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REARRANGEMENTS OF β,γ-EPOXYSILANES TO β-SILYL ALDEHYDES AND KETONES

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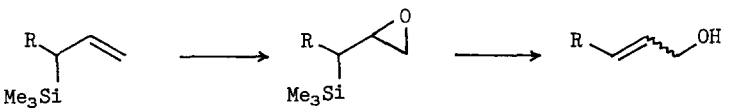
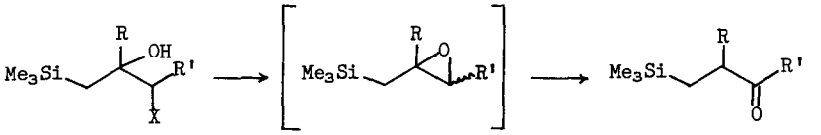
We have been interested in the possibility that β,γ-epoxysilanes[1] might serve as precursors to allylic alcohols via the sequence shown below.[6] Few examples of β,γ-epoxysilanes are



known.[1] Epoxidations of allylsilanes are reported to give poorly characterized mixtures of cleavage products.[1,3,7] We have therefore investigated the cyclizations of halohydrins[5,8] as an alternative approach to the synthesis of β,γ-epoxysilanes. Instead of the expected epoxides (2,[9] 5, and 8), we have isolated rearranged β-silyl carbonyl compounds (3, 6, and 9) from these reactions. These rearrangements are surprising in view of the mild conditions employed and because of the fact that the trimethylsilyl group is retained in the products.



1a, R = Me, R' = H, X = Cl
1b, R = Me, R' = H, X = Br
4, R = Ph, R' = H, X = Cl
7, R = H, R' = Et, X = Cl

2, R = Me, R' = H
5, R = Ph, R' = H
8, R = H, R' = Et

3, R = Me, R' = H
6, R = Ph, R' = H
9, R = H, R' = Et

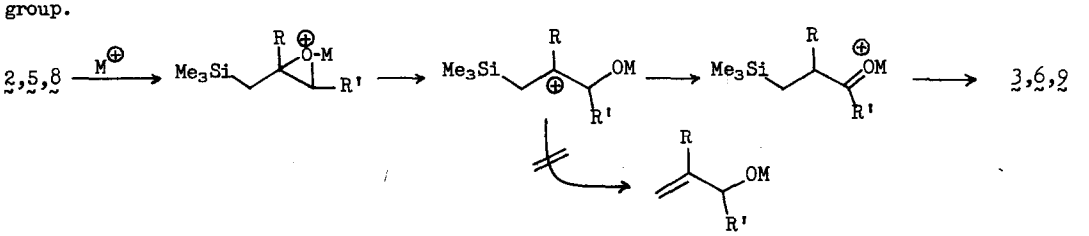
The chlorohydrin 1a[5,10] was prepared in 66% yield from chloroacetone by reaction with trimethylsilylmethylmagnesium chloride (Et_2O, room temp, 13 hr). Treatment of 1a with LiH (6 equiv) and t-BuOH (0.7 equiv) (THF, reflux 21 hr) gave a 40% yield[11] of the silyl aldehyde 3.[12,13] The aldehyde 3 was also the major product when NaH (THF, reflux 13 hr) or NaOH (Et_2O)

was employed as the base,[14] and could also be formed from the bromohydrin 1b (NaH, THF, room temp, or NaOH, Et_2O, room temp).[15]

To examine the generality of this reaction, the chlorohydrins 4 and 7 were similarly treated with LiH, NaH, and KH. Under all of these conditions, the β-silyl carbonyl compounds 6 and 9, respectively, were formed as one of the major components of a mixture; under some conditions, compounds 6 and 9 could be obtained in good yields by treatment of the initial reaction mixtures with magnesium bromide etherate. Thus, the chlorohydrin 4[10] (prepared from $PhCOCH_2Cl$ as above in 67% yield) was treated with NaH (5 equiv) and t-BuOH (1 equiv) (THF, 0°, 3 hr), followed by $MgBr_2 \cdot 2Et_2O$ (1 equiv) (THF, 0°, 4 hr) to give the silyl aldehyde 6[10,16] (ir (film) 5.81 μ) in 70% yield. Similarly, the chlorohydrin 7[10] (prepared from 2-chlorobutanal[17] in 80% yield) was treated with KH (2 equiv) (THF, -25°, 9 hr),[16] followed by $MgBr_2 \cdot 2Et_2O$ (Et_2O, 0°, 3.5 hr), to give the γ-ketosilane 9[10,19,20] (ir (film) 5.84 μ) in 59% yield.

