The Nickel-catalyzed Cyclodimerization of Butadiene. The Synthesis of 2-Methylenevinylcyclopentane and the Isomerization of 1,3,7-Octatriene

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A catalyst system of $NiX_2(R_3P)_2$–$NaBH_4$ or –R′ONa (X=halogen, R and R′=alkyl) was found to yield 2-methylenevinylcyclopentane (MVCP) and *n*-octatrienes (OT), depending on the amount of $NaBH_4$ or R′ONa, which act as a reducing agent for the nickel halide. Less than an equimolar amount of the reducing agent provides a catalyst for MVCP, whereas an excess amount provides that for *n*-octatrienes. In the latter case, the nickel halide is reduced to zero-valent nickel, which then reacts with hydrogen halide to give a catalyst for MVCP again. The catalyst (<2 : 1 ratio of reducing agent : Ni) was also effective in the isomerization of 1,3,7-octatriene to MVCP.

Some nickel catalysts have been reported to be effective catalysts for the novel cyclodimerization of butadiene to give 2-methylenevinylcyclopentane (MVCP).[1–3] Organonickels, such as arylnickel- or π-allylnickel halide, are typical catalysts which are used in the presence of a controlled amount of alcohol. The other type of the catalyst is a phosphine complex of nickel halide combined with organolithium. In both cases, the nickel compounds might be reduced by alcohols or organolithium to an active nickel species. On the other hand, sodium borohydride is an effective reducing agent for the preparation of transition-metal catalysts and is also used for the linear dimerization of butadiene by a nickel catalyst.[4,5] A mixture of cobalt halide and sodium borohydride is also effective for the dimerization of butadiene; an important intermediate has been isolated, and its structure has been studied crystallographically.[6]

It is well-known that the phosphine complex of platinum halide is also reduced to a stable platinum hydride by the action of alcoholic potassium hydroxide.[7] A similar reduction can be anticipated for nickel salts.

$$PtCl_2(Et_3P)_2 + CH_3CH_2OH + KOH \rightarrow PtHCl(Et_3P)_2 + CH_3CHO + KCl + H_2O \qquad (1)$$

It has now been found that tri-*n*-butylphosphine complexes of nickel halides $NiX_2(n\text{-}Bu_3P)_2$, combined with sodium borohydride or sodium alkoxide, are also effective for the cyclodimerization of butadiene to MVCP, when the reducing agent is controlled to an equimolar amount. This paper will deal with the cyclodimerization of butadiene and the isomerization of 1,3,7-octatriene. An effort has been made to find the relationship between the two catalysts, which give linear dimers or MVCP.

Results and Discussion

When bis(tri-*n*-butylphosphine)dibromonickel and sodium borohydride or sodium alkoxide were mixed in equimolar quantities in alcohol, a yellowish-brown solution was obtained. This solution smoothly dimerized butadiene under a slightly high pressure at between 80 and 100 °C to give 2-methylenevinylcyclopentane(MVCP). In the catalyst system, the amount of sodium borohydride or sodium alkoxide plays an important role and has a strong influence on the product distribution. First, the conditions were decided under which MVCP could be formed selectively. Table 1 summarizes the effect of the amount of the reducing agent on the distribution of the dimers. In most cases, butadiene was not unchanged by the reaction. The product other than the dimers was *trans*-1,4-polybutadiene. To obtain MVCP selectively, an amount of sodium borohydride or sodium alkoxide equimolar to the nickel salt was necessary. The effect of the amount of alkoxide is shown in Fig. 1. If the nickel salt was combined with an excess (more than 1 mol) of the reducing agent, a conventional linear dimerization occurred and *n*-octatrienes were the main products.

