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PYROLYTIC REARRANGEMENTS OF α,β-EPOXYSILANES TO SILYL ENOL ETHERS[1]

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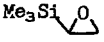
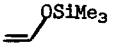
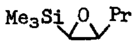
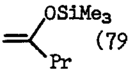
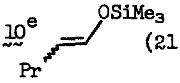
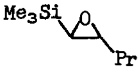
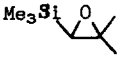
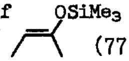
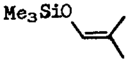
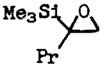
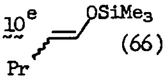
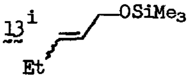
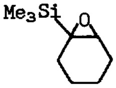
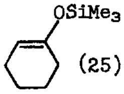
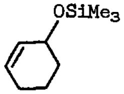
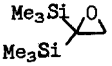
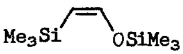
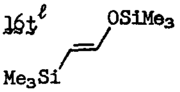
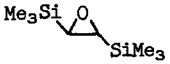
α,β-Epoxysilanes are beginning to show promise as versatile synthetic intermediates. Stork has demonstrated that they can be converted to carbonyl compounds by hydrolysis,[2] and we have recently shown that they can be stereospecifically converted to olefins by treatment with organometallic reagents,[3] followed by elimination reactions of the resulting β-hydroxyalkylsilanes.[3,4] We now report the flash-vacuum pyrolysis of α,β-epoxysilanes in which rearrangement to the isomeric silyl enol ethers is observed.[5] Brook has just reported his results of an independent study of the thermal rearrangement of α,β-epoxysilanes at 160-320° for extended periods.[6]

The silyl epoxides **1**-**7** were prepared by epoxidation of the corresponding vinylsilanes.[7] The pyrolysis apparatus was a horizontal 22 mm Vycor tube which was heated in an oven over a 33 cm length. Before each run, the tube was conditioned with dichlorodimethylsilane.[9] Pyrolyses were carried out at 600° by reducing the pressure to 0.2-0.7 mm and allowing the epoxide to vaporize and pass through the heated tube. The volatile products were collected in a receiver cooled in liquid nitrogen, purified by evaporative (bulb to bulb) distillation, and analyzed by NMR, IR, and VPC. The results are shown in Table 1.

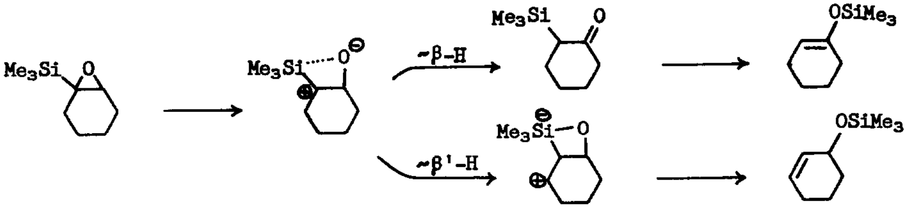
A comparison with simple epoxides shows that the presence of the trimethylsilyl group facilitates the rearrangement. Under our standard pyrolysis conditions described above, we found that propylene oxide and cyclohexene oxide were completely unchanged, while styrene oxide was only partially rearranged (to $PhCH_2CHO$).[10]

Although several of the products can be accounted for by mechanisms involving cleavage of either the α or β C-O bond of the epoxide, most of the products can be accounted for by cleavage of the C-O bond α to silicon[11,12] (perhaps facilitated by prior interaction between silicon and oxygen),[12e] and migration of a group (H, Me_3Si, or alkyl) from the β (and β' in the case of **4** and **5**) carbon to the α carbon; a conceivable pathway is shown below.[13] Such a process would account for all of the products[14] except **12** and **17**.[15] The preference for α-cleavage is perhaps most convincingly demonstrated in the pyrolysis of **3**, the epoxide most likely to undergo β-cleavage. The major product (**11**) must have resulted from α-cleavage with methyl migration,[16] while the product derived from β-cleavage (**12**) was formed only to the extent of 23%. The preference for α-cleavage is further supported by the fact that epoxide **4** underwent rearrangement at lower temperatures than epoxides **2** and **3**.

