# Isomerization of 3-Carene over MgO and CaO

KATSUAKI SHIMAZU, HIDESHI HATTORI, AND KOZO TANABE

*Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060, Japan*

The isomerization of 3-carene was studied over MgO, and CaO. The main product was 2-carene which resulted from a double bond migration within a six-membered ring. The catalytic activity and selectivity varied with starting materials and pretreatment temperature of the catalysts. Two kinds of magnesium oxides were prepared. From magnesium hydroxide, MgO(I) was prepared and MgO(II) from magnesium carbonate hydroxide. Both MgO(I) and MgO(II) became active when pretreated at 400°C, and attained their maximum activities when pretreated at 900 and 500°C, respectively. Active sites on both kinds of MgO were strongly poisoned by carbon dioxide and butylamine but were only slightly poisoned by triethylamine. The activities of CaO(I), which was prepared from calcium hydroxide, and CaO(II), prepared from calcium carbonate, appeared when pretreated at 300 and 600°C, respectively, and reached their maximum activities when pretreated at 600 and 1000°C, respectively.

Over MgO(I) and MgO(II) pretreated at 500°C, 3-carene and 2-carene exchanged their allylic hydrogen atoms in the six-membered ring more easily than the allylic hydrogen atoms in the methyl group.

Dehydrogenation of 3-carene to *m*- and *p*-cymenes occurred over CaO(II) pretreated at 600–800°C but it hardly took place over CaO(I), MgO(I), and MgO(II) pretreated at any temperatures.

## INTRODUCTION

3-Carene is a major constitutent of turpentines in commercially important pine species, but most of its utilization had been limited to a solvent. However, Booth (*1*) found the utility value of 3-carene as an industrial raw material for *l*-menthol which is used in perfumery, in pharmaceuticals as a local anodyne, and as a flavoring in tooth paste, chewing gum and cigarettes. The first step in ths process in a conversion of 3-carene to 2-carene.

In addition to industrial importance, some academic interests exist in the isomerization of 3-carene. 3-Carene has different kinds of reactive groups such as a double bond in a six membered ring, three kinds of allylic hydrogen atoms, and a cyclopropane ring. The most reactive part in the molecule may vary with the property of a catalyst. The surface property of a catalyst is expected to be reflected directly on the products which may indicate the reactive part of 3-carene.

A selective formation of 2-carene was reported to take place over Na or K metal on $Al_2O_3$ (*1*) and the compounds or complexes of alkali metals with organic compound such as Na-xylene–*o*-chlorotoluene (*1*), potassium *tert*-butoxide–dimethyl sulfoxide (*1, 2*), Li-ethylenediamine (*1–3*), etc. Over hydrogenation catalysts such as Raney nickel, Pd on carbon, and copper chromite, 2-carene was produced in addition to the hydrogenated products under a hydrogen atmosphere (*1*). On the other

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hand, 3-carene is converted to various menthadienes and cymenes in the presence of liquid acids (*4*, *5*) or solid acids (*6*, *7*).

In our previous paper (*8*), the catalytic action of 15 kinds of metal oxides were examined from the viewpoint of the acidic and basic properties of the catalyst surface. 3-Carene undergoes isomerization substantially to 2-carene over basic catalysts such as MgO, CaO, SrO, $Y_2O_3$. $La_2O_3$, and $ZrO_2$. On the other hand, 3-carene is isomerized to menthadienes and dehydrogenated mainly to *m*- and *p*-cymenes over acidic catalysts such as $SiO_2$–$Al_2O_3$, $Ce_2O_3$, and $TiO_2$.

In this paper, the reaction has been studied in detail over MgO and CaO. The reaction mechanism was also investigated by means of a tracer study where deuterium was used as the tracer.

