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Preparation of New Solid Superbase and Its Catalytic Activity

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A solid superbase whose basicity (H_-) was higher than 37 was prepared by the successive treatment of γ-alumina with sodium hydroxide and sodium at 280—350 °C under nitrogen. The base was highly effective in the catalytic isomerization of 5-vinylbicyclo[2.2.1]hept-2-ene to 5-ethylidenebicyclo[2.2.1]hept-2-ene.

There has been a great interest in the superacidity and the superbasicity of solid catalysts.$^{1)}$ In spite of intense activities in the field of the solid super acid, there have appeared only a few reports on solid superbase catalysts, which involve magnesium oxide,$^{2)}$ magnesium oxide doped with sodium,$^{3)}$ rubidium oxide, and caesium oxide.$^{4)}$ Here we wish to report the preparation of a novel solid superbase which exhibited remarkably strong basicity and its application to the olefin isomerization.

A typical preparation procedure is as follows. To 30.0 g of calcined γ-alumina$^{5)}$ was added 4.5 g of sodium hydroxide by portions at 310—320 °C with stirring and the water generated was removed by a flow of nitrogen. The stirring was continued for 3 h at the same temperature to give white solid (A). Then, 1.2 g of sodium was added thereto, and the reaction mixture was stirred for 1 h at the same temperature to give pale blue solid (B).

It is interesting to compare the property of the intermediate solid A and the final product B. The basicity(H_-) of A was less than 26.5 measured by the benzoic acid titration method using Hammet indicators.$^{1,6)}$ Its X-ray analysis revealed that β-sodium aluminate with much disorder was formed on the α-alumina.$^{7)}$ On the other hand, the basicity(H_-) of B was found to be more than 37. The distribution of the basicity of each solid base is shown in Table 1.

The superbase B did not show diffraction peaks of sodium metal in X-ray analysis. In contrast to the great difference in the basicity between solids A and B, their X-ray diffraction patterns were quite similar except that the peaks of sodium aluminate in B became somewhat broader and weaker than those in A. The solid-state ^{23}Na NMR spectrum of B showed only a peak for ionized sodium.[8] These data suggest that ionization of sodium on the disordered aluminate in B plays a key role in giving extremely strong basic sites on the solid.[9]

When the same procedure was carried out with α-alumina and sodium hydroxide, sharp peaks of β-sodium aluminate were observed in the X-ray analysis of the intermediate solid. In this case, the final product clearly showed the diffraction peaks of sodium metal. This one exhibited no catalytic activity for the olefin isomerization.

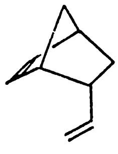
Table 1. Base strength distribution of A and B

Solid base	Basicity H_- range/mmol·g^{-1} a)		
	26.5—35.0	35.0—37.0	37.0≤
γ-Al_2O_3-NaOH (A)	0.0	0.0	0.0
γ-Al_2O_3-NaOH-Na (B)	b)	1.0	1.3

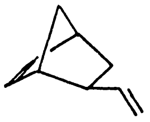
a) The indicators employed are 4-chloroaniline(H_-=26.5), diphenylmethane(H_-=35.0), and cumene(H_-=37.0).

b) Accurate result was not obtained because of the indistinct color change of the indicator.

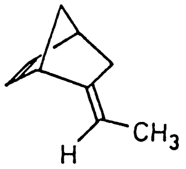
We have applied the solid superbase B to a catalyst for the isomerization of 5-vinylbicyclo[2.2.1]hept-2-ene (1) to 5-ethylidenebicyclo[2.2.1]hept-2-ene (2) which is an important third comonomer of ethylene-propylene synthetic rubber.[10] Since diene 1 undergoes thermal rearrangement easily,[11] comparatively low reaction temperatures are required to accomplish the reaction selectively. It was found that the smooth isomerization of 1 to 2 took place stoichiometrically even at -30 °C in the presence of the solid catalyst.