Table 1. Pyrolysis of α,β-Epoxysilanes at 600°.

Epoxide	Products (ratio)^a						Yields^a
1 	8^b 						68%
$2c^c$ 	9^d 	(79)	10^e 	(21)			72%
$2t^c$ 	9	(59)	10	(41)			66%
3^c 	11^f 	(77)	12^g 	(23)			77%
4^h 	10^e 	(66)	13^i 	(34)			75%
5 	14^j 	(25)	15^k 	(75)			77%
6 	$16c^\ell$ 	(71)	$16t^\ell$ 	(29)			67%
7 	16c	(20)	16t	(58)	17^m 	(22)	83%

(a) Yields and isomer ratios were determined by NMR, using chloroform as an internal standard. (b) Reported in ref 20; IR in agreement with that reported;^{20e,f} NMR (CCl_4) δ 0.19 (Me_3Si), 3.99 (d, J = 6 Hz, 1 H), 4.26 (d, J = 14 Hz, 1 H), 6.26 (dd, J = 6, 14 Hz, 1 H). (c) Pyrolysis at 500° gave a very similar ratio of products, with 40-50% of recovered epoxide (less than 0.5% cis-trans isomerization of epoxides 2c and 2t). (d) NMR (CCl_4) δ 3.94 (s, $C{=}CH_2$); by NMR and VPC, this compound corresponds to one component of a mixture of silyl enol ethers prepared from 2-pentanone by treatment with $Me_3SiCl/Et_3N/DMF$.^{21} (e) Reported in ref 22. The product was a mixture of cis and trans isomers, by NMR and VPC comparison with a mixture of silyl enol ethers prepared independently from valeraldehyde by treatment with $Me_3SiCl/Et_3N/ZnCl_2$.^{20b,c,d,g} (f) This was formed as a mixture of cis and trans isomers; the isomer with cis methyls was predominant, by NMR and VPC comparison with a mixture of silyl enol ethers prepared independently from 2-butanone as described by House.^{21} (g) Reported in refs 20b, 22; identical with a sample prepared independently from isobutyraldehyde by treatment with $Me_3SiCl/Et_3N/ZnCl_2/DMF$. (h) Pyrolysis at 500° gave a similar result; pyrolysis at 400° gave the same ratio of 10 and 13, with 34% of recovered epoxide 4. (i) Identified by comparison with a sample prepared independently from trans-2-penten-1-ol^{23} by treatment with Me_3SiCl/Et_3N. (j) Identical with an authentic sample.^{20b,c,21} (k) Identical with a sample prepared independently from 2-cyclohexen-1-ol by treatment with Me_3SiCl/Et_3N. (ℓ) Compounds 16c and 16t were separated by preparative VPC (Carbowax, column temp 75°). Compound 16c (see ref 17) had the following spectra: IR (CCl_4) 3.41, 6.27, 8.02, 9.34, 11.9 μ; NMR (CCl_4) δ 0.02 (s, 9 H), 0.14 (s, 9 H), 4.26 (d, J = 7 Hz, 1 H), 6.69 (d, J = 7 Hz, 1 H); mass spectrum m/e 188 (M^+), 173, 147, 131, 75, 73, 66, 59, 45, 43. Compound 16t had the following spectra: IR (CCl_4) 3.41, 6.23, 8.02, 8.70, 11.8 μ; NMR (CCl_4) δ 0.02 (s, 9 H), 0.19 (s, 9 H), 4.59 (d, J = 14 Hz, 1 H), 6.22 (d, J = 14 Hz, 1 H); mass spectrum similar to that of 16c. (m) A sample was separated by preparative VPC (SE-30, column temp 100°) and identified as trimethylsilylketene by its IR and NMR spectra and by its reaction with diisopropylamine (see ref 24).



