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CONVERSION OF 1-ALKOXY-2-(TRIMETHYLSILYL)-3-HYDROXY MOIETY TO OLEFINS IN PETERSON OLEFINATION; AN UNPRECEDENTED STEREOCHEMICAL CONSEQUENCE

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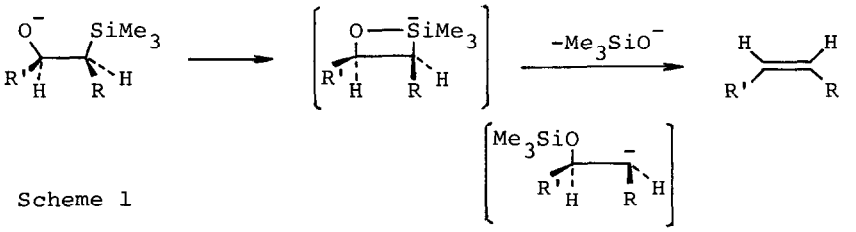
Summary: In the Peterson olefination of a β-oxidoalkylsilane which accommodates a diastereomerically pure 1-alkoxy-2-(trimethylsilyl)-3-hydroxy moiety, anti pathway to eliminate an alkoxide ion was found to predominate over the amply precedented *syn*-elimination of a trimethylsilanolate ion.

Peterson olefination is referred to as a stereospecific syn or anti elimination of β-hydroxyalkylsilanes under basic or acidic conditions, respectively. Thus, once a diastereomerically pure β-hydroxyalkylsilane is in hand, either (*E*)- or (*Z*)-olefin can be prepared at will from the single precursor by a choice of conditions for the elimination.[1,2]

From a mechanistic standpoint, it is clear that, in the acid-catalyzed process, the usual stereoelectronic factors determine the antiperiplanar geometry of elimination. It is then felt that the base-induced process, which forms a β-oxidoalkylsilane first, does not generally involve the intervention of a carbanion despite a seemingly facile 1,3-carbon to oxygen migration of the silyl group.[3] Therefore, the elimination of β-oxidoalkylsilane assumes that both acyclic and cyclic systems having geometry suitable for a facile elimination take a genuine syn pathway (Scheme 1).[4,5]



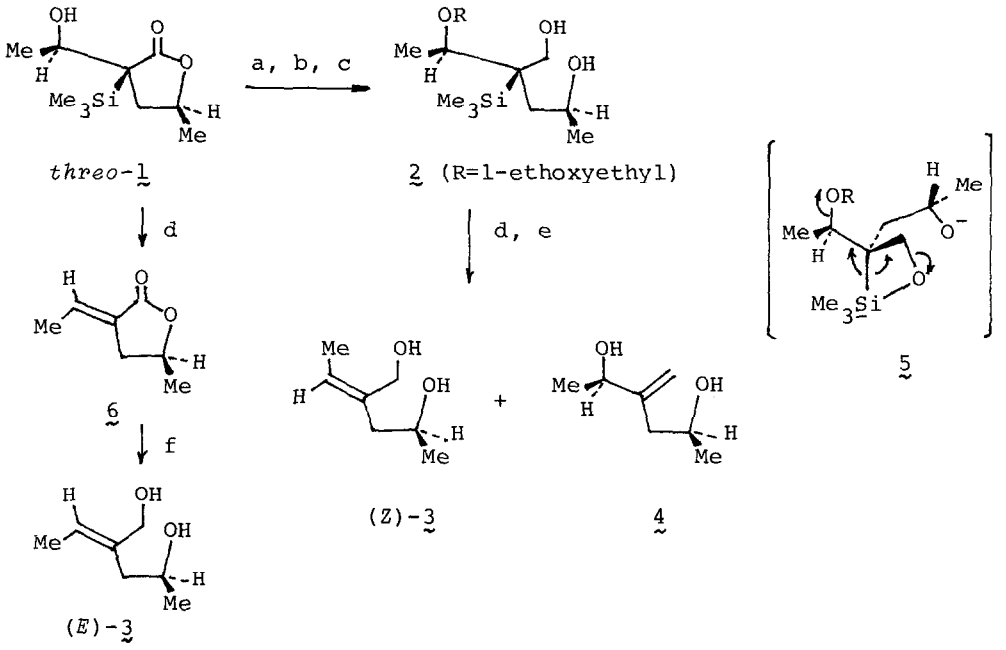
Scheme 1

We describe herein that, when a β-hydroxyalkylsilane accommodates an alkoxy group on another β-position to the silicon atom, elimination of an alkoxide ion predominated over the *syn*-elimination pathway of a silanolate ion.

