JOURNAL OF CATALYSIS **65**, 245–252 (1980)

Double-Bond Migration of Allylamine to Enamine over Basic Oxide Catalysts

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Received January 30, 1979; revised March 31, 1980

Double-bond migration of 1-*N*-pyrrolidino-2-propene to 1-*N*-pyrrolidino-1-propene

was carried out at 40°C with a microcatalytic pulse reactor over basic oxide catalysts such as MgO, CaO, SrO, BaO, ThO_2, La_2O_3, ZrO_2, and ZnO. Magnesium oxide and CaO exhibit a high activity. Strontium oxide, BaO, and La_2O_3 rapidly reduce their activities with pulse number, though the initial activities are high. Thorium oxide shows an intermediate nature between these two groups. Zirconium oxide and ZnO are completely inactive. Activities of MgO and CaO vary with the pretreatment temperature of the catalysts, and the maximum activities are obtained when pretreated in the temperature range 400–1000°C for MgO and 700°C for CaO. In the double-bond migration of *N*,*N*-dimethyl-2-propenylamine over CaO, 100% *cis*-*N*,*N*-dimethyl-1-propenylamine is initially formed. It is suggested that the double-bond migration of allylamines proceeds via anionic intermediates in which the *cis* form is much more stable than the *trans* form.

INTRODUCTION

Since Stork and colleagues' demonstration (*1*, *2*) of the general utility of enamines for the acylation and alkylation of carbonyl compounds, the potential use of enamines has expanded in organic synthesis (*3*). The most versatile method for preparing enamines involves the condensation of aldehydes and ketones with secondary amines (*3*, *4*). Base-catalyzed double-bond migration of allylamines is one of the special ways to prepare enamines. By this method, stereospecific synthesis is possible. The ratio of the two isomers, *cis* and *trans* enamines, was determined by kinetic control in contrast to the case of the condensation which gives the thermodynamically equilibrated ratio of *cis*/*trans* isomers. For base-catalyzed double-bond migration, strong bases such as t-BuOK in dimethyl sulfoxide and sodium amide in liquid ammonia are commonly used as homogeneous catalysts (*5*–*8*).

Although heterogeneous catalysts have several advantages compared with homogeneous catalysts, only a few solid base catalysts have been examined for the double-bond migration of allylamines. Kondrat'eva and Dol'skaya (*9*) reported that double-bond migration of allylamines proceeded over potassium hydroxide supported on alumina at 260–270°C. Hubert (*10*) presented potassium amide on alumina as an effective catalyst for the reaction. Allylamines were isomerized cleanly at 25°C, though activity degradation was observed during the reaction.

Besides supported base catalysts, a variety of metal oxides have been recently presented as base catalysts. Those are zinc oxide (*11*), alkaline earth oxides (*12*–*17*), thorium oxide (*18*), lanthanum oxide (*19*), and zirconium oxide (*20*). We studied the double-bond migration of allylamines over these metal oxides and reported briefly the catalytic activities of alkaline earth oxides (*21*). In this paper, catalytic activities of the

0021-9517/80/100245-08$02.00/0

above basic catalysts in addition to those of alkaline earth oxides are reported in detail and the reaction mechanism is discussed.

