

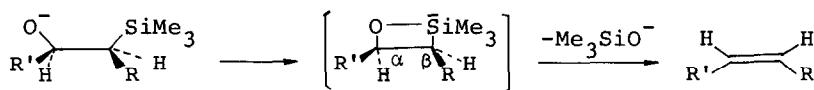
NOVEL COMPETING REACTION OF 1-METHOXY-2-(TRIMETHYLSILYL)-3-HYDROXY MOIETY IN
BASE-INDUCED PETERSON OLEFINATION; MECHANISTIC RATIONALE OF THE REACTION

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Summary: In the base-induced Peterson olefination of diastereomerically pure 8-methoxy-7-(trimethylsilyl)-6-tridecanol, anti pathway to eliminate a methoxide ion was found to compete significantly with amply precedented *syn*-elimination of a trimethylsilyl anion. On the basis of an extent of the competing reactions which depend markedly on the respective diastereomers (three from four diastereomers) the detailed mechanism of the *syn*-elimination emerged.

The stereochemical outcome of Peterson olefination has become clear, by using a diastereomerically pure β -hydroxyalkylsilane, to proceed stereospecifically with *syn* or anti pathway under basic or acidic conditions, respectively.¹

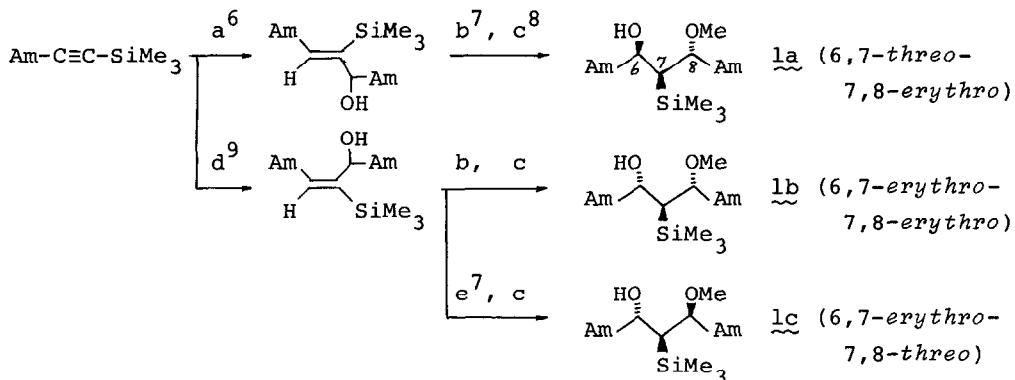
From a mechanistic viewpoint, it is evident that the usual stereoelectronic factors determine the antiperiplanar geometry of elimination in the acid-catalyzed process. On the other hand, the base-induced process, which forms a β -oxidoalkylsilane first, assumes the four-membered ring species (or incipient carbanion) in the transition state for a rigorous *syn*-elimination to occur. However, it should be emphasized that detailed mechanism of the base-induced elimination is not known, especially for the stereoelectronic factors in the fragmentation of the postulated four-membered ring species^{1c, 2} (Scheme 1).



Scheme 1

Several instances where a competing reaction prohibits the Peterson base-induced olefination of unactivated β -hydroxyalkylsilanes involve retro-aldol³ and Darzens-like reactions⁴ and most interestingly homo-Brook rearrangement.⁵ The latter protiodesilylation must take place *via* the postulated four-membered transition state.

We have found that a β -hydroxyalkylsilane which accommodates an alkoxyl group on another vicinal position to the silicon atom can undergo elimination of the alkoxide ion predominantly over the *syn*-elimination pathway of a silanol anion.^{2b} Intrigued by the novel competing reaction, we initiated studies designed to help distinguish between the existing two competitive eliminations of 1-methoxy-2-(trimethylsilyl)-3-hydroxy moiety, which are both considered to be



a: i) $i\text{-BuMgBr/cat. Cp}_2\text{TiCl}_2/\text{Et}_2\text{O}$, ii) AmCHO . b: i) $t\text{-BuO}_2\text{H/VO(acac)}_2/\text{CH}_2\text{Cl}_2$.
 c: i) KH/MeI/THF , ii) AlH_3 (2 eq)/THF. d: i) Dibah/hexane, ii) I_2 ,
 iii) $t\text{-BuLi}$, iv) AmCHO . e: $\text{Mcpba/CH}_2\text{Cl}_2$.

Scheme 2 ($\text{Am} = \text{C}_5\text{H}_{11}$)

concerted processes. Thus, requisite three of four possible diastereomers of 8-methoxy-7-(trimethylsilyl)-6-tridecanol (1a - 1c) were prepared in pure state, respectively (Scheme 2).

To our chagrin, preparation of the fourth diastereomer (1d , 6,7-*threo*-7,8-*threo*) failed due to exclusive isomerization of an immediate precursor during methylation (step c) into a silyl ether.

