JOURNAL OF CATALYSIS **80**, 307–314 (1983)

Hydrogenation of Conjugated Dienes over ZrO_2 by H_2 and Cyclohexadiene

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Received August 12, 1982; revised November 22, 1982

Hydrogenation of 1,3-butadiene and 2-methyl-1,3-butadiene and equilibration reaction of H_2–D_2 were carried out over ZrO_2 using H_2 and cyclohexadiene as hydrogen sources. Reaction rates were measured by changing the activation temperature of the catalyst. While the hydrogenation with H_2 and H_2–D_2 equilibration reaction gave an optimum activity at 600°C, another optimum was obtained for transfer hydrogenation at 800°C. Hence it is concluded that the sites responsible for the transfer hydrogenation are not the same as those which catalyze hydrogenation with H_2 and H_2–D_2 equilibration. Product distributions in *n*-butenes and methylated butenes were compared on ZrO_2, ThO_2, La_2O_3, and MgO and were also compared in direct hydrogenation with H_2 and transfer hydrogenation with cyclohexadiene. Assuming an ionic intermediate, selectivity changes in the monoolefins produced over different catalysts and by different hydrogen sources were interpreted in terms of the variation of the anionic character of the intermediate and the shift of anionic to neutral or cationic intermediate, respectively.

INTRODUCTION

The reduction of multiple bonds with the aid of an organic molecule as the hydrogen donor in the presence of a catalyst is known as catalytic transfer hydrogenation. Although the catalytic transfer hydrogenation over transition metals has been extensively investigated (see review by Brieger and Nestrick (*1*)), only recently have papers appeared which describe such reactions over nontransition metal oxides (*2, 3*). Over these catalysts hydrogen donor molecules such as cyclohexadiene (CHD) quite readily hydrogenate 1,3-butadiene (1,3-BD) to *n*-butenes. One characteristic feature of these reactions is that the products formed are quite specific. For example, the catalyst ZrO_2 will promote hydrogenation of 1,3-BD with both CHD and H_2 gas, but the *n*-butene products are distinctly different for the two hydrogen sources. With CHD, the major product is 1-butene; with H_2, *trans*-2-butene predominates. Another characteristic is that donor molecules hydrogenate 1,3-BD to *n*-butenes under conditions where neither H_2–D_2 equilibration nor hydrogenation by H_2 gas occurs (*3*).

The application of hydrogen donor molecules to control the product selectivity has important potential in both applied and fundamental research. One significant area where these reactions may have an impact is the selective removal of sulfur and nitrogen from synthetic crude oil that has been derived from coal, a process that is thought to occur homogeneously under more severe conditions (*4*).

We (*5*) have recently reported the results of studies designed to examine the catalytic behavior of ZrO_2, specifically, how the acid–base properties affect the isomerization of 1-butene. This report deals with the influence of the acidic and basic properties on the hydrogenation of 1,3-BD with H_2 and with CHD over ZrO_2, together with some ancillary reactions that occur simultaneously.

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0021-9517/83 $3.00

EXPERIMENTAL

Zirconium oxide was prepared by hydrolysis of $ZrOCl_2$ with aqueous ammonia to form an insoluble hydroxide which was washed by deionized water until no Cl^- ions were found in the filtrate. The precipitate was dried at 100°C in air and calcined in air at various temperatures for several hours. Prior to use, the catalyst was evacuated for 2 h at the same temperatures that the catalyst was calcined at. 1,3-Butadiene, 2-methyl-1,3-butadiene (2-M-1,3-BD), and methylacetylene were purified by passing them through 4A molecular sieves at −78°C. Cylinder hydrogen was purified by passage at −78°C through a column containing 4A molecular sieves and previously evacuated MgO. Deuterium gas was obtained by electrolysis of D_2O, followed by purification through a Pd thimble. After repeated freeze–pump–thaw cycles, 1,3-cyclohexadiene was vacuum-distilled from a 4A molecular sieve trap at 0°C.