## EXPERIMENTAL METHODS

### Catalysts

Two kinds of MgO and CaO were obtained by heating different starting materials. MgO(I) and CaO(I) were prepared from their hydroxides (Kanto Chemical Co., Inc.). MgO(II) and CaO(II) were prepared from magnesium carbonate hydroxide (Merck & Co., Inc.) and calcium carbonate (Merck & Co., Inc.), respectively.

### Reagents

3-Carene was supplied by Glidden-Durkee Div., SCM Corp., and its purity was 98.6%. Before use, 3-carene was dried with 4A molecular sieves for the activity measurements, and the freeze–thaw technique was employed to exclude $CO_2$ and $O_2$ for the exchange reaction with deuterium.

Butylamine (Wako Pure Chemical Industries, Ltd.) and triethylamine (Nakarai Chemicals, Ltd.) were dried with 4A molecular sieves before use. Helium carrier gas and deuterium were purified by passage through 13X molecular sieves at $-196°C$.

TABLE 1

Surface Area of Catalyst

| Catalyst | Pretreatment | | Surface area $(m^2/g)$ |
|---|---|---|---|
| | Temp (°C) | Atmosphere | |
| MgO(I) | 500 | Vacuo | 145 |
| | 500 | He | 87 |
| | 900 | Vacuo | 43 |
| | 900 | He | 100 |
| MgO(II) | 500 | Vacuo | 281 |
| | 500 | He | 77 |
| | 900 | Vacuo | 54 |
| | 900 | He | 27 |
| CaO(I) | 500 | Vacuo | 71 |
| | 500 | He | 70 |
| | 900 | Vacuo | 34 |
| | 900 | He | 2.4 |
| CaO(II) | 500 | Vacuo | 3.3 |
| | 500 | He | 1.2 |
| | 900 | Vacuo | 4.9 |
| | 900 | He | 3.5 |

### Reaction Procedure

For isomerization of 3-carene, a microcatalytic pulse reactor which was directly combined with a gas chromatographic column was employed (*9*). The catalyst was pretreated under a helium stream for 2 hr. A 1 or 3 $\mu$l pulse of 3-carene was injected into a helium stream by a microsyringe. The reaction products were trapped at $-196°C$ and then flash evaporated into a gas chromatographic column. A column (5-m, 6 mm o.d.) was packed with polyethylene glycol, 20M, on Celite 545, which was operated at 100°C with a flow rate of about 60 ml/min.

Poisoning effects with carbon dioxide, butylamine and triethylamine were tested as follows. A pulse of the poison, amounts of which were just sufficient to cover a monolayer of the catalyst, was introduced after the third pulse of 3-carene. Then the catalytic activities of the successive two pulses of 3-carene were measured.

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TABLE 2

Exchange Reaction of 3-Carene with Deuterium[a]

| Catalyst wt (mg) | Evacuation temp (°C) | Reaction | | Conversion of isomerization (%) | $\bar{\phi}$ value | Number of H atoms | | |
|---|---|---|---|---|---|---|---|---|
| | | Temp (°C) | Time (min) | | | Region | Calcd. | Obsd. |
| MgO(I) | | | | | | | | |
| 50.4 | 500 | 80 | 30 | 21.1 | 0.57 | A | 3.3 | 3.4 |
| | | | | | | B | 3.7 | 3.1 |
| | | | | | | V | 1.0 | 1.0 |
| 124.9 | 500 | Room temp | 90 | 37.4 | 0.37 | A | 3.5 | 3.6 |
| | | | | | | B | 3.5 | 3.1 |
| | | | | | | V | 1.0 | 1.0 |
| 101.2 | 900 | 80 | 30 | 28.2 | 0.24 | A | 3.4 | 3.4 |
| | | | | | | B | 3.7 | 3.5 |
| | | | | | | V | 1.0 | 0.9 |
| MgO(II) | | | | | | | | |
| 50.5 | 500 | 80 | 30 | 26.0 | 1.56 | A | 3.4 | 2.8 |
| | | | | | | B | 3.6 | 2.7 |
| | | | | | | V | 1.0 | 1.0 |
| 125.5 | 500 | Room temp | 90 | 38.8 | 2.69 | A | 3.5 | 2.4: |
| | | | | | | B | 3.5 | 1.8 |
| | | | | | | V | 1.0 | 1.1 |
| 251.6[b] | 500 | Room temp | 180 | 41.2 | 4.89 | A | 3.5 | 1.2 |
| | | | | | | B | 3.5 | 0.9 |
| | | | | | | V | 1.0 | 1.0 |
| 251.6 | 500 | Room temp | 1200 | 41.0 | 5.76 | A | 3.5 | 0.8 |
| | | | | | | B | 3.5 | 0.8 |
| | | | | | | V | 1.0 | 0.7 |