The isomeric silyl enol ethers (**16c**[17] and **16t**) obtained on pyrolysis of the bis(trimethylsilyl) epoxides **6** and **7** are noteworthy in that they are formally derived from trimethylsilylacetaldehyde, a molecule which has not yet been reported.[18] However, attempted hydrolysis of a mixture of **16c** and **16t** in acid yielded only acetaldehyde, and treatment of the mixture of **16c** and **16t** with 2,4-DNP reagent gave the 2,4-DNP of acetaldehyde.

It should be noted that hydrolysis of the silyl enol ethers obtained from these pyrolyses would give carbonyl compounds which are structurally isomeric with those which would be obtained by hydrolysis[2] of the epoxysilanes. This fact, coupled with the manifold synthetic uses of silyl enol ethers,[19] indicates the synthetic potential of this rearrangement.

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References and Notes

1. A portion of this work was presented at the 169th National ACS Meeting, Philadelphia, Pennsylvania, April 1975; Abstracts, ORGN 14.
2. (a) G. Stork and E. Colvin, J. Am. Chem. Soc., 93, 2080 (1971); (b) G. Stork and M. E. Jung, ibid., 96, 3682 (1974); see also (c) B.-Th. Gröbel and D. Seebach, Angew. Chem., Int. Ed. Engl., 13, 83 (1974); (d) R. K. Boeckman, Jr., and K. J. Bruza, Tetrahedron Lett., 3365 (1974).
3. P. F. Hudrlik, D. Peterson, and R. J. Rona, J. Org. Chem., 40, 2263 (1975).
4. P. F. Hudrlik and D. Peterson, J. Am. Chem. Soc., 97, 1464 (1975).
5. The partial rearrangement of phenyldimethylsilylethylene oxide to the isomeric silyl enol ether upon gas chromatography at 187° has been reported: J. W. Wilt, O. Kolewe, and J. F. Kraemer, J. Am. Chem. Soc., 91, 2624 (1969).
6. A. R. Bassindale, A. G. Brook, P. Chen, and J. Lennon, J. Organometal. Chem., 94, C21 (1975).
7. Trimethylsilylethylene oxide (**1**)[3,5,6,8] and epoxides **2**-**3**[3] have been previously described. The synthesis of epoxides **4**-**7** is described in the following communication.
8. V. Bažant and V. Matoušek, Coll. Czech. Chem. Commun., 24, 3758 (1959).
9. The tube was filled with a 5% solution of dichlorodimethylsilane in benzene and allowed to stand for several hours at room temperature, then rinsed with petroleum ether and with ether and allowed to dry. On some occasions when the tube was not freshly conditioned, positional isomerization of double bonds in the products was observed.
10. Pyrolyses of simple epoxides are reported to give complex mixtures of products, predominantly aldehydes and ketones. For example, see (a) S. W. Benson, J. Chem. Phys., 40, 105 (1964); (b) T. J. Hardwick, Can. J. Chem., 46, 2454 (1968); (c) M. C. Flowers and R. M. Parker, J. Chem. Soc. B, 1980 (1971); (d) M. C. Flowers and R. M. Parker, Internat. J. Chem. Kinetics, 3, 443 (1971); (e) J. M. Watson and B. L. Young, J. Org. Chem., 39, 116 (1974); (f) P. Dowd and K. Kang, Chem. Commun., 258 (1974); and references cited in each of the above.

11. Thermal and acid-catalyzed rearrangements of several other heteroatom-substituted epoxides are reported to take place with initial cleavage of the β C-O bond of the epoxide. For example, see (a) R. N. McDonald, in "Mechanisms of Molecular Migrations," B. S. Thyagarajan, Ed., Vol. 3, Wiley, New York, N. Y., 1971; pp 67-107; (b) M. Sprecher and D. Kost, Tetrahedron Lett., 703 (1969); (c) D. F. Tavares and R. E. Estep, ibid., 1229 (1973); and references cited therein.