The reaction was carried out in a closed recirculation reactor (740 cm^3) which was equipped with a sampling manifold for gas chromatographic analysis of hydrocarbons. Temperatures between 50 and 75°C and catalyst weights from 50 to 300 mg were used for both the direct hydrogenation of 1,3-BD with H_2 and the transfer hydrogenation of 1,3-BD with CHD. Conditions were the same for the H_2–D_2 equilibration reaction. A 5-m VZ-7 column (Gasukuro Kogyo Co., Ltd.) was operated at 0°C to separate the lower hydrocarbons. A 2-m column of polyethylene glycol 200 maintained at 50°C provided separation of the cyclic hydrocarbons. Samples separated gas chromatographically were subjected to mass spectrometric (Hitachi M52) or ^{13}C NMR spectroscopic analysis. The ^{13}C NMR spectra were recorded by a JNM-FX 100 PET spectrometer at 25 MHz using proton noise decoupling in $CDCl_3$ with tetramethylsilane as an internal reference. Composition of gaseous H_2, HD, and D_2 was determined mass spectrometrically. Surface areas were measured by the BET method using N_2 as the adsorbent at −195°C.

RESULTS AND DISCUSSION

1. Hydrogenation of 1,3-BD with H_2 and 1,3-CHD; Equilibration of H_2–D_2

When a mixture of 1,3-BD (40 Torr) and H_2 (100 Torr) was passed over the catalyst at 50°C, hydrogenation took place smoothly to yield *n*-butenes, *trans*-2-butene being the major product. A negligible amount of *n*-butane was produced. Deuteration (using D_2 in place of H_2) of 1,3-BD produced exclusively butene-d_2 products, and ^{13}C NMR of the products indicated that the two D atoms were located almost exclusively on the C_1 and C_4 atoms of *trans*-2-butene (*2*).

A characteristic feature of basic oxides such as alkaline earth oxides is that their catalytic activities for certain reactions are often sensitive to activation temperature (*6*). A maximum in activity at 800°C for 1-butene isomerization has been reported on ZrO_2 catalysts (*5*).

The specific reaction rates, normalized to unit surface area, for the H_2–D_2 equilibration and for hydrogenation of 1,3-BD with H_2 are plotted against evacuation temperature in Fig. 1. The initial composition of the

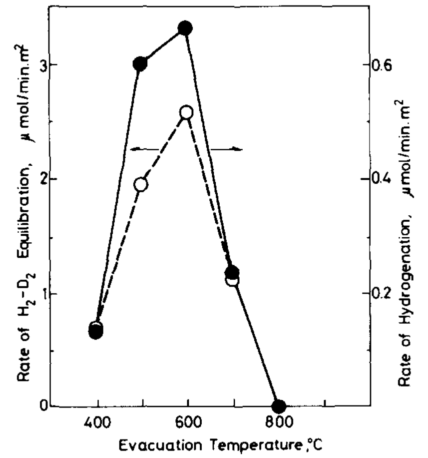


FIG. 1. Changes of the rate of H_2–D_2 equilibration (○) and direct hydrogenation of 1,3-BD by H_2 (●) with pretreatment temperature of ZrO_2.

n-butene products for the various evacuation temperatures is shown in Fig. 2 when H_2 was the hydrogen source. Note that a maximum was obtained at 600°C for both equilibration and hydrogenation reactions, although the product distribution did not change significantly. Coincidence of the optimum temperature of evacuation for both reactions indicates the importance of the dissociation of H_2 molecules in the hydrogenation reaction.

Figure 3 shows the dependence on evacuation temperature of the reaction rate for transfer hydrogenation of 1,3-BD with 1,3-CHD. While the hydrogenation with H_2 gave an optimum activity at 600°C, another optimum was obtained for transfer hydrogenation at about 800°C. Considerable catalytic activity remains in transfer hydrogenation even at 900°C, the highest evacuation temperature investigated, whereas at that temperature the direct hydrogenation reaction with H_2 ceased. These findings suggest that the sites responsible for the transfer hydrogenation are not the same as those which catalyze direct hydrogenation with H_2.

