

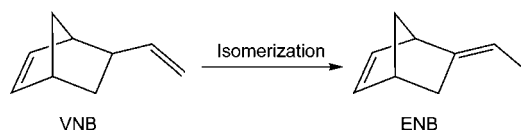
Mechanistic Investigation of the Isomerization of 5-Vinyl-2-norbornene

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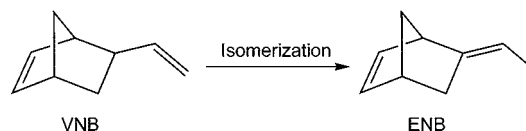
The isomerization reaction of 5-vinyl-2-norbornene (VNB) to 5-ethylidene-2-norbornene (ENB) has been performed using a catalytic system consisting of an alkali metal hydride and an amine. Among various amines tested, only aliphatic 1,2-diamines exhibited the activity for the isomerization. The isomerization was also affected by the alkali metal hydride employed. The activity of the alkali metal hydride increased with the increasing size of alkali metal: $\text{KH} > \text{NaH} > \text{LiH}$. A series of electron paramagnetic resonance (EPR) and UV-vis experiments on the active species suggest that the isomerization of VNB proceeds through a radical mechanism.

Introduction

There has been a great industrial interest in the synthesis of 5-ethylidene-2-norbornene (ENB) as a third component of a terpolymer of ethylene, propylene, and diene monomers (EPDM rubber).^{1–3} Currently, ENB is being manufactured by the catalytic isomerization of 5-vinyl-2-norbornene (VNB), which is produced by the Diels–Alder reaction between 1,3-butadiene and cyclopentadiene (Scheme 1).⁴

There are known solid super base catalysts that act as isomerization catalysts, such as alkali metal supported on alumina, silica gel, or active carbon with a large surface area, but these solid catalysts are hard to handle because they are easily ignited and lose activity upon contact with air.^{5–7}

SCHEME 1



There are also known liquid bases, for example, mixtures of an alkali metal hydroxide and an aprotic organic solvent and of an alkali metal amide and an amine. Organometallic complexes including Ti ,^{4,8} Co ,^{9,10} and Fe ¹¹ are other types of catalysts used for the isomerization. The industrial application of these liquid bases and organometallic complexes, however, has been restricted because of their low catalytic activities. Accordingly, many attempts have been made to increase the activities of liquid base catalysts. A major improvement has been made in the patent literature by using a catalytic system consisting of an alkali metal hydride and a polyamine.¹²

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(1) Fritz, M. E.; Atkins, K. E. U.S. Patent 3,347,944, 1967.

(2) Grozdreva, E. A.; Belikova, N. A.; Plate, A. F.; Shatenshtein, A. I. *Dokl. Chem.* **1969**, 189, 967.

(3) Mirzoyan, Z. A.; Kovaleva, G. V.; Pisman, I. I.; Livshits, I. A.; Korobova, L. M.; Dalin, M. A. *Dokl. Akad. Nauk SSSR* **1974**, 30, 28.

(4) Ishii, Y.; Saitoh, A.; Hamanaka, S.; Ogawa, M. *Sekiyo Gakkaiishi* **1986**, 29, 20.

(5) Haag, W. O.; Pines, H. *J. Am. Chem. Soc.* **1960**, 82, 387.

(6) Suzukamo, G.; Fukao, M.; Minobe, M. *Chem. Lett.* **1987**, 585.

(7) Caubere, P. *Chem. Rev.* **1993**, 93, 2317.

(8) Wolfgang, S. U.S. Patent 3,696,157, 1972.

(9) Pillai, S. M. *React. Kinet. Catal. Lett.* **1994**, 52, 35.

(10) Samnani, P. B.; Bhattacharya, P. K.; Pillai, S. M.; Satish, S. *J. Chem. Res. (S)* **1994**, 338, 1868.

(11) Osokyn, Y.; Grinberg, Y.; Fel'dblyum, V.; Toetlin, I.; Belikoba, N.; Plate, A. *Neftekhimiya* **1980**, 20, 354.

TABLE 1. Effect of Amine on the Isomerization of VNB^a

amine	temp (°C)	yield ^b (%)
ethylenediamine	25	96.3
diethylenetriamine	25	96.2
1,2-diaminopropane	25	95.8
1,2-diaminocyclohexane	25	n.r. ^c
1,2-diaminocyclohexane	100	80.5
1,3-diaminocyclohexane	25, 100	n.r.
1,4-diaminocyclohexane	25, 100	n.r.
ethylamine	25, 100	n.r.
cyclohexylamine	25, 100	n.r.