EXPERIMENTAL METHODS

The MgO, CaO, SrO, and BaO catalysts were prepared from $Mg(OH)_2$ (Kanto Chemical Co., Inc.), $Ca(OH)_2$ (Kanto Chemical Co., Inc.), $SrCO_3$ (E. Merck), and granular BaO (E. Merck) by thermal decomposition under a helium stream. The ThO_2 catalyst was prepared from $Th(C_2O_4)_2$ (Wako Pure Chemical Industry Ltd.) by thermal decomposition at 500°C in air. The La_2O_3 catalyst was obtained by thermal decomposition of $La(OH)_3$ at 700°C under a helium stream. Lanthanum hydroxide was prepared by hydrolysis of an aqueous solution of $La(NO_3)_3$ with aqueous ammonia followed by washing with deionized water and drying at 120°C. The ZrO_2 catalyst was obtained by thermal decomposition of $Zr(OH)_4$ at 700°C in air. Zirconium hydroxide was prepared by hydrolysis of an aqueous solution of $ZrOCl_3$ with aqueous ammonia followed by washing and drying. The ZnO catalyst was prepared by hydrolysis of an aqueous solution of $Zn(NO_3)_2$ with aqueous ammonia followed by washing and calcination at 450°C in air. The Al_2O_3 catalyst was prepared by hydrolysis of an alcoholic solultion of aluminum isopropoxide with aqueous ammonia followed by washing and calcination at 500°C in air. The silica–alumina catalyst was type SA-N of Nikki Chemical Industry. Prior to the reaction, all catalysts were pretreated at proper temperatures in a reactor under a helium stream for 3 h.

1-*N*-Pyrrolidino-2-propene was prepared from allyl bromide and pyrrolidine by condensation according to the method of Sauer and Prahl (*6*). *N*,*N*-Dimethyl-2-propenylamine was purchased from Tokyo Kasei Kogyo Company, Ltd. Amines were distilled under a reduced pressure and purified by passage through KOH columns.

A microcatalytic pulse reactor was employed for carrying out the reaction at 40°C. One microliter of 1-*N*-pyrrolidino-2-propene was introduced by a microsyringe into the helium stream ahead of the catalyst, and the products were trapped by liquid nitrogen before being flash evaporated into a gas chromatographic column, which was directly connected to a mass spectrometer. Apiezone L on KOH-treated Chromosorb was packed in a 3-m glass column which was operated at 100°C.

Stereoselectivity in the isomerization of *N*,*N*-dimethyl-2-propenylamine over the CaO catalyst was examined by NMR spectroscopic analysis. An all-glass static reactor was employed. Calcium oxide was outgassed at 500°C in a reactor and sealed. A reactant was introduced through breakable seals. After the reaction, the product was directly trapped in an NMR cell, and the cell was sealed. The products in the cell were kept at liquid-nitrogen temperature to prevent the produced enamine from undergoing *cis–trans* isomerization, and melted immediately before the NMR measurement. The NMR spectrum was recorded on an R 20B Hitachi spectrometer at 60 MHz.

RESULTS

In the reaction of 1-*N*-pyrrolidino-2-propene, the conversion to 1-*N*-pyrrolidino-1-propene is plotted against the pulse number in Fig. 1. Over MgO pretreated at 1100°C, the conversion was not lowered by increasing the flow rate. The conversion was al-

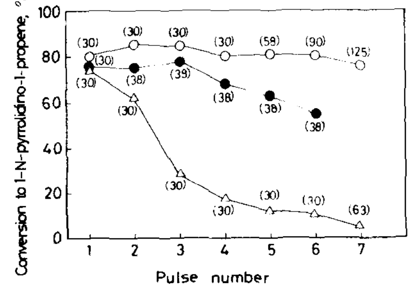


FIG. 1. Conversion to 1-*N*-pyrrolidino-1-propene against pulse number. (○) 30 mg MgO pretreated at 1100°C; (●) 30 mg MgO pretreated at 450°C; (△) 300 mg SrO pretreated at 1000°C. The figures in parentheses show flow rate in milliliters per minute.