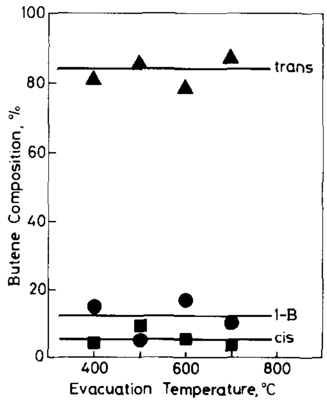


FIG. 2. Initial composition of *n*-butene in the hydrogenation of 1,3-BD with H_2. ●, 1-B; ▲, *trans*; ■, *cis*.

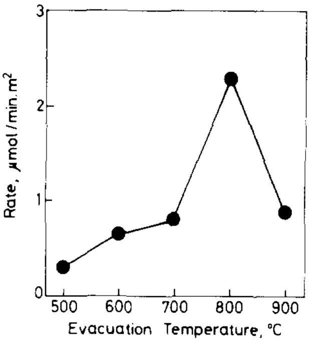


FIG. 3. Changes of the rate of transfer hydrogenation with pretreatment temperature of ZrO_2.

During the transfer hydrogenation, several additional catalytic reactions occur. Isomerization, dehydrogenation, and hydrogen disproportionation take place to give 1,4-CHD, benzene, and cyclohexene. A separate reaction was performed using 40 Torr of 1,3-CHD as the sole reactant at 75°C. Figure 4 shows the changes that occur in the rates of these reactions as a function of the evacuation temperature. An optimum evacuation temperature near 800°C was obtained for all three reactions. In a previous paper (*5*) we showed that the rate of 1-butene isomerization also goes through a maximum at 800°C. We speculated that this double-bond migration is initiated by abstraction of an allyl hydrogen to form a π-allyl anion on an acid–base pair site and that successive intramolecular H migrations lead to isomerization. The fact that

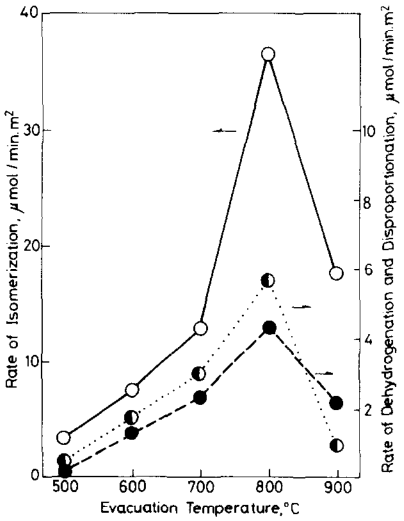
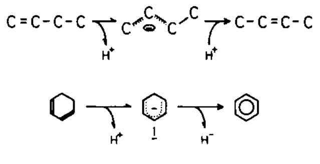


FIG. 4. Changes of the rate of isomerization, dehydrogenation, and disproportionation of 1,3-CHD with pretreatment temperature. ○, Isomerization; ●, disproportionation; ◐, dehydrogenation.

the same optimum temperature is observed for the isomerization of both 1-butene and 1,3-CHD indicates that the same active sites are operative for both reactions. We would thus propose that both reactions take place intramolecularly via a π-allyl anion initiated by abstraction of an allyl hydrogen atom, viz.,



SCHEME 1

Removal of another hydrogen atom from **1** results in the formation of a benzene molecule. Addition of hydrogen atoms, thus liberated from the 1,3-CHD, to another CHD molecule yields cyclohexene; this accounts for the observed hydrogen disproportionation reaction.

A similar set of reactions has been reported by Hofmann *et al.* (*7*) in a homogeneous system. When 1,3-CHD was treated with t-butOK in dimethyl sulfoxide at 55°C, 1,4-CHD was observed. However, in the presence of equimolar, 1,3-BD and 1,3-CHD, *cis*- and *trans*-2-butene were formed. The rate of butene formation was faster than that of cyclohexene; the authors attributed this to the preferential hydride-accepting ability of 1,3-BD.