[a] 0.32 mmol of 3-carene and 7.3 mmol (90 Torr) of $D_2$ are reacted.
[b] Pressure of $D_2$, 189 Torr.

For the exchange reaction of 3-carene with deuterium, a recirculation reactor was used. The catalyst was pretreated *in vacuo* for 2 hr. The system had a volume of about 1500 ml and was attached with a cold trap at 0°C. The starting materials were evacuated at 500°C for 2 hr prior to the reaction. About 50 μl of 3-carene (0.32 mmol) and 90 Torr of deuterium (7.3 mmol) were introduced into the reaction system. A portion of the 3-carene was condensed in the cold trap kept at 0°C during the reaction. Separated product isomers were trapped at −196°C and subjected to mass spectroscopic analysis by low voltage electrons using a Hitachi mass spectrometer

RMU-2. All nmr spectra in solution with carbon tetrachloride were recorded with a JEOL PS-100 high resolution nmr spectrometer with an operating frequency of 100 MHz. Chemical shifts were recorded in ppm ($\delta$) from tetramethyl silane ($\delta = 0.00$).

Specific surface areas of catalysts were determined by applying the BET equation to the nitrogen adsorption isotherm at −196°C.

## RESULTS

*Surface Area*

Specific surface areas of catalysts which were pretreated at 500 and 900°C under

a vacuum or helium stream are listed in Table 1. Surface areas are greater for the evacuated samples than for helium treated samples except MgO(I) pretreated at 900°C.

## Activity of MgO and CaO

The reaction products of 3-carene (**I**) were 2-carene (**II**), m-mentha-1,5-diene (**III**), p-mentha-1,5-diene (α-phellandrene) (**IV**), m-cymene (**V**) and p-cymene (**VI**).



(**I**)     (**II**) (**III**)   (**IV**)   (**V**)     (**VI**)
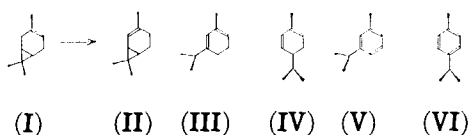
In Fig. 1 are shown conversions of 3-carene to 2-carene over MgO(I) and MgO(II) as a function of the pretreatment temperature. The activities of MgO(I) and MgO(II) appeared when pretreated at 400°C. At a high pretreatment temperature, the activity of the MgO(II) decreased, while the activity of MgO(I) increased and attained a maximum value at 900°C. Although m- and p-cymenes were produced slightly (2%) in all regions of the pretreat-
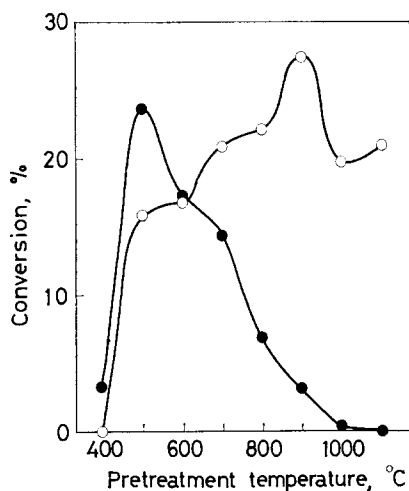


