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CLEAVAGE OF THE SILICON-CARBON BOND BY FLUORIDE ION IN TRIORGANOSILYLOXIRANES. THE STEREOCHEMISTRY OF SUBSTITUTION AT OXIRANYL CARBON.

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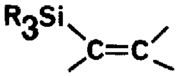
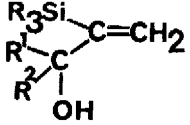
The cleavage of silicon-alkynyl carbon bond (in I) by fluoride ion is relatively facile[1] whereas the cleavage of silicon-vinyl carbon bond (in II) is difficult[1,2]. This is attributed in part to the ability of the alkynyl anion to act as a better leaving group in what is probably an S_N2-Si reaction[3]. We found that when there is a β-hydroxy group present, cleavage of silicon-vinyl carbon bond (in III) by fluoride ion can occur. A β-hydroxy effect was proposed to account for the observation[2]. However, even with the anchimeric assistance of the β-hydroxy group, cleavage of the silicon-alkyl carbon bond (in IV) by fluoride ion could not be achieved[2].

I $R_3Si{-}C{\equiv}C{-}$

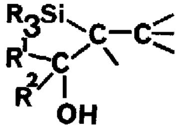
II



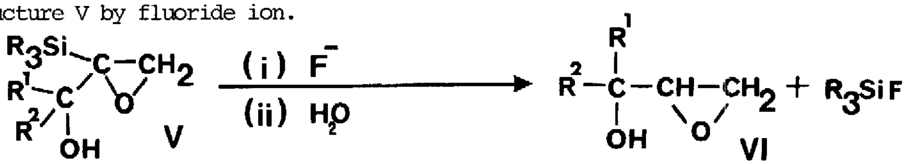
III



IV



In view of the increasing interest of silyloxiranes in organic synthesis[4-7] and the expectation that the oxiranyl anion may be somewhere in-between the vinyl anion and the alkyl anion in terms of basicity[8], we have examined the cleavage of silicon-carbon bond in compounds of general structure V by fluoride ion.



(1)

a: $R{=}R^1{=}C_6H_5$, $R^2{=}H$ b: $R{=}CH_3$, $R^1{=}C_6H_5$, $R^2{=}H$

c: $R{=}C_6H_5$, $R^1{=}CH_3$, $R^2{=}H$ d: $R^1R^2{=}(CH_2)_5$, $R{=}CH_3$

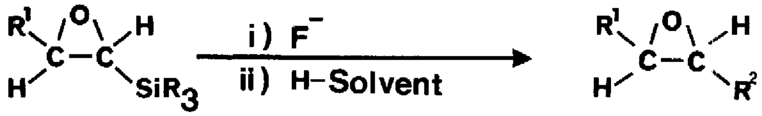
a: $R^1{=}C_6H_5$, $R^2{=}H$ c: $R^1{=}CH_3$, $R^2{=}H$

d: $R^1R^2{=}(CH_2)_5$

We wish to report the remarkable observation that the replacement of silyl group by hydrogen (equation 1) can indeed be achieved with relative ease.

Compounds V were obtained by epoxidation of III[9] with m-chloroperbenzoic acid in methylene chloride at room temperature. A mixture of V and Tetraethylammonium fluoride (1.1 equivalent) in dimethylsulfoxide or acetonitrile was stirred at room temperature for 2 hours. When the reaction mixture was quenched with water and extracted with ether, there was obtained in essentially quantitative yield the compound VI. The identities of compounds VI were secured by standard spectroscopic means as well as by comparison with authentic compounds prepared by epoxidation of the corresponding allylic alcohols.

Comparison of the relative rates of reaction with fluoride ion indicated that it is easier to cleave the silicon-carbon bond in V than in III[2]. This led us to investigate the reaction of simple triorganosilyloxiranes with fluoride ion. Indeed, triphenylsilyloxirane (VIIa), on reaction with potassium fluoride in ethanol-dimethylsulfoxide gave triphenylfluorosilane[10] as well as ethylene oxide[11]. Similarly, <u>trans</u>-1-phenyl-2-trimethylsilyloxirane[12] (VIIb) on treatment with tetraethylammonium fluoride in DMSO followed by quenching with water gave styrene oxide (VIIIb) in quantitative yield.