TABLE 1

Double-Bond Migration of 1-*N*-Pyrrolidino-2-propene at 40°C

Catalyst	Pretreatment temperature (°C)	Specific surface area (m^2/g)	Weight of catalyst (mg)	Pulse No.	Flow rate (ml/min)	Percentage of each product			
						1-*N*-Pyrrolidino-2-propene	1-*N*-pyrrolidino-1-propene	Pyrrolidine	Propion-alde-hyde
MgO	600	135	30	1	30	0	79.8	9.9	10.3
				3	30	0.1	85.6	11.5	2.7
				5	88	1.0	83.9	12.3	2.7
CaO	400	81	30	1	30	4.4	64.3	25.5	5.7
				3	30	28.5	49.9	18.8	2.8
				5	30	56.0	35.1	7.1	1.8
CaO	700	52	34	1	30	0.5	61.2	26.1	11.7
				3	30	0.2	81.8	15.7	2.2
				5	113	0.4	76.7	19.8	3.2
SrO	1000	10	302	1	30	0.2	77.7	11.8	10.3
				3	30	62.4	31.2	5.3	1.2
				5	30	86.3	12.9	0.6	0.1
BaO	800	0.2	313	1	30	0.4	71.9	19.1	8.7
				2	30	96.5	2.9	0.4	0.2
ThO_2	700	59	102	1	30	16.6	50.8	17.0	15.6
				3	30	50.8	40.6	5.9	2.4
				5	120	72.2	19.7	5.2	2.8
La_2O_3	700	27	31	1	30	0.6	67.9	19.3	12.2
				3	30	71.9	20.8	5.6	1.7
				4	30	97.8	0.4	1.8	0

most saturated. Over MgO pretreated at 450°C, the conversion decreased gradually with the pulse number. Rapid decrease in the conversion was observed for SrO. At the first pulse with MgO pretreated at 1100°C, about 60% of a slug remained on the catalyst. The amounts of the remained molecules corresponded to 0.12 mmol of the reactant/g catalyst.

The compositions of the products for each catalyst are given in Table 1. Although a main product was 1-*N*-pyrrolidino-1-propene, considerable amounts of pyrrolidine and propionaldehyde were produced over all catalysts. The formation of propionaldehyde was facile especially at the first pulse. Since neither the reactant nor the carrier gas contained oxygen atoms, the oxygen atom in propionaldehyde should originate from the catalyst surface. With SrO, BaO, and La_2O_3, the activity degradation with the pulse number was prominent, though they showed high conversions to 1-*N*-pyrrolidino-1-propene at the first pulse. The activity degradations of MgO and CaO were very small. Thorium oxide gradually lost its activity with successive pulses. No activities were observed with ZrO_2, ZnO, Al_2O_3, and SiO_2–Al_2O_3 at 40°C.

The variations of the conversion to 1-*N*-pyrrolidino-1-propene at the second pulse as a function of the pretreatment temperature are shown in Fig. 2 for MgO, CaO, and BaO. The activity of MgO appeared on pretreatment above 300°C, and it was nearly saturated when pretreated in the temperature range 400–1000°C. Calcium oxide exhibited the activity on pretreatment above 100°C and showed roughly equal conversions in the pretreatment temperature range 300–900°C. Barium oxide showed almost no activity at the second pulse on pretreatment at any temperature.

Stereochemistry was examined for the double-bond migration of *N*,*N*-dimethyl-2-propenylamine over CaO that was outgassed at 500°C. Since *N*,*N*-dimethyl-2-propenylamine has a molecular structure in which a methyne group of 4-methyl-1-pentene is replaced by a nitrogen atom, stereochemistry in the double-bond migration of 4-methyl-1-pentene was also studied for comparison.

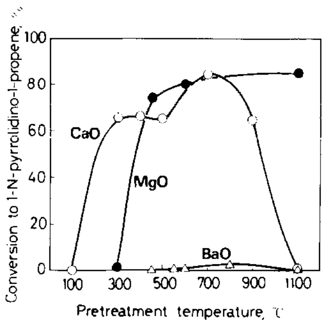


FIG. 2. Variations of conversion to 1-*N*-pyrrolidino-1-propene as a function of pretreatment temperature. Weight of catalyst: MgO, 30 mg; CaO, 30 mg; BaO, 300 mg. Flow rate, 30 ml/g. Reaction temperature, 40°C.

