Pergamon

Tetrahedron Letters, Vol. 38, No. 46, pp. 8117-8120, 1997
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0040-4039/97 $17.00 + 0.00

PII: S0040-4039(97)10123-X

Regio- and Stereospecific Cleavage of α,β-Epoxysilanes with Lithium Diphenylphosphide

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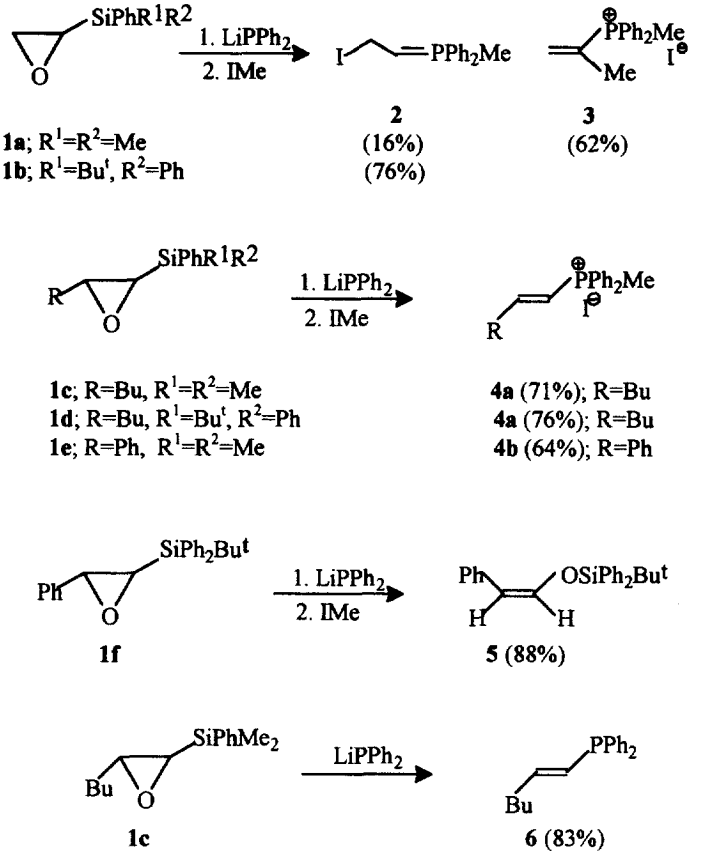
Abstract: Silyl epoxides **1a-e** react with lithium diphenylphosphide and then with methyl iodide to give vinylphosphonium iodides resulting from α-opening of the epoxide ring and subsequent Peterson elimination. In the same conditions, the E-β-phenyl-α-*tert*-butyldiphenylsilylepoxide **1f** leads to the corresponding silyl enol ether **5** by β-opening followed by Brook rearrangement. Both processes are regio- and stereospecific. © 1997 Elsevier Science Ltd.

It is well known that α,β-epoxysilanes exhibit a high order of reactivity toward nucleophiles. They undergo regio- and stereospecific α-opening by a variety of nucleophiles to produce diastereomerically pure β-hydroxysilanes,[1,2] and these β-hydroxysilanes undergo stereospecific *syn* or *anti* β-elimination reactions under basic or acidic conditions, respectively, leading to heteroatom-substituted olefins of known stereochemistry.[3]

We have now found that dimethylphenylsilyl- and *tert*-butyldiphenylsilylepoxides prepared by epoxidation[4,5] of vinylsilanes, obtained, in turn, by dimethylphenylsilyl-[6] and *tert*-butyldiphenylsilyl cupration[5] from alkynes, react with lithium diphenylphosphide and then with methyl iodide[7] to give different products depending on the structure of the epoxysilane (Scheme 1). All new compounds showed satisfactory spectral and analytical data.[8]

When both types of epoxysilanes are unsubstituted or β–alkyl substituted , the nucleophilic attack by diphenylphosphide occurs on the backside of the α–carbon atom with α–opening of the epoxide ring and formation of intermediates which, even when methylated, undergo exclusively Peterson-elimination leading to stereodefined vinylphosphonium iodides **4** (Scheme 2). If methylation is omitted vinylphosphines **6** are isolated (Scheme 1). The iodoalkylidenephosphorane **2** is probably formed by addition of iodide at β–unsubstituted vinylphosphonium **4** (R=H) and the 1-methylvinylphosphonium iodide **3** may result by methylation of ylide formed from α–deprotonation by the smaller dimethylphenylsilyloxide (Scheme 2).

