present as a co-catalyst (*4*). Table 1 shows the effects of the co-catalyst when 3-methylpyridine is the enhancing amine. Of the co-catalysts, water is extraordinarily effective. The principal products obtained in the presence of 3-methylpyridine were dimethylcyclooctadienes (DMCOD), dipentene (DP), and dimethyloctadienes (DMOD). Dimethyloctatriene (DMOT), however, which was the principal product when alkylamines were used, is a minor product (*3*). Ethanol and acetic acid were less effective than water.

Conversions and yields of products with reaction time, are shown in Figs. 1 and 2, using water or ethanol as co-catalyst,

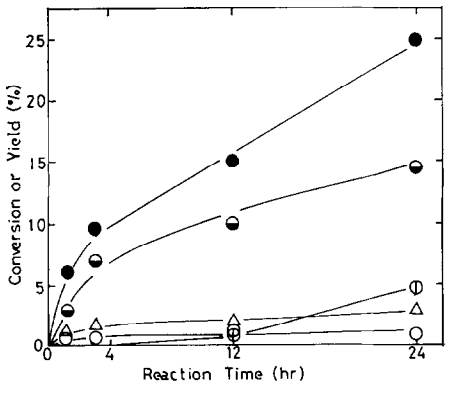

FIG. 1. Reaction profile of dimerization catalyzed by $Ni(PPh_3)_2Cl_2$–$NaBH_4$–3-methylpyridine in the presence of catalyst water. $Ni(PPh_3)_2Cl_2$, 0.5 mmol; $NaBH_4$, 1.5 mmol; 3-methylpyridine, 1 ml; H_2O, 1.5 mmol; isoprene, 1 ml; *n*-pentane, 1 ml; benzene, 5 ml; reaction temperature, 80°C. ●, conversion; ○, DMOD; △, DMOT; ◒, DP; ⊕, DMCOD.

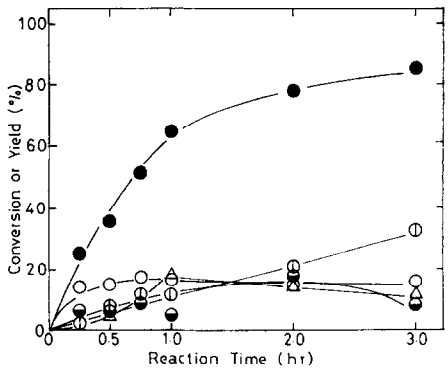

FIG. 2. Reaction profile of dimerization catalyzed by $Ni(PPh_3)_2Cl_2$–$NaBH_4$–3-methylpyridine in the presence of catalyst ethanol. The conditions and symbols are the same as those in Fig. 1 except that 1.5 mmol of ethanol was used instead of the same amount of water.

respectively. With water, the yield of DMCOD increased linearly with the reaction time until completion. Yields of DMOT and DP, however, decreased with the time after passing through a maximum, indicating that they may be converted to DMCOD. For ethanol, there were significant differences. Conversions reached only 25% and showed no change with increasing reaction time. The product distributions were also different. With ethanol, DP was the principal product with low conversion even after 24 hr. The life-time or turnover number of the catalyst should be improved for industrial applications. The authors have no definite explanation for the co-catalytic role of water at present. Recently, some aprotic polar solvents such as HMPA were shown to provide a high catalytic activity without any water. This fact suggests that water may help the reduction of nickel ion in the nonpolar solvent.

Effects of amine concentrations on conversions and product distributions are shown in Fig. 3. Although the yields of all products increased with additions of amine, the relative yields of DMCOD and DMOD were sensitive to the concentrations of the amine. Yields reached maximum values of 35 and 25%, respectively, at the amine/Ni ratio of 20, but decreased sharply at a higher ratio.

Enhanced Activity of Various Cyclic Amines

As activity enhancement by cyclic amines is dependent on structure, some 28 cyclic amines, essentially pyridine derivatives, were examined because Swift *et al.* (*6*) reported an excellent catalyst of iron–N-donor complex and discussed the electronic and steric factors of ligands. Activity enhancement is summarized in Tables 2–6, for variable water contents and reaction times. The dependence on activity on water content (for 24-hr duration) can be deduced from Tables 2, 4, and 6 for a series of cyclic amines. For all amines the maximum activity occurred with additions of 1.5 mmol of water, i.e., three times the concentration of nickel complex.

