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Regioselective Ring-opening Reactions of 2,3-Epoxy Alcohols with Sodium Azide Supported on Zeolite CaY

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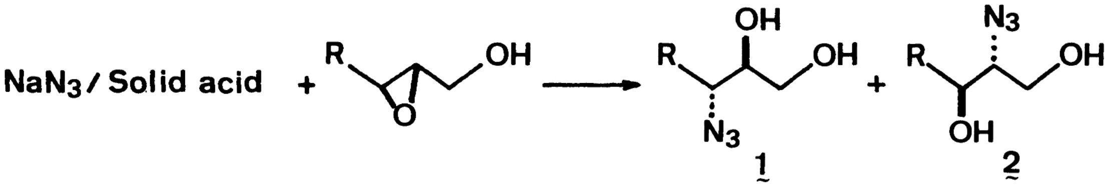
Sodium azide supported on zeolite CaY induces C-3 ring-opening of 2,3-epoxy alcohols to afford 3-azido-1,2-diols in much higher regioselectivity than a conventional reagent system of NaN_3-NH_4Cl in MeOH-H_2O. The cation in zeolite greatly influences the regioselectivity of the reaction.

Since an efficient method for syntheses of enantiomerically pure 2,3-epoxy alcohols has been developed,[1] regioselective ring-opening reactions of 2,3-epoxy alcohols with various nucleophiles are recognized as a promising route for synthesizing multifunctionalized chiral molecules.[2] Recently the combined use of trimethylsilyl azide and Lewis acid ($Ti(O-^iPr)_4$[3] or Et_2AlF[4]) was reported to bring about C-3 opening of 2,3-epoxy alcohols to give 3-azido-1,2-diols in high selectivity. Here we wish to report regioselective ring-opening of 2,3-epoxy alcohols by use of sodium azide supported on solid acid.



As solid acid supports were selected calcium cation-exchanged Y-type zeolite (CaY),[5] γ-alumina (JRC-ALO-4),[6] and silica gel (Fuji-Davison B-type). Sodium azide was impregnated on the supports and treated with 2,3-epoxy alcohols (Table 1). As a control experiment the treatment of the epoxides with a conventional reagent (NaN_3-NH_4Cl in MeOH-H_2O) was investigated.

It should be noted that NaN_3 supported on CaY rapidly induced C-3 opening in much higher selectivity compared with NaN_3 supported on Al_2O_3 or SiO_2 and the NaN_3-NH_4Cl system. In reactions of 2,3-epoxy-3-cyclohexylpropan-1-ol with zeolite-supported NaN_3 reagents the regioselectivity of 1/2 was found to be sensitive to the cation in Y-type zeolite used: CaY (94:6), LaY (79:21), HY (76:24), NaY (77:23).

A typical experimental procedure is as follows: In a flask solid acid (CaY (0.8 g), γ-Al_2O_3 (1.9 g), or SiO_2 (2.6 g))[7] was immersed in an aqueous solution (3 ml) of NaN_3 (3 mmol) and water was evaporated at 40 °C/20 Torr for 2 h.

Table 1. Regioselective ring-opening of 2,3-epoxy alcohols with azide reagents

NaN_3-Reagent	R=Cyclohexyl Time/h	Yield/% (**1**:**2**)	R=n-C_7H_{15} Time/h	Yield/% (**1**:**2**)	R=Isopropyl Time/h	Yield/% (**1**:**2**)
NaN_3/CaY	1.5	85 (94: 6)	1.5	82 (97: 3)	2.0 16.0[a]	86 (88:12) 81 (91: 9)[a]
NaN_3/Al_2O_3	5.0	65 (66:34)	5.0	64 (78:22)		
NaN_3/SiO_2	10.0	35 (78:22)				
NaN_3-NH_4Cl[b]	21.0	88 (76:24)	7.0	84 (87:13)	21.0	58 (64:36)

a) Reaction was carried out at 50 °C.

b) A control experiment: A mixture of epoxy alcohol (1 mmol), NaN_3 (10 mmol), NH_4Cl (2.2 mmol), MeOH (8 ml), and H_2O (1 ml) was refluxed.

The content of residual water in the reagent was estimated by an increase in the total weight of the reagent: NaN_3/CaY (20 wt%[8]), NaN_3/Al_2O_3 (1.5 wt%[8]), and NaN_3/SiO_2 (18 wt%[8]). To a suspended mixture of the supported reagent and benzene (3 ml) was added a benzene solution (2 ml) of 2,3-epoxy alcohol (1 mmol), and the mixture was refluxed with stirring. As work-up, water (3 ml) was added and the mixture was stirred for 0.5 h and filtered. Organic products were extracted from the filtrate and purified by TLC. The regioselectivity of the reaction was determined by GLC after the products were converted to diacetates with Ac_2O and pyridine.

The use of the zeolite-supported azide reagent in ring-opening of epoxides has the following advantages: rapid promotion of highly selective reactions, simple preparation and manipulation of the reagent, and easy separation of the reagent from products.

References

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5) CaY(cation content:Ca^{2+} 67%, Na^+ 33%) was prepared from NaY (Shokubai Kasei Co.) by cation-exchange.

6) A reference catalyst supplied from Catalysis Society of Japan.

7) The amount of solid acid affected the reaction rate. The optimum amount of each solid acid is shown.

8) (The weight of the adsorbed water)/(the weight of the supported reagent)x100. The amount of the residual water in the reagent greatly influenced the reaction rate. An effect of water was discussed: T. Ando, T. Kawate, J. Yamawaki, and T. Hanafusa, Chem. Lett., 1982, 935, and references cited therein.

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