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RING OPENING AND REARRANGEMENT OF TRIMETHYLSILYLOXIRANES. AN IMPROVED PREPARATION OF α-TRIMETHYLSILYLKETONES

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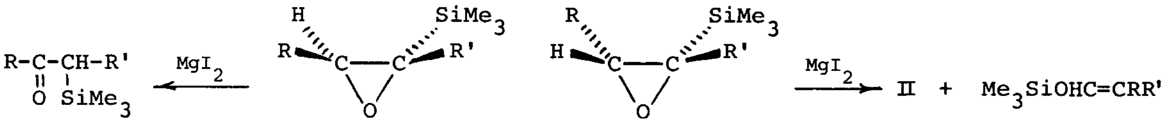
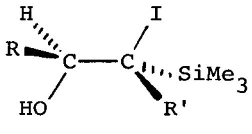
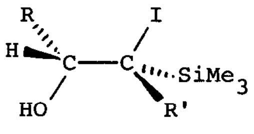
α-Trimethylsilylketones[1] (II) have attracted considerable attention as precursors for E- and Z-olefins with predictable geometry.[2,3] The silylated ketones have usually been prepared by oxidation of the corresponding β-trimethylsilylalcohols,[2] because direct silylation of the corresponding ketones has not given the expected products.[4] Although the recently reported synthesis of II via MgI_2-induced rearrangement of easily accessible silyloxiranes I seems to be promising,[5] we have to clarify the reason why the same treatment of the diastereomer III produces a mixture of II and IV. This paper describes a preparatively improved procedure for the transformation which involves iodohydrins (V and VI) as discrete intermediates.[6]



II I III IV



V



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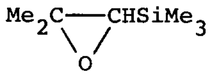
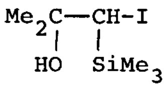


VII



$Me_2C(OH)\text{—}CH(SiMe_3)\text{—}I$

VIII

a: R = R' = Hex. b: R = Pr, R' = Am.

To a solution of trimethylsilyloxirane Ia (0.284 g, 1 mmol, purity >99%)[5] in 5 ml of ether was added 1 ml of 57% HI at 0°C. Alkaline work up and chromatographic purification (silica gel column, benzene) gave iodohydrin Va in a quantitative yield.[7] Silyloxiranes IIIa (purity 91%) and IIIb (purity 97%) were transformed analogously into iodohydrin VIa and VIb, respectively. Another silyloxirane VII produced VIII regioselectively.[8] The stereochemistry of the iodohydrins was determined by regeneration of the starting silyloxiranes by the action of excess potassium t-butoxide: thus Ia (purity >99%) from Va, IIIa (purity 91%) from VIa, and IIIb (purity 96%) from VIb, respectively.

The above described results indicate that iodide ion is attached regio- and stereoselectively on the silylated carbon.[9,10]

Treatment of Va with n-BuLi (1 equiv.) in hexane-ether at room temperature for 1.5 h gave IIa in a quantitative yield.[11] Analogously the diastereomer VIa produced the same product IIa in 90% yield. Exclusive 1,2-migration of H in both isomers accounts for the same product. Iodohydrin VIb gave IIb in a quantitative yield. The present procedure involving iodohydrin intermediates improves the yields of II over the ones of previously reported one-pot transformation.

In contrast, magnesium salts of diastereomeric iodohydrins behaved differently. Treatment of Va with MeMgI (1 equiv.) and MgI_2 (10 equiv.) in ether at reflux for 2 h gave IIa in 92% yield. Iodohydrin VIa, on the other hand, was transformed into a mixture of IIa (29%) and trimethylsilyl enolate IVa (43%).[12] Previously reported MgI_2-induced rearrangement of silyloxiranes showed similar product distributions depending upon the sorts of the starting diastereomers.[5] In order to obtain mechanistic information, the reaction has further been reinvestigated.

Treatment of Ia with MgI_2 at 20°C provided Va (28%) along with IIa (30%), while repeating the reaction at 40°C yielded no trace of Va but a pure sample of IIa (93%). Clearly the Mg salt of iodohydrin should be an intermediate, giving II or IV in the successive reaction. The above described product distributions depending upon diastereomers are consistent with this view.[14]

REFERENCES AND NOTES

(1) α-Trimethylsilylketone means α-trimethylsilyl-substituted ketone in this paper.

(2) P. F. Hudrlik and D. Peterson, *J. Am. Chem. Soc.*, **97**, 1467 (1975).

(3) K. Utimoto, M. Obayashi, and H. Nozaki, *J. Org. Chem.*, **41**, 2940 (1976).

(4) Generally trimethylsilyl enolates were obtained; see (a) G. Stork and P. F. Hudrlik, *J. Am. Chem. Soc.*, **90**, 4462, 4464 (1968). (b) H. O. House, M. Gall, and H. D. Olmstead, *J. Org. Chem.*, **34**, 2324 (1969), **36**, 2361 (1971) and references cited therein.