^a Reaction conditions: reaction time = 1 h, molar ratio of NaH/amine/VNB = 1:30:50. ^b ENB yield (%) = (moles ENB produced/initial moles VNB) × 100. ^c n.r. = no reaction.

TABLE 2. Effect of Alkali Metal Hydride on the Isomerization of VNB^a

alkali metal hydride	temp (°C)	yield ^b (%)
LiH	25	4.0
LiH	100	92.6
NaH	25	96.3
KH	25	99.9

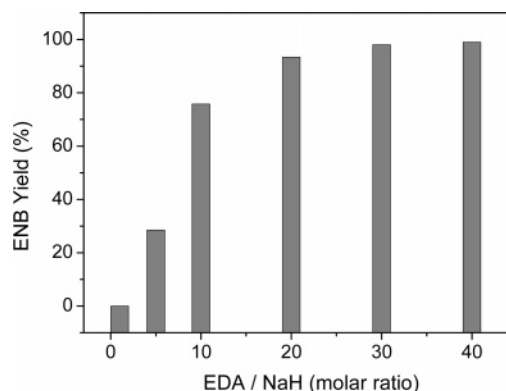
^a Reaction time = 1 h. Molar ratio of MH/EDA/VNB = 1:30:50. ^b ENB yield (%) = (moles ENB produced/initial moles VNB).

Even though various catalysts have been developed, some of which have been successfully used in the commercial production of ENB, the mechanistic details on the isomerization of VNB have rarely been investigated. For this reason, we have undertaken a mechanistic study on the isomerization process with a hope that understanding the mechanism might help to develop isomerization catalysts with better performance. Among the catalysts reported, we are particularly interested in the liquid base catalysts consisting of an alkali metal hydride and a polyamine because they are highly active and relatively easy to handle for the mechanistic investigation.

In this paper, we report our observations on the mechanistic aspects of the VNB isomerization conducted in the presence of a catalytic system based on a polyamine and an alkali metal hydride.

Results and Discussion

Effects of Amines and Alkali Metal Hydrides. The isomerization reactions of VNB were performed using a catalytic system consisting of an amine and an alkali metal hydride. Tables 1 and 2 show the effects of amines and alkali metal hydrides on the isomerization of VNB, respectively. As can be seen in Table 1, ENB was produced in high yields at room temperature in the presence of a di- or triamine including ethylenediamine (EDA), 1,2-diaminopropane, and diethylenetriamine. The isomerization also proceeded in the presence of 1,2-diaminocyclohexane but at a much higher temperature of 100 °C. Interestingly, however, no ENB was produced even at 100 °C when 1,3- or 1,4-diaminocyclohexane was used instead of 1,2-diaminocyclohexane, supporting the importance of the locations of two amino groups. It is likely that the formation of the active species from a 1,2-diamine and NaH is more facilitated through resonance stabilization when the two amino groups of the diamine are located at the vicinal positions. As expected from the above results, monoamines such as ethylamine and cyclohexylamine were not effective for the isomerization.

**FIGURE 1.** Effect of the molar ratio of EDA/NaH on the isomerization.

The isomerization was greatly affected by the alkali metal hydride employed. As shown in Table 2, KH produced ENB almost quantitatively at room temperature, but LiH gave ENB in very low yield (e.g., about 4%) at room temperature. The activity of the alkali metal hydride increased with the increasing size of alkali metal: KH > NaH > LiH. It seems that the formation of the active species and the evolution of hydrogen gas are more facilitated in the presence of a hydride of larger-sized alkali metal because the dissociation energy of alkali metal hydride decreases with the increasing size of alkali metal.

The influence of the molar ratio of EDA/NaH on the VNB isomerization was also examined. The yield of ENB increased with an increasing molar ratio of EDA/NaH up to 30 and remained nearly constant thereafter on further increases in the molar ratio (Figure 1). This phenomenon can be ascribed to the polar character of the active species produced from the reaction of EDA with NaH. The active species formed from the interaction of NaH and EDA is soluble in EDA but completely insoluble in VNB or ENB. Therefore, at a lower molar ratio of EDA/NaH, the majority of active species exists as a heterogeneous oily state in the reaction mixture, thereby limiting the interaction with VNB. However, with an increasing molar ratio of EDA/NaH, the oily active species becomes soluble in the bottom EDA layer and thus the interaction of the active species with the VNB layer is more facilitated when stirring is applied.