FIG. 1. Conversion of 3-carene over MgO at the fifth pulse vs pretreatment temperature. (○) MgO(I); (●) MgO(II): reaction temperature, 80°C; contact time, 4 s ml⁻¹ mg.
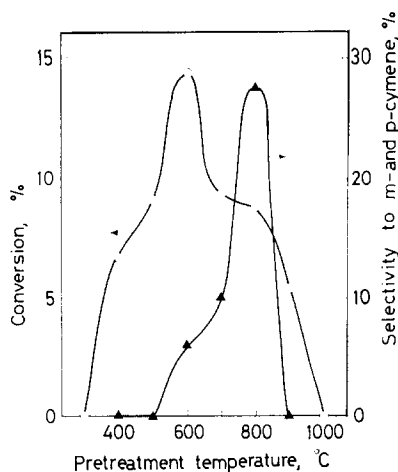


FIG. 2. Conversion of 3-carene and selectivity to m- and p-cymene over CaO(I) at the third pulse vs pretreatment temperature. (○) Conversion of 3-carene; (▲) selectivity to p-cymene; reaction temperature, 80°C; contact time, 2.5 s ml⁻¹ mg.

ment temperature, the selectivity for the formation of 2-carene was almost constant.

The activity of the CaO(I) appeared by the pretreatment at 300°C and increased with an increase of the pretreatment temperature and the maximum activity was observed when pretreated at 600°C as shown in Fig. 2. By pretreatment above 500°C, the formation of m- and p-cymene was observed and attained a maximum at 800°C of the pretreatment temperature. Mole percentages of each porduct are plotted against contact time in Fig. 3. The rate of double bond migration is much faster than that of dehydrogenation and an induction period was observed for the formation of m- and p-cymenes.

Since CaO(II) was much more rapidly poisoned with successive pulses of 3-carene and showed a lower activity than the CaO(I), the conversions of the first pulse at a contact time of 10 S ml⁻¹ mg are plotted against the pretreatment temperature as shown in Fig. 4. CaO(II) began to be active by the pretreatment at 600°C as expected from a higher decomposition temperature for calcium carbonate than for calcium hydroxide. m-Cymene and
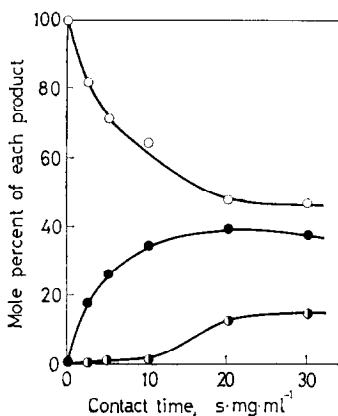
FIG. 3. Variation of product percentage with contact time over CaO(I). (○) 3-Carene; (●) 2-carene; (◐) *m*- and *p*-cymene; reaction temperature, 80°C.

*p*-cymene were not produced over CaO(II) in contrast to the case of CaO(I) where cymenes were produced with a selectivity of 34% at the first pulse when pretreated at 800°C.

It should be noted that 4-carene was not produced for all catalysts.

## Poisoning Effect

In Fig. 5 are shown poisoning effects on the MgO(II) with triethylamine, butylamine, and carbon dioxide. Triethylamine hardly influences the catalytic activity. Butylamine poisoned a considerable portion of the active sites, though its basicity ($pK_b = 3.38$) is almost the same as that of triethylamine ($pK_b = 3.25$). Carbon dioxide poisoned the active sites almost completely. Similar results were obtained for MgO(I) pretreated at 500 and 900°C, and for CaO(I) pretreated at 600°C.

## Exchange Reaction of 3-Carene with $D_2$

Experimental conditions and results are summarized in Table 2. A $\phi$ value is defined as $\Sigma i \cdot d_i$, where $d_i$ is a mole fraction of the isotopic species $C_{10}H_{16-i}D_i$, and represents the average number of D atoms in a molecule. Distributions of D atoms in the molecule are listed in Table 3. Larger $\phi$

values for MgO(II) than for MgO(I) indicate that the rate of the exchange reaction with $D_2$ over MgO(II) is faster than that for MgO(I).