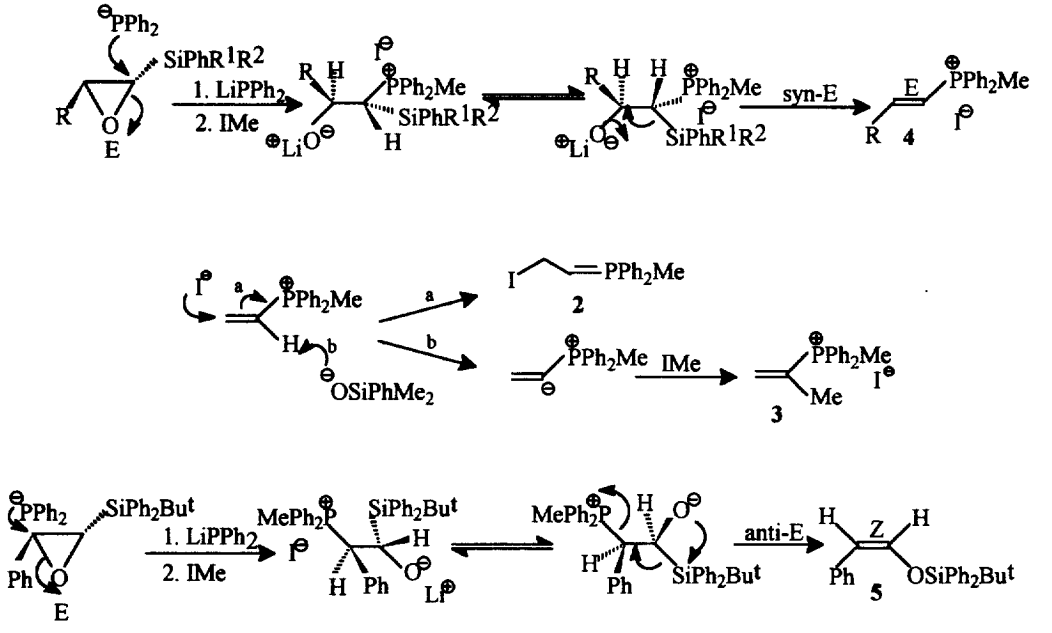


Scheme 1

On the other hand, when the β-substituent is phenyl, the α-dimethylphenylsilylepoxide **1e** is opened in the same way. However, when the β-substituent is also phenyl but the silyl group is the voluminous *tert*-butyldiphenyl group,[9] the reaction follows a very different pathway. The formation of the silyl enol ether **5** may take place by initial nucleophilic attack at benzylic β-carbon with β-opening followed by Brook rearrangement of an α-oxidosilane with elimination of a good β-leaving group.[10] The *cis* configuration of silyl enol ether **5** demonstrates that this elimination takes place with *anti* stereochemistry (Scheme 2).

In conclusion, since epoxysilanes have been obtained by epoxidation of vinylsilanes, the overall process provides a regio- and stereospecific method for converting vinylsilanes to vinylphosphonium salts with retention of configuration. We have developed a simple and efficient method for preparing vinylphosphonium salts, which are suitable reagents for the synthesis of a variety of heterocyclic, carbocyclic and chain-extended systems.[11] Furthermore, we have obtained a stereodefined silyl enol ether, one of the

more useful and versatile functional groups in organic synthesis.[12] Although many methods exist for their preparation, few provide stereochemical control.[13]



Scheme 2

ACKNOWLEDGEMENTS

Our thanks are due to Prof. Antonio García Martínez (Departamento de Química Orgánica, Madrid, Spain) for his helpful suggestions and for providing us with the experimental procedure. We also thank DGICYT of the Spanish Ministerio de Educación y Ciencia for financial support (nº. PB93-0227).

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7. The experimental procedure is the same as that described by García-Martínez, A.; Oliver, M. *Synthesis* **1983**, 663, for converting E-epoxides to Z-olefins.
8. Selected spectroscopy data: **2**: IR vmax (nujol)/cm^{-1} 1200 (C=P); ^{1}H NMR ($CDCl_3$) δ 8.12-7.68 (11H, m, Ph and HC=), 3.78 (2H, d, J 5.4, CH_2I) and 3.14 (3H, d, J 13.8, MeP); ^{13}CNMR (CD_3SOCD_3 + $CDCl_3$) δ 135.35 (=CH para), 132.96 (=CH orto), 130.52 (=CH meta), 118.77 (d, J_{PC} 86.7, =C, PhP), 133.51 (d, J_{PC} 186.7, HC=P), 15.87 (CH_2I) and 8.71 (d, J_{PC} 56.7, MeP); MS m/z 354 (M^+, 1%), 277 (M-Ph, 5), 227 (M-I, 12), 200 (M-2Ph or M-IC_2H_3,99), 185 (39), 183 (ICH=C=P^+, 100), 128 (22), 127 (13) and 77 (15).

   3: ^{1}H NMR ($CDCl_3$) δ 7.66-7.34 (10H, m, Ph), 7.22 and 5.99 (total 2H, d, J 2.0, $=CH_2$), 3.78 (3H, d, J 19.6, MeP) and 2.26 (3H, s, MeC=).

   4a: ^{1}H NMR ($CDCl_3$) δ 7.93-7.61 (10H, m, Ph), 6.86 (1H, tt, J 6.6 and 16.5, =C<u>H</u>CH_2), 6.68 (1H, dd, J 16.5 and 23.8, =CHP), 2.92 (3H, d, J 13.6, MeP), 2.50 (2H, m, $C\underline{H_2}CH$=), 1.53 (2H, m, $C\underline{H_2}CH_2CH$=), 1.36 (2H, m, $C\underline{H_2}(CH_2)_2CH$=) and 0.91 (3H, t, J 7.2, Me).

   5: ^{1}H NMR ($CDCl_3$) δ 7.83-7.19 (15H, m, PhSi and PhC), 6.38 (1H, d, J 6.6, =CHOSi), 5.35 (1H, d, J 6.6, =CHPh) and 1.18 (9H, s, Me_3CSi).
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13. The hydrolysis of α,β-epoxysilanes and treatment of resulting α,β-dihydroxysilanes with KH followed by Me_3SiCl led to *cis-trans* mixtures of silyl enol ethers: Hudrlik, P. F. ; Schwartz, R. H.; Kulkarni, A. K. *Tetrahedron Lett.* **1979**, 2233.

(*Received in UK* 19 *August* 1997; *revised* 11 *September* 1997; *accepted* 12 *September* 1997)