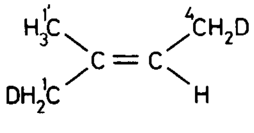
The agreement of the optimum temperature for transfer hydrogenation and the reactions stated above emphasizes the common importance of the dissociation of hydrogen atoms from a CHD molecule. There is apparently a competition between 1,3-BD and 1,3-CHD for the adsorption sites, since the presence of the latter decreases the direct hydrogenation of the former as may be seen in our previous paper (*2a*).

Propadiene is not hydrogenated by either H_2 or CHD, although it does isomerize to methylacetylene. In this reaction, neither isomerization nor dehydrogenation of CHD occurs, which suggests that propadiene and/or methylacetylene strongly inhibit adsorption of H_2 or CHD molecules.

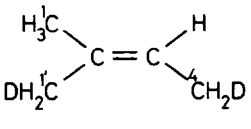
2. *Hydrogenation of 2-Methyl-1,3-butadiene with H_2 and 1,3-CHD*

When 2-M-1,3-BD was hydrogenated at 50°C with H_2 over ZrO_2 activated at 500°C, the following hydrogenated products were obtained: 60% 2-methyl-2-butene (2-M-2-B), 35% 2-methyl-1-butene (2-M-1-B), and 5% 3-methyl-1-butene (3-M-1-B). This means that hydrogenation involves 60% 1,4-addition and 40% 1,2- (and 3,4-) addition of hydrogen. However, when 1,3-CHD was used as the hydrogen source, 15% 1,4-addition and 85% 1,2- (and 3,4-) addition (55% 2-M-1-B and 30% 3-M-1-B) products were obtained (see Table 1). Again, a pronounced change in the course of hydrogenation was found when 1,3-CHD was used, as was observed in 1,3-BD hydrogenation.

Both mass spectral and ^{13}C NMR analyses of the deuterated products revealed that the molecular identity of D_2 was conserved in all the products, i.e., 100% of the molecules containing deuterium were doubly labeled with d_2 and all the D atoms were located in the terminal methyl groups. Furthermore, 2-M-2-B-1,4-d_2 existed in the form of two isomers, (E)-2-M-2-B-d_2 and (Z)-2-M-2-B-d_2, which could be readily distinguished by ^{13}C NMR analysis of the D content of each methyl group (*8*, *9*), viz.,



(E)-2-M-2-B



(Z)-2-M-2-B

Carbon-13 NMR measurement revealed that the percentages of monodeuterio methyl carbon (CH_2D) in the C-1, C-1′, and C-4 positions were 89, 11, and 100%, respectively; these values indicate that the 2-M-2-B-1,4-d_2 is 89% in the (E)-form and 11% in the (Z)-form. Quite similar values have been observed on ThO_2 (*9*) (see Table 1).

3. *Possible Mechanisms of Hydrogenation of Conjugated Dienes by H_2 and CHD on ZrO_2*

Hydrogenation of olefins by H_2 over nonmetallic catalysts has been discussed in terms of coordinative unsaturation (*10*) and heterolytic dissociation of H_2 molecules (*11*).

In a previous paper (*2*), we suggested that the reaction involves a mechanism with H_2 from the gas phase reacting directly with adsorbed 1,3-BD (Rideal–Eley mechanism). This mechanism accounted successfully for the retention of molecular identity (H_2 or D_2 addition during hydrogenation), the absence of H_2–D_2 equilibration in the presence of unsaturated hydrocarbons, and the temperature-independent isotope effect of 1.4. However, the correlations observed between the H_2–D_2 exchange rate (in the absence of unsaturated hydrocarbons) and the direct hydrogenation rate (with H_2) as a function of pretreatment temperature indicate that the reaction may be more complicated than originally suspected. Specifically, the data suggest that the H_2 molecules are probably dissociated on the surface and that a simple Rideal–Eley mechanism is inadequate to account for these latest observations.

