Tetrahedron Letters,Vol.29,No.7,pp 835-836,1988 0040-4039/88 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

MIGRATION AND STABILITY OF THE SILYL GROUP IN THE USE OF PHENYLTHIOMETHYLTRIMETHYLSILANE AS A FORMYL SYNTHON

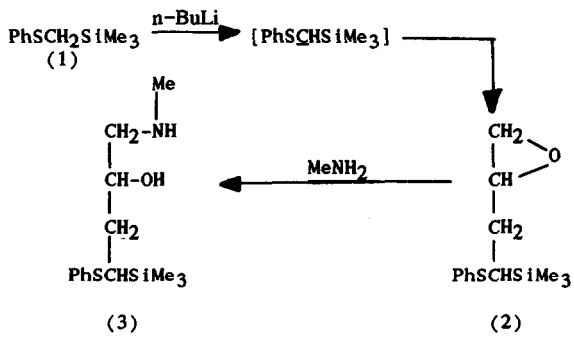
Paul L. Coe, A. Stanley Jones, Ajit Kumar and Richard T. Walker*
Department of Chemistry, University of Birmingham,
P.O. Box 363, Birmingham B15 2TT, U.K.

Summary: 1,4-Silyl group migration from carbon to oxygen in the reaction between phenylthiomethyltrimethylsilane and epibromohydrin is reported.

Recently a new formyl anion synthon, phenylthiomethyltrimethylsilane (1),[1] having the virtues of at least moderate nucleophilicity, stability to a wide range of reaction conditions, and facile conversion to the unmasked aldehyde, has been suggested as a replacement for 1,3-dithianes (4)[2] which have found wide use in organic synthesis for the past two decades.

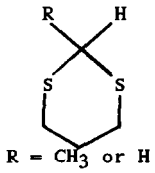
Phenylthiomethyltrimethylsilane is indeed a versatile formyl anion synthon[3] as long as the alkylating reagents do not have oxygen atoms which might allow 1,4 silyl group migration from carbon to oxygen thus leading to unexpected products.[4] This type of rearrangement has been reported by Takeda et al. in 1983 who observed this effect in the reaction of α,α-bis(trimethylsilyl)phenylthiomethyllithium with epichlorohydrin. Problems arising from the migration of a silyl group are outlined in this paper.

Our synthetic route to a nucleosidic aldehyde compound required the synthesis of a key intermediate (3) which seemed possible using the anion synthon as shown in Scheme 1:

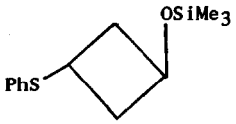


Scheme 1

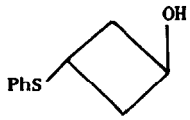
However, the reaction of epibromohydrin with the synthon did not yield the epoxide (2) required to carry out the reaction with methylamine to obtain the amine alcohol intermediate (3). Analysis of the products showed that the major components were 1-phenylthio-3-hydroxycyclobutane (6),[5] 1-phenylthio-3-trimethylsiloxycyclobutane (5)[6] and 1,5-di(phenylthio)-pentan-3-ol (8).[7]



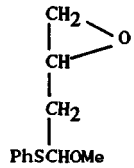
(4)



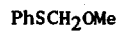
(5)



(6)

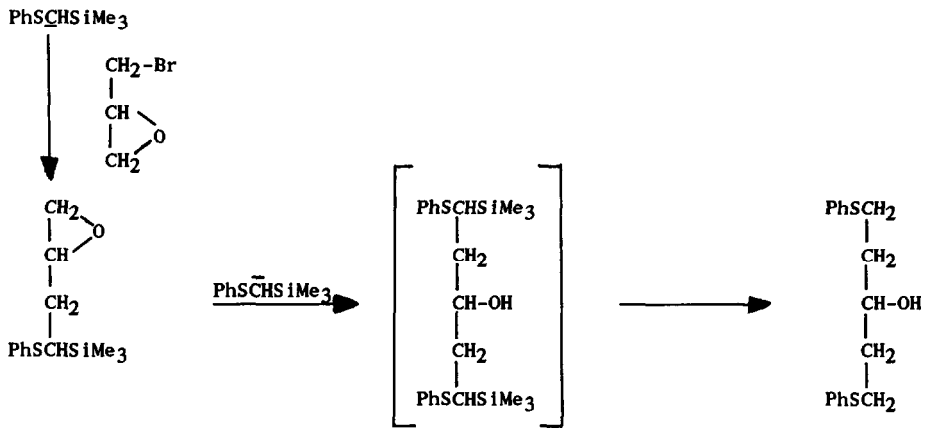


(7)



(9)

The most probable explanation for the production of compounds (5) and (6) is migration of the trimethylsilyl group from carbon to oxygen and then formation of the cyclobutane ring to give (5), which being hydrolytically unstable, would give (6). Formation of the minor product (8) is postulated in Scheme 2, whereby initial formation of the required epoxide is followed by further attack by the anion synthon and subsequent loss of the silyl group by migration. To show further that products 5, 6 and 8 result from silyl group rearrangement, epoxide (7) was synthesised by treating the anion of methoxymethylphenylsulphide (9) with an equivalent amount of epibromohydrin.



(8)

Scheme 2

Phenylthiomethyltrimethylsilane, when used as a formyl anion synthon with alkylating reagents containing oxygen atoms, may result in unexpected products.

Acknowledgements: We gratefully thank the Medical Research Council for a Fellowship (to A.K.).

REFERENCES and NOTES

1. P.J. Kocienski, Tet. Letters, 1980, 21, 1559.
2. D. Seebach and E.J. Corey, J. Org. Chem., 1975, 40 (2), 231.
3. D.J. Ager and R.C. Cookson, Tet. Letters, 1980, 21, 1677.
4. T. Takeda, S. Naito, K. Ando and T. Fujiwara, Bull. Chem. Soc. Jpn., 1983, 56, 967.
5. ^{1}H NMR (CCl_4) δ = 1.4–1.85 (4H, m, CH_2 x 2), 2.65–2.89 (1H, brs, CH–SPh), 3.5–4.8 (1H, m, CH–OH), 7.1–7.5 (5H, m, PhS).
6. ^{1}H NMR (CCl_4) δ = 0.05 (9H, s, Me_3), 1.4–1.85 (4H, m, CH_2 x 2), 2.4–2.8 (1H, m, CH–SPh), 3.9–4.2 (1H, m, CH–OH), 7.1–7.5 (5H, m, PhS).
7. ^{1}H NMR ($CDCl_3$) δ = 1.85–2.0 (5H, m, CH_2 x 2 + CH–OH), 2.9–3.1 (4H, t, CH_2 x 2), 3.8–4.1 (1H, m, CH–OH), 7.1–7.4 (5H, m, PhS).
8. All new compounds described gave satisfactory elemental analyses and exhibited spectra completely in accord with their assigned structures.

(Received in UK 4 January 1988)