Then the diastereomeric compounds (1a - 1c) were subjected to elimination conditions with KH (4 eq) in dry THF (0.05-0.1 M solution) first at -78°C , the reaction temperature being allowed to elevate gradually to start elimination. Critical temperature was observed for completion of respective elimination of 1a - 1c . Reaction products, (*E*)- or (*Z*)-8-methoxy-6-tridecene (2) and (*E*)-8-(trimethylsiloxy)-6-tridecene (3) resulting from either base-induced Peterson *syn*-elimination or competing methoxide elimination (supposed to be E2), were analyzed directly by GLC and identified, after isolation by column chromatography, by ^1H and ^{13}C NMR spectra. Results are summarized in the Table.

At a glance the product ratios of two competing eliminations of 1a - 1c appear very divergent. However, geometrical integrity of two olefin products, (*E*)- or (*Z*)- 2 and (*E*)- 3 (Entries 1 and 3), firmly established the Peterson *syn*-elimination and at the same time *anti*-elimination of a methoxide ion with concomitant silyl group migration to oxygen (E2). It should be mentioned that a better leaving group (MeOCH_2O^-)¹⁰ than methoxyl facilitates remarkably the E2 elimination (Entry 2) and that the Peterson reaction to afford an *E* olefin must proceed faster than that for the formation of *Z* olefin by a factor of four (Entry 1 *vs.* 3), provided that the difference between the steric environment of 1a and 1b in the transition state does not significantly change the rate of *anti*-elimination as depicted in Scheme 3.

The most intriguing results were obtained in the cases of 1c and $\text{1c}'$ ¹¹ (Entries 4 and 5). Thus, it was found that the Peterson *syn*-elimination by far predominated over the methoxide elimination from which unexpected (*E*)- 3 was sole-

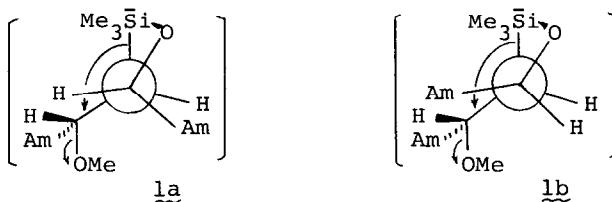
Table. Base-Induced Competitive Elimination of Diastereomeric 8-Methoxy-7-(trimethylsilyl)-6-tridecanols (la-lc).

Entry	Compound	Reaction temp. (°C)	Product ^{a)} Peterson	(ratio)	E2	
1	<u>la</u>	-60		(1)		(1)
2	<u>la'</u> (MeOCH ₂) ^{c)}	0	"	(1)	"	(5)
3	<u>lb</u>	-40		(1)	"	(4)
4	<u>lc</u>	+10	"	(5.8)	"	(1)
5	<u>lc'</u> (PhMe ₂ Si) ^{d)}	0	"	(7)	"	(1)

a) Combined yield almost quantitative. b) Free allylic alcohol on GLC.

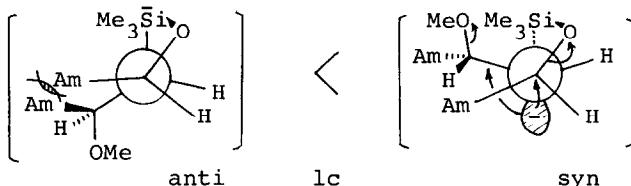
c) Instead of a methyl group. d) Instead of a trimethylsilyl group.

ly obtained. The implication of these results is the detection of unusual *syn*-elimination of a methoxide ion to take place from diastereomer lc. Inspection of a similar model for transition state of lc to those of la and lb (given in Scheme 3) clearly shows prohibitive congesion between two alkyl groups for



Scheme 3

anti entry with respect to the methoxyl group (Scheme 4, anti). Under these



Scheme 4 (*syn*-elimination with stereoelectronic antiperiplanar pathway)

circumstances, therefore, the methoxyl group in lc is forced to occupy *syn* to geminal silyl group in a strained ring as far as β -elimination is concerned (Scheme 4, syn). The fact that doubly eclipsed conformation of lc to give the observed olefins must require high energy of activation may well explain both higher reaction temperature for elimination to occur and predominant Peterson *syn* pathway over *syn* methoxide expulsion to proceed.

Finally, the work described here seems to help obtain insight into the exact nature of *syn*-elimination pathway, represented by the Peterson olefination of simple unactivated β -oxidoalkylsilanes. We have observed decisive change in the mode of elimination of methoxide ion from anti pathway (la and lb) to *syn*

(1c) both of which compete with necessary Peterson *syn*-elimination, even though the postulated four-membered ring species is transient in nature.¹²

More recently, Bach and collaborators¹³ have reported theoretical evidence that the less favored mode of *syn* elimination occurs by the concerted process of leaving group expulsion and the concomitant *inversion of configuration* at the more or less developing carbanionic center (C_β). If this is the case, one can easily explain the unusual *syn* elimination of a methoxide ion from 1c with stereoelectronic antiperiplanar pathway which also applies to the Peterson *syn* pathway.

We thank Toshiba Silicone Co., Ltd. for a generous gift of chlorosilanes.

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