

**BASE-CATALYZED HOMO-BROOK REARRANGEMENT OF DIASTEREOMERIC 7,8-EPOXY-
7-(TRIMETHYLSILYL)-6-TRIDECANOLS**

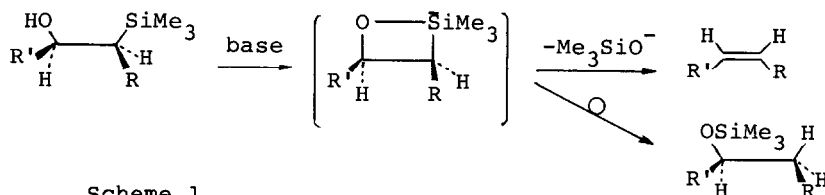
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Summary: Semi-quantitative rate measurement of base-catalyzed 1,3-migration of a silyl group from carbon to oxygen (homo-Brook rearrangement) using four diastereomerically pure title compounds revealed that the aptitude for the migration depends markedly on the configurational environment around the trimethylsilyl group of the respective substrate.

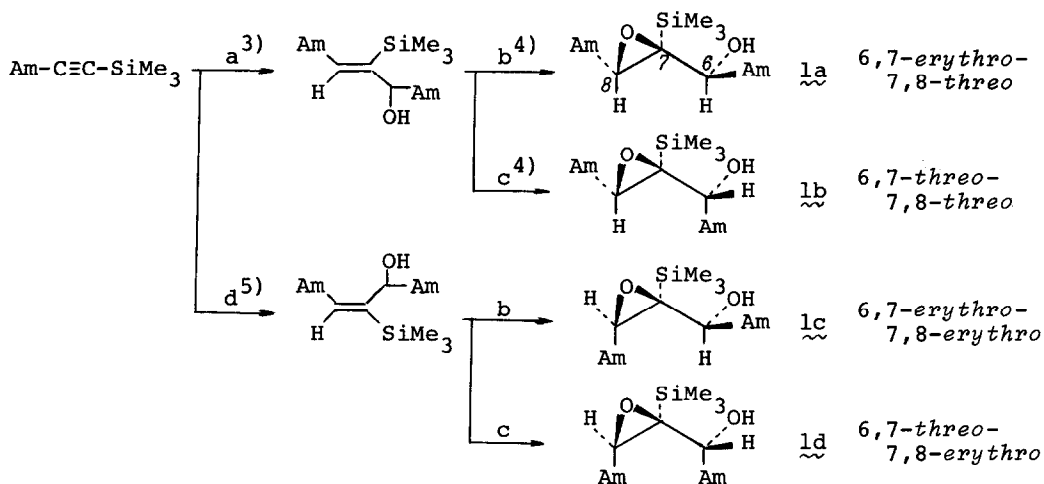
We have reported¹⁾ that, in the base-induced Peterson olefination of diastereomerically pure 8-methoxy-7-(trimethylsilyl)-6-tridecanol, anti pathway to eliminate a methoxide ion was found to compete profoundly with amply preceded syn-elimination of a trimethylsilanolate ion.

The Peterson olefination of unactivated β -hydroxyalkylsilanes