Regioselective Reductive Cleavage of Terminal Epoxides with Polymer-supported Chloroaluminium Tetrahydroborate†

J. Chem. Research (S), 1997, 330–331†

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Epoxides are reduced exclusively to the less substituted alcohols with regenerable polyvinylpyridine-supported chloroaluminium tetrahydroborate in high yields.

The reductive cleavage of epoxides to alcohols is one of the most useful reactions in organic synthesis.[1] Cleavage of unsymmetrical substituted epoxides with most conventional reducing agents generally results in the more substituted alcohols.[2] Considerable effort has focused on the development of methods for regioselective epoxide cleavage to the less substituted alcohols, and for this purpose several types of reagents have been used.[2,3] However, in most cases mixtures of alcohols have been obtained. The most satisfactory results have been achieved only with a limited number of reagents such as sodium cyanotrihydroborate–BF_3 etherate,[3b] potassium triphenylhydroborate–Ph_3B[3c] system and recently silica gel-supported zinc tetrahydroborate reported by Ranu[3e,f] and the sodium tetrahydroborate–amine system *via* a photochemical approach.[3h]

Polymer-supported reducing agents have received considerable attention in recent years and a variety of them, while exhibiting the advantages of polymeric reagents, have been used in the mild and selective reduction of organic compounds.[4] The only reported polymer-supported tetrahydroborate reagents are Amberlyst anion exchange resin-supported tetrahydroborate and cyanotrihydroborate[5] as well as polymer-supported zinc[6] and zirconium[7] tetrahydroborates which we recently reported as stable, efficient and selective reducing agents for a variety of organic functional groups.[8] With these polymer-supported metal tetrahydroborates, however, the regioselective reduction of epoxides was not possible and a mixture of alcohols was obtained with the more substituted alcohols being the major products.[8]

We now report that in the course of our studies on a new polymer-supported metal tetrahydroborate, namely, polyvinylpyridine-supported chloroaluminium tetrahydroborate, we found that it can reduce epoxides exclusively to their lesser substituted alcohols in almost quantitative yields.

Aluminium chloride was supported on crosslinked poly(4-vinylpyridine) by adding a solution of the metal salt to an alcoholic suspension of the polymer. The polymeric reagent was then obtained by an exchange reaction between the polymer-supported aluminium chloride and lithium tetrahydroborate. It was a white-cream, stable and non-hygroscopic powder. The capacity of the reagent was 1.8 mmol BH_4 per gram. Data obtained on the Al and Cl content by atomic absorption and potentiometric titration techniques showed, within experimental error, that the reducing species are in the form of $AlCl_2(BH_4)$ supported on the polymeric ligand (such species are known to be formed as unstable intermediates in the formation of aluminium tetrahydroborate from the reaction of $AlCl_3$ and $LiBH_4$).[9] Attempts to prepare polymer-supported aluminium tetrahydroborate, $Al(BH_4)_3$, were not successful.

Regioselective reduction of various epoxides to their corresponding less substituted alcohols were performed using this reagent and the results are shown in Table 1. The reductions were performed in solvents such as diethyl ether, tetrahydrofuran, dichloromethane, acetonitrile, methanol and ethanol under reflux. The reagent was most efficient in absolute ethanol. No solvolytic ring opening of the epoxides was detected in this solvent. Identification and analysis of the products were made on the basis of IR, ^1H NMR and GLC evidence compared with the authentic samples. Regeneration of the reagent was achieved by washing with acid and then base to obtain the original polymer followed by complexation and exchange reactions. The regenerated polymeric reagent, except for a small weight loss in each cycle, had almost the same capacity and performance as the original reagent.

In conclusion, this regenerable polymer-supported reducing agent provides an efficient methodology for excellent regioselective cleavage of terminal epoxides to the less substituted alcohols. Moreover, the mildness, convenience and high yield make this reagent an attractive reagent for such an epoxide cleavage. Further utilization of this new stable polymer-supported metal tetrahydroborate reducing agent for different reductive transformations will be reported in due course.

Experimental

Preparation of Poly(4-vinylpyridine)-supported Chloroaluminium Tetrahydroborate.—Crosslinked poly(4-vinylpyridine) (2% divinyl benzene, Fluka AG) (5.0 g) was suspended in methanol (50 ml) and stirred for 1 h. A solution of $AlCl_3$ (20 g, 0.15 mol) in THF–MeOH (4:1, 150 ml) was added to the polymer suspension. The mixture was then stirred for 12 h at room temperature and the precipitate filtered off, washed with excess methanol and diethyl ether and then dried in vacuum at 40 °C to yield 7.39 g polymer-supported aluminium chloride as a light yellow powder.

To a solution of $LiBH_4$ (3.0 g, 0.14 mol) in dry THF (100 ml), the above supported polymer was added portionwise at 0–5 °C and stirred for 3 h. The resulting material was separated and washed several times with THF and diethyl ether and then dried under vacuum to produce a white-cream stable and non-hygroscopic powder. The capacity of the reagent was determined by iodometric titration method to be 1.8 mmol BH_4^- per gram. The amount of aluminium determined by atomic absorption spectroscopy and the Cl^- content determined by potentiometric titration were 1.90 and 3.85 mmol per gram of polymer respectively.

General Procedure for the Reductive Cleavage of Epoxides.—In a flask (100 ml) equipped with a condenser and a magnetic stirrer, a solution of epoxide (1 mmol) in absolute ethanol (10 ml) was prepared. The supported reagent (1.5 g) was added and the reaction mixture stirred while being refluxed. Progress of the reaction was monitored by TLC (CCl_4–diethyl ether as 5:1) or GC. On completion of the reaction, water (100 ml) was added and the solution stirred for 5 min. The mixture was then filtered and the filter cake washed several times with diethyl ether. The organic layer was separated and dried over $MgSO_4$. On evaporation of solvent the pure product was obtained in high yield.

Regeneration of the Reagent.—The spent reagent (5 g) was treated with hydrochloric acid (20 ml, 0.1 M), stirred for 0.5 h and then filtered. The resulting filter cake was washed first with sodium hydroxide (3 × 10 ml, 0.1 M) and then with distilled water, acetone and diethyl ether. The solid was dried in vacuum at 60 °C to give the original polymer (4.8 g) which could then be supported and used again.

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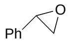
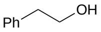
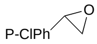
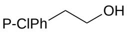
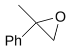
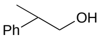
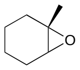
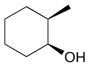
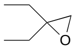
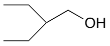
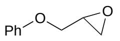
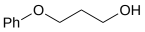
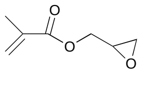
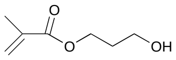
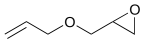
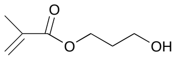
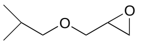
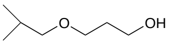
†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1997, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

Table 1 Reductive cleavage of terminal epoxides with poly(4-vinylpyridine)-supported chloroaluminium tetrahydroborate[a]

Epoxide	Product[b]	t/h	Yield (%)[c]
		8	98
		10	95
		5	90
		6	85
		9	90
		10	92
		7	98
		10	89
		10	98

[a]All reactions carried out in refluxing absolute ethanol. [b]Characterized by comparison with authentic samples (IR, ^{1}H NMR and GC). [c]Isolated yield.

We are grateful to Shiraz University research council for partial support of this work.

Received, 13th May 1997; Accepted, 15th May 1997
Paper E/7/03327C

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