By analogy to the reaction of platinum with alcoholic potassium hydroxide, the formation of the

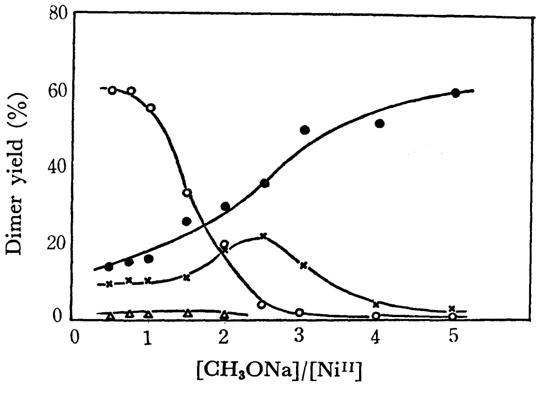

Fig. 1. Effect of [Alkoxide] on the dimerization at 80 °C for 22 hr.
(○), MVCP; (●), 2,4,6-OT; (×), 1,3,6-OT; (△), 1,3,7-OT.
Conditions: $[NiBr_2(n\text{-}Bu_3P)_2]=0.3$ mmol, [Butadiene]=25 mmol.

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[1] J. Kiji, K. Masui, and J. Furukawa, *Tetrahedron Lett.*, **1970**, 2561.

[2] J. Kiji, K. Masui, and J. Furukawa, *Chem. Commun.*, **1970**, 1310.

[3] J. Kiji, K. Masui, and J. Furukawa, This Bulletin, **44**, 1956 (1971).

[4] T. Yoshida and S. Yuguchi, Presented at the 18th Annual Meeting of the Chemical Society of Japan, 1965, Osaka.

[5] N. Yamazaki and T. Ohta, *J. Macromol. Sci.- Chem.*, **A3**, 1571 (1969).

[6] G. Natta, V. Giannini, P. Pino, and A. Cassata, *Chim. Ind.* (Milan), **47**, 524 (1965).

[7] J. Chatt and B. L. Shaw, *Chem. Ind.* (London), **1960**, 931.

TABLE 1. DIMERIZATION OF BUTADIENE[a)]

Ni Compd.	(mmol)	Reducing agent	(mmol)	Butadiene (mmol)	Solvent	Product[b)] (Yield, %)			
						MVCP	OT	VCH	COD
$NiBr_2(n\text{-}Bu_3P)_2$	(0.3)	$NaBH_4$	(0.12)	24	Ethanol	82	—	—	—
$NiBr_2(n\text{-}Bu_3P)_2$	(1.0)	$NaBH_4$	(1.0)	24	Ethanol	80	7	—	—
$NiBr_2(n\text{-}Bu_3P)_2$	(0.3)	$NaBH_4$	(2.4)	24	Ethanol	—	12	8	1
$NiCl_2(n\text{-}Bu_3P)_2$	(0.5)	$NaBH_4$	(0.5)	12	Ethanol	30	11	—	—
$Ni(NO_3)_2(n\text{-}Bu_3P)_2$	(0.5)	$NaBH_4$	(0.5)	12	Ethanol	26	18	—	—
$Ni(SCN)_2(n\text{-}Bu_3P)_2$	(0.5)	$NaBH_4$	(0.5)	12	Ethanol		(No reaction)		
$Ni(CN)_2(n\text{-}Bu_3P)_2$	(0.5)	$NaBH_4$	(0.5)	12	Ethanol		(Polymerization)		
$NiBr_2(Et_2PhP)_2$	(0.5)	$NaBH_4$	(0.5)	12	Ethanol	71	—	—	—
$NiBr_2(Ph_3P)_2$	(0.3)	$NaBH_4$	(0.3)	25	Ethanol	27	40	—	—
$NiCl_2(Ph_3P)_2$	(0.3)	$NaBH_4$	(0.3)	25	Ethanol	33	22	—	—
$NiBr_2(n\text{-}Bu_3P)_2$	(0.3)	CH_3ONa	(0.3)	25	2-Propanol	58	28	<1	—
$NiCl_2(n\text{-}Bu_3P)_2$	(0.3)	CH_3ONa	(0.3)	25	2-Propanol	43	19	<1	—
$Ni(NO_3)_2(n\text{-}Bu_3P)_2$	(0.3)	CH_3ONa	(0.3)	25	2-Propanol	25	16	<1	—
$Ni(SCN)_2(n\text{-}Bu_3P)_2$	(0.3)	CH_3ONa	(0.3)	25	2-Propanol	—	0.3	—	—
$Ni(CN)_2(n\text{-}Bu_3P)_2$	(0.3)	CH_3ONa	(0.3)	25	2-Propanol		(No reaction)		
$NiBr_2(Ph_3P)_2$	(0.3)	CH_3ONa	(0.3)	25	2-Propanol		(No reaction)		

