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Electronic and Steric Effects of Amines on the Dimerization of Isoprene Catalyzed by Nickel Complex

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Electronic and steric effects of amines on the dimerization of isoprene catalyzed by bis-triphenylphosphinenickel (II) dichloride-$NaBH_4$ have been studied from the viewpoint of substituent effects. Alkylamines accelerated the formation of linear dimers. The rates of DMOT formation were well correlated with the combination of σ^* and *Es* values of alkyl groups, indicating that the steric as well as electronic factors of the amines may play some roles in the catalytic process of the dimerization. Pyridine and its methyl-substituted derivatives accelerated the cyclic dimerization; however, the activity of γ-picoline was much larger than that of α-picoline, indicating again the importance of the steric effect of the amine. The roles of amine in the dimerization reaction are discussed in terms of the proposed mechanism.

INTRODUCTION

Dimerization reactions of conjugated dienes have been intensively studied using various catalyst systems that contain transition metal ions of various coordination structures (*1*). Nickel ion, especially in its phosphine complexes, is such a metal ion, and a number of studies (*2*) after the pioneer study by Wilke and his co-workers (*3*) suggested the intermediate reaction, the role of the phosphine ligand, the effect of the solvent and reducing reagents, and the mechanism. A protonic solvent accelerates the formation of linear dimers, whereas an aprotic one accelerates that of cyclic dimers (*3, 4*). The present authors (*5*) found that the structure of amines introduced into the catalytic system brought about significant effects on the selectivity and activity of this reaction as catalyzed by the $NiCl_2$-$(PPh_3)_2$-$NaBH_4$ system.

In the present study, such effects were investigated for alkylamines, pyridine, and its derivatives from the viewpoint of substituent effects by the aid of linear free energy relationships (*6*). By using isoprene as the substrate, some details of the reaction mechanism can be discussed from the positions of the methyl groups in the dimers produced as were those of Takahashi *et al.* (*7a*) and Josey (*7b*), because they should be determined at the step of intermediate formation.

EXPERIMENTAL

Reagents. The amines used in the present study are listed in Table 1. They are all of GR grade from Tokyo Kasei Co.

Reaction and products. The dimerization reaction was carried out in a sealed glass tube that was kept in an oil bath at constant temperature (80°). The reacting components consisted of 0.5 mmole $Ni(PPh_3)_2X_2$, 1.5 mmole $NaBH_4$, 1 ml isoprene, 1 ml

[1] I.M.

TABLE 1

EFFECT OF MONO ALKYLAMINES ON THE DIMERIZATION ACTIVITY[a]

	Amine	Conversion	Selectivity				Others[b]
			Linear dimer		Cyclic dimer		
			DMOD	DMOT	DMCOD	DP	
1	n-$PrNH_2$	98.0[c]	16.2	45.0	1.24	5.5	20.9
2	n-$BuNH_2$	86.5	23.8	37.5	11.7	8.3	18.7
3	Iso-$PrNH_2$	86.0	16.0	45.6	15.6	4.7	18.1
4	Iso-$BuNH_2$	73.2	19.3	47.7	11.8	8.8	12.4
5	Sec-$BuNH_2$	24.6	23.2	30.8	21.2	9.7	13.1
6	Tert-$BuNH_2$	8.3	44.2	0.3	14.2	31.2	9.9

[a] Reaction conditions: temp., 80°C; reaction time, 24 hr; $Ni(PPh_3)_2Cl_2$, 0.5 mmole; $NaBH_4$, 1.5 mmole; isoprene, 1 ml; amine, 1 ml; pentane, 1 ml.

[b] Unidentified dimers.

[c] Reaction time: 14 hr.

amine, and 1 ml pentane (internal standard). Identified products from the present study were 2,6-dimethyl-1,3,6-octatriene (DMOT), dimethyloctadienes (DMOD) such as 2, 6-dimethyl-2,6-octadiene, 2,7-dimethyl-1,6-octadine, and 2,6-dimethyl-1,6-octadiene, dimethylcyclooctadiene (DMCOD), and dipentenes (DP; V, VII in Fig. 7). It should be noted that the dimethyloctatriene produced was almost exclusively 2,6-dimethyl-1,3,6-octatriene. Experimental details were described in a preliminary communication (*5*).

Addition products (*8*) were not detected under the present conditions, perhaps because the higher reaction temperature favored the dimerization over the addition reaction, as Heimbach *et al.* (*9*) pointed out, or because the promoting acids were absent (*8*).