UV–Vis and EPR Experiments. In the course of investigating the isomerization reaction with a catalytic system consisting of an alkali metal hydride and an amine, we have found that the activity of the catalytic system is strongly related to the color of the solution. The active solution containing EDA and NaH exhibited a purple color at room temperature and showed a strong peak centered at 581 nm in the UV–vis spectrum (Figure 2). However, neither the color nor the absorption band at visible regions was observed for the solution consisting of NaH and an inactive amine such as 1,3-cyclohexane diamine. The intensity of the absorption band at 581 nm was affected by the activity of alkali metal hydride. For instance, the mixture of EDA and LiH gave much lower intensity than that of EDA and NaH, demonstrating the importance of the peak at 581 nm. Such an UV absorption band was also observed in many delocalized radical species containing nitrogen atoms in the range 400–800 nm.^{13,14}

Interestingly, the solution containing 1,2-diaminocyclohexane and NaH showed a purple color only when the solution was heated to 100 °C. Once the purple color persisted, the isomer-

(12) Ishihara, T. JP Patent 6-40956, 1994.

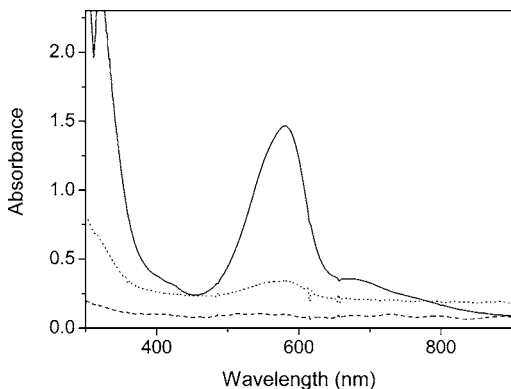
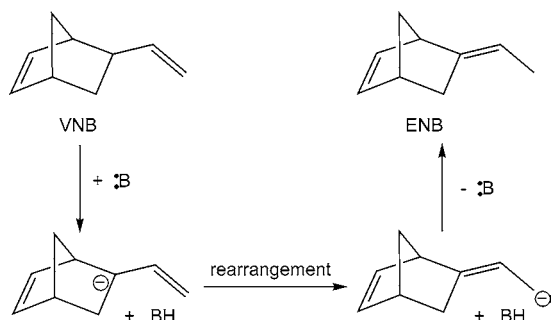


FIGURE 2. UV spectra of the solutions containing EDA and alkali metal hydride. (—): EDA/NaH (30:1) under Ar (after 10 min). (···): EDA/LiH (30:1) under Ar (after 10 min). (---): After exposure of EDA/NaH to dioxygen.

SCHEME 2



ization proceeded even at room temperature, irrespective of the amine and alkali metal hydride used.

In general, the isomerization of VNB is known to proceed through a carboanionic mechanism (Scheme 2).⁶ However, this seems not to be the case for the isomerization mediated by a catalytic system consisting of EDA and an alkali metal hydride. When benzophenone dissolved in EDA was added to the purple solution containing EDA and NaH, the solution immediately turned to greenish-blue, a characteristic color of the phenyl ketyl radical, and became inactive for the VNB isomerization. It is conceivable that the active radical species is captured by phenyl ketyl radicals and transformed into an inactive species. A similar phenomenon was also observed when a stable organic radical, 1,1,6,6-tetramethylpiperidinyl-oxide (TEMPO), was added to the purple solution, strongly suggesting that the isomerization proceeds through a radical mechanism.

To confirm this postulate, electron paramagnetic resonance (EPR) experiments were performed. The active purple species prepared from NaH and EDA diluted in THF exhibited a complicated hyperfine splitted signal centered at $g = 2.0034$ (3363 G) (Figure 3a). This pattern of hyperfine splitting is very similar to that of the Na^+ ion pair of the delocalized bisdiazene radical anion.^{13b} Therefore, it is conceivable that the active purple species could be a delocalized radical anion paired with

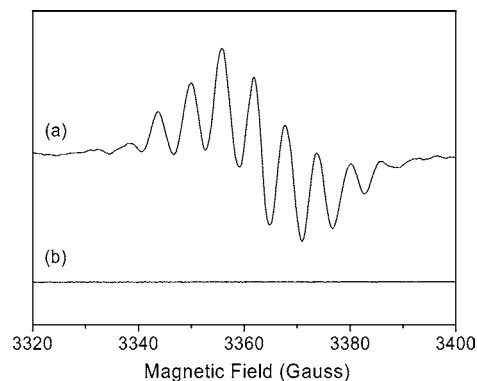
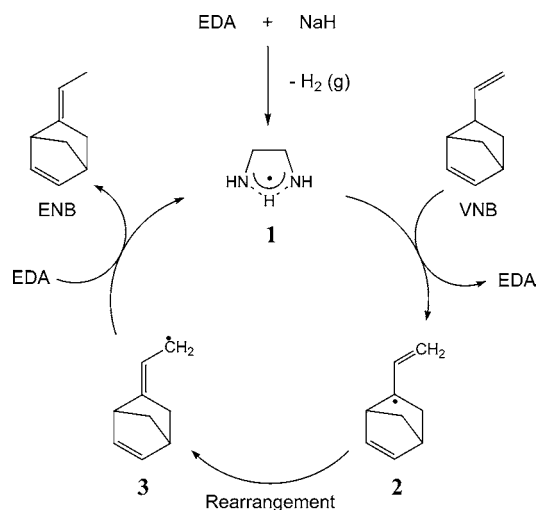


FIGURE 3. EPR spectrum of purple species at 298 K under Ar in THF: (a) active species (NaH/EDA = 30, NaH in THF = 5 mM) and (b) after exposure of (a) to dioxygen.