a) At 80 °C for 24 hr. b) MVCP, 2-methylenevinylcyclopentane; OT, mixture of isomeric *n*-octatrienes; VCH, 4-vinyl-1-cyclohexene; COD, 1,5-cyclooctadiene.

nickel hydride caused by alkoxide may be assumed (Eq. 2) when an equimolar amount of alkoxide is used. Until now only a few nickel hydrides have, however, been isolated in a stable form.

$$NiBr_2(n\text{-}Bu_3P)_2 + CH_3ONa \rightarrow [HNiBr(n\text{-}Bu_3P)_2] + NaBr + CH_2O \qquad (2)$$

It has been reported that bis(tri-propylphosphine)-hydridochloronickel, $HNiCl(i\text{-}Pr_3P)_2$, is unstable and decomposes at room temperature.[9)] Therefore, the hydride transiently formed according to Eq. 2 may be assumed to decompose at the reaction temperature, probably through the reductive elimination of hydrogen bromide to give an active nickel catalyst for the cyclodimerization.

$$HNiBr(n\text{-}Bu_3P)_2 \rightarrow HBr + [Ni(n\text{-}Bu_3P)_2] \qquad (3)$$

Another possibility for the activation of the catalyst is that the nickel-hydrogen bond is activated by the coordination of butadiene, as in the case of the alkylnickel catalyst.[10,11)] Stable $HNiCl[(C_6H_{11})_3P]_2$ has been synthesized by the reaction of $NiCl_2[(C_6H_{11})_3P]_2$ with sodium borohydride,[8)] but it has no catalytic activity by itself. However, it shows a catalytic activity for the linear dimerization of butadiene in the presence of alcohol, although not for that of amine and phenol, and gives octatrienes.[12)] The cyclodimerization proceeds satisfactorily in the presence of strong donor phosphines, such as tri-*n*-butylphosphine. Tricyclohexylphosphine possesses a basicity similar to that of tri-*n*-butylphosphine.[13)] In the dimerization of butadiene, the bulky cyclohexyl group on phosphorus prevents the cyclodimerization to the five-membered cycle.[3)] It seems reasonable to assume, on the basis of the reduction of organometals by alcohol,[14)] that stable $HNiCl[(C_6H_{11})_3P]_2$ is reduced further by alcohol in the presence of butadiene, and that only after the reduction does it show the catalytic activity for the dimerization.

$$HNiCl[(C_6H_{11})_3P]_2 + C_2H_5OH \rightarrow H_2 + \{Ni[(C_6H_{11})_3P]_2\} + CH_3CHO + HCl \qquad (4)$$

During this reduction or during the decomposition described above, hydrogen halide is liberated; it appears to play an important role as a cocatalyst, and