The type of substituent and location in the pyridine ring influences the activity, suggesting both steric and electron effects (*3*).

Substitutions in β or γ positions cause small steric effects so that enhancement is

TABLE 2

Effects of Water on the Catalytic Activity Enhanced by Amines[a]

	Conversion (%)	Yield (%)					DMCOD/DP
		DMOD	DMOT	DP	DMCOD	Others	
Pyridine	31.2	12.5	2.3	0.3	6.5	9.6	22
2-Methylpyridine	16.2	2.9	1.6	9.7	0.9	1.1	0.09
3-Methylpyridine	10.9	0.7	—	5.6	4.6	—	0.80
4-Methylpyridine	22.9	4.4	1.8	7.1	4.4	5.2	0.62
2-Ethylpyridine	5.8	0.6	1.0	3.2	0.8	0.2	0.25
3-Ethylpyridine	12.2	2.1	2.2	1.2	4.2	2.5	3.5
4-Ethylpyridine	48.2	4.0	3.2	12.3	22.5	6.2	1.8
2-*n*-Propylpyridine	10.9	3.5	—	4.2	0.2	3.0	0.04
4-Isopropylpyridine	30.6	4.8	3.5	3.6	15.2	3.5	4.2
4-t-Butylpyridine	34.6	10.7	2.1	5.6	7.6	8.6	1.4
2,4-Dimethylpyridine	45.6*	1.8	9.8	3.2	23.2	7.6	7.3
3,4-Dimethylpyridine	30.1	7.8	—	2.3	10.2	9.8	4.5

[a] $Ni(PPh_3)_2Cl_2$, 0.5 mmol; $NaBH_4$, 1.5 mmol; H_2O, 0.5 mmol; amine, 1 ml; other reaction conditions are the same as those in Table 1.

TABLE 3

Effects of Pyridine and its Derivatives with Substituents at β and/or γ Positions on Dimerization[a]

Amines	Conversion (%)	Yield (%)					DMCOD/DP	Yield of cyclic dimers (%)
		DMOD	DMOT	DP	DMCOD	Others		
Pyridine	28.4	12.3	0.9	3.7	3.7	7.9	1.00	7.4
3-Methylpyridine	64.6	17.5	18.9	5.5	14.1	8.6	2.56	19.6
4-Methylpyridine	38.5	5.6	11.2	6.8	9.8	5.1	1.44	16.6
3-Ethylpyridine	35.5	10.8	8.5	4.2	9.1	2.9	2.17	13.3
4-Ethylpyridine	24.4	11.1	0.1	0.4	0.3	12.5	0.75	0.7
4-Isopropylpyridine	32.5	7.2	6.8	3.4	11.5	3.7	3.38	14.9
4-t-Butylpyridine	26.8	8.5	1.9	7.1	5.2	4.1	0.73	12.3
3,4-Dimethylpyridine	64.3	9.1	29.9	5.1	15.6	4.6	3.06	20.7
3,5-Dimethylpyridine	12.4	3.6	1.5	1.6	4.1	1.7	2.56	5.7
3-Chloropyridine	6.9	4.8	—	2.1	—	Trace	—	2.1
4-Chloropyridine–HCl[b]	3.1	1.1	0.3	1.7	—	—	—	1.7
3-Cyanopyridine	7.5	2.1	1.2	4.2	—	—	—	4.2
4-Cyanopyridine	2.3	1.1	—	1.2	—	Trace	—	1.2
3-Aminopyridine	16.3	3.2	1.1	1.8	—	2.1	—	1.8
4-Aminopyridine	16.5	2.8	1.0	2.1	5.2	—	—	7.3
3-Hydroxypyridine	25.4	11.2	4.6	1.7	1.1	3.9	0.65	2.8
4-Hydroxypyridine	2.2	2.2	—	—	—	—	—	—

[a] $Ni(PPh_3)_2Cl_2$, 0.5 mmol; $NaBH_4$, 1.5 mmol; H_2O, 1.5 mmol; isoprene, 1 ml; *n*-pentane, 1 ml; amine, 10 mmol; benzene, 5 ml; reaction temperature, 80°C; reaction time, 1 hr.