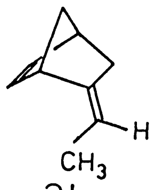
1a



1b



2a



2b

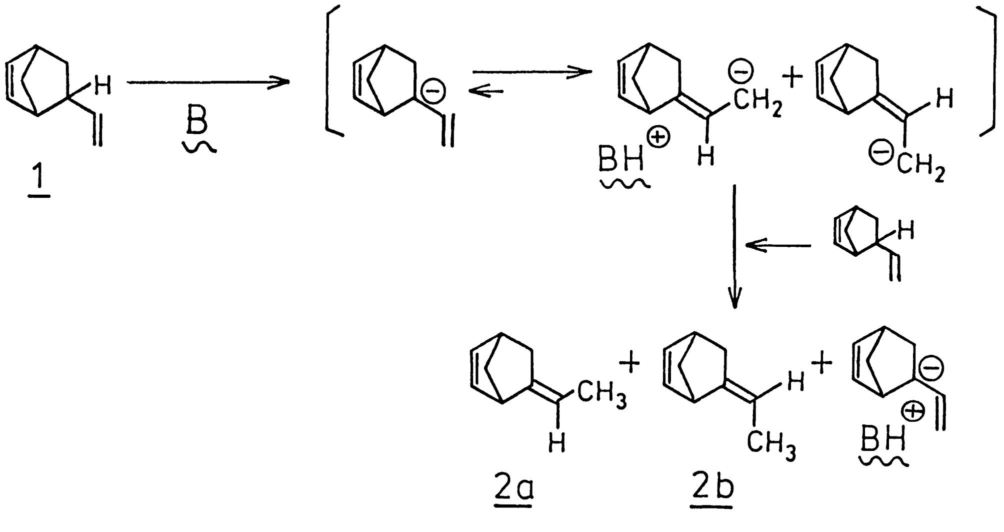
In a typical experiment, 0.20 g of solid B was added to 30.0 g of diene 1 (endo/exo mixture) under nitrogen and the heterogeneous reaction mixture was stirred at 25 °C for 3 h. The solid base was filtered off to give the product (29.8 g) which contained 99.7% of 2 and 0.3% of 1.$^{12)}$ Solid A showed no activity for the isomerization.

The starting material 1 consists of a mixture of endo/exo (1a,1b) isomers,$^{11)}$ and the isomerized product 2 has also two isomers of E/Z (2a,2b).$^{13)}$
It was verified that the E/Z ratio of the product 2 depends on the reaction temperature regardless of the exo/endo ratio of the starting material 1 as shown in Table 2. The result demonstrates that the E/Z ratio can be thermodynamically controlled.

Table 2. Isomerization of 5-vinylbicyclo[2.2.1]hept-2-ene

Starting material 1	Product 2 2a/2b			
1a/1b	-30 °C	25 °C	70 °C	100 °C
75/25	91/9	83/17		76/24
13/87	90/10	81/19	77/23	

The isomerization is presumed to proceed through intermolecular reaction on the strong basic sites of the solid as illustrated in Scheme 1.$^{14)}$



Scheme 1.

Further application of this solid superbase to other carbanion mediated reactions is in progress.

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References

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5) γ-Al_2O_3 of Sumitomo Chemical Company's Product was used after calcination at 500 °C for 20 h. Specific surface area: 150 m^2g^{-1}, Mean particle size: 80 μm.
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7) Shimadzu X-ray diffractometer (VD-II) was used with Ni filtered-Cu Kα radiation. The diffraction pattern of solid A was composed of broad peaks of β-sodium aluminate and those of γ-alumina.
8) Solid-state ^{23}Na NMR spectra were measured on a Bruker CXP-200 spectrometer (52.94 MHz). The peak(δ=-9 ppm) was assigned to Na^+ by comparison with the chemical shifts of NaCl(δ=0 ppm) and metallic Na(δ=1000 ppm) using 3 M NaCl aq solution as an external reference standard.
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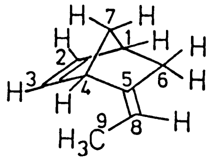
11) The starting material 1 was prepared by Diels-Alder reaction of cyclopentadiene with butadiene; A. F. Plate and N. A. Belikova, J. Gen. Chem. USSR, 30, 3902 (1960).
12) The product was analyzed by gas chromatography.
13) Rectification of these two isomers of 2 was carried out on a 80 plate packed column to give 2a (bp 76.0 °C/13.3 kPa) and 2b (bp 76.5 °C/13.3 kPa). In order to confirm their configurations, ^{1}H NOE experiment was performed on isomer 2b. Irradiation of the H-9 (δ=1.65) produced a 17.2% enhancement of the signal of the H-4 (δ=3.36), thus 2b was assigned to Z-isomer.



2b

14) The surface of the solid turned greenish yellow during the reaction. The sodium cation was not eluted by the reactant, which was confirmed by atomic absorption spectroscopy.

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