The NMR spectrum of the products in the reaction of *N*,*N*-dimethyl-2-propenylamine at the conversion level of 84% is shown in Fig. 3. The assignment is based on the literature (*6*) in which the chemical shift of each hydrogen of the neat substance is presented. The values of the chemical shifts observed are slightly different from those in the literature, probably because of the reactant remaining in the products. The *cis*/*trans* ratio of *N*,*N*-dimethyl-1-propenylamine was obtained from the intensities of the quartet peaks (CH_3(c)) at 0.95 ppm for the *cis* isomer and at 0.86 ppm for the *trans* isomer. The separation was possible when the spectrum was taken at 60 MHz. Percentages of the *cis* isomer in *N*,*N*-dimethyl-1-propenylamines produced are plotted against the conversion in Fig. 4. Extrapolation to zero conversion gives 100% *cis*-*N*,*N*-dimethyl-1-propenylamine. Percentages of the *cis* isomer in 4-methyl-2-pentenes from 4-methyl-1-pentene are also shown in Fig. 4. The percentage of *cis*-4-methyl-2-pentene at zero conversion was about 50%. The stereoselectivity to the *cis* form is much higher for the isomerization of the allylamine than for the olefin.

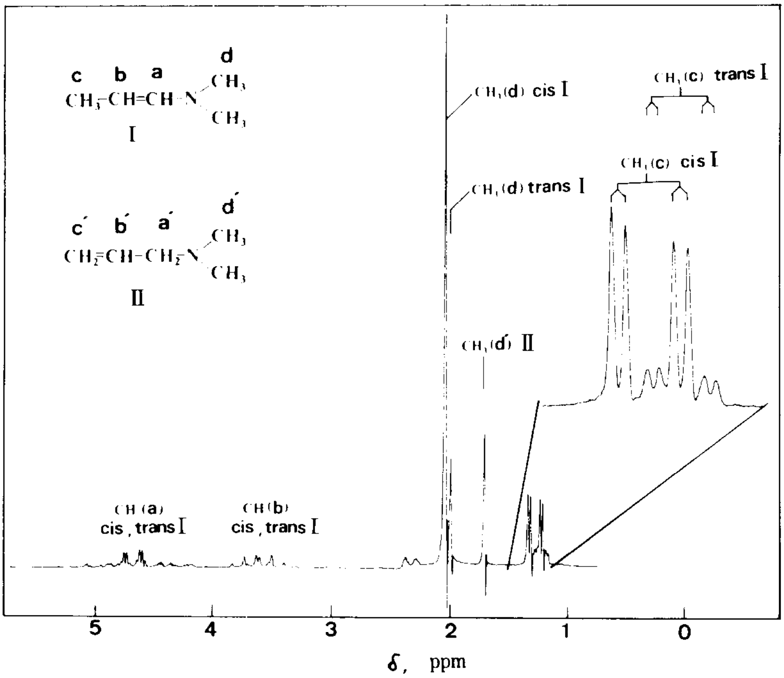


FIG. 3. NMR spectrum of the products at 84% conversion level in the reaction of *N*,*N*-dimethyl-2-propenylamine.

DISCUSSION

Among the metal oxides that were examined for the double-bond migration of 1-*N*-pyrrolidino-2-propene, MgO, CaO, SrO, BaO, La_2O_3, and ThO_2 exhibited activities at least in the first pulse. As mentioned earlier, these oxides are known to possess basic sites on their surface and to catalyze butene isomerization in which the basic sites act as active sites. It has been reported that the double-bond migration of allylamines occurs in liquid phase with homogeneous bases. Therefore, it is suggested that the active sites of MgO, CaO, SrO, BaO, La_2O_3, and ThO_2 for the double-bond migration of allylamines are basic sites.