[b] 4-Chloropyridine hydrochloride.

TABLE 4

Effects of Pyridine and its Derivatives with Substituents at β and/or γ Positions on Dimerization[a]

Amines	Conversion (%)	Selectivity (%)					DMCOD/DP	Yield of cyclic dimers (%)
		DMOD	DMOT	DP	DMCOD	Others		
Pyridine	79.6	40.6	11.4	8.4	23.7	15.9	2.82	25.6
3-Methylpyridine	93.7	27.6	2.3	13.0	33.6	23.5	2.58	43.7
4-Methylpyridine	72.4	7.8	35.4	9.9	28.4	17.8	2.87	27.7
3-Ethylpyridine	91.6	12.5	22.8	11.1	30.9	22.8	2.78	38.5
4-Ethylpyridine	90.3	8.2	7.3	26.0	44.2	14.2	1.70	63.4
4-Isopropylpyridine	72.5	13.5	7.0	14.4	46.9	18.3	3.26	44.4
4-t-Butylpyridine	47.3	25.6	—	17.1	25.3	39.3	1.48	20.1
3,4-Dimethylpyridine	93.5	15.7	—	10.0	28.5	43.3	2.85	36.0
3,5-Dimethylpyridine	31.1	38.3	—	23.0	21.7	17.1	0.94	13.9
3-Chloropyridine	35.7	—	13.1	7.5	—	19.4	—	24.1
4-Chloropyridine[b]	7.2	34.7	15.3	50.0	—	—	—	3.6
3-Cyanopyridine	5.8	17.8	5.6	43.2	7.8	25.6	0.18	3.0
4-Cyanopyridine	11.5	14.0	4.8	47.6	10.3	23.3	0.22	6.7
3-Aminopyridine	45.2	35.0	15.2	4.3	13.1	7.2	3.05	7.9
4-Aminopyridine	50.0	38.0	18.4	5.6	10.2	8.8	1.82	7.9
3-Hydroxypyridine	33.8	66.3	17.8	5.0	—	10.0	—	1.7
4-Hydroxypyridine	10.3	70.2	23.3	3.5	—	3.0	—	0.4

[a] $Ni(PPh_3)_2Cl_2$, 0.5 mmol; $NaBH_4$, 1.5 mmol; H_2O, 1.5 mmol; isoprene, 1 ml; *n*-pentane, 1 ml; amine, 10 mmol; benzene, 5 ml; reaction temperature, 80°C; reaction time, 24 hr.

[b] 4-Chloropyridine hydrochloride.

TABLE 5

Effects of α-Substituted Pyridines on Dimerization[a]

Amines	Conversion (%)	Yield (%)					DMCOD/DP	Yield of cyclic dimers (%)
		DMOD	DMOT	DP	DMCOD	Others		
2-Methylpyridine	46.5	3.4	20.4	2.8	11.6	8.2	4.14	14.4
2-Ethylpyridine	26.8	8.4	0.4	6.7	5.5	5.8	0.82	12.2
2-*n*-Propylpyridine	6.2	—	—	4.3	—	1.9	0	4.3
2,3-Dimethylpyridine	19.1	3.7	2.5	2.0	7.7	3.3	3.85	9.7
2,4-Dimethylpyridine	30.6	6.6	8.5	1.4	5.3	8.9	3.79	6.7
2,5-Dimethylpyridine	41.0	5.5	14.4	3.3	16.8	1.1	5.09	20.1
2,6-Dimethylpyridine	1.6	1.3	—	0.2	—	0.1	0	0.2
2-Chloropyridine	10.5	6.4	—	4.1	—	Trace	0	4.1
2-Cyanopyridine	4.9	2.9	—	1.3	—	Trace	0	1.3
2-Aminopyridine	14.1	4.9	1.5	0.5	0.2	1.8	0.40	0.7
2-Hydroxypyridine	55.0	21.5	7.8	1.3	Trace	2.0	0	1.3

