Silica Gel-supported Zinc Borohydride. Part 3.¹ Regioselective Reductive Cleavage of Methylenecycloalkane Oxides to the Less-substituted Alcohols

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Highly selective reductive cleavage of methylenecycloalkane oxides to less-substituted alcohols has been achieved by a simple procedure using silica gel supported zinc borohydride in tetrahydrofuran.

Current interest in regioselective ring opening of epoxides arises from their importance.² Reductive cleavage of unsymmetrical alkyl-substituted epoxides with most conventional reducing agents generally produces the more substituted alcohols,³ few reagents⁴ being known to give less substituted alcohols. Recently, we introduced silica gel-supported zinc borohydride as a reagent of choice for general regioselective cleavage of the C-O bond to the more substituted carbon atom.⁵ Also, because of the difficulty in obtaining less-substituted alcohols from the reductive cleavage of methylenecycloalkane oxides with commonly available reagents, Yamamoto et al.⁶ used diisobutylaluminium 2,6-di-tert-butyl-4-substituted phenolates for this purpose. This reagent, however, gives the unsaturated alcohol as an undesirable side-product whilst the regioselectivity is less than satisfactory. This prompted us to investigate the reduction of methylenecycloalkane oxides with our reagent-silica gelsupported zinc borohydride; the results reported here are very promising.

In a typical procedure, the oxide was treated with silica gelsupported zinc borohydride in THF at room temperature for 24 h after which the product was isolated by simple work-up. Several structurally varied methylenecycloalkane oxides were subjected to cleavage by this procedure to produce stereoselectively one isomer of the corresponding less substituted alcohols[†] (see Table 1). The cleavage was very clean and no side-products other than the more substituted alcohol were observed.

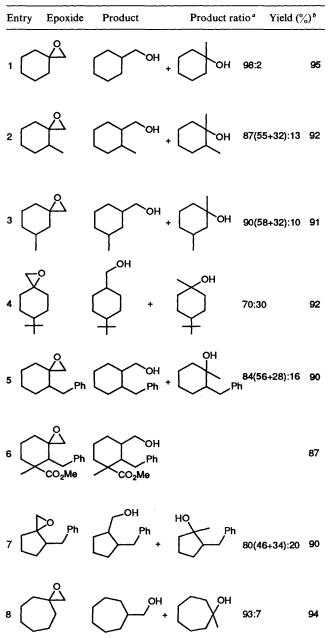
The synthetic potential for alcohols⁶ of the type made by this procedure, we believe, is considerable.

Experimental

A solution of zinc borohydride in 1,2-dimethoxyethane was prepared from zinc chloride and sodium borohydride following the reported procedure.⁷ Silica gel-supported zinc borohydride was then obtained by a method reported earlier.^{1.5}

General Procedure for Reductive Cleavage of Oxides.—The methylenecycloalkane oxide (prepared from the corresponding cycloalkanone through Wittig olefination⁸ and epoxidation⁹) (1 mmol) was stirred with silica gel-supported zinc borohydride (3 mmol) in dry THF (5 cm³) at room temperature for 24 h. The reaction mixture was then decomposed with careful dropwise addition of water and filtered. The filtrate was extracted with ether and the extract was washed with aqueous sodium hydrogen carbonate and brine, dried (Na₂SO₄) and then evaporated to leave the product. Identification and analysis of the products were made on the basis of ¹H NMR and GLC
 Table 1
 Reductive cleavage of methylenecycloalkane oxides with silica

 gel-supported zinc borohydride in THF



^a The percentage compositions of products were determined by GC; the figures in parentheses showed the percentage ratio of stereoisomers in the less substituted alcohol. ^b Yields refer to total isolated products.

[†] The major isomer was expected to be the thermodynamically more stable *trans* alcohol by analogy with the reduction of similar oxides with other reducing agents.⁶

evidence at comparison with authentic samples (the more substituted alcohols were prepared from the parent cyclo-alkanones).

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