In Scheme 2 is outlined an unprecedented stereochemical consequence in the elimination of a β-oxidoalkylsilane which was derived from diastereomerically pure

threo-(3*R**, 5*R**, 1'*S**)-4,5-dihydro-3-(1'-hydroxyethyl)-3-(trimethylsilyl)-5-methyl-2(3*H*)furanone (1).[6,7]

Thus, protection of the hydroxyl group with ethyl vinyl ether and reduction of the lactone moiety of 1 with lithium aluminum hydride followed by careful aqueous workup gave compound 2[8] with relative configuration as indicated in quantitative yield.



Scheme 2. a) CH_2=CHOEt/*p*-TsOH/CH_2Cl_2, b) $LiAlH_4$/THF, c) aq. NH_4Cl, d) $KN(SiMe_3)_2$/PhH-THF, e) H_3O^+, f) *i*-Bu_2AlH/Pentane.

To a solution of 2 (234 mg, 1.15 mmol) dissolved in dry tetrahydrofuran (THF) (25 mL) was added 2.2 equivalents of potassium bis(trimethylsilyl)amide (0.4 *M* in benzene) at -70 °C. The mixture was stirred for 3 h during which time reaction temperature was allowed to raise to room temperature, and quenched with saturated ammonium chloride. Careful separation of the reaction products by column chromatography (silica gel with gradual elution with hexane-ether) afforded a mixture of (5*R**, 2*Z*)-3-(hydroxymethyl)-2-hexen-5-ol (3) and its trimethylsily ether at the allylic alcohol and an ethoxyethyl derivative of (2*R**, 5*S**)-3-methylene-2,5-hexanediol (4). These primary products were hydrolyzed to give 3[9] and 4[10], respectively, in a pure state in 68.4% combined yield.

This novel base-induced elimination of 2 possesses two striking features. First, 3 was formed as a major product rather than 4 in a ratio of 63:37, which can not be explained simply by a foregoing *syn*-elimination pathway.

In order to rationalize this unexpected result, it is presumed that the β-oxidosilane formed from 2 experiences the postulated penta-coordinate silicon species 5 having geometry suitable for a facile elimination of an alkoxide ion as depicted in Scheme 2. Thus, the transient species 5 may give rise to either 3 or 4, the ratio depending both on the geometry of elimination (anti *vs.* syn) and on the aptitude for the leaving group of an alkoxy or a trimethylsiloxy group. There seems to be an alternative where a silicon migration to form a carbanion precedes the elimination (ElcB mechanism). The fact that protiodesilylation, *via* the carbanion, is faster than elimination[5] may substantiate this alternative. However, it was found to be not the case (*vide infra*).

Second, both 3 and 4 were found to be diastereomerically pure, respectively. Since we have obtained easily pure *threo*-(3*R**, 5*R**, 1'*S**)-1, preparation of 4 represents a new method for attaining 1,4-remote acyclic stereoselection.

That 3 is also one diastereomer with purely Z olefin moiety[11] is significant. It follows that the geometry between a trimethylsilyl and an alkoxy group should be anti to afford (Z)-olefin stereoselectively. Therefore, it is unreasonable to assume that the common carbanion formed, if any, can enter into elimination with either anti or syn pathway depending on the leaving groups present on the position β to the carbanion.

In conclusion, all data presented here are best understood through a mechanism that involves concomitant and preferred *anti*-elimination in competition with the *syn*-elimination pathway from the common species 5 which is shown in the Scheme. Extensions of the present studies to include preparation and conversion of more generalized 1-alkoxy-2-(trimethylsilyl)-3-hydroxy systems to olefins are in progress.

Generous gift of trimethylchlorosilane from Toshiba Silicone Co., Ltd. is gratefully acknowledged.

REFERENCES AND NOTES

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b) E. W. Colvin, "Silicon in Organic Synthesis", Butterworth (1981), Chapt. 12.
2) K. Yamamoto, Y. Tomo, and S. Suzuki, Tetrahedron Lett., 21, 2861 (1980).
3) We have already suggested that, in the presence of a carbanion-stabilizing group, a facile 1,3-carbon to oxygen migration of the silyl group very likely takes part in the elimination (ref. 2).
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b) P. F. Hudrlik, D. Peterson, and R. J. Rona, J. Org. Chem., 40, 2263 (1975).