An nmr spectrum of nondeuterated 3-carene is shown in Fig. 6a. Each signal is assigned as shown in Table 4. Since the peaks due to 2-H and 5-H are partly superposed with the peak of 10-H (10-methyl hydrogen), the region from $\delta = 1.32$ to $\delta = 3.20$ was divided into two parts at $\delta = 1.74$ which corresponded to a minimum point in the spectrum. The first part, **A**, ranging from $\delta = 1.32$ to $\delta = 1.74$ contains 3.15 hydrogen atoms, and the other part, **B**, ranging from $\delta = 1.74$ to $\delta = 3.20$ contains 3.85 hydrogen atoms. Division of the spectrum of 2-carene in the same way gives **A** containing 4.00 hydrogen atoms and **B** containing 3.00 hydrogen atoms. In Fig. 6b is shown an nmr spectrum of a mixture of 3-carene and 2-carene which was obtained by the exchange reaction of 3-carene with deuterium over MgO(I) pretreated at 500°C. The conversion of 3-carene to 2-carene was 19.7%. Since it was difficult to separate carenes distinctly into each isomer and to collect a sufficient amount, a mixture of 3-carene and 2-carene was subjected to the nmr measurement.
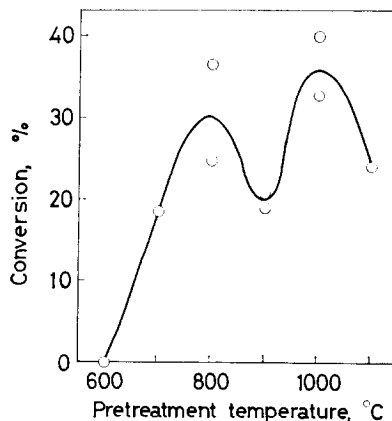


FIG. 4. Conversion of 3-carene over CaO(II) at the first pulse vs pretreatment temperature. Reaction temperature, 80°C; contact time, 10 s ml$^{-1}$ mg.

TABLE 3

Distribution of D Atoms in Carene Isomer

| Expt | Catalyst | Product | % Each Product | Isotopic distribution (%) | | | | | | | | | |
|------|----------|---------|------------------|------|------|------|------|------|------|------|------|------|-----------|
| | | | | $d_0$ | $d_1$ | $d_2$ | $d_3$ | $d_4$ | $d_5$ | $d_6$ | $d_7$ | $d_8$ | $\phi$ value |
| 1 | MgO(I) | 2- | 19.4 | 44.1 | 24.7 | 16.9 | 9.2 | 4.0 | 1.0 | 0.2 | 0 | 0 | 1.08 |
| | | 3- | 78.9 | 74.5 | 12.8 | 8.0 | 3.3 | 1.2 | 1.2 | 0 | 0 | 0 | 0.45 |
| 4 | MgO(II) | 2- | 24.5 | 28.5 | 11.7 | 11.7 | 12.4 | 15.0 | 14.1 | 5.0 | 1.3 | 0.2 | 2.40 |
| | | 3- | 74.0 | 52.8 | 13.6 | 11.0 | 7.7 | 7.2 | 5.9 | 1.6 | 0.2 | 0 | 1.28 |

The hydrogen atoms which underwent the exchange reaction with $D_2$ could be estimated by comparison of each peak area with the total peak area which corresponds equivalent to $(16-\bar{\phi})$ hydrogen atoms, where $\bar{\phi}$ is a $\phi$ value of a mixture of carenes. The fractional peak area for the hydrogen atoms whose $\bar{\phi}$ values are less than 1.32 was equivalent to $8/(16-\bar{\phi})$. This indicates that the hydrogen atoms which are attached to the carbon atoms 1, 6, 8, and 9 are not exchanged with $D_2$.