An anionic intermediate was proposed to interpret the results for the hydrogenation of dienes with H_2 on MgO, La_2O_3, and ThO_2 (*9, 11*). Table 1 lists the product distributions observed in the hydrogenation of 1,3-BD and 2-M-1,3-BD on MgO, La_2O_3, and ThO_2, together with observed distributions over ZrO_2. The relative amounts of the (E)- and (Z)-forms of 2-M-2-B-d_2 obtained during deuteration of 2-M-1,3-BD are also included in Table 1. From these results, the catalysts can be divided into several classifications.

(a) 1,3-BD + H_2: (i) MgO gives *cis*-2-butene preferentially while La_2O_3, ThO_2, and ZrO_2 give primarily *trans*-2-butene. (ii) More than 90% 1,4-addition to yield 2-butene may be observed over MgO, La_2O_3,

TABLE 1

Product Composition in Hydrogenation of 1,3-BD and 2-M-1,3-BD

Catalyst	Hydrogenation of 1,3-BD			Hydrogenation of 2-M-1,3-BD					Ref.
	Product %			Percentage (E)-form[a]	Percentage (Z)-form[a]	Product %			
	1-B	*trans*	*cis*			2-M-1-B	3-M-1-B	2-M-2-B	
MgO	7	16	77	60	40	5.8	0.6	92.6	(*11*)
La_2O_3	2	84	14	64	36	7.8	0.5	91.6	(*11*)
ThO_2	8	83	9	89	11	13.3	1.0	85.7	(*9, 11*)
ZrO_2	15	80	5	89	11	34	4	62	This work
ZrO_2[b]	64	14	22	—	—	55	30	15	This work
eq[c]	3.2	76.8	20.0	—	—	10.9	0.2	88.9	

[a] Composition of (E)- and (Z)-forms was obtained by ^{13}C NMR measurement for 2-M-2-B-d_2.

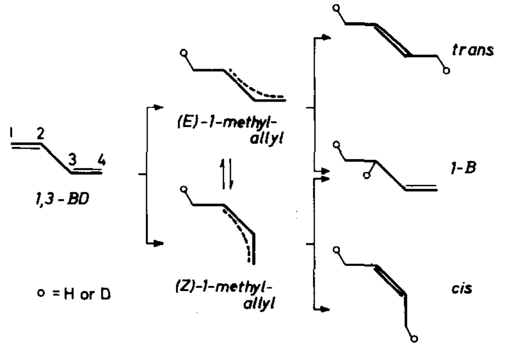
[b] Hydrogen source was 1,3-CHD.

[c] Equilibrium composition at 50°C (K. W. Egger, D. M. Golden, and S. W. Benson, *J. Amer. Chem. Soc.* **86,** 5420 (1964)).

and ThO_2, and the selectivity for 1,4-addition is only slightly lower on ZrO_2.

(b) 2-M-1,3-BD + H_2: (i) the relative amounts of the (E)- and (Z)-forms of 2-M-2-B-d_2 are markedly different on MgO and La_2O_3 from those on ThO_2 and ZrO_2. (ii) The selectivity toward 1,4-addition was highest for MgO and La_2O_3, lower for ThO_2, and lowest for ZrO_2.