5) Very recently, there has been reported that the base-catalyzed protiodesilylation of β-hydroxyalkylsilanes involving 1,3-carbon to oxygen migration of the silyl group took place exclusively; F. Sato, Y. Tanaka, and M. Sato, J. Chem. Soc., Chem. Commun., in press and P. F. Hudrlik, A. M. Hudrlik, and A. K. Kulkarni, J. Am. Chem. Soc., 104, 6809 (1982).

6) According to Noyori's proposal [R. Noyori, I. Nishida, and J. Sakata, J. Am. Chem. Soc., 103, 2106 (1981)], *threo*-1 has a relative configuration shown.

7) Preparation of compounds 1 and 6 has been presented at the 46th Fall Meeting of the Chem. Soc. Japan (1982), Abstr. 3D14. All compounds reported here gave satisfactory elemental analyses.
threo-1, mp 112-113 °C (hexane-benzene). ^{1}H NMR(90 MHz, $CDCl_3$, TMS) δ0.18(s, 9H), 1.27(d, *J*=6.0 Hz, 3H), 1.41(d, *J*=6.0 Hz, 3H), 1.78(dd, *J*=14.4, 8.3 Hz, 1H), 2.38(d, *J*=2.8 Hz, 1H), 2.58(dd, *J*=14.4, 7.5 Hz, 1H), 4.15-4.55(br.m, 1H), and 4.60 ppm(sym. m, 1H). ^{13}C NMR(22.5 MHz, $CDCl_3$, ext. TMS) δ-3.0, 20.4, 22.0, 33.1, 46.7, 69.9, 76.0, and 180.5 ppm.

8) Diastereomeric mixture of (2*R**, 3*R**, 5*S**)-2-(1'-ethoxyethoxy)-3-(hydroxymethyl)-3-(trimethylsilyl)-5-hexanol (2): ^{1}H NMR($CDCl_3$, TMS) δ0.00(s, 9H), 1.00-1.25(m, 12H), 1.26-1.80(m, 2H), 3.2-4.3(m, 6H), 4.50(q, *J*=5.1 Hz, 1H), 4.75(q, *J*=5.1 Hz,1H), and 4.6-5.0(br, 1H). ^{13}C NMR($CDCl_3$, TMS) δ-1.26, -0.74, 14.95, 15.15, 18.24, 18.59, 20.02, 20.36, 24.22, 25.05, 36.14, 37.23, 42.08, 42.82, 57.81, 59.85, 62.67, 64.97, 61.72, 63.10, 72.42, 76.02, 98.86, and 101.03.

9) (Z)-3: ^{1}H NMR δ1.19(d, *J*=6.4 Hz, 3H), 1.69(d, *J*=6.8 Hz, 3H), 1.9-2.5(m, AB, 2H), 3.7-4.0(m, 3H), 4.09 and 4.20(AB, *J*=12.1 Hz, 2H), and 5.45(q, *J*=6.8 Hz, 1H). ^{13}C NMR δ13.2, 23.2, 49.1, 60.1, 67.8, 126.1, and 136.4.

10) Spectral data of 4: ^{1}H NMR δ1.24(d, *J*=6.2 Hz, 3H), 1.28(d, *J*=6.6 Hz, 3H), 2.91 and 2.26(AB, 2H), 3.59(br. s, 1H), 3.90(q, *J*=5.8 Hz, 1H), 4.31(q, *J*=6.2 Hz, 1H), and 4.88-5.11(vinylic H). ^{13}C NMR δ22.4, 23.6, 41.6, 68.0, 70.9, 113.0, and 150.2.

11) This apparent total absence of the corresponding *E*-isomer is confirmed by umambiguous preparation of the latter which is also depicted in Scheme 2. The base-induced olefination of *threo*-1 gave (*E*)-α-ethylidene-γ-methyl-γ-butyrolactone (6).[7] The latter was reduced to give (*E*)-3: ^{1}H NMR δ1.23(d, *J*=6.2 Hz, 3H), 1.65(d, *J*=6.8 Hz, 3H), 2.0-2.6(m, AB, 2H), 3.2-4.2(m, 5H), and 5.66(q, *J*=7.5 Hz, 1H). ^{13}C NMR δ13.5, 23.4, 38.7, 67.1, 68.7, 125.8, and 136.9.

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