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Double-bond isomerization of olefinic amines over potassium amide loaded on alumina

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Potassium amine loaded on alumina heated under vacuum at 573 K (KNH_2/Al_2O_3) readily isomerizes N,N-diethyl-3,7-dimethyl-octa-2(Z),6-dienylamine to N,N-diethyl-3,7-dimethyl-octa-1(E),3-dienylamine, which was obtained in 99% yield at 313 K for 1 h with or without solvent. The double bond at the 1 position was 100% E. The ratio of E/Z of the double bond at the 3 position was almost 1/1.

Keywords: potassium amide, alumina, double-bond isomerization, olefinic amines

1. Introduction

Not only the isomerizations of simple alkenes, but also the isomerizations of olefinic amines are catalyzed by base catalysts [1–5]. KNH_2 supported on alumina, which had been proposed as a solid base catalyst by Hubert, could isomerize allyl amines in good yield [6–8].

Recently, Baba et al. reported that potassium amide which was loaded on alumina and heated under vacuum at about 573 K [9] has much higher activity for alkene isomerization than alkali metals loaded on metal oxides by vapor deposition [10–14]. It should be noted that high-temperature (573 K) treatment under vacuum was essential for obtaining the superactive catalyst [9]. For example, the catalyst readily isomerized 2,3-dimethylbut-1-ene to 2,3-dimethylbut-2-ene even at 201 K.

This work is aimed at showing that potassium amide loaded on alumina and heated under vacuum at 573 K has a very high activity for the selective isomerization of olefinic amines, i.e. N,N-diethyl-3,7-dimethyl-oct-2-enylamine, **1**, and N,N-diethyl-3,7-dimethyl-octa-2(Z),6-dienylamine, **2**. As shown later, the selective isomerization of **2** to N,N-diethyl-3,7-dimethyl-octa-1(E),3-dienylamine, **4** offers a convenient route to monoterpene aldehyde, since **2** can be easily prepared by the dimeric addition of isoprene to dialkylamine over base catalysts [15].

2. Experimental

The starting alkenes, **1** and **2**, kindly provided by Kuraray Co. Ltd., were distilled under vacuum prior to the reactions. The purities of **1** and **2** were 99.5% as determined by gas chromatography.

The catalysts, KNH_2 and $NaNH_2$ loaded on alumina, were prepared in an ammoniacal solution of the metal by an impregnation method as follows: 125 mg of alumina (surface area: 124 $m^2\,g^{-1}$, average pore diameter: 15 nm) was heated in a quartz reactor under vacuum at 773 K for 3 h. A piece of potassium (or sodium) metal was then introduced to the reactor under nitrogen together with a piece of Fe_2O_3, which served as a catalyst for the formation of amide [16]. The Fe_2O_3 did not contribute to the catalytic behavior. Thus, the catalytic activity did not change by separating from the catalyst with a magnet. The amounts of the metals were 10 wt% and 6 wt% for K and Na, respectively. After evacuating the system to 10^{-3} Pa at room temperature, ammonia was liquefied into the reactor cooled with a dry-ice–ethanol mixture, in order to dissolve the metal. A blue color due to solvated electrons developed. This color gradually faded and disappeared, indicating the transformation of the metal into the amide. The solution was kept in contact with alumina for 1 h and then warmed up to room temperature to pump out the most of ammonia. The system was further heated under vacuum at 573 K (523 K for $NaNH_2$) for 1 h. The catalysts thus prepared are denoted as KNH_2/Al_2O_3 and $NaNH_2/Al_2O_3$, respectively. As reported earlier, KNH_2 species was identified by infrared spectroscopy [6].

CaO and MgO were prepared by heating $CaCO_3$ and $Mg(OH)_2$ under vacuum for 3 h at 998 K and 773 K, respectively.

The reactions were carried out at 313 K in the quartz reactor. The reactants were introduced to the reactor from its side-arm, after the catalyst was prepared. The products were identified with ^1H NMR. The conversion of the reactants and the yields of the products were determined with a gas chromatograph (an OV 101 glass column) using propylbenzene as an internal standard.

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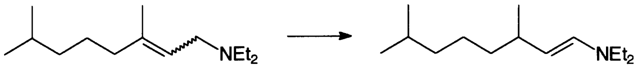
3. Results and discussion

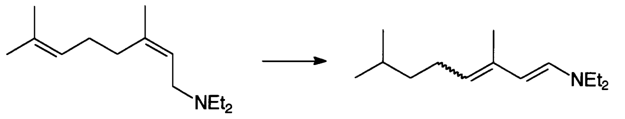
The isomerization of **1** was carried out with 0.2 ml of the reactant in 2 ml hexane with 0.125 g of KNH_2/Al_2O_3 at 353 K for 1 h. The E/Z ratio of the starting alkene was 4/1. The product was the corresponding enamine, **3**, which was obtained in a 91% yield with a 95% selectivity. The isomerized product, **3**, has 100% E configuration. This proves that the catalyst KNH_2/Al_2O_3 is very effective for the isomerization of olefinic amines as well as simple alkenes.



