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Regioselective Reduction of Epoxides and Conjugated Carbonyl Compounds Using Zeolite Supported Zinc Borohydride.

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Abstract: Zeolite supported zinc borohydride is a versatile catalyst for the regeoselective reduction of epoxides, conjugated ketones, and aldehydes to the corresponding alcohols in good yields.

Zeolites as catalysts for selective organic reactions have received considerable attention in recent decades due to their unique physical and chemical properties such as shape selectivity, acidic and basic nature, and their thermal stability.[1] Besides the general advantages associated with heterogeneous catalysts like convenient use, easy separation, and being inexpensive, zeolites can also be prepared with different porosity, hydrophobicity, varying acid and basic strength and site distribution. This makes zeolites versatile catalysts for a variety of reactions.[2] In this communication, we wish to report the regeoselective reduction of epoxides, conjugated ketones and aldehydes to the corresponding alcohols in good yields under mild conditions, using zeolite supported zinc borohydride.

The reductive ring opening of epoxides to the corresponding alcohols is one of the most useful reactions in organic synthesis.[3] Reductive cleavage of unsymmetrically substituted epoxides with most reducing agents generally produces the more substituted alcohols; whereas few reagents are known to give the less substituted alcohols.[4] Among these few reagents however, satisfactory results have been obtained only with reagents like zinc borohydride supported on silica gel, potassium triphenyl borohydride and sodium cyanoborohydride with boron trifluoride etharate.[4] But, the highly toxic nature and the cost of these reagents often restrict their use. Thus, there is a need for developing novel reducing agents that are easy to use, inexpensive, and environmentally benign.

The reduction of conjugated ketones and aldehydes to the corresponding allylic alcohols are usually associated with simultaneous reduction of the double bonds, and this leads to the formation of saturated alcohols or ketones due to the competing 1,2- vs 1,4- reduction.[5] Eventhough there are several reports in literature about the development of various reducing agents for the selective 1,2- reduction of conjugated ketones and aldehydes, only few have proven to be practical and general in scope.[6]

In recent years, organic transformations on solid supports have attracted attention because of their enhanced selectivity and milder reaction conditions.[7] In view of the established beneficial effects of the solid supports, we developed zeolite supported zinc borohydride for the reduction of a variety of structurally different epoxides and conjugated carbonyl compounds under mild conditions.

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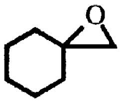
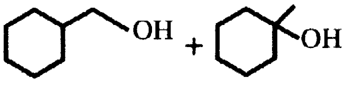
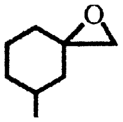
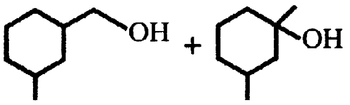
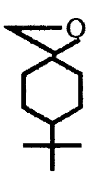
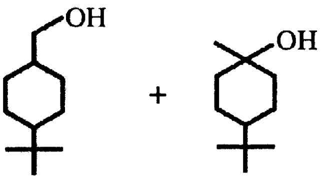
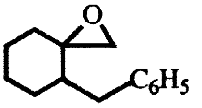
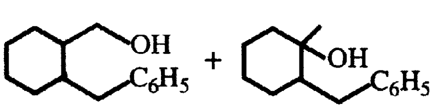
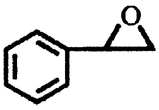
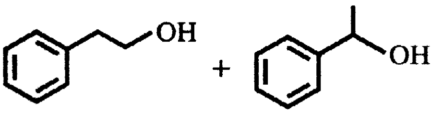
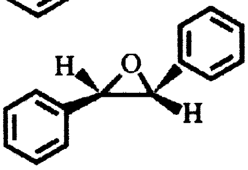
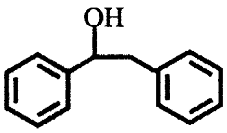
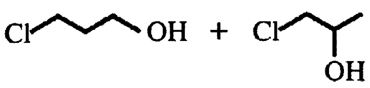
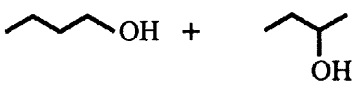
The methylene cycloalkane oxide was prepared from the corresponding cycloalkanone through wittig olefination followed by epoxidation, and the zeolites (Y-Zeolite and Zeolite beta) were synthesized as reported elsewhere.[8] Prior to use, zeolites were calcined at 500 °C for 5h in the presence of air.