VII a: R^1=H, R=C_6H_5 b: R^1=C_6H_5, R=CH_3

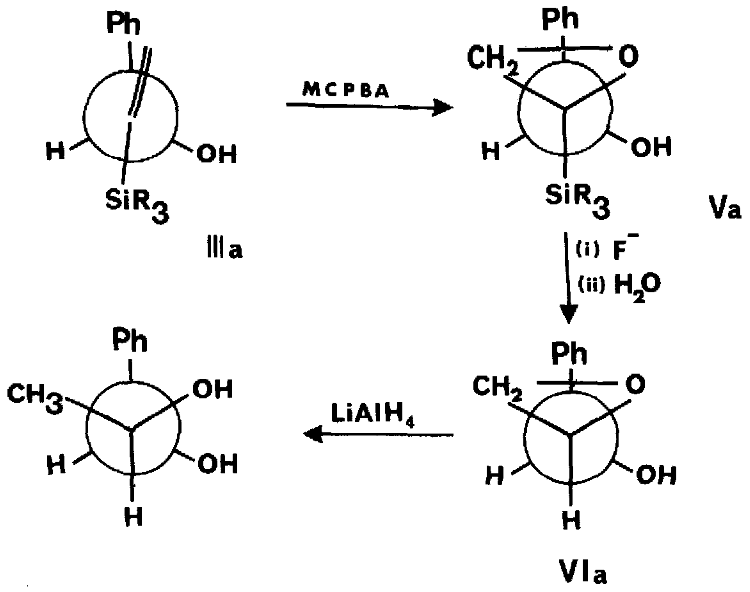
VIII a: R^1=R^2=H b: R^1=C_6H_5, R^2=H
c: R^1=C_6H_5, R^2=D.

The stereochemistry of substitution at the oxiranyl carbon has been examined on the basis of the following experiments. Epoxidation of IIIa occurred in a stereoselective manner to give the epoxy compound Va as one diastereomer. While the stereochemistry of Va has not been established with certainty, it is argued that the preferred conformation of IIIa is likely to have the vinyl group eclipsing with the phenyl group[16]; epoxidation of IIIa then occurred on the same side as the hydroxy group[17]. The stereochemistry of VIa was however deduced definitely by lithium aluminum hydride reduction to give erythro-1-phenylpropane-1,2-diol[13]. The overall transformation can be depicted by scheme I. The replacement of the silyl group by hydrogen (Va ⟶ VIa) occurred thus with retention of configuration at carbon. Similar stereospecific transformations were obtained for the sequence IIIb ⟶ Vb ⟶ VIa.

Retention of configuration at the oxiranyl carbon can however be demonstrated in the conversion of VIIb to VIIc. A solution of VIIb (1 mmole), tetraethylammonium fluoride in 1 ml of DMSO-d_6 was stirred for one minute at room temperature. The reaction mixture was poured into 20 ml D_2O. Styrene oxide (VIIIc) was isolated in 70% yield and found to have 33% deuterium incorporation (mass spectrometry) with all the deuterium confined to the trans-position (nmr).[18]

Two mechanisms can be considered to account for the observed results. The first one involves a frontside electrophilic substitution at the oxiranyl carbon[19]. This is considered less likely in view of the relative order of reactivity of alkynyl > vinyl > alkyl. Some carbanionic character must have developed at the carbon center. In the case of the second mechanism, an oxiranyl anion is postulated as the intermediate[19]. Oxiranyl anion has previously been implicated in the base-catalysed rearrangement of epoxides[20]. Information about the nature of the oxiranyl anion has however been scanty. In as much as the present reaction gives an indication of the nature of carbanionic character at the carbon center, our results suggest that (1) oxiranyl anion is comparable to alkynyl anion as leaving group and (2) the rate of inversion of the oxiranyl anion is sufficiently slow[21] with respect to proton transfer so that the stereochemical integrity at the oxiranyl carbon is maintained.