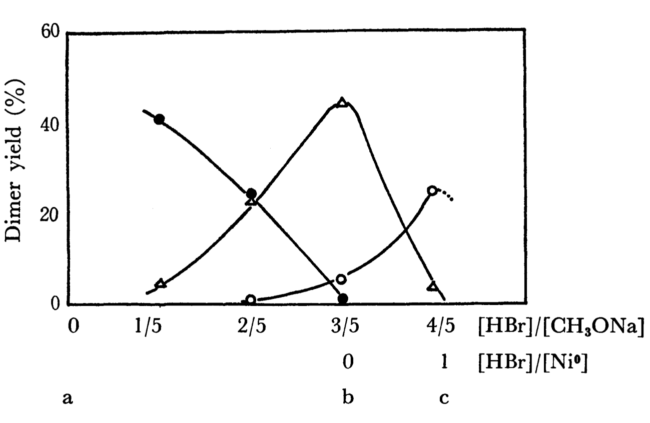

Fig. 2. Effect of [HBr] on the dimerization at 80 °C for 22 hr.
(○), MVCP; (●), 2,4,6-OT; (△), 1,3,7-OT.
Conditions: $[NiBr_2(n\text{-}Bu_3P)_2] = 0.3$ mmol, $[CH_3ONa] = 1.5$ mmol. [Butadiene] = 20 mmol.

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8) M. L. H. Green and T. Saito, *Chem. Commun.*, **1969**, 208.

9) M. L. H. Green, C. N. Street, and G. Wilkinson, *Z. Naturforsch.*, *B*, **14**, 738 (1959).

10) A. Yamamoto, K. Morifuji, S. Ikeda, T. Saito, Y. Uchida, and A. Misono, *J. Amer. Chem. Soc.*, **87**, 4652 (1965).

11) T. Yamamoto, A. Yamamoto, and S. Ikeda, *ibid.*, **93**, 3350 (1971).

12) J. Furukawa, J. Kiji, and S. Mitani, unpublished work.

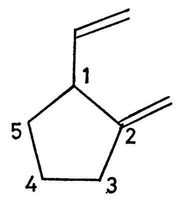
13) C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 2953 (1970).

14) D. A. White and G. W. Parshall, *Inorg. Chem.*, **9**, 2358 (1970).

the product distribution seems to vary with the concentration of hydrogen bromide. To confirm this, we examined the effect of hydrogen halide on the catalyst composed of $NiBr_2(n\text{-}Bu_3P)_2$ and an excess of sodium alkoxide. Hydrogen bromide was added incrementally to the catalyst, which gives linear dimers. The results of this study are shown graphically in Fig. 2; the reversibility of the cyclodimerization catalyst formation is there demonstrated.

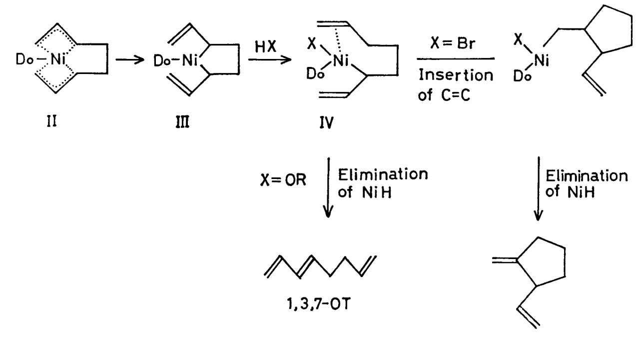
The catalyst was prepared by the reaction of $NiBr_2(n\text{-}Bu_3P)_2$ with sodium methoxide (molar ratio 1 : 5) in 2-propanol. After confirming that the catalyst of this composition is effective for the linear dimerization, but not for MVCP, dry hydrogen bromide was added; the cyclodimerization catalyst was found to be thus regenerated. It is assumed that the decomposition or the reduction of the nickel hydride proceeds according to Eq. 3 or 4, and that the hydrogen bromide formed during this process in neutralized with the excess of alkoxide. It has been observed that the addition of hydrogen bromide in a 3 : 5 molar ratio of HBr: alkoxide (point (b) in Fig. 2) is still ineffective for the cyclodimerization and that *n*-octatrienes are thus formed mainly. In this region (from (a) to (b)), the isomerization of 1,3,7-octatriene to 2,4,6-octatriene decreases with an increase in the amount of hydrogen bromide, because the isomerization is catalyzed by a strong base.[15] Under these conditions, all the hydrogen bromide is neutralized by alkoxide; thus, the solution is "basic." When more hydrogen bromide (point (c)) is added, the solution reveals the catalytic activity for the cyclodimerization. At this point the molar ratio of free hydrogen bromide to nickel is assumed to be 1 : 1. Beyond this point, the further addition of hydrogen bromide produces a color change from yellow to green; this change can reasonably be attributed to the formation of the original nickel bromide, and no reaction of butadiene occurs. These observations lead to a conclusion concerning the hydrogen bromide (generally speaking, hydrogen halide) stoichiometry for the activation of the catalyst. The ratio of hydrogen bromide to zero-valent nickel must be 1 : 1 for the cyclodimerization. This reaction is demonstrated by Eq. 2. Zero-valent nickel and hydrogen bromide are formed through the transient formation of the nickel hydride, followed by rapid decomposition (Eq. (3)) or by further reduction by alcohol (Eq. (4)), when the catalyst is prepared by the equimolar reaction of $NiBr_2(n\text{-}Bu_3P)_2$ with sodium borohydride or sodium alkoxide in alcohol. The catalyst which have been reported in the previons paper[3] also satisfy these conditions. Once zero-valent nickel is formed, the formation of the bis-π-allylic intermediate (II), which is described below, is a well-known reaction.[16,17] The stabilization by forming a chelating bis-π-allylic complex seems to be a driving force for this reaction.