RESULTS AND DISCUSSION

Effects of alkylamines. Addition of n-propylamine into the reaction system accelerated the dimerization reaction 20-fold. The effect of amine concentration on the product distribution is shown in Fig. 1; the dependence of DMOT formation on the concentration was marked, whereas the formation of DMOD was rather independent of amine concentration except for quite low concentrations of the amine.

The following facts were found in a previous study (*5*). (1) Two kinds of linear dimers were produced via parallel reactions. (2) The formation of DMOD was complete at an early stage of the reaction, whereas that of DMOT increased with reaction time. (3) The hydrogen used for the formation of DMOD came from $NaBH_4$.

These results suggest that the formation

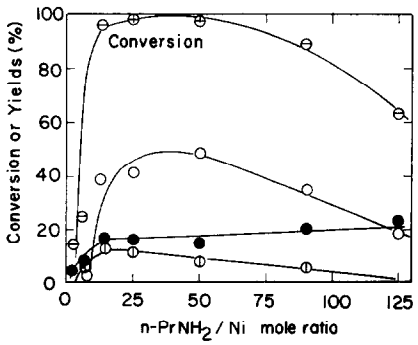

FIG. 1. Effect of n-propylamine concentration on catalytic activities. Reaction conditions: temp. and time, 80°, 24 hr; $Ni(PPh_3)_2Cl_2$, 0.5 mmole; $NaBH_4$, 1.5 mmole; Isoprene, 1 ml; n-pentane, 1 ml. ⊖, conversion; ○, DMOT; ●, DMOD; ⓓ, DMCOD.

of DMOT was expected to be most affected by the nature of the amine. The structures of the added amines brought about significant effects on the yields of DMOT. The alkylamine is believed to accelerate the linear dimerization of DMOT formation through its hydrogen-transfer ability (*9*), so that it is to be expected that the structures of the amines would have such effects. These effects are expected to be correlated with the electronic or steric factors of the substituent group (Figs. 2 and 3, where Taft's σ^* and *Es* are used as the measure of electronic and steric factors for the alkyl groups of the amines). Both figures show fair correlations, although isopropylamine and isobutylamine are out of line in Figs. 2 and 3, respectively. Taking account of a relation between *Es* and σ^* except for isobutyl and isopropyl groups (Fig. 4), deviation of isopropyl and isobutyl groups in Figs. 2 and 3 are considered to be due to the small steric effect of the isopropyl group in spite of its high electron-donating effect, and alternatively, due to the small σ^* value of the isobutyl group in spite of its large *Es* value. Thus, the substituent effects of alkyl groups are described more appropriately by taking both factors into account. Taft's equation can be used for such a purpose.

$$\log v = \rho^*\sigma^* + sEs + C. \qquad (1)$$

The values of ρ^*, s, and C, determined by the least-squares mean, are 8.2, 0.80, and 1.4, respectively. The relative activities obtained by using these values are compared with the observed values in Fig. 5, which shows a close correlation with the activities observed. Even if the slope (3.5) of the linear relation of Fig. 4 is taken into account, the contribution of electronic effect seems predominant.

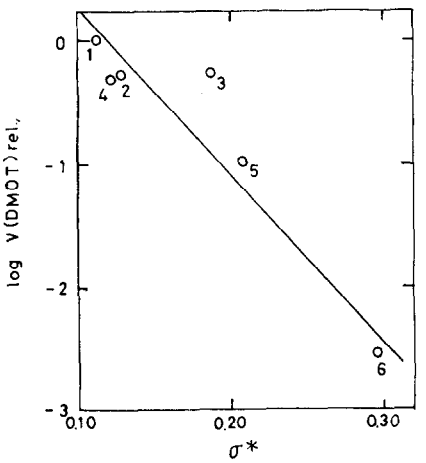

FIG. 2. Relative activities of DMOT formation vs σ^* values of alkyl groups. Numbers and reaction conditions refer to Table 1.

