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# Copper(II) Exchanged Cation Exchange Resin: Useful Activator in the Reduction of Ketones

A. Sarkar<sup>a</sup>, B. R. Rao<sup>ab</sup> & B. Ram<sup>a</sup>

<sup>a</sup> Department of Applied Chemistry, Indian School of Mines, Dhanbad, 826004, INDIA

<sup>b</sup> R. R. Lab., Bhopal, 462026, India Published online: 23 Sep 2006.

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## COPPER(II) EXCHANGED CATION EXCHANGE RESIN: USEFUL ACTIVATOR IN THE REDUCTION OF KETONES

A. Sarkar\*, B.R. Rao\*\* and B. Ram Department of Applied Chemistry Indian School of Mines Dhanbad - 826004, INDIA

Abstract : A copper(II) exchanged cation exchange resin used been as support for reduction of ketones has with sodium borohydride.Supported Cu(II) ions activate the reduction of ketones to a large extent and control stereochemistry of reductions of cyclic the ketones resulting in preponderance of equatorial alcohol in most cases.

In continuation of our search for supported reagents<sup>1-3</sup> which can reduce ketones, particularly cyclic ketones with considerable ease and a fair degree of stereoselectivity, we wished to explore the possibility of .using some modified polymer based reagent to serve this purpose. In this connection, it appeared that cation exchange resin suitably exchanged with cupric ions may be useful, in view of the fact that both cupric<sup>4</sup> and cuprous<sup>5</sup> salts have been used together reduction with sodium borohydride for of organic compounds under homogeneous condition. Triphenyl copper(II) borohydride used for phosphine has been almost stereoselective reduction of 4-t-butylcyclohexanone (94% trans alcohol)<sup>6</sup>.

\* To whom correspondence should be addressed. \*\*Presently, in R.R. Lab., Bhopal- 462026, India.

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These reports prompted us to use  $Cu^{+2}$  exchanged cation exchange resins as activators in the reduction of ketones under heterogeneous condition. In this connection it may be mentioned that although borohydride exchanged-anion exchange resin has been used for reduction of a variety of compounds,<sup>7-10</sup> the stereoselectivity of the reagent as far as reduction of cyclic ketones is concerned had not been very encouraging. Hence, it was also a point of interest to see whether there can be any improvement of stereoselectivity when the present system is used.

The copper (II) support prepared by elution of (Na<sup>+</sup> form, cation exchanger) with Amberlite IRA-120 solution of copper (II) acetate (subsequently 5% а washed with water and dried over P205) was found to be quite stable and could be stored as a stable One of the advantages of the support was material. is recoverable and reusable with almost that it no associated loss in activity.

The reductions were quite facile. Cyclic ketones could be reduced rather easily as compared to acyclic ketones. Probably complexation of the carbonyl group with  $Cu^{+2}$  ions takes place more readily with the cyclic ketones.

reductions stereochemistry of The of some of the cyclic ketones almost in all the cases pointed involvement of the copper (II) in towards forming a weak complex from the equatorial side of the cyclic 4-t-butylcyclohexanone ketone. The reduction of associated with formation of 96% trans-alcohol, was 4-methylcyclohexanone, a conformationally whereas unlocked cyclohexanone, was reduced with an overall ratio of 94:6 for trans and cis isomers of the alcohol.

	Fntry	System I		System II	
		Yield % o (%) ria iso	f Equato- l/endo mer	Yield (%)	% of equato- rial/endo isomer
1.	4-t-butyl cyclohex- anone	98(3)	98	92(2)	91
2.	4-methyl cyclohex- anone	97(4.5)	94	85(3)	82
3.	3,3,5-tri- methyl cyclo hexanone	96(24) -	58	88(5)	57
4.	Camphor	52(58)	33	90(7)	26
5.	Cyclohexa- none	98(1.5)	-	90(0.5)	) –
6.	Fluorenone	97(4)	-	94(1)	-
7.	Ethyl methyl ketone	92(1)		83(0.5)	) –
8.	Acetophe- none	96(5)	-	86(2),	-

TABLE - 1

Results of Reduction of Ketones

a. All reductions were carried out in ethanol, somewarming. times with

b. Incomplete reduction in case of camphor was observed (60% reduction).

c. With BER (see text) the percentage of trans-4-tbutyl cyclohexanol and 4-methylcyclohexanol formed, were 82% and 80% respectively. Cis-3,3,5 trimethyl cyclohexanol was formed to the extent of 43%.

I: Presently reported reagent: System II: d. System

 $CuSO_4$  and NaBH<sub>4</sub> in ethanol. e. The values in parentheses refer to time in hr. for complete reduction.

3,3,5-trimethylcyclohexanone, a hindered ketone was reduced with opposite stereochemistry (42% trans and 58% cis) than normally obtained with sodium borohydride reduction. Camphor was also reduced with the formation of higher percentage of endo alcohol (33%) as compared to that obtained in reduction with borohydride.

establish unequivocally the role played by То  $Cu^{+2}$ the ions in controlling the stereochemistry, the reductions of the cyclic ketones were also carried out under homogeneous condition using copper sulphateborohydride system following the procedure of Yoo et al4. The stereochemical results of the reductions of towards involvement copper (II)ions point in controlling the stereochemistry (see table). Reduction 4-t-butylcyclohexanone under these conditions of 91% resulted in the formation of trans-alcohol, 3,3,5-trimethylcyclohexanone on reduction yielded 57% cis alcohol. All these results clearly point participation of towards copper (II)ions in the formation of some complex from the equatorial side of the cyclic ketones. The effect is. enhanced when the copper (II) ions are grafted on the polymeric bed of the cation exchange resin.

comparison of the stereochemical results А of reductions of the cyclic ketones using copper (II)exchanger and sodium borohydride, with cation that borohydride exchanged anion exchange resin(BER) of the former reveals that system improves upon the stereochemistry of the reductions obtained with the latter to a very large extent. In fact BER is not at all stereoselective in the reduction of cyclic ketones.

Another interesting observation is that the copper (II) cation exchange resin is totally recoverable

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and reusable. On addition of sodium borohydride during (II) ions were converted to reduction, the copper copper (I) state but was again reconverted back to the same oxidation state after 24h (the original bluish green colour of the resin was restored), with minimum loss in activity.

To summarise, it may be stated that the Copper (II) cation exchanger could be very useful activator for various reactions which normally proceed slowly in presence of polymer supports.

#### Experimental

Preparation of Cu (II) exchanged cation exchange resin: A solution (250 ml) of cupric acetate (5%) was slowly passed through cation exchange resin (Na<sup>+</sup> from, 15 g). The elution was completed within 10 hrs and the resin was washed with distilled water and dried over  $P_2O_5$  in vacuo. The Cu (II) equivalent of the resin determined by reeluting 2g of the Cu(II) exchange resin (and subsequent standard iodometric titration) was found to be 3 meq/g.

Reduction of the Ketones : General Procedure :

In a typical experiment a mixture of 4-t-butylcyclohexanone (0.85 g, 5 meq) and copper (II) exchange resin (3 g, 9 meg) was stirred in ethanol for 0.5 h. Sodium borohydride (0.2 g, 0.55 meq in aqueous ethanol (5 ml) added slowly at 0°C. The mixture was stirred was temperature/40-50<sup>0</sup>C, and the reaction was at room monitored using TLC. On completion of the reaction the mixture was filtered, residue washed with ethanol and combined filtrate was evaporated to afford the the desired alcohol.

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