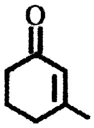
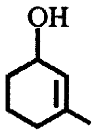
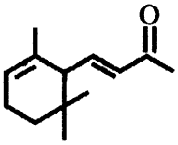
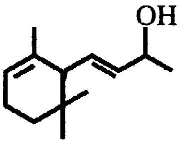
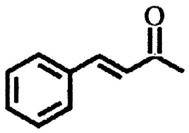
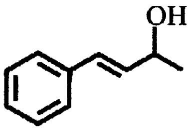
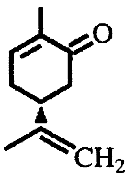
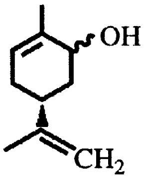
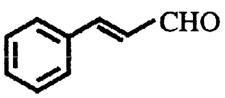
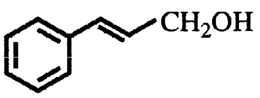
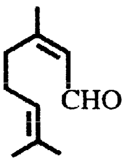
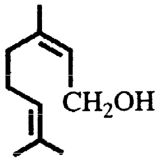
Table 1. Comparison of the yields of various alcohols over Y-Zeolite and Zeolite beta supported zinc borohydride. T = r.t, t = 12 h.

Substrates	Products[a]	Product ratio[b]	Yield[c]	
			Y-Zeolite	Zeolite beta
		(94:6)	88	84
		(83:17)	90	87
		(76:24)	84	82
		(80:20)	78	75
		(91:9)	81	78
		-	77	72
		(75:25)	85	80
		(89:11)	82	84

[a] All products were characterized by their IR, ^{1}HNMR and Mass Spectra. [b] Product ratio was determined by GC (Hewlett packard, 5890 series II Gas Chromatograph, Ultra 2 capillary column, analysis temperature = 150 °C, flame ionization detector. [c] Isolated pure products.

A solution of zinc borohydride in 1,2-dimethoxyethane (DME) was prepared from sodium borohydride and zinc chloride as reported elsewhere.[9] The zeolite supported zinc borohydride was prepared by the addition of zinc borohydride (190 mg, 2 mmol) in DME (10 mL) to activated zeolite (1 g) and stirred at room temperature for 1 h. Then the solvent was removed and the reagent was dried under vacuum (5 Torr, 2h) to give the zeolite supported zinc borohydride, which was used for the reduction of epoxides and conjugated carbonyl compounds on the same day.

Table 2. Comparison of the yields of various conjugated alcohols over Y-Zeolite and Zeolite beta supported zinc borohydride. T = 0 °C, t = 12 h.

Substrates	Products[a]	Yield[b]	
		Y-Zeolite	Zeolite beta
		82	79
		85	87
		78	72
		74	70
		80	83
		86	78
		71	67

[a] All products were characterized by their IR, ^{1}HNMR and Mass Spectra.. [b] Isolated pure products.

The general procedure for the reduction of epoxides, conjugated ketones and aldehydes is as follows. The epoxides or conjugated carbonyl compounds (0.5 mmol) was stirred with zeolite supported zinc borohydride (2 mmol) in dry THF (10 mL) at room temperature or 0 °C for 12 h. Then the reaction mixture was filtered and the zeolite was treated with methanol (3 x 15 mL). The combined THF/methanol mixture was partitioned between water (50 mL) and ether (45 mL). The ether layer was washed with saturated solution of $NaHCO_3$ and brine. It was then dried over anhydrous sodium sulfate followed by the removal of solvent to furnish the crude product, which was further purified by column chromatography using hexane/ethylacetate. This methodology has been successfully applied for the regioselective reduction of various epoxides, conjugated ketones, and aldehydes, and the results are summarized in Tables 1 and 2. In the case of conjugated carbonyl compounds reduction, no appreciable 1,4-reduction products were formed. Whereas the reduction of conjugated ketones and aldehydes using zinc borohydride under similar conditions produce 1,4-reduction product as the major component.

In summary, we have developed a facile heterogeneous catalytic methodology for the regioselective reduction of epoxides, conjugated ketones, and aldehydes to the corresponding alcohols in good yield using zeolite supported zinc borohydride. The positive features of these inexpensive zeolites includes ease of work up and separation of the product, lack of corrosiveness and other environmental hazards, and regeneration and reuse of the catalyst.

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