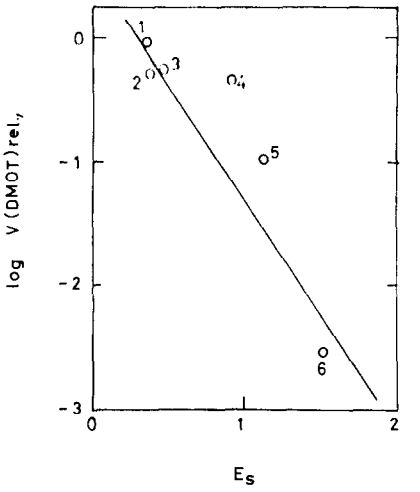

FIG. 3. Relative activities of DMOT formations vs *Es* values of alkyl groups. Numbers and reaction conditions refer to Table 1.

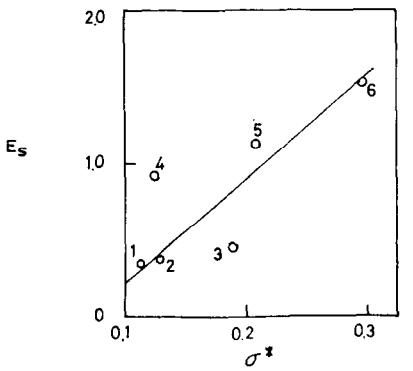

FIG. 4. Relation between σ^* and *Es* values of alkyl groups. Numbers refer to Table 1.

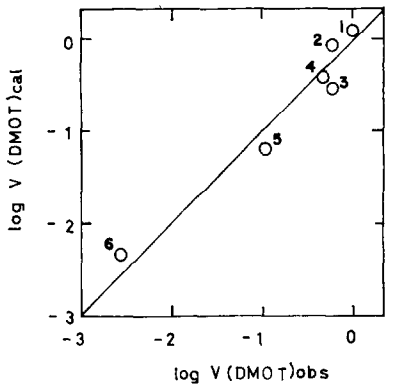

FIG. 5. Comparison of calculated and observed activities of DMOT formation. Numbers refer to Table 1. The following equation was used: $\log V = \rho^*\sigma^* + sEs + C$, where ρ^*, s, and C are 8.2, 0.8, and 1.4, respectively.

The effects of the halide anion on the catalytic activities in the presence of *n*-propylamine are summarized in Table 2, which shows small differences in activities, indicating that the anion was not contained in the active species of the catalyst. In spite of the presence of the amine, the structure of the phosphine ligand changed the activity significantly, as observed in the absence of amines (*10*).

Effects of cyclic amines. Catalytic activities in the presence of cyclic amines are summarized in Table 3, together with their basic strength. It should be noted that activity for the formation of cyclic dimers was significantly increased by the addition of pyridine and γ-picoline: However, α-picoline and 2,6-lutidine of the same or greater basic strength showed only limited acceleration. Such an acceleration by cyclic amines may be explained in terms of the electronic and steric contribution of the methyl group.

A large increase of DMCOD/DP formation ratios was observed by the addition of cyclic amines to the catalytic system, as shown in Table 3. The small value of α-picoline may be noted.[2] The effect of the ligand on the formation of DMCOD is larger than that on DP.

The nucleophilic activities of pyridine and methylpyridines have been extensively studied (*11*). Methyl substituents in the pyridine nucleus increase the basic strength [as measured by the pK value in aqueous solution (Table 3)] in a regular and additive manner, with the implication that their effect is essentially electronic and not steric in origin. However, even methyl groups in the α-position reduce the catalytic power of these compounds in some hydrolysis reactions, in spite of the fact that the Brönsted catalysis law was observable among these compounds without a methyl group in α-position. Thus, it can be reasonably assumed that the coordinated cyclic amines alter the catalytic activity of the

[2] A DMCOD/DP ratio of 5.3 was reported in our preliminary communication (*5*); however, repeated experiments revealed the value to be 0.3 in the present study.

TABLE 2

EFFECTS OF LIGANDS ON THE DIMERIZATION[a]

Catalyst	Conversion (%)	Selectivity (%)				
		DMOD	DMOT	DP	DMCOD	Others[b]
$Ni(PPh_3)_2Cl_2$	98.0	16.2	45.0	5.5	12.4	20.5
$Ni(PPh_3)_2I_2$	98.0	36.9	34.9	6.4	8.3	13.4
$Ni[P(n\text{-}Bu)_3]_2Br_2$	11.7	60.4	Trace	12.7	Trace	25.9

[a] Reaction conditions: temp., 80°C; reaction time, 14 hr; $Ni(PPh_3)_2X_2$, 0.5 mmole; $NaBH_4$, 1.5 mmole; isoprene, 1 ml; n-$PrNH_2$, 1 ml; n-pentane, 1 ml.