If butadiene reacts with the nickel hydride before the reduction (Eq. (4)) or the decomposition (Eq. (3)), it forms a π-crotyl nickel.[18] This possibility can also be excluded by the observation that the position of the deuteration of the dimer (I) is at the 3-carbon atom when the dimerization is carried out in deuterium-labelling alcohol.[1]



I

Therefore, in contrast to the rhodium-catalyzed dimerization of ethylene studied by Cramer,[19] where a metal hydride initiates the dimerization, nickel hydride or hydrogen bromide does not participate in the initiation reaction. Detailed information on the role of hydrogen bromide could not be obtained from the present study, but it appears that the bromide promotes the further insertion of one terminal double bond into the Ni–C bond to give the cyclic dimer before the elimination of nickel hydride.



Scheme 1

Solvent. This cyclodimerization involves the migration of one hydrogen atom. It has been already proposed that alcohol participates in this reaction.[3] For this reason, in most of our studies alcohol was employed. Primary and secondary alcohols were effective for the reaction, but tertiary alcohol, benzene, tetrahydrofuran, and dimethyl sulfoxide were ineffective. In *t*-butylalcohol and dimethyl sulfoxide, *trans*-1,4-polybutadiene was the main product, while in benzene and tetrahydrofuran no appreciable reaction occurred and butadiene was recovered unchanged. In triethylsilane, no reaction of the nickel salt with sodium borohydride occurred, butadiene and triethylsilane being recovered. However, if ethanol was present in the silane, MVCP was formed in a considerable amount (≈30%). In this case, though, no product due to hydrosilation was detected.

Other Nickel Salts. The best results were obtained with tri-*n*-butylphosphine complexes of nickel

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15) C. G. Cardenas, *J. Org. Chem.*, **35**, 264 (1970).

16) P. Heimbach, P. W. Jolly, and G. Wilke, *Advan. Organometal. Chem.*, **8**, 29 (1970).

17) B. Barnett, B. Büssemeier, P. Heimbach, P. W. Jolly, G. Krüger, I. Tkatchenko, and G. Wilke, *Tetrahedron Lett.*, **1972**, 1457.

18) C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 6777 (1970).

19) R. Cramer, *ibid.*, **87**, 4717 (1965).

bromide and chloride. Since a crystalline complex could not be obtained by the reaction of nickel iodide with tri-*n*-butylphosphine, the catalytic activity of the iodide analogue has not been examined. However, it has been previously reported that (*o*-tolyl)NiI-$[(C_2H_5)_3P]_2$ is highly effective for the cyclodimerization in the presence of alcohol.[2] Therefore, hydrogen iodide has a similar effect on the reaction. The tri-*n*-butylphosphine complex of the nitrate and triphenylphosphine complexes of the bromide and the chloride gave a mixture of MVCP, *n*-octatrienes, and low-molecular-weight polybutadiene. No reaction of butadiene occurred when the isothiocyanate was used as a catalyst. The cyanate complex gave polybutadiene.

