

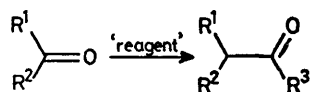
# Organosilicon Chemistry: New Applications to Reductive Nucleophilic Acylation

By FRANK COOKE and PHILIP MAGNUS\*

(Evans Chemistry Laboratory, The Ohio State University, 140 West 18th Avenue, Columbus, Ohio 43210)

**Summary**  $\alpha$ -Chloroethyltrimethylsilane (**1**) is deprotonated to give (**2**) which reacts with ketones and aldehydes to give  $\alpha,\beta$ -epoxysilanes, useful precursors to methyl ketones.

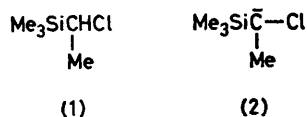
THE recent surge in the development of organosilicon chemistry into the more general areas of organic synthesis has produced many interesting reactions that demonstrate the synthetically useful properties associated with silicon.<sup>1</sup> Unfortunately apart from the Peterson reaction<sup>2</sup> and



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associated procedures,<sup>3</sup> little synthetic use is made of organosilicon chemistry since silicon reagents to a large extent are comparatively inaccessible to the non-specialist.

Here we describe synthetic applications of reductive nucleophilic acylation<sup>4</sup> (Scheme). Deprotonation of the readily available  $\alpha$ -chloroethyltrimethylsilane<sup>5</sup> (**1**) using *s*-butyl-lithium in tetrahydrofuran at  $-78^\circ\text{C}$  gave the anion (**2**). The results of reactions of this anion with a variety of carbonyl compounds are listed in the Table.



Hydrolysis ( $\text{H}_2\text{SO}_4\text{-MeOH-H}_2\text{O}$ )<sup>6</sup> of the  $\alpha,\beta$ -epoxysilanes gave the corresponding methyl ketones. Consequently the new reagent (**2**) has acted as a nucleophilic acylating species and reduction has taken place at the original carbonyl group. Whilst reagents exist that accomplish this transformation,<sup>4</sup> none offer the convenience and ease of operation, nor the mild conditions. Furthermore the intermediate  $\alpha,\beta$ -epoxysilane can be converted into an enol ether, enol acetate, alkenyl bromide, or enamide,<sup>7</sup> and other functional groups (acetals, dithians, and vinyl selenides),<sup>8</sup> thus enhancing the scope and usefulness of this new procedure.

Substrate	$\alpha,\beta$ -Epoxysilane (% yield) <sup>a</sup>	Methyl ketone
Ph <sub>2</sub> CO		
		—

<sup>a</sup> All yields refer to isolated material. None are optimised and actual yields in all cases are probably higher. <sup>b</sup> 2,4-Dinitrophenyl-hydrazone (DNP) m.p.  $150\text{--}153^\circ\text{C}$  (from benzene-light petroleum); lit.: J. Burkhard, J. Vais, and S. Landa, *Z. Chem.*, 1969, 9(1), 29, m.p.  $153.4\text{--}153.9^\circ\text{C}$ . <sup>c</sup> DNP m.p.  $145\text{--}146^\circ\text{C}$  (from benzene-light petroleum); lit.: J. Graefe, M. Muehlstadt, and D. M. Mueller, *Tetrahedron*, 1970, 2677, m.p.  $144.5^\circ\text{C}$  (from ethanol).

It should be noted that  $\alpha,\beta$ -epoxysilanes were, prior to this work, only available by epoxidation of vinylsilanes and were, as a consequence, relatively inaccessible.

We thank the National Cancer Institute for a grant.

(Received, 2nd May 1977; Com. 425.)

<sup>1</sup> For reviews covering general synthetic applications of organosilicon chemistry see: S. S. Washburne, *J. Organometallic Chem.*, 1974, 83, 155; 1976, 123, 1; R. F. Cunico, *ibid.*, 1976, 109, 1; I. Fleming, *Chem. and Ind.*, 1975, 449.

<sup>2</sup> D. J. Peterson, *J. Org. Chem.*, 1968, 33, 780; T. H. Chan, E. Chang, and E. Vinokur, *Tetrahedron Letters*, 1970, 1137.

<sup>3</sup> F. A. Carey and A. S. Court, *J. Org. Chem.*, 1972, 37, 939; H. Gilman and R. Tomasi, *ibid.*, 1962, 27, 3647.

<sup>4</sup> O. W. Lever, Jr., *Tetrahedron*, Report No. 19, 1976, 1965.

<sup>5</sup> L. H. Sumner and F. C. Whitmore, *J. Amer. Chem. Soc.*, 1949, 68, 485.  $\alpha$ -Chloroethyltrimethylsilane (**1**) is prepared from commercially available  $\alpha$ -chloroethyltrichlorosilane (Petrasch Systems, Inc.), by reaction with methylmagnesium bromide. A more convenient method is methylation of the  $\alpha$ -chloro- $\alpha$ -trimethylsilylcarbanion: C. Burford, F. Cooke, E. Ehlinger, and P. D. Magnus, *J. Amer. Chem. Soc.*, in the press.

<sup>6</sup> G. Stork and B. Ganem, *J. Amer. Chem. Soc.*, 1973, 95, 6152; G. Stork and E. Colvin, *ibid.*, 1971, 93, 2080.

<sup>7</sup> P. F. Hudrlík, A. M. Hudrlík, R. J. Rona, R. N. Misra, and G. P. Withers, *J. Amer. Chem. Soc.*, 1977, 99, 1993.

<sup>8</sup> P. D. Magnus, G. Roy, and W. Hsin, unpublished results.