[b] Unidentified dimers.

TABLE 3

EFFECTS OF CYCLIC AMINES ON THE DIMERIZATION[a]

Amines	Selectivity (%)					Conversion (%)	Yield of cyclic dimers	DMCOD/DP	pKa
	DMOD	DMOT	DP[b]	DMCOD[b]	Others[c]				
Pyridine	24.7	23.8	14.1 (11.8)	26.5 (22.1)	10.6	83.5	33.9	1.9	5.22
γ-Picoline	11.3	Trace	22.8 (20.0)	34.6 (30.2)	31.2	87.5	50.4	1.5	5.98
β-Picoline	24.0	7.0	19.3 (17.8)	37.5 (34.5)	12.2 (11.2)	92.0	52.3	1.9	5.63
α-Picoline	44.7	—	27.1 (9.7)	8.4 (3.0)	19.8	35.8	12.7	0.3	5.96
2,6-Lutidine	—	—	—	—	—	No react.	—	—	6.72
None[d]			79.0 (4.2)	4.1 (0.2)	16.9	5.3	4.4	0.05	—

[a] Reaction conditions: temp., 80°C; reaction time, 24 hr; $Ni(PPh_3)_2Cl_2$, 0.5 mmole; $NaBH_4$, 1.5 mmole; amine, 1 ml; isoprene, 1 ml; *n*-pentane, 1 ml.

[b] Numbers in parentheses represent the yields.

[c] Unidentified trimers.

[d] Without amine.

nickel complexes through their steric as well as electronic influences.

Anion effects in the presence of cyclic amines are summarized in Table 4; the amount of $NaBH_4$ used was equivalent to the amount of nickel ion.[3] Unlike the results obtained with the alkylamines, the halide anions brought about significant effects on the activity and selectivity. This may imply that the active species of the catalyst contains the anion in the coordination sphere. The values of the DMCOD/DP ratio increased markedly in the order of Cl > Br > I. The yield of DMCOD, also, was markedly dependent on the nature of the ligand.

[3] The amount of $NaBH_4$ used showed a significant effect on the catalytic activity. In the case of alkylamines, 2 moles of $NaBH_4$ for each nickel ion were necessary to get the maximum activity, whereas in pyridine, 1 mole was enough.

TABLE 4

EFFECTS OF LIGANDS[a] ON THE DIMERIZATION IN THE PRESENCE OF PYRIDINE

Catalyst	Conversion (%)	Selectivity (%)					DMCOD/DP
		DMOD	DMOT	DP	DMCOD	Others[b]	
$Ni(PPh_3)_2Cl_2$	71.9	13.2	34.8	12.5	25.0	14.5	2.0
$Ni(PPh_3)_2Br_2$	15.9	36.0	—	12.1	12.7	39.5	1.0
$Ni(PPh_3)_2I_2$	10.0	33.0	—	23.3	Trace	43.9	0

[a] Reaction conditions: temp., 80°C; reaction time, 24 hr; $Ni(PPh_3)_2X_2$, 0.5 mmole; $NaBH_4$, 0.5 mmole; isoprene, 1 ml; pyridine, 1 ml; *n*-pentane, 1 ml.

[b] Unidentified trimers.

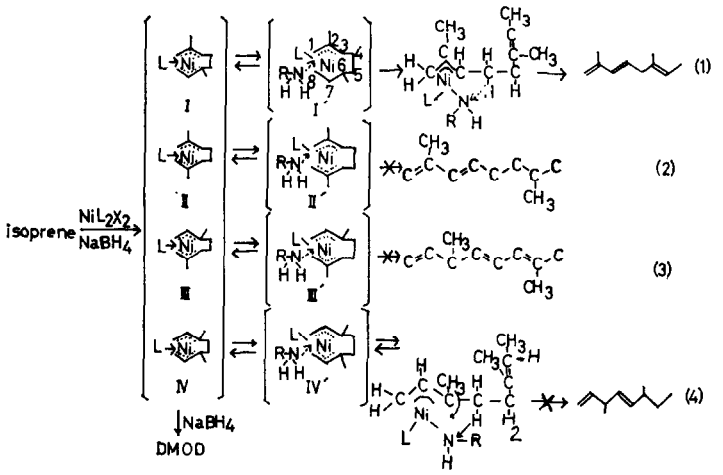

FIG. 6. Mechanism of linear dimerization.

