

Chitosan-supported Borohydride Reducing Agent

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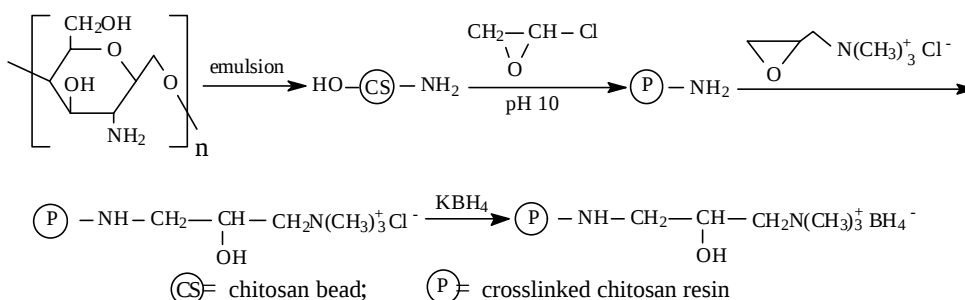
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Abstract: A new chitosan-supported borohydride reducing reagent (CBER) was prepared by treatment of KBH_4 with the resin of chitosan derivative, which was first synthesized from the reaction of cross-linked chitosan microsphere with glycidyl trimethylammonium chloride. CBER could reduce aromatic carbonyl compound to corresponding alcohol.

Keywords: Polymer-support borohydride reducing agent, chitosan resin.

Borohydride exchange resin (BER) a useful reducing reagent has been used in reduction of some carbonyl compounds and acyl halides¹. When BER combines with a transition metal catalyst, it can reduce $\text{C}=\text{C}$ double bonds², halides², nitro compounds³, cyano, diazo³ and azide compounds⁴. The support of BER is the synthetic macromolecule polystyrene. Here, we used chitosan as the support of borohydride. As known, chitosan is a renewable and abundant natural polysaccharide.

Scheme 1 Preparation of CBER



The highly porous chitosan beads were made by emulsion method using 5% chitosan in acetic acid (2%) solution and paraffin oil with Span 80. The beads were cross-linked with epichlorohydrin in order to make the particles inert to acid and chemicals. The cross-linked chitosan resin ($d=150 \mu\text{m}$) reacted with glycidyl trimethylammonium chloride in water at 60°C to form the quaternary ammonium resin. Finally, the resin exchanged with potassium borohydride to get the borohydride exchange resin (CBER), whose average capacity was 1.92 mmol per gram dried resin.

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As shown in **Table 1**, the new CBER can reduce aromatic carbonyl compounds to corresponding alcohols. The CBER reduced aromatic aldehyde faster than aromatic ketone. The reduction of less hindered carbonyl group was much faster. More interestingly, the para-electron-donating substituent enhanced the reaction rate whereas the para-electron-withdrawing substituent retarded the rate (entries 3 and 4>entry 1>entry 6), suggesting that the more reactive aldehyde was easier bound by amino group in resin before reduction.

The CBER was milder than NaBH_4 ⁵. The high degree of swelling of CBER in 95% ethanol made reaction like solution-phase reaction, but the chemoselectivity was greater than using BER^1 . A simple filtration of resin gave essentially pure products free from boron moiety in most cases. The CBER can be reused repeatedly. After treating with KBH_4 solution it can keep the initial activity. Thus, CBER is a reagent of choice for the reduction of carbonyl compounds.

Table 1 Reduction of aromatic carbonyl compounds with CBER in ethanol

Entry	Substrates ^a	Products	% Reduction ^b
1	$\text{C}_6\text{H}_5\text{CHO}$	$\text{C}_6\text{H}_5\text{CH}_2\text{OH}$	96.4
2	$4\text{-Cl-C}_6\text{H}_4\text{CHO}$	$4\text{-Cl-C}_6\text{H}_4\text{CH}_2\text{OH}$	>99 (96) ^c
3	$4\text{-CH}_3\text{O-C}_6\text{H}_4\text{CHO}$	$4\text{-CH}_3\text{O-C}_6\text{H}_4\text{CH}_2\text{OH}$	>99
4	$4\text{-(CH}_3)_2\text{N-C}_6\text{H}_4\text{CHO}$	$4\text{-(CH}_3)_2\text{N-C}_6\text{H}_4\text{CH}_2\text{OH}$	>99
5	$4\text{-OHC-C}_6\text{H}_4\text{CHO}$	$4\text{-HOCH}_2\text{-C}_6\text{H}_4\text{CH}_2\text{OH}$	>99 (95) ^c
6	$4\text{-NO}_2\text{-C}_6\text{H}_4\text{CHO}$	$4\text{-NO}_2\text{-C}_6\text{H}_4\text{CH}_2\text{OH}$	92.8 (91) ^c
7	$2\text{-NO}_2\text{-C}_6\text{H}_4\text{CHO}$	$2\text{-NO}_2\text{-C}_6\text{H}_4\text{CH}_2\text{OH}$	82.6
8	$2\text{-OH-C}_6\text{H}_4\text{CHO}$	$2\text{-OH-C}_6\text{H}_4\text{CH}_2\text{OH}$	93.5 (47) ^c
9	$\text{C}_6\text{H}_5\text{COCH}_3$	$\text{C}_6\text{H}_5\text{CH(OH)CH}_3$	64.8
10	$\text{C}_6\text{H}_5\text{COC}_6\text{H}_5$	$\text{C}_6\text{H}_5\text{CH(OH)C}_6\text{H}_5$	31.2

a. CBER (10 mmol) and the carbonyl (10 mmol) compound in 50 mL 95% ethanol at 20°C for 4 h, monitored by LC; b. by 300 MHz NMR; c. isolated yield.

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