For a nondeuterated mixture containing $X$ fraction of 3-carene and $Y$ fraction of 2-carene, the number of hydrogen atoms in the A region and in the B region can be calculated from $3.15X + 4.00Y$ and $3.85X +3.00Y$, respectively. These values are listed in Table 2 as calculated values. For a deuterated mixture, the total numbers of hydrogen atoms in the regions A and B, and olefinic hydrogen atoms are equivalent to $(8-\bar{\phi})$. The numbers of hydrogen atoms in each region are calculated and listed in Table 2 as observed values. The difference between the calculated value and the observed value represents the number of hydrogen atoms exchanged with deuterium atoms. The region A includes all hydrogen atoms attached to carbon atom 10 and a part of hydrogen atoms attached to carbon atoms 2 and 5 in 3-carene and carbon atoms 4 and 5 in 2-carene. The region B includes the rest of the hydrogen atoms attached to carbon atoms 2 and 5 in 3-carene and carbon atoms 4 and 5 in

2-carene but no hydrogen atoms at carbon atom 10.

Over MgO(I) pretreated at both 500 and 900°C, the hydrogen atoms attached to carbon atom 10 were not exchanged, since the observed number of hydrogen atoms was substantially the same as the calculated value. Considerable differences between observed values and calculated ones were shown in the B region. This indicates that only the allylic hydrogen atoms in the six-membered ring are exchanged with deuterium. Although some differences were observed in the A region for MgO(II), the differences were much smaller for the A region than for the B region. This indicates
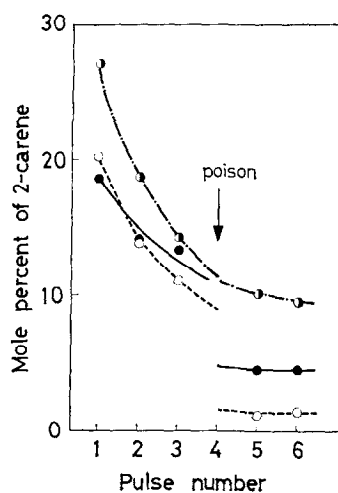


FIG. 5. Poisoning of MgO(II) pretreated at 500°C with triethylamine (◑); Butylamine (●); and carbon dioxide (○); reaction temperature, 80°C.
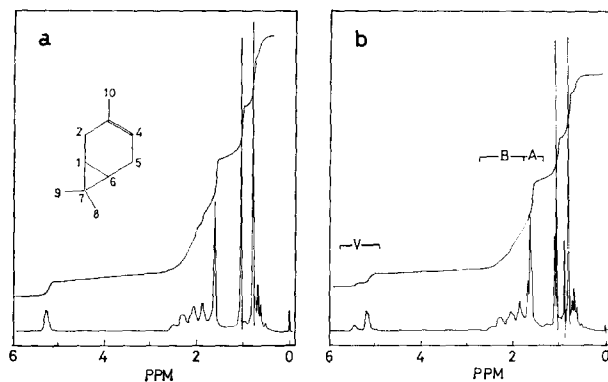
FIG. 6. Nuclear magnetic resonance spectra of carenes. (a) Nondeuterated 3-carene, (b) a mixture containing 80.3% of 3-carene and 19.7% of 2-carene, which was obtained by exchange reaction of 3-carene with deuterium over MgO(I) evacuated at 500°C. Reaction temperature, 80°C; reaction time, 30 min; catalyst weight, 50 mg.

that the allylic hydrogen atoms in the six-membered ring (at carbon atoms 2 and 5) are more easily exchanged with deuterium than the allylic hydrogen atoms of the methyl group carbon atom 10). The olefinic hydrogen atom was hardly exchanged over all catalysts.

