Chemical Modification of Polymers.[1] Borohydride Reducing Agents Derived from Anion Exchange Resins

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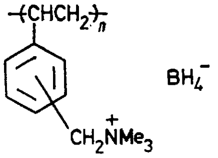
Summary Exchange of quaternary ammonium type anion exchange beads with $NaBH_4$ leads to useful reducing agents possessing the advantage of easy work-up.

In recent years the use of insoluble polymer-bound reagents for organic synthesis has increased.[2,3] While several polymer-bound insoluble reduction catalysts have been described,[4,5] to our knowledge no polymer supported reducing agents have been reported; we now report the preparation of such reagents.

Anion exchange resins of the quaternary ammonium type with chloride counterions of various porosities were stirred once with a 2—3-fold excess of aqueous $NaBH_4$ to afford resin beads containing units of structure (**1**). The beads were characterized by elemental analysis.



(1)

The insoluble beads readily reduced aldehydes. Therefore, the reducing capacity of the beads was determined by exposure to an excess of benzaldehyde in ethanol. The residual benzaldehyde was determined by g.l.c. The following reducing capacities in mmol benzaldehyde per gram dry weight were obtained (% of theoretical capacity based upon analysis of starting beads in parenthesis): Amberlite IRA-400, 11·0 (65%); Amberlite IRA-401S CP, 11·2 (82); Amberlite IRA-938, 9·8 (66); Amberlyst A-26, 13·3 (79).†

The kinetics of reduction of benzaldehyde were similarly examined using the beads derived from Amberlite IRA-400 and IRA-401S CP in ten-fold excess relative to the aldehyde. The relative initial rates of reduction using these beads were in a 2:1 ratio. Under equivalent conditions $NaBH_4$ reduction is at least 25 times faster than reduction with the treated IRA-401S CP beads. These results are interesting in that the more porous beads (IRA-401S CP) are less reactive than the less porous beads (IRA-400).

The lower rates of reaction of the polymer-bound reducing agents suggest that they may possess greater selectivity than $NaBH_4$; *e.g.*, the rate of reduction may depend on the chain length of aliphatic ketones as observed for olefin hydrogenation using resin-bound catalysts.[5] Indeed, a slightly greater (2%) preference for equatorial attack on 4-t-butylcyclohexanone, yielding the *cis*-alcohol, is observed with the beads from Amberlite IRA-400 relative to $NaBH_4$. We are at present characterizing further these reagents, which possess the advantage of very simple work-up by filtration or use in columns.

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† Amberlite and Amberlyst are trademarks of Rohm and Haas Co., Philadelphia, Pennsylvania.

[1] For previous paper in this series see: H. W. Gibson and F. C. Bailey, *Macromolecules*, 1976, **9**, 688.

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