Although we have not yet been able to isolate the epoxides in most of the above reactions,[15,18] they are the expected intermediates.[8,9,21] Further support for the intermediacy of epoxide 2 is our observation that the rearranged aldehyde 3 was also a major product when trimethylsilylacetone[22] was treated with dimethylsulfonium methylide.[23]

Although Lewis acid-catalyzed rearrangements of epoxides to carbonyl compounds are well known,[24] the above rearrangements are remarkable in that they occur under conditions (e.g. NaOH, NaH, or KH[18]) where Lewis acid catalysis would not be expected. The stability of the developing positive charge β to silicon[6a] may be a driving force for these rearrangements; it is noteworthy that hydride migration[25] to form the carbonyl occurs rather than loss of the trimethylsilyl group.[26]



This new rearrangement may provide a potential method for the synthesis of γ-functional organosilanes[27,28]

References and Notes

1. For a review of the chemistry of epoxysilanes, see L. V. Nozdrina, Y. I. Mindlin, and K. A. Andrianov, Russ. Chem. Rev., 42, 509 (1973). The only examples of β,γ-epoxysilanes for

which spectral data are given were prepared by epoxidation of silacyclopentenes.[2] The epoxidation of simple allylsilanes is reported to be unsuccessful,[3] although a few groups report successful preparations of β,γ-epoxysilanes by this method.[4] The synthesis of β,γ-epoxysilanes by other methods is also claimed.[3a,5]

2. (a) G. Manuel, P. Mazerolles, and J.-C. Florence, C. R. Acad. Sci. Paris, Ser. C, 269, 1553 (1969); (b) G. Manuel, P. Mazerolles, and J.-C. Florence, J. Organometal. Chem., 30, 5 (1971); (c) G. Manuel, P. Mazerolles, M. Lesbre, and J.-P. Pradel, J. Organometal. Chem., 61, 147 (1973).

3. (a) E. P. Plueddemann and G. Fanger, J. Am. Chem. Soc., 81, 2632 (1959); (b) V. Bažant and V. Matoušek, Coll. Czech. Chem. Comm., 24, 3758 (1959); (c) T. Tsuruta, S. Inoue, and H. Koenuma, Makromol. Chem., 112, 58 (1968).

4. (a) A. Wende and A. Gesierich, Plaste u. Kautschuk, 8, 399 (1961); Chem. Abstr., 56, 11611e (1962); (b) P. Brison and M. Lefort, Fr. Patent 1526231 (1968); Chem. Abstr., 70, 115319y (1969).

5. (a) S. I. Sadykh-Zade, L. V. Nozdrina, and A. D. Petrov, Doklady Akad. Nauk SSSR, 118, 723 (1958); Chem. Abstr., 52, 11805f (1958); (b) S. I. Sadykh-Zade and A. D. Petrov, Azerb. Khim. Zh., (No. 5), 105 (1962); Chem. Abstr., 59, 2847b (1963).

6. An example of this reaction in a cyclic organosilane is known; see ref 2c. For other elimination reactions of β-functional organosilanes, see (a) A. W. P. Jarvie, Organometal. Chem. Rev. A, 6, 153 (1970); (b) T. H. Chan and E. Chang, J. Org. Chem., 39, 3264 (1974); (c) P. F. Hudrlik and D. Peterson, J. Am. Chem. Soc., 97, 1464 (1975).

7. In accordance with the literature results,[3] our attempts to epoxidize allyltrimethylsilane and other simple allylsilanes have so far given many-component mixtures.

8. For examples of epoxide formation by cyclization of halohydrins, see (a) A. Rosowsky, in "Heterocyclic Compounds with Three and Four-Membered Rings," Part One, A. Weissberger, Ed., Interscience, New York, N. Y., 1964, pp 94-147; (b) H. O. House, "Modern Synthetic Reactions," 2nd ed, W. A. Benjamin, Inc., Menlo Park, California, 1972, pp 432-36; (c) G. J. Matthews and A. Hassner, in "Organic Reactions in Steroid Chemistry," Volume II, J. Fried and J. A. Edwards, Ed., Van Nostrand Reinhold, New York, N. Y., 1972, pp 15-17.

9. The synthesis of epoxide 2 by base treatment of chlorohydrin 1a has been claimed;[5] the structural assignment was not supported by any spectral data.

10. Satisfactory ir, NMR, and mass spectra were obtained.

11. In addition to the major fraction, other fractions from the distillation contained an estimated additional 10% of 3.

12. A compound, bp 95° (25 mm), assigned this structure was prepared from methacrylyl chloride via a reductive silylation procedure: J. Dunoguès, M. Bolourtchian, R. Calas, N. Duffaut, and J.-P. Picard, J. Organometal. Chem., 43, 157 (1972). An earlier report for the preparation of this compound is open to question: C. A. Burkhard and D. T. Hurd, U. S. Patent 2588083 (1952); Chem. Abstr., 46, 9120i (1952); C. A. Burkhard and D. T. Hurd, J. Org. Chem., 17, 1107 (1952).