Acknowledgement: Financial support by the National Research Council of Canada and the Ministry of Education, Quebec, is gratefully acknowledged.



Scheme 1

References and Footnotes

(1) C.S. Kraihanzel and J.E. Poist, J. Organometal. Chem., 8, 239 (1967).

(2) T.H. Chan and W. Mychajlowskij, Tetrahedron Letters, 3479 (1974).

(3) L. Sommer, "Stereochemistry, Mechanism and Silicon", McGraw Hill, 1965.

(4) G. Stork and E. Colvin, J. Amer. Chem. Soc., 93, 2080 (1971).

(5) T.H. Chan, M.P. Li, W. Mychajlowskij and D.N. Harpp, Tetrahedron Letters, 3511 (1974).

(6) B.T. Gröbel and D. Seebach, Angew. Chem. Internat. Ed., 13, 83 (1974).

(7) R.K. Boeckman Jr. and K.J. Bruza, Tetrahedron Letters, 3365 (1974).

(8) The similarity of oxirane and cyclopropane in possessing properties of unsaturation was first cogently argued by A.D. Walsh, Trans. Faraday Soc., 45, 179 (1949). For recent works, see W.C. Danen, J. Amer. Chem. Soc., 94, 4835 (1972) and references cited therein.

(9) For preparation of compounds III, see T.H. Chan and W. Mychajlowskij, Tetrahedron Letters, 171 (1974).

(10) On isolation by TLC, a mixture of triphenylfluorosilane and triphenylsilanol was obtained.

(11) Ethylene oxide was isolated into a cold-trap by passing N_2 gas through the reaction mixture. Its identity was established by pmr comparison with authentic sample.

(12) Prepared by the *epoxidation of E-1-phenyl-2-trimethylsilylethylene which was synthesized* according to D. Seyferth, L.G. Vaughan and R. Suzuki, J. Organometal. Chem., 1, 444 (1964).

(13) Identified by both pmr[14] and m.p.[15].

(14) G. Schmid, Can. J. Chem. 46, 3415 (1968).

(15) M. Sbododa and J. Sicher, Coll. Czech. Chem. Commun., 20, 1452 (1955).

(16) Eclipsing conformation has been found to be general for alkenes. See G.J. Karabatsos and D.J. Fenoglio in "Topics in Stereochemistry", ed. E.L. Eliel and N.L. Allinger, Vol. 5, Wiley-Interscience, New York, 1970.

(17) The directing effect of allylic hydroxy group in epoxidation has been well documented. P. Chamberlain, M.L. Roberts and G.H. Whitham, J. Chem. Soc., B, 1374 (1970) and references cited therein.

(18) The proton trans- to the phenyl group in styrene oxide was assigned by C.A. Reilly and J.D. Swalen, J. Chem. Phys., 32, 1378 (1960). In the present case, p.m.r. integration gave the relative rations of the trans-proton, the cis-proton and the benzylic proton, as 0.67/1.00/1.00. The modest deuterium incorporation was due in part to the trace of water inevitably present in tetraethylammonium fluoride.

(19) See D.J. Cram, "Fundamentals of Carbanion Chemistry", Academic Press, New York, 1965 for a general discussion of aliphatic electrophilic substitution.

(20) See for example A.C. Cope, P.A. Trumbull and E.R. Trumbull, J. Amer. Chem. Soc., 80, 2844 (1958). Also the review by A. Rosowsky in "Heterocyclic Compounds", ed. A. Weissberger, vol. 19, p. 262. Interscience, New York, 1964.

(21) Inversion barrier for the nitrogen pyramid of the isoelectronic oxaziridine was found to be high. See F. Montanari, I. Moretti and G. Torre, Chem. Commun. 1086 (1969). A. Mannschreck, J. Lines and W. Seitz, Ann. 727, 224 (1969).