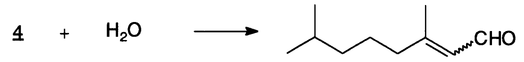
1 3

It is known that Z-enamines are initially formed in the isomerization of allylic amines, but that they are subsequently isomerized to the more stable E-enamines [3].

Tanaka and Hata reported that **2** was isomerized to **4** in the presence of a soluble catalyst, alkali metal 2-aminoethylamide [17][1]. For example, potassium 2-aminoethylamide prepared in situ by adding KH_2 to ethylenediamine gave a 80.9% yield of **4** as a chromatographic yield in 3 h at 343 K. Moreover, they reported that **4** was converted to 3,7-dimethyl-oct-2-en-1-al (dihydrocitral, **5**) in 86% yield by the hydrolysis in an aqueous solution of acetic acid [17][1]. Thus, **5** was prepared in 69% yield based on **2**. Development of solid catalysts for this isomerization is highly desirable because of easier work up after the reaction.



2 4



5

The isomerization of **2** to **4** was carried out with various heterogeneous catalysts at 313 K for 1 h without solvent or in hexane. The catalysts used are KNH_2/Al_2O_3, $NaNH_2/Al_2O_3$, CaO and MgO and the results are shown in table 1. KNH_2/Al_2O_3 showed the highest catalytic activity for this isomerization. The reaction proceeded almost quantitatively with or without a solvent (hexane). The ratio of E/Z of the double bond at the 3 position in the product, **4**, was almost 1/1. The double bond at the 1 position was 100% E.

Though **4** was a sole product at 313 K, the selectivity was not always so high. When the reaction was carried out over KNH_2/Al_2O_3 at 273 K, the conversion of **2** was 57%, and the yield of **4** was 37%. Other products identified by ^1H NMR were N,N-diethyl-3,7-dimethylocta-4,6-dienylamine (yield: 8%), and N,N-diethyl-3,7-dimethylocta-3,5-dienylamine (yield: 1%). The rest of the products could not be identified. The very high yield of **4** at 313 K indicates that this product is obtained as the thermodynamically most stable isomer. KNH_2/Al_2O_3 gave a higher yield of **4** with a higher selectivity, compared with alkali metal 2-aminoethylamide as a homogeneous catalyst [17].

The activity of $NaNH_2/Al_2O_3$ was lower than that of KNH_2/Al_2O_3, and Al_2O_3 itself showed no catalytic activity.

It is well known that CaO and MgO prepared by the decomposition of $CaCO_3$ and $Mg(OH)_2$ under vacuum show high catalytic activities for the isomerization of alkenes such as but-1-ene [18]. These oxides showed catalytic activities for the isomerization, but the activities were lower than that of KNH_2/Al_2O_3. CaO gave 97% yield of **2** with a 99% selectivity in 20 h.

We found that the hydrolysis of **2** proceeded quantitatively to yield **5** upon passing an ethyl acetate–hexane solution of **4** through a column of SiO_2 at room temperature. This result shows that **5** is easily prepared from **2** via the isomerization to **4** over KNH_2/Al_2O_3, followed by the hydrolysis of **4**. The E/Z ratio of **5** was 12/1.

Table 1
Isomerization of N,N-diethyl-3,7-dimethyl-octa-2(Z),6-dienylamine **2** to N,N-diethyl-3,7-dimethyl-octa-1(E),3-dienylamine **4**

Catalyst[a]	Reactant (mmol)	Solvent[b]	Reaction temp. (K)	Reaction time (h)	Conversion of **2** (%)	Yield of **4** (%)	Selectivity to **4** (%)
KNH_2/Al_2O_3	4.0	no solvent	313	1	99	99	100
(K = 10 wt%)	4.0	hexane	313	1	99	99	100
	4.0	no solvent	273	1	57	35	61
$NaNH_2/Al_2O_3$ (Na = 6 wt%)	0.8	hexane	313	1	89	68	76
CaO	4.0	no solvent	313	20	98	97	99
	4.0	no solvent	273	1	23	7	30
MgO	4.0	no solvent	313	1	4	1	25
Al_2O_3	4.0	no solvent	313	20	0	0	

[a] The catalyst weight: 0.125 g. The amounts of metal species loaded on Al_2O_3 are shown as metal base.
[b] Solvent: 2.0 ml.

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[1] H NMR data of **4** and **5** were in accord with the reported data in refs. [19,20], respectively.

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