[a] $Ni(PPh_3)_2Cl_2$, 0.5 mmol; $NaBH_4$, 1.5 mmol; H_2O, 1.5 mmol; isoprene, 1 ml; *n*-pentane, 1 ml; amine, 10 mmol; benzene, 5 ml; reaction temperature, 80°C; reaction time, 1 hr.

due to the electronic effects: Substitution in the α position with the strong electron-drawing or releasing groups decreases the activity. Thus, the relative enhancements by cyclic amines can approximately be correlated with values of σ for substituents at the β or γ positions (Fig. 4). Of the substituents, a β-methyl was most effective, the σ value being slightly negative. For 4-aminopyridine and 4-chloropyridine hydrochloride, no correlation was found (Fig. 4). The former amine may accelerate the formation of linear dimers via amino group as well as the cyclic amine. The decreased basicity of hydrochloride may not be adequately reflected in the value of σ of the substituent.

α-Methylpyridines, e.g., 2-methylpyridine, gave activities comparable with 3-methyl- and 4-methylpyridines. The very

TABLE 6

Effects of α-Substituted Pyridines on Dimerization[a]

Amines	Conversion (%)	Selectivity (%)					DMCOD/DP	Yield of cyclic dimers (%)
		DMOD	DMOT	DP	DMCOD	Others		
2-Methylpyridine	91.1	13.6	20.8	7.0	33.1	20.7	4.73	36.5
2-Ethylpyridine	25.7	4.7	7.5	63.2	5.3	19.3	0.08	17.6
2-*n*-Propylpyridine	26.5	22.4	—	35.3	3.4	38.9	0.10	10.3
2,3-Dimethylpyridine	58.3	13.0	6.9	6.0	54.5	19.6	9.08	35.3
2,4-Dimethylpyridine	90.9	5.9	24.6	6.8	42.2	20.5	6.21	44.5
2,5-Dimethylpyridine	91.8	12.4	10.6	8.4	46.6	22.0	5.55	51.4
2,6-Dimethylpyridine	20.2	38.5	5.9	39.2	2.2	14.2	0.06	8.4
2-Chloropyridine	14.5	—	9.8	70.5	—	19.7	~0	10.2
2-Cyanopyridine	28.4	28.2	—	47.2	4.2	20.8	0.09	14.6
2-Aminopyridine	24.1	18.2	31.8	39.6	—	10.4	~0	9.5
2-Hydroxypyridine	57.1	44.3	—	14.4	—	6.3	~0	8.2
Quinoline	30.8	48.1	—	11.4	4.9	35.7	0.48	5.0

[a] $Ni(PPh_3)_2Cl_2$, 0.5 mmol; $NaBH_4$, 1.5 mmol; H_2O, 1.5 mmol; isoprene, 1 ml; *n*-pentane, 1 ml; amine, 10 mmol; benzene, 5 ml; reaction temperature, 80°C; reaction time, 24 hr.

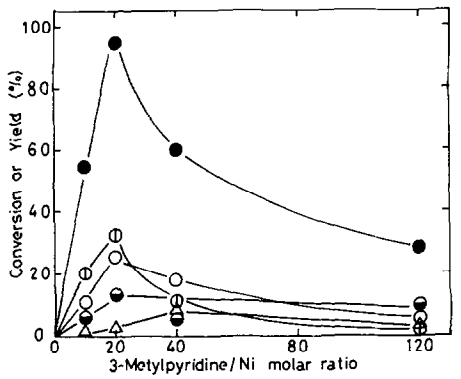

FIG. 3. Effects of the amount of 3-methylpyridine on the catalytic activity of $Ni(PPh_3)_2Cl_2$–$NaBH_4$. The reaction conditions and symbols are the same as those in Fig. 1 except for the variable amount of 3-methylpyridine and the fixed reaction time of 24 hr.

low activity of 2-methylpyridine (*3*) may be attributed to amounts of water present which are below that required for the maximum effect as a co-catalyst. On the other hand, larger groups, e.g., ethyl or *n*-propyl, decrease the activity considerably, quite different from substitutions in the β or γ positions. The second methyl group at the other α position also decreases the activity very much, implying that the two methyl groups may block both sides of the active nitrogen site. Substitution at the β position on the same side as the α substituent on the pyridine ring also decreases the activity to some extent. In contrast, substitution of the second methyl group at β or γ on the opposite side of the ring caused no decrease in activity. Strong releasing or attracting groups at the α position decrease the activity by electronic effects as for the β or γ substitutions.

