

## Silica Gel-supported Zinc Borohydride. Part 3.<sup>1</sup> Regioselective Reductive Cleavage of Methylene-cycloalkane Oxides to the Less-substituted Alcohols

Brindaban C. Ranu\* and Asish R. Das

Department of Organic Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta 700 032, India

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.<sup>2</sup> Reductive cleavage of unsymmetrical alkyl-substituted epoxides with most conventional reducing agents generally produces the more substituted alcohols,<sup>3</sup> few reagents<sup>4</sup> 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.<sup>5</sup> Also, because of the difficulty in obtaining less-substituted alcohols from the reductive cleavage of methylenecycloalkane oxides with commonly available reagents, Yamamoto *et al.*<sup>6</sup> used diisobutyl-aluminium 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 gel-supported zinc borohydride; the results reported here are very promising.

In a typical procedure, the oxide was treated with silica gel-supported 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 alcohols<sup>6</sup> 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.<sup>7</sup> Silica gel-supported zinc borohydride was then obtained by a method reported earlier.<sup>1,5</sup>

**General Procedure for Reductive Cleavage of Oxides.**—The methylenecycloalkane oxide (prepared from the corresponding cycloalkanone through Wittig olefination<sup>8</sup> and epoxidation<sup>9</sup>) (1 mmol) was stirred with silica gel-supported zinc borohydride (3 mmol) in dry THF (5 cm<sup>3</sup>) at room temperature for 24 h. The reaction mixture was then decomposed with careful drop-wise addition of water and filtered. The filtrate was extracted with ether and the extract was washed with aqueous sodium hydrogen carbonate and brine, dried (Na<sub>2</sub>SO<sub>4</sub>) and then evaporated to leave the product. Identification and analysis of the products were made on the basis of <sup>1</sup>H NMR and GLC

**Table 1** Reductive cleavage of methylenecycloalkane oxides with silica gel-supported zinc borohydride in THF

Entry	Epoxide	Product	Product ratio <sup>a</sup>	Yield (%) <sup>b</sup>
1			98:2	95
2			87(55+32):13	92
3			90(58+32):10	91
4			70:30	92
5			84(56+28):16	90
6				87
7			80(46+34):20	90
8			93:7	94

† 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.<sup>6</sup>

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

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

#### Acknowledgements

Financial support from CSIR for this investigation is highly appreciated. A. R. D. also thanks CSIR for the award of his research fellowship.

#### References

- 1 Part 2, B. C. Ranu and A. R. Das, *J. Org. Chem.*, 1991, **56**, 4796.
- 2 (a) C. Bonini and G. Righi, *Tetrahedron*, 1992, **48**, 1992; (b) G. K. Biswas and P. Bhattacharyya, *Synth. Commun.*, 1991, **21**, 569; (c) J. M. Chong, *Tetrahedron Lett.*, 1992, **33**, 33; (d) T. K. Chakraborty and G. V. Reddy, *Tetrahedron Lett.*, 1991, **32**, 679.

- 3 M. Hudlicky, *Reductions in Organic Chemistry*, Ellis Horwood Ltd., Chichester, 1984.
- 4 (a) H. C. Brown and N. M. Yoon, *J. Chem. Soc., Chem. Commun.*, 1968, 1549; (b) R. O. Hutchins, I. M. Taffer and W. Burgoyne, *J. Org. Chem.*, 1981, **46**, 5214; (c) N. M. Yoon and K. E. Kim, *J. Org. Chem.*, 1987, **52**, 5564; (d) J. J. Eisch, Z.-R. Liu and M. Singh, *J. Org. Chem.*, 1992, **57**, 1618.
- 5 B. C. Ranu and A. R. Das, *J. Chem. Soc., Chem. Commun.*, 1990, 1334.
- 6 K. Maruoka, S. Saito, T. Ooi and H. Yamamoto, *Synlett*, 1991, 255.
- 7 P. Crabbe, G. A. Garcia and C. Rius, *J. Chem. Soc., Perkin Trans. 1*, 1973, 810.
- 8 (a) R. Greenwald, M. Chaykovsky and E. J. Corey, *J. Org. Chem.*, 1963, **28**, 1128; (b) W. G. Dauben and D. M. Walker, *J. Org. Chem.*, 1981, **46**, 1103.
- 9 F. Fringuelli, R. Germani, F. Pizzo and G. Sovelli, *Tetrahedron Lett.*, 1989, **30**, 1427.

Paper 2/02662G

Received 21st May 1992

Accepted 10th June 1992