DISCUSSION

The appearances of the activities of MgO(I) and CaO(I) for the isomerization of 3-carene to 2-carene with an increase in the pretreatment temperature roughly coincide with the appearances of the activities for the isomerization of butenes (10), the conversion of benzaldehyde to benzyl benzoate (11), and the decomposition of diacetone alcohol (12). The basic sites appear on MgO and CaO when $H_2O$ and/or $CO_2$ are removed from the surfaces by heating (10). The temperatures of the appearances of the basic sites coincide with those of the activities for the above reactions. Like for the other reactions, it is suggested that the active sites on MgO(I) and CaO(I) for the isomerization of 3-carene to 2-carene are generated by the removal of $H_2O$ and/or $CO_2$ from the surfaces, and these sites have basic properties. The active sites on

MgO(II) and CaO(II) could also have basic properties, though a higher pretreatment temperature was required to remove $CO_2$ for the preparation of CaO(II) than for CaO(I).

The basic sites generated in this way are considered to be $O^{2-}$ (12). Since butylamine exchanges the two hydrogen atoms attached to the nitrogen atom with deuterium over MgO(II), which is revealed by nmr spectroscopy (13), it is suggested that butylamine is dissociatively adsorbed on MgO. A proton and the remainder $(C_4H_9NH^-)$ may be adsorbed on the $O^{2-}$ and its adjacent metal cation, respectively. Although the basicities of butylamine and triethylamine do not considerably differ, triethylamine has no hydrogen atoms at the nitrogen atom. It may be coordinatively adsorbed on the metal cation with its lone pair of electrons of nitrogen atom. Therefore, the adsorption of triethylamine is considered to be much weaker than that of butylamine. A small poisoning effect of triethylamine suggests that the metal cations on the surface are not sufficiently strong to adsorb triethylamine irreversibly.

Carbon dioxide was reported to be strongly adsorbed on MgO and CaO in a bidentate or unidentate form according to

an adsorption condition (*14*). Metal cations may be blocked if $CO_2$ is adsorbed in a bidentate form, but they may not be blocked if $CO_2$ is adsorbed in a unidentate form. In both adsorption forms, $O^{2-}$, ions are blocked, and therefore the catalyst becomes inactive.

Over CaO(II) pretreated at 600–800°C, dehydrogenation to *m*- and *p*-cymenes occurred in addition to the isomerization. Schächter and Pines (*15*) have reported that cyclohexadienes and cyclohexene underwent dehydrogenation to benzene, and simultaneously hydrogen disproportionation to benzene, cyclohexene and cyclohexane. In this work, however, menthenes were not detected, which were expected to be produced if disproportionation of 3-carene occurred. This discrepancy may be caused by the difference either in the reactivity of the reactants or in the reaction temperature. The disproportionations of cyclohexadienes and cyclohexene were carried out at 240°C and higher. The variation of the selectivity for the formation of *m*- and *p*-cymenes with increasing pretreatment temperature coincides essentially with the variations of activities for hydrogenation of olefins (*16*, *17*). Consequently, the dehydrogenation of 3-carene and the hydrogenation of olefins proceed on the same active sites. The activity of MgO(I) for the hydrogenation of olefins is lower than that of CaO(I) by one order of magnitude (*16*), which explains a negligible activity of MgO(I) for the formation of *m*- and *p*-cymenes.

For double bond migration of olefins, mechanisms involving a $\pi$-allylic anion intermediate are proposed over basic catalysts such as MgO (*10*), CaO (*10*), and ZnO (*18*). The isomerizations of 3-carene to 2-carene over MgO and CaO are most likely to proceed by a $\pi$-allylic anion mechanism.

Two kinds of the reaction paths involving a $\pi$-allylic anion can be considered. One involves 3(10)-carene (**X**) as an intermediate

(path 1) and the other involves the anion (**XI**) (path 2).
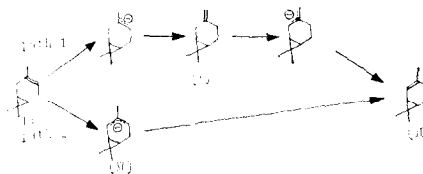


The reaction is initiated by the abstraction of the hydrogen atom at carbon atom 10 in the path 1, and by the abstraction of the hydrogen atom at carbon atom 2 in the path 2.