Product Distribution

Products in catalytic reactions enhanced by the cyclic amines are cyclic dimers of DP and DMCOD, although considerable amounts of DMOD and DMOT are also found. The latter products may result from the action of sodium borohydride (a hydrogen donor) which is present in excess for the reduction of the nickel complex.

Water concentration influences the product distribution, especially for 2-methylpyridine, where a small amount gives a low ratio of DMCOD/DP, and the optimum concentration gives quite a large ratio. The rather random ratios of DMCOD/DP already published may be due to uncontrolled amounts of water in the reaction system.

As described above, some of DP was converted into DMCOD, so that the selectivity between these cyclic dimers depends on the conversion. The conversion, however, is not the only factor influencing selectivity: The structure of the amine is also influential. In Fig. 5, the DMCOD/DP ratios are correlated with conversions (1 and 24 hr) using various cyclic amines with the optimum concentration of water. The data fall into two groups. In the first group, higher DMCOD/DP ratios are shown even

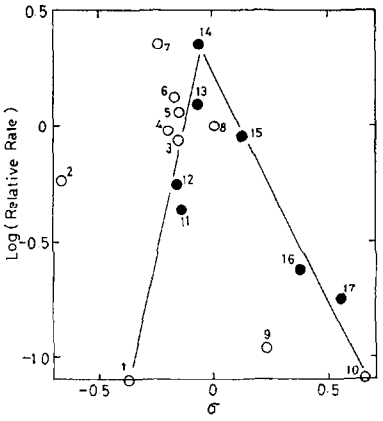

FIG. 4. Relative activity enhancement by pyridine and its derivatives. The reaction conditions are the same as those in Fig. 1 except that different amines were used instead of 3-methylpyridine shown in Fig. 1. (1) 4-hydroxy P, (2) 4-amino P, (3) 4-ethyl P, (4) 4-t-butyl P, (5) 4-isopropyl P, (6) 4-methyl P, (7) 3,4-dimethyl P, (8) pyridine (P), (9) 4-chloro P hydrochloride, (10) 4-cyano P, (11) 3,5-dimethyl P, (12) 3-amino-P, (13) 3-ethyl P, (14) 3-methyl P, (15) 3-hydroxyl P, (16) 3-chloro P, (17) 3-cyano P (pyridine is abbreviated as P). Open and closed circles refer to γ- and β-substituted pyridines, respectively.

at low conversions, rising as high as nine at higher conversions. This group consists of 2-methyl-, 2,3-dimethyl, 2,4-dimethyl-, and 2,5-dimethylpyridines, each of which carries a methyl group at the α position. In the second group the ratios rose from near to zero at low conversion, increasing to three at 90% conversion. The order, 2,3-dimethyl > 2,5-dimethyl > 2-methyl exhibiting increasing ratios of DMCOD/DP, may correspond to increasing steric hindrances. 2,3-Dimethylpyridine induced a rather small catalytic activity, caused by a large steric hindrance as mentioned above. Despite the above comment, the DMCOD/DP ratio of 2,6-dimethylpyridine was very low, its large steric hindrance probably being caused by lack of coordination activity to the catalyst.

Mechanistic Consideration

Heimbach and his co-workers (*2c*) studied the cyclic dimerization of butadiene extensively and proposed a mechanism, where the ring closure of the π-allyl intermediate

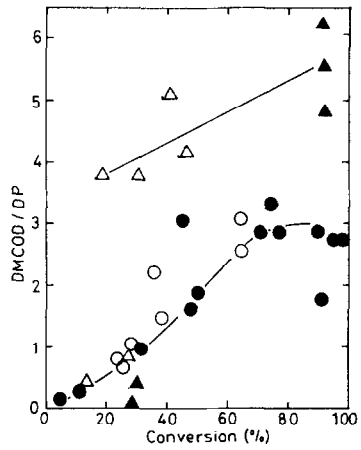

FIG. 5. The change of DMCOD/DP ratio against the conversion. The reaction conditions are the same as those in Fig. 1 except for the variable amine and the reaction times of 1 as well as 24 hr. Closed and open symbols refer to the reaction times of 24 and 1 hr, respectively. Triangle, α- and/or β-substituted pyridine; circle, β- and/or γ-substituted pyridine. Data refer to Tables 3–6.