SCHEME 3



a sodium cation. However, the possibility of the presence of a sodium radical cation cannot be excluded. When the above purple solution was exposed to dry dioxygen, the solution turned a brownish-yellow (Figure 2) and the EPR signal completely disappeared (Figure 3b). As can be expected from the absence of the EPR signal, the isomerization of VNB did not proceed after the purple solution was exposed to dioxygen for a few seconds, implying that the active radical species in the purple solution were extinguished upon interaction with dioxygen, a known diradical species.

Mechanism of the Isomerization Reaction of VNB. From the experimental and spectroscopic results, the plausible reaction mechanism of the isomerization is suggested in Scheme 3. The active radical species **1** is likely to form by the reaction of EDA and NaH with the evolution of H_2 . The evolution of hydrogen gas was confirmed by means of a gas chromatographic analysis (see Supporting Information). The interaction of **1** with VNB would produce EDA and radical species **2**, which in turn rearranges to give **3**. The interaction of radical species **3** with EDA will produce ENB with the regeneration of the active species **1**.

Conclusions

The isomerization of VNB produced ENB in high yields in the presence of a catalytic system consisting of an aliphatic 1,2-diamine and an alkali metal hydride. The activity of the catalytic

(13) (a) Exner, K.; Hunkler, D.; Gescheidt, G.; Prinzbach, H. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1910. (b) Exner, K.; Cullmann, O.; Vogtle, M.; Prinzbach, H.; Grossmann, B.; Heinze, J.; Liesum, L.; Bachmann, R.; Schweiger, A.; Gescheidt, G. *J. Am. Chem. Soc.* **2000**, *122*, 10650.

(14) Zwier, J. M.; Brouwer, A. M.; Keszthelyi, T.; Balakrishnan, G.; Offersgaard, J. F.; Wilbrandt, R.; Barbosa, F.; Buser, U.; Amaudrut, J.; Gescheidt, G.; Nelsen, S. F.; Little, C. D. *J. Am. Chem. Soc.* **2002**, *124*, 159.

system was strongly related to the color of the solution and the absorption band at 581 nm. The active catalytic system produced a purple color and showed a strong absorption band at 581 nm in the UV-vis spectrum. The yield of ENB increased with an increasing molar ratio of EDA/NaH up to 30 and remained unchanged thereafter on further increases in the molar ratio. The activity of the alkali metal hydride increased with the increasing size of alkali metal: $\text{KH} > \text{NaH} > \text{LiH}$. A series of EPR and UV-vis experiments on the active species suggest that the isomerization of VNB proceeds through a radical mechanism.

Experimental Section

Materials. Amines, ENB, and VNB were purchased and purified according to the literature procedures just prior to use.¹⁵ LiH, NaH, and KH were used as received. All the glassware was completely dried at 120 °C to remove water.

Isomerization Reactions. Isomerization reactions were carried out under an inert atmosphere. A typical reaction was as follows: ethylenediamine (7 mL, 50 mmol) was added to a 100 mL round-

bottomed flask containing NaH (0.04 g, 1.67 mmol), and the mixture was vigorously stirred until the solution turned to purple and the evolution of H₂ gas was ceased. VNB (12 mL, 83 mmol) was then added to the purple solution and reacted for 1 h to produce ENB.

Instrumentation. The product mixture was analyzed by a gas chromatograph equipped with a flame-ionized detector and GC mass spectrometry. Hydrogen gas evolved and was analyzed by a gas chromatograph equipped with a thermal conductivity detector (TCD). Electron paramagnetic resonance (EPR) spectra were recorded on a EPR spectrometer (microwave frequency, 9.43 GHz; power, 1 mW; modulation frequency, 100 kHz; modulation amplitude, 3.0; time constant, 0.3 s). UV-vis spectra were obtained using a specially designed gas cell containing two 25 × 4 mm quartz windows.

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Supporting Information Available: EPR spectra of active purple species at different concentrations and GC data of evolved hydrogen gas. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(15) Perrin, D. D.; Armarego, W. L. F. In *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: New York, 1988.