12. For experiments relating to stabilities of radicals and cations α and β to silicon, see (a) A. W. P. Jarvie, Organometal. Chem. Rev. A, 6, 153 (1970); (b) P. J. Krusic and J. K. Kochi, J. Am. Chem. Soc., 91, 6161 (1969); (c) T. Kawamura, P. Meakin, and J. K. Kochi, ibid., 94, 8065 (1972); (d) C. Eaborn, F. Feichtmayr, M. Horn, and J. N. Murrell, J. Organometal. Chem., 77, 39 (1974); (e) see also A. R. Bassindale, A. G. Brook, P. F. Jones, and J. M. Lennon, Can. J. Chem., 53, 332 (1975).

13. Thermal isomerizations of β-ketosilanes to silyl enol ethers are known: (a) A. G. Brook, D. M. MacRae, and W. W. Limburg, J. Am. Chem. Soc., 89, 5493 (1967); (b) A. G. Brook, D. M. MacRae, and A. R. Bassindale, J. Organometal. Chem., 86, 185 (1975); (c) G. L. Larson and Y. V. Fernandez, ibid., 86, 193 (1975).

14. This mechanism does not account for Brook's results with cis and trans trimethylsilylstyrene oxides.[6] In these cases, the presence of the β-phenyl group presumably favors β-cleavage.

15. Thermal dehydrosilylations are known; for example, see C. Eaborn and R. W. Bott in "Organometallic Compounds of the Group IV Elements," A. G. MacDiarmid, Ed., Volume 1, "The Bond to Carbon," Part I, Marcel Dekker, New York, 1968, pp 353-355.

16. In contrast to these results, Brook,[6] under his conditions, observed **12** to be the only product formed from pyrolysis of epoxide **3**, except in one set of runs where some methyl migration (presumably giving **11**) was reported to occur. Additionally, in Brook's epoxide (isopropenyltrimethylsilane epoxide) having β' hydrogens, formation of allyl silyl ether (as in **4** → **13** and **5** → **15**) was not observed. Brook observed no trimethylsilylketene in the pyrolysis of epoxide **7**; we have not determined the lower temperature limit for effecting rearrangement of epoxide **7** under our conditions.

17. Compound **16c** has been previously reported, and tentatively identified by its NMR spectrum (solvent not specified), which differs from that given here. J. Dunoguès, E. Jousseaume, J.-P. Pillot, and R. Calas, J. Organometal. Chem., 52, C11 (1973).

18. For some unsuccessful attempts to prepare trimethylsilylacetaldehyde, see ref 5.

19. For a comprehensive bibliography of synthetic applications of trimethylsilyl enol ethers, see R. M. Coates, L. O. Sandefur, and R. D. Smillie, J. Am. Chem. Soc., 97, 1619 (1975).

20. (a) A. N. Nesmeyanov, I. F. Lutsenko, and V. A. Brattsev, Dokl. Akad. Nauk SSSR, 128, 551 (1959); Chem. Abstr., 54, 7537i (1960); (b) Belg. Patent 670769 (1966); Chem. Abstr., 65, 5487d (1966); (c) A. Bazouin, J. Dunoguès, and M. Lefort, Fr. Patent 1436568 (1966); Chem. Abstr., 66, 18764z (1967); (d) F. Runge and W. Abel, Makromol. Chem., 120, 148 (1968); (e) A. N. Lazarev, I. S. Ignat'ev, L. L. Shchukovskaya, and R. I. Pal'chik, Spectrochim. Acta, 27A, 2291 (1971); (f) J. Dedier, A. Marchand, M. T. Forel, and E. Frainnet, J. Organometal. Chem., 81, 161 (1974); (g) H. K. Hall, Jr., and P. Ykman, J. Am. Chem. Soc., 97, 800 (1975).

21. H. O. House, L. J. Czuba, M. Gall, and H. D. Olmstead, J. Org. Chem., 34, 2324 (1969).

22. P. J. Stang, M. G. Mangum, D. P. Fox, and P. Haak, J. Am. Chem. Soc., 96, 4562 (1974).

23. L. D. Bergel'son, V. D. Solodovnik, and M. M. Shemyakin, Izv. Akad. Nauk SSSR, 499 (1966); Chem. Abstr., 65, 10614h (1966).

24. R. A. Ruden, J. Org. Chem., 39, 3607 (1974).