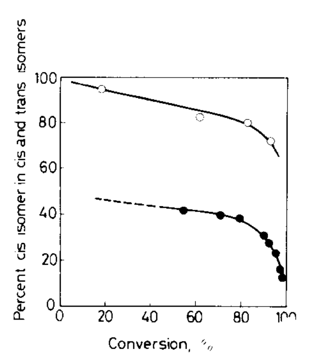
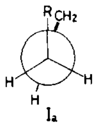


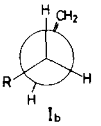
FIG. 4. Percentages of *cis* isomer in isomerized products for the double-bond isomerizations of *N*,*N*-dimethyl-2-propenylamine (○) and 4-methyl-1-pentene (●).

Although ZrO_2 and ZnO act as basic catalysts for butene isomerization, they showed no activities for the double-bond migration of allylamines. One explanation could be that the basic sites of ZrO_2 and ZnO are too weak to abstract a proton from allylamines. An alternative explanation might be that the acidic sites which are supposed to be adjacent to the basic sites strongly adsorb allylamines which block the basic sites.

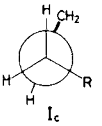
Similar to the isomerization of olefins, the double-bond migration of allylamine is considered to be initiated by abstraction of an allylic proton by the basic site of the catalyst to form π-allylic anions. For drawing the reaction pathway, it is necessary to take into account the conformation of the reactant. The π-allylic anion has two configurations, *trans* and *cis* forms. The *trans*-π-allylic anion would be formed from the *anti* conformer of the reactant, whereas the *cis*-π-allylic anion would be formed from the *syn* conformer. The terms *anti* and *syn* conformers represent those whose angle of torsion between the terminal methylene group and the amino group are +90 to +270° and −90 to +90°, respectively. Conformational determination of the allylamines is not available in the literature. However, conformational analysis of substituted propene has been summarized (*22*). According to Ref. (*22*), the three conformers shown below have the same stability for 1-butene in which R = CH_3.



I_a



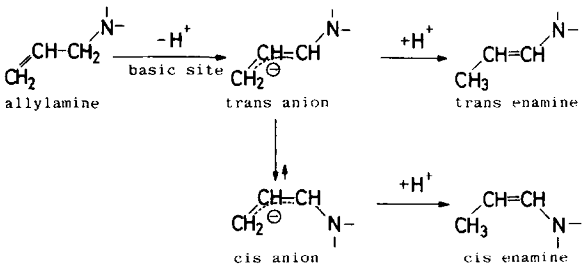
I_b



I_c

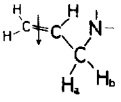
As the R group becomes bulkier, the populations of forms I_b and I_c increase; the steric repulsion between the methylene group and the R group increases. This could be applied to unsaturated compounds containing a nitrogen atom. The steric repulsion between the pyrrolidino group or the dimethyl amino group and the methylene group may be great. In addition, the repulsion between π-electron and p-electron at the N atom favors the *anti* conformer. Therefore, it is expected that the *anti* conformer is preferential for both pyrrolidino-2-propene and *N*,*N*-dimethyl-2-propenylamine.

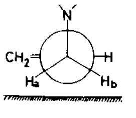
Abstraction of the allylic proton from allylamine of the *anti* conformer by the basic sites of the catalyst would produce the *trans*-π-allylic anion. If the *trans*-π-allylic anion were attacked by a proton at carbon atom 3 before it interconverted to the more stable *cis*-π-allylic anion, *trans*-enamine would be preferentially produced. This was not the observed result. If the interconversion between the *trans*- and *cis*-π-allylic anions were fast, the *cis*-π-allylic anion would be predominant on the surface and *cis*-enamine would be preferred in the initial products. This was observed. The reaction pathway would be as follows:



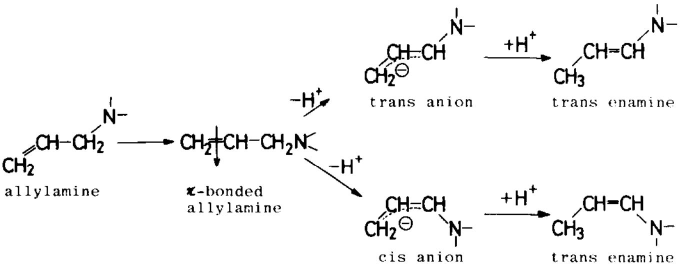
SCHEME I. Reaction scheme of double-bond migration of allylamine to enamine over basic catalyst.