13. Bp 60-64° (25 mm); ir (film) 3.70, 5.78, 8.00, 11.85 μ; NMR ($CHCl_3$) δ 9.89 (d, 1 H, J = 2 Hz), 2.22 (m, 1 H), 0.94 (d, 3 H, J = 6.5 Hz), 0.7-0.4 (m, 2 H, appearing as 0.7, d, J = 6 Hz, and 0.42, d, J = 8 Hz), 0.15 (s, 9 H); mass spectrum m/e 147, 144 (M^+), 130, 129, 115, 75, 74, 73, 59, 45, 43; 2,4-dinitrophenylhydrazone (from MeOH), mp 123.5-124°. Anal. Calcd for $C_{13}H_{20}N_4O_4Si$: C, 48.13; H, 6.21. Found: C, 48.04; H, 6.34.

14. Treatment of 1a with MeLi in Et_2O or with LiH in THF also gave significant quantities of the aldehyde 3.

15. To ascertain that the rearrangement was not taking place on aqueous workup, the reaction mixture from some experiments (1b with NaOH and with NaH) was distilled without aqueous workup, giving the same product (2) by VPC and NMR.

16. 2,4-Dinitrophenylhydrazone (from EtOH), mp 144.5-145.5°.

17. C. L. Stevens, E. Farkas, and B. Gillis, J. Am. Chem. Soc., 76, 2695 (1954).

18. Under carefully controlled conditions, treatment of the chlorohydrin 7 with KH (THF, -25°,

8 hr) gave a 1:3 mixture of the ketosilane 9 and another component; the latter was purified by preparative VPC and had spectra consistent with the epoxide structure 8: ir (CCl_4) 3.38, 6.88, 8.00, 8.42, 11.21, 11.8 μ; NMR (CCl_4) δ 2.55-2.21 (m, 2 H), 1.68-1.18 (m, 2 H), 1.11-0.55 (m, 5 H), -0.04 (s, 9 H). On treatment with $MgBr_2 \cdot 2Et_2O$, this compound was converted to the ketosilane 9.

19. Compound 9 has been previously reported by N. V. Komarov, V. K. Roman, and L. I. Komarova, Izv. Akad. Nauk SSSR, 1464 (1966); Engl. p 1405.

20. 2,4-Dinitrophenylhydrazone (from MeOH), mp 97-97.5°. Anal. Calcd for $C_{14}H_{22}N_4O_4Si$: C, 49.68; H, 6.55. Found: C, 49.60; H, 6.56.

21. Alternative β-elimination reactions of the initially formed alkoxides, with loss of silicon, were not observed. For conditions where this type of elimination would be expected, see ref 6c.

22. C. R. Hauser and C. R. Hance, J. Am. Chem. Soc., 74, 5091 (1952).

23. E. J. Corey and M. Chaykovsky, J. Am. Chem. Soc., 87, 1353 (1965); see also ref 8b, pp 715-719.

24. For example, see B. Rickborn and R. M. Gerkin, J. Am. Chem. Soc., 93, 1693 (1971), and references cited therein.

25. Although alternative mechanisms involving a proton-abstraction step rather than hydride migration are conceivable, we believe they are less likely under our conditions. For example, see J. K. Crandall, L. C. Crawley, D. B. Banks, and L. C. Lin, J. Org. Chem., 36, 510 (1971).

26. The novel zinc iodide-induced isomerizations of cyclopropyl silyl ethers to allyl silyl ethers are superficially similar to the rearrangement of 2 to 3 except that carbon and oxygen are interchanged. S. Murai, T. Aya, T. Renge, I. Ryu, and N. Sonoda, J. Org. Chem., 39, 858 (1974).

27. For some previous methods of synthesizing γ-functional organosilanes, see refs 12 and 19 and the following: L. H. Sommer and R. P. Pioch, J. Am. Chem. Soc., 76, 1606 (1954); J. W. Curry and G. W. Harrison, Jr., J. Org. Chem., 23, 627 (1958); A. D. Petrov, S. I. Sadykh-Zade, and E. I. Filatova, J. Gen. Chem. USSR, 29, 2896 (1959); J. Dunoguès, A. Ekouya, R. Calas, and N. Duffaut, J. Organometal. Chem., 87, 151 (1975); V. Bažant, V. Chvalovský, and J. Rathouský, "Organosilicon Compounds," Vol. 1, Academic Press, New York, N. Y., 1965, pp 139-150, 256-268.

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