Over basic catalysts, olefins exchange their allylic hydrogen atoms with deuterium (*19–21*). The intermediates for exchange reactions are suggested to be allylic carbanions which also undergo isomerization, though there is another type of site which catalyzes only isomerization (*20*). The location of D atoms in carenes which resulted from the exchange with deuterium may indicate the reaction path for the isomerization of 3-carene. If the reaction proceeds via the path 1, the hydrogen atoms at carbon atom 10 would be most easily exchanged with deuterium. If the reaction proceeds via the path 2, the hydrogen atoms at carbon atom 2 would be easily exchanged.

Since the hydrogen atoms at carbon atom 10 did not exchange over MgO(I) and the hydrogen atoms at carbon atoms 5 and/or

TABLE 4

Assignments of Nmr Signals

| Position[a] | Chemical shift (ppm) | |
| --- | --- | --- |
| | 3-Carene | 2-Carene |
| 4(2)[b] | 5.24 | 5.48 |
| 2(4),[b] 5 | 2.5   1.6 | 2.5   1.6 |
| 10 | 1.60 | 1.68 |
| 8, 9 | 1.04, 0.78 | 1.08, 0.88 |
| 1, 6 | 1.0 | 1.0 |

[a] Refer to Fig. 6a.
[b] The parentheses for 2-carene.

2 exchanged, it is suggested that the iso-merization proceeds *via* the path 2. Over MgO(II), the hydrogen atoms at carbon atom 5 and/or 2 exchanged more easily than the hydrogen atoms at carbon atom 10, which exchanged to some extent. There-fore, it is suggested that the path 2 is pre-dominant over the path 1.

The olefinic positions of 2-carene and 3-carene can be converted by isomerization into allyl positions of 3-carene and 2-carene, respectively. The allylic hydrogen atoms at carbon atom 4 of 2-carene and at carbon atom 2 of 3-carene seem to be exchanged by the reverse reaction of path 2. The olefinic hydrogen atoms are expected to be exchanged with deuterium. Experi-mental results showed that the olefinic hydrogen atoms were not substantially ex-changed. According to Acharya (*22*), 3-carene exists preferentially in a boat con-formation as shown below.
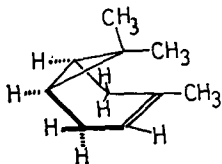


Since one side of 3-carene in the boat form is strongly shielded by the cyclopropane ring and its *gem*-dimethyl group, only the other side may interact with the surface of catalyst. One of the allylic hydrogen atoms at carbon atom 2, which is toward the catalyst surface, may be abstracted, and a $\pi$-allyl anion may be formed. A deuterium ion may approach carbon atom 2 or 4 from the surface, and produce 3-carene-2-$d_1$ or 2-carene-4-$d_1$. In the $d_1$-species, a deuterium atom in the allylic position may be always on a side accessible to the surface. Corre-sponding abstraction–addition occurs in the reverse reaction during which the deu-terium atom in the $d_1$-species will be taken away, while the hydrogen atom which is attached to the same carbon atom as the deuterium may remain as an olefinic hy-drogen atom.

Since hydrogen atoms are exchanged with deuterium at carbon atom 5, it is suggested that the intermediate,



is formed in the reaction. However, drawing (below) the intermediate and showing the addition of a hydrogen atom to carbon atom 3 with formation of a double bond between carbon atoms 4 and 5 show a serious nonbonded interaction between 8-methyl group and 10-methyl group, which could explain no formation of 4-carene.
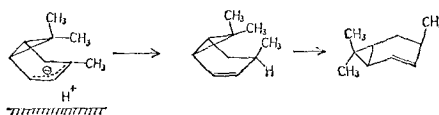


## ACKNOWLEDGMENTS

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