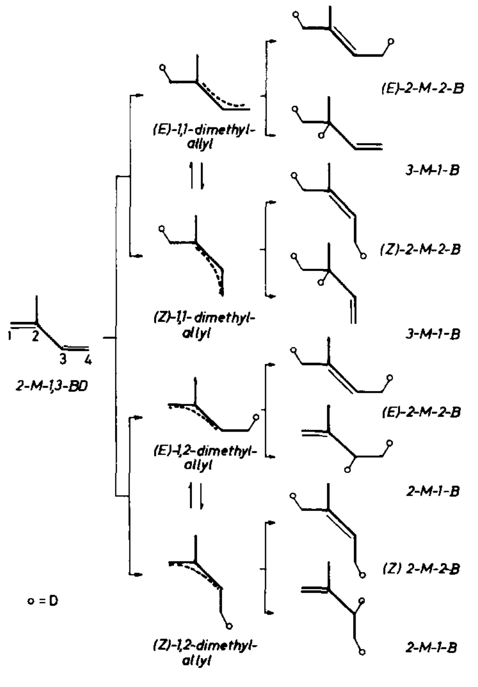
These observations can be interpreted in the following way. The *s-trans* conformations of 1,3-BD (*12*) and 2-M-1,3-BD (*13*) are preferred in the gas phase (about 98%), and we assume that this conformational selectivity is retained in the half-hydrogenated states initially formed by additions of one hydrogen. The added hydrogen is an anion (H^-) which forms by the heterolytic dissociation of H_2 into H^+ and H^- on a strong base such as MgO (*14*). The half-hydrogenated species thus formed is a π-allylic carbanion intermediate. The (E)-π-allylic carbanion may interconvert to a more stable (Z)-π-allylic carbanion (*14*). Scheme 2 shows a probable reaction route of the 1,3-BD hydrogenation. Such an interconversion is influenced by a rotational barrier of the allylic anion which may be affected by an alkyl substitution to the anion and by countercations. Thompson and Ford (*15*) have reported that barriers to the rotation about the carbon–carbon bonds of allylalkali metal compounds increased in the order of: Li^+ (10.7 kcal/mol), K^+ (16.7 kcal/mol), Cs^+ (18.0 kcal/mol).



SCHEME 2

These observations could be interpreted in terms of the size or the electronegativity of the alkali cations. A high yield of *cis*-2-butene in the hydrogenation of 1,3-BD over MgO could be interpreted in the same manner, since Mg^{2+} cation has the smallest ionic radius and the lowest electronegativity among the oxides tested. A high rotational barrier of the 1-methyl-π-allylic system found in the isomerization of butene on La_2O_3 was also attributed to the contribution of the lanthanum cation (*16*). Thus, the role of the metal cation for the rotational barrier should be taken into account in the heterogeneous catalysis system including the allylic anion, though semiempirical calculation by CNDO/2 suggested that the (Z)-allylic anion is stabilized by interacting with a basic center (*14b*).

In the hydrogenation of 2-M-1,3-BD by D_2, four products are expected as shown in Scheme 3. An addition of one D atom at the C-1 position leads to the formation of 1,1-dimethyl-π-allylic ion, while an addition to the C-4 position results in the formation of 1,2-dimethyl-π-allylic ion. The former is



SCHEME 3

the intermediate to 2-M-2-B and 3-M-1-B and the latter is the intermediate to 2-M-2-B and 2-M-1-B. Considering the product distribution, especially the production ratio of 2-M-1-B to 3-M-1-B shown in Table 1, the most likely conclusion is that the hydrogenation proceeds via 1,2-dimethyl-π-allylic ion, since the production of 3-M-1-B was far less than that of 2-M-1-B over four catalysts.

Introduction of a methyl group to 1,3-BD or the 1-methyl-π-allylic system enhanced the favorable production of (Z)-2-M-2-B-d_2 on La_2O_3 as on MgO. Thompson and Ford (*15*) have shown that the rotational barriers of 2-methylallyl- (15.9 kcal/mol) and (E)-1-isopropylallylpotassium (14.0 kcal/mol) are lower than that of allylpotassium (16.7 kcal/mol). Alkyl substitution to the 1-methyl-π-allylic anion seems to reduce the rotational barrier in the half-hydrogenated state of 2-M-1,3-BD on La_2O_3. Thus, the resulting composition of 2-M-2-B resembles that of MgO. On ThO_2 and ZrO_2, in which the cation has higher electronegativity, the effect of the alkyl substitution to the rotational barrier does not seem significant and hence, the production of (E)-2-M-2-B-d_2 was still high.