An alternative explanation is possible (*23*). If allylamine is initially π-bonded to the surface, the amino group would be off from the surface:





Abstraction of the H_a and the H_b will give *cis* anion and *trans* anion, respectively. If the *cis* anion is more stable than the *trans* anion, the H_a would be preferentially abstracted, which will give *cis*-enamine. This coincides with the observed results. The reaction pathway would be as follows:



SCHEME II. Reaction scheme of double-bond migration of allylamine to enamine over basic catalyst.

So far, there have been no definite results which might indicate the correct reaction pathway. However, the preferential formation of *cis*-enamine in the initial stage of the reaction suggests that the *cis* form is much more stable than the *trans* form in the anionic intermediate, whichever the reaction pathway is.

In base-catalyzed double-bond migration of 1-olefins, preferential formation of *cis*-2-olefins was observed in many cases. However, in some cases (*14, 24*), almost equal amounts of the *cis* and *trans* isomers were produced; nevertheless the *cis* form of the intermediate is more stable than the *trans* form (*25–27*). In the double-bond migration of 4-methyl-1-pentene over the CaO catalyst that had been pretreated at 500°C, about equal amounts of the *cis* and *trans* forms of 4-methyl-2-pentene were produced in the initial stage of the reaction. Over the same catalyst, a *cis*/*trans* ratio of 6 was observed for 1-butene isomerization (*14*). Since the *anti* conformer is favored in 4-methyl-1-pentene, if the double-bond migration of 4-methyl-1-pentene occurred by a process similar to Scheme I, the rate of the addition of an H^+ to the anionic intermediates should be comparable to that of the interconversion of the *trans* anion to *cis* anion. On the other hand, if the reaction involved the initial π-bonding as shown in Scheme II, the rate of the abstraction of the protons should be the same for two allylic protons, which would result in the formation of about equal amounts of *cis* and *trans* anionic intermediates. Since the *cis* anion is believed to be more stable and the π-bonded species would give preferentially the *cis* anion, the latter seems not to be plausible.

The variations of the activities of CaO and MgO for the double-bond migration of 1-*N*-pyrrolidino-2-propene with the pretreatment temperature are slightly different from those for olefins such as 1-butene and 3-carene. When CaO was outgassed at 300°C, the activity for the double-bond migration of 1-*N*-pyrrolidino-2-propene became almost saturated, while the activity for 1-butene isomerization was very small (*14*) and that for 3-carene isomerization was negligible (*28*). Over MgO catlyst outgassed at 400°C, the activity for 1-butene isomerization was very small (*14, 29*), but the activity for the double-bond migration of 1-*N*-pyrrolidino-2-propene was an attainable one. With both CaO and MgO, the activities appeared at slightly lower outgassing temperatures of the catalyst for the double-bond migration of 1-*N*-pyrrolidino-2-propene than for the isomerization of olefins. The activities for the double-bond migration of 1-*N*-pyrrolidino-2-propene are considered to vary with the pretreatment temperature above 400°C for CaO and 300°C for MgO, but the saturated conversions may hide the changes in activity.

The activity degradation with the pulse number which was distinctly observed for SrO, BaO, and La_2O_3 could be caused by the following two reasons. First, the reactivity of enamine is so high that it reacts with the surface oxygen atoms to form propion aldehyde, and the active site structure is inactivated. Second, enamine decomposes on the surface, and the decomposed products react with enamine or polymerize.

ACKNOWLEDGMENTS

This work was supported by Grant-in Aid for Scientific Research 311706 from the Ministry of Education of Japan. The authors thank Dr. H. Shirahama of Hokkaido University for his valuable advice on NMR measurements.

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