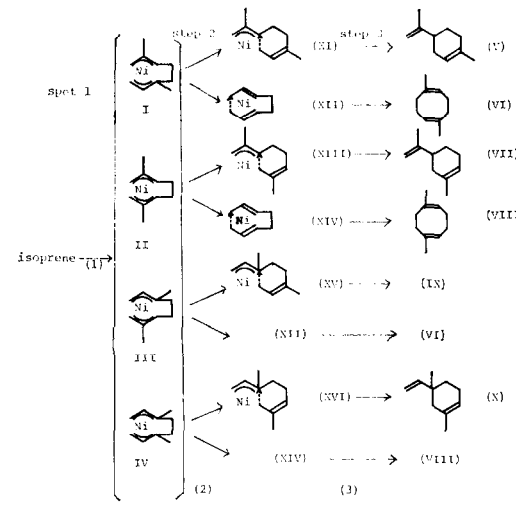

FIG. 6. Reaction scheme for the cyclic dimerization of isoprene (*2c*).

led to cyclic dimers. This reaction scheme is presented in Fig. 6. No IX and X in DP produced may rule out the intermediates III and IV (*3b*).

The dimerization reaction of the present study is of zero order with respect to isoprene, indicating that the coordination of two molecules of isoprene to form the π-allyl intermediate may not be the slow step and that the ring-closure or the removal of the dimeric product is rate-determining. Thus, the amine may work via step 2, where the π-allyl intermediates are transformed into the π-complex. The amine may coordinate the nickel complex to some extent. Diminishing the number of coordination sites of the catalyst ring may accelerate the ring closure of the π-allyl chain into the π-complexes. The coordination of a conjugate amine without a labile hydrogen may help the coordination of cyclic intermediates, whereas the alkyl amine accelerates the formation of the linear dimers through the reversible hydrogen transfer (*3b*).

The strength of coordination of the enhancing amine to the catalyst should be moderate if it is to accelerate the catalytic reaction through this mechanism. Too weak

a coordination may bring about no acceleration in the elimination of the dimerized isoprene. Too strong a coordination would strongly bond to the catalyst sites of nickel ion which would then not be open to the substrate. Thus, the moderate basicity, which is known by the σ value to be slightly smaller than zero, is reasonably assumed to be most effective for the acceleration for the dimerization reaction. The high activity of 3,4-dimethylpyridine compared to 3,5-dimethylpyridine cannot be explained at present. Some secondary steric factor may effect these disubstituted pyridines.

The selectivity between DMCOD and DP is influenced by the extent of the consecutive conversion of DP into DMCOD. Even if this selectivity change is taken into account, some pyridine derivatives with a methyl group at the α position produce DMCOD at extraordinarily high selectivity. Such selectivity can be discussed from a mechanistic aspect. The intermediates after the ring closure which lead to DP or DMCOD should have different steric factors as shown in Fig. 6. The intermediate leading to DMCOD which may coordinate to nickel ion through two π-bonds is assumed to be planar, being separate from the other coordinating ligands. The intermediate to DP with a π-bond, however, is expected to be nonplanar according to Jolly and Wilke (*2b*). The pyridine derivatives with a methyl group at the α position may prefer the planar intermediate to the nonplanar one, because the methyl groups of the ligand may sterically interact with the ring part of the nonplanar intermediate located near the ligand. Thus, the formation of DMCOD becomes selective when bulky cyclic amines were used. Such hindrance should decrease in the order 2,3-dimethyl > 2,4-dimethyl > 2,5-dimethyl $\approx$ 2-dimethyl, coinciding with the decreasing order of selectivity.

The catalytic activity of the nickel phosphine complex for the dimerization of isoprene into a linear or cyclic dimer was found to be increased and controlled by the addition of a suitable amine and an optimum concentration of water. However, the turnover number of the catalyst is too small for practical utilization. Further study to lengthen the catalyst life is necessary.

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