Since electron density of 1-methyl-π-allylic anion is high at the C-3 position, a H^+ attacks this position and favorable formation of 2-butene was usually observed. Hence, 1,4-addition of hydrogen to 1,3-BD on basic oxides is more favorable than 1,2-addition. Selectivity to 1,4-addition varies from catalyst to catalyst: the higher the electronegativity of the cation in oxides, the lower the formation of the 1,4-addition products (*17*). Similar behavior is also found in the hydrogenation of 2-M-1,3-BD (*18*). So, when a π-allylic anion is assumed in the hydrogenation of conjugated dienes, it seems likely to consider that the selectivity of H^+ addition to the allylic system is affected by the electronegativity and/or the size of cations of oxides which may lead to the change in a charge distribution of an anionic intermediate.

An optimum temperature of pretreatment for the H_2–D_2 equilibration reaction was observed at 600°C. This is markedly different from the optimum temperature (800°C) for the 1-butene isomerization and 1,3-CHD dehydrogenation, where π-allylic anions presumably play an important role. This difference suggests that the sites responsible for the H_2–D_2 equilibration and the hydrogenation by H_2 should be different from those which promote the isomerization and the dehydrogenation. Though basic properties likely play an important role in the abstraction of a proton from a butene molecule or a CHD molecule, these properties do not seem to influence the dissociation of H_2 molecules on ZrO_2. It has been reported (*19*) that the low-temperature tetragonal form (or metastable tetragonal form) of zirconia is converted into the monoclinic form around 600–700°C. Perhaps the sites for the dissociation of hydrogen molecules may be related to a change in the crystal form, and such sites may have a different cation–anion configuration than the sites corresponding to the monoclinic structure and such sites may not have strong basicity.

When CHD is used as a hydrogen source over ZrO_2, the resulting *n*-butene and methylated butene product distributions are markedly different from those obtained from the hydrogenation by H_2. The tendency toward 1,2-addition is greatly enhanced by using CHD, in both 1,3-BD and 2-M-1,3-BD hydrogenation. We believe that the hydrogenations by H_2 and CHD take place independently (*2*). Hydrogen from H_2 tends to add to the C-1 and C-4 atoms of diolefins, while hydrogen from CHD adds to the C-1 and C-2 atoms or to the C-3 and C-4 atoms. An enhanced production of 3-M-1-B in the 2-M-1,3-BD hydrogenation is indicative of the possible intermediate. As in the case of the hydrogenation by H_2, 2-M-1-B and 3-M-1-B may be formed via 1,2- and 1,1-dimethyl-π-allylic ions, respectively. When we consider the resonance forms of these allylic ions, the anionic form is favorable in the 1,2-dimethylallylic system, while the cationic form is favorable in the 1,1-dimethylallylic system, since primary anion and tertiary cation are most stable. Enhanced selectivity to 3-M-1-B may be attributed to the favorable contribution of 1,1-dimethylallylic cation. A CHD molecule liberates a proton at a basic site of the catalyst and leaves a cyclohexyl-π-anion as the first step. The proton may add to the C-1 carbon atom of a diene molecule to form 1,1-dimethylallylic cation. Proton addition to the C-2 or C-3 position seems unlikely, since the resulting intermediate involves primary cation and is not stabilized. The question of why the addition of a second hydrogen (H^-) takes place at the C-3 position is difficult on the basis of the π-allylic system. However, if one assumes that a π-allylic ion converts to the σ-allylic system in a transition state and H^- adds to this σ-allylic cation, favorable position which accepts H^- could be a tertiary carbon, since a tertiary σ-allylic cation is more stable than a primary σ-allylic cation. Such an interconversion between (E)- and (Z)-allylic anion systems through σ-allylic complex was also speculated by several authors (*15, 16*). If this speculation is valid, preferred formation of 3-M-1-B from 1,1-dimethylallylic cation intermediate could be understood. This interpretation can also explain the preferred formation of 2-M-1-B from 2-M-1,3-BD and of 1-B from 1,3-BD by using CHD as a hydrogen source.

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