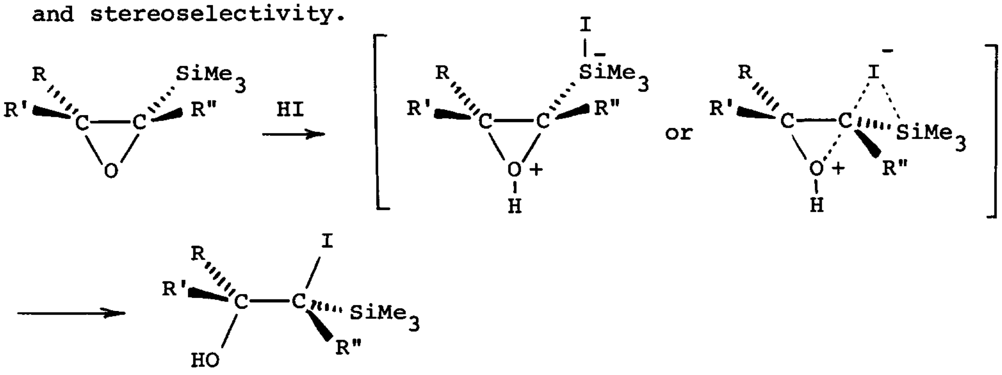
(5) M. Obayashi, K. Utimoto, and H. Nozaki, *Tetrahedron Letters*, 1807 (1977).

(6) When preparation of this paper was completed, Dr. I. Kuwajima and his co-workers published another type of α-trimethylsilylketone synthesis by the rearrangement of silyl-substituted chlorohydrin; T. Sato, T. Abe, and I. Kuwajima, *Tetrahedron Letters*, 259 (1978).

(7) Iodohydrin II, ir (neat) 3475, 1240, 840, 756, 690 cm^{-1}; pmr (CCl_4) δ ppm, 0.23 (9H, s), 0.90 (6H, t, J = 6 Hz), 1.07-1.80 (20H, m), 1.50 (1H, d, J = 6.6 Hz, CH-O$\underline{H}$), 3.44 (1H, m, C$\underline{H}$-OH). Hydroxy proton was checked by D_2O-added pmr as well as double resonance irradiated at 3.44. Other iodohydrins were determined analogously.

(8) Structure of VIII was determined by selective formation of 1-iodo-2-methylpropene by the action of BF_3-etherate.

(9) Penta-coordinated silicon intermediate may explain the observed regio- and stereoselectivity.



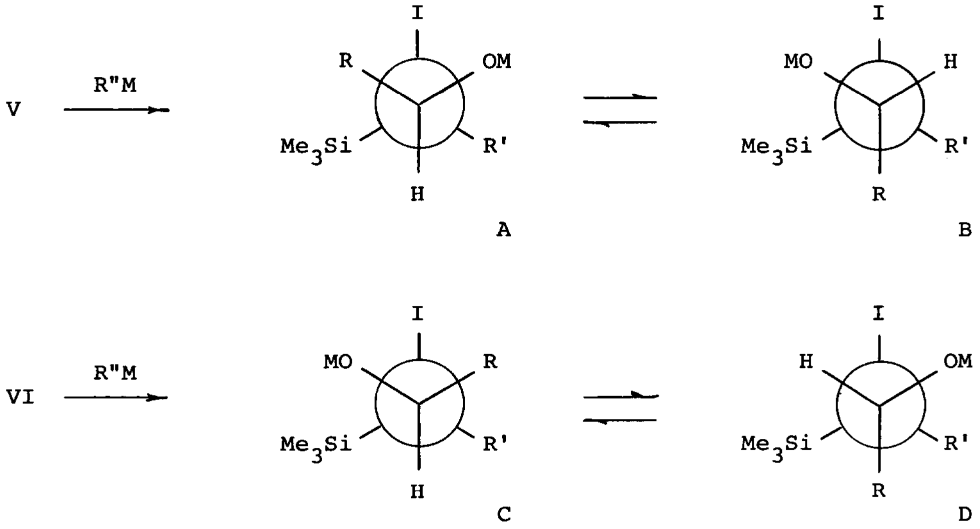
Analogous penta-coordinated silicon intermediates were suggested:

M. T. Reetz and N. Greif, Angew. Chem. Int. Ed., 16, 712 (1977).

(10) Analogous α-cleavage of silyloxiranes has appeared: (a) P. F. Hudrlik and J. P. Arcoleo, Tetrahedron Letters, 591 (1977). (b) P. F. Hudrlik, A. M. Hudrlik, R. J. Rona, R. J. Misra, and G. P. Withers, J. Am. Chem. Soc., 99, 1993 (1977) and references cited therein.

(11) Direct treatment of III with LiI gave no rearranged product.

(12) Rearrangement of iodohydrin to α-trimethylsilylketone (II) is ascribed to MI-elimination (following scheme) under 1,2-hydrogen migration, while the one affording IV to MI-elimination under 1,2-R migration and the subsequent 1,3-migration of Me_3Si. The observed selectivity is explained on the following assumptions: (i) migratory aptitude H > R; (ii) anti conformation of the migrating group and iodine (ref. 13); (iii) Me_3Si > R, I in effective size; (iv) if M = Li, A (→ II) > B (→ IV) and C (→ II) > D (→ IV) in populations as R > OLi > H in effective size; (v) if M = MgI, A > B but C < D as OMgI and Me_3Si should be in anti-positions each other because of the larger effective size of OMgI group. Possibly $\Delta F^{\ddagger}$ (D → IV) is comparable with $\Delta F^{\ddagger}$ (D → C → II).



(13) B. Rickborn and R. M. Gerkin, J. Am. Chem. Soc., 93, 1693 (1971).

(14) The authors wish to thank The Ministry of Education, Japan, for Grant-in-Aid (110309, 203014).