MECHANISTIC REASONING

The fact that 2,6-dimethyl-1,3,6-octatriene was the exclusive product of DMOT permits some discussion of the linear dimerization mechanism. First, the reaction mechanism proposed for butadiene by Heimbach (*4b, 9*) may also be valid for the reaction of isoprene under the present conditions because 1,3,6-triene was similarly the exclusive product from butadiene. The reaction steps can be described as shown in Fig. 6. The alkyl amine may work as the hydrogen transfer agent in the linear dimerization. Second, the reaction routes (2)–(4) seem not to occur because of the steric retardation by the methyl group. The methyl group may hinder the approach of the amine to the reaction point of the bisallyl C_8 intermediate in the hydrogen transfer steps. In intermediates II′ and III′, the hydrogen-donating amine should interact with the methyl group in the 7 position. The reaction described by Eq. (4) may not proceed to completion because the methyl group at the 3 position hinders the hydrogen transfer at the 4 position. Such an explanation seems consistent with the fact that steric as well as electronic factors have a considerable effect on the catalytic activity of DMOT formation.

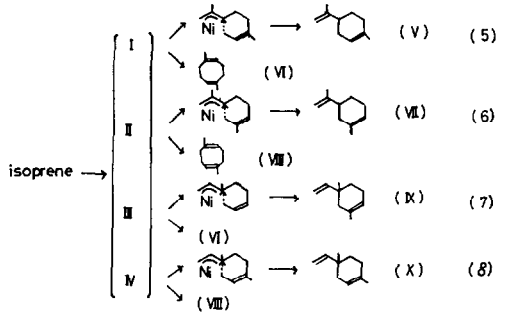

FIG. 7. Mechanism of cyclic dimerization.

Heimbach and his co-workers studied the cyclic dimerization of butadiene extensively and proposed the mechanism shown in Fig. 7 (*12*). Groups IX and X were not detected in the products, so the methyl group may hinder the ring closure of the π-allyl intermediates [III, IV].

A further study dealing with more kinds of cyclic amines and anion ligands is necessary to summarize the determining factors of the DMCOD/DP selectivity.

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REFERENCES

1. Bird, C. W., "Transition Metal Intermediates in Organic Synthesis," Logos Press, London, 1967.

2. Buchholz, H., Heimbach, P., Hey, J. J., Selbek, H., Wiese, W., and Wilke, G., *Amer. Chem. Soc.; Div. Petroleum Chem.* Preprints **17**, B80 (1972).

3. Wilke, G., *Angew. Chem.*, **75**, 10 (1963).

4. (*a*) Feldman, J., Frampton, O., Suffer, B., and Thomas, M., *American Chem. Soc.; Div. Petroleum Chem. Preprints* **9**, A55 (1964). (*b*) Heimbach, P., *Angew. Chem.* **80**, 967 (1968).

5. Mochida, I., Yuasa, S., and Seiyama, T., *Chem. Lett.*, in press.

6. Leffler, J. E., and Granwald, E., "Rates and Equilibria of Organic Reactions," Wiley, New York, 1963.

7. (*a*) Takahashi, K., Hata, G., and Miyake, A., *Bull. Chem. Soc. Jap.* **46**, 600 (1973); (*b*) Josey, A. D., *J. Org. Chem.* **39**, 139 (1974).

8. Baker, R., Halliday, D. E., Smith, T. N., *Chem. Commun.* 1583 (1971); Becker, R., Cook, A. H., and Smith, T. N., *Tetrahedron Lett.* 503 (1973); Furukawa, J., Kiji, J., Mitani, S., Yoshikawa, S., Yamamoto, K., and Sasakawa, E., *Chem. Lett.* 1211 (1972).

9. Heimbach, P., Jolly, P. W., and Wilke, G., "Advances in Organometallic Chemistry," Vol. 8, p. 81. Academic Press, New York, 1970.

10. Brenner, W., Heimbach, P., Hey, H., Müller, E. W., and Wilke, G., *Ann. Chem.* **727**, 161 (1969).

11. Feather, J. A., and Gold, V., *J. Chem. Soc.* 1752 (1964).

12. Heimbach, P., Jolly, P. W., and Wilke, G., "Advances in Organometallic Chemistry," pp. 54–59. Academic Press, New York, 1970.