The effects of the other electron donors as auxiliary ligands have also been studied. Strong electron donors, such as tri-*n*-butylphosphine and diethylphenylphosphine, are best. The presence of an excess amount of phosphine (>2 : 1 ratio of phosphine : Ni) suppresses the formation of the dimers. The strong electron donors favor the formation of the σ-allyl complex (III), which is a transient form occurring before the alcoholysis and the cyclization. Bidentate phosphines and amines are not effective.

Isomerization of 1,3,7-*Octatriene*. 1,3,7-Octatriene may be expected to react further in the presence of the catalyst. One possibility is an isomerization through the π-allyl nickel intermediate (II), which is assumed to be formed by an intramolecular transfer of hydrogen, followed by alcoholysis. Another possibility is the direct reaction of 1,3,7-octatriene with nickel hydride to form the intermediate (IV). If this is true, it is possible to isomerize 1,3,7-octatriene to MVCP. From this point of view, the isomerization has been studied. The results are shown in Fig. 3. The nickel complex, when combined with less than 2 moles of alkoxide, isomerized 1,3,7-octatriene to MVCP. If more alkoxide was used, only the isomerization of the double bond occurred to give 2,4,6-octatriene; *e. g.*, the base-catalyzed isomerization was predominant. The other products were high-boiling oligomers.

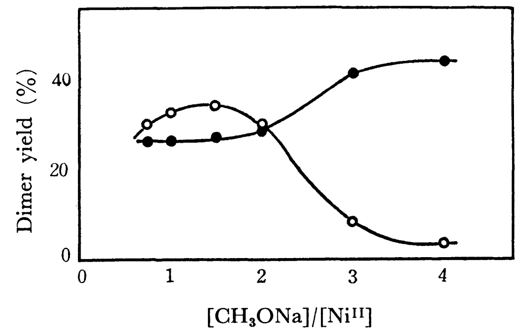
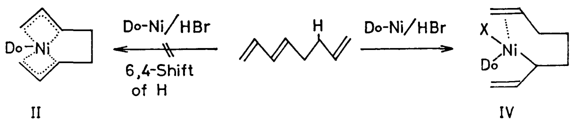


Fig. 3. Effect of [Alkoxide] on the isomerization of 1,3,7-octatriene at 80 °C for 24 hr.
(○), MVCP; (●), 2,4,6-OT.
Conditions: $[NiBr_2(n\text{-}Bu_3P)_2] = 0.3$ mmol, $[1,3,7\text{-OT}] = 10$ mmol.

To gain insight into the isomerization, the deuterium-labelling experiment was particularly instructive; it will, therefore, be described in some detail. Hexadeutero-1,3-butadiene and its dimer (1,3,7-OT) were used for this purpose. A solution of 0.5 mmol of $NiBr_2(n\text{-}Bu_3P)_2$, 10 mg of sodium borohydride, and 1 ml of liquified hexadeuterobutadiene were heated in 1 ml of ethanol in a sealed glass tube at 80 °C for 24 hr. The deuterated MVCP thus formed showed only one broad singlet, around 7.7 τ. Isotope (H)-labelling occurred on the 3-carbon atom. The position of the hydrogen can be explained by the assumption that the reaction proceeds through the bis-allylic nickel intermediate (II), which has been discussed previously.[1] On the other hand, 0.5 ml of perdeutero-1,3,7-octatriene was treated with 1 mmol of $NiBr_2(n\text{-}Br_3P)_2$ and sodium ethoxide in 1 ml of ethanol at 80 °C for 24 hr. The MVCP which was obtained from this isomerization showed a broad singlet around 8.2 τ. This signal is assigned to a hydrogen on the 4- or 5-carbon atom (in I). In a separate experiment we have confirmed that MVCP is stable toward the action of the catalyst under these conditions and that no appreciable exchange of hydrogen with a solvent occurs after it is formed.[20] Thus, the position of the hydrogen is quite different between these two experiments. This fact shows that the isomerization of 1,3,7-octatriene to MVCP does not proceed through the bis-π-allylic intermediate (II), which is anticipated to be formed by the nickel-catalyzed C_6—C_4 shift of hydrogen. In this case, an addition of nickel hydride occurs on the 3- and 4-carbon atoms, followed by cyclization to give the five-membered cycle, *i. e.*, nickel hydride-initiated isomerization. This is different from the cyclodimerization of butadiene described above, which is not initiated by the addition of butadiene to the nickel hydride.



Scheme 2

Experimental

The phosphine complexes of nickel salts were prepared by a method described earlier.[3] Commercially-available butadiene was dried over a 3A Molecular Sieve. The hexadeuterobutadiene was prepared from hexachlorobutadiene by the method of Morse.[21] The 1,3,7-octatriene was synthesized by the dimerization of butadiene with a palladium catalyst.[22] The dry hydrogen bromide was generated by adding bromine to tetralin.[23] All the solvents were purified by the conventional method and were distilled under a nitrogen atmosphere.

Gas-chromatographic analyses were carried out on a column, Silicone DC 550 on Celite, 3 m, at 100 °C. The products were identified by comparing the retention times and,

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20) J. Kiji, K. Masui, K. Ueo, and J. Furukawa, presented at the 24th Annual Meeting of the Chemical Society of Japan, 1971, Osaka.

21) A. T. Morse and L. C. Leitch, *J. Org. Chem.*, **23**, 990 (1958).

22) N. Takahashi, T. Shibano, and N. Hagihara, *Tetrahedron Lett.*, **1967**, 2451.

23) A. H. Blatt, "Organic Syntheses," Coll. Vol. II, (1943), p. 338.

if necessary, the infrared and NMR spectra with those of authentic samples after separation by gas chromatography.

Cyclodimerization of Butadiene. *(i) Sodium Borohydride Method*: The nickel phosphine complex and the sodium borohydride were placed in a glass tube (20 mm in diameter). The tube was immediately fitted with a three-way stapcock. The system was placed under nitrogen by evacuating and by then filling it with nitrogen several times. When the solvent was added at room temperature, the solution turned brown or yellow, depending on the amount of sodium borohydride used. The reaction was instantaneous. The tube was cooled to −78 °C in a dry ice-acetone bath; then, liquified butadiene was added by means of a syringe through the three-way stopcock under a nitrogen atmosphere. The tube was sealed with a flame and heated. The yields of the products were determined gas chromatographically.

(ii) Alkoxide Method: To an alcoholic solution of the nickel complex in the glass tube we slowly added a 1 M solution of alkoxide by means of a syringe. At −78 °C, liquified butadiene was added, after which the tube was sealed with a flame and heated. The detailed reaction conditions and the results are given in Table 1.

Studies on Reversibility of Catalyst. The catalyst solution was prepared by the reaction of 10 ml of a 0.15 M 2-propanol solution of $NiBr_2(PBu_3)_2$ with 1.5 ml of a 5 M methanol solution of sodium methoxide. To this solution, a small amount of butadiene was then added; the mixture was allowed to stand overnight at room temperature. Five sets of experiments were made with this solution. After confirming that the only products were *n*-octatrienes and octadienyl ether, 2 ml of this solution was transferred to the glass tube under a nitrogen atmosphere. To each solution a definite amount of dry hydragen bromide was added as a 1.5 M 2-propanol solution, and then a 20-mmol portions of liquified butadiene was added at −78 °C. The tube was subsequently sealed and heated at 80 °C for 18 hr. The results are shown in Fig. 2.

Isomerization of 1,3,7-Octatriene. To the catalyst solution, 1,3,7-octatriene, instead of butadiene, was added. The mixture was then allowed to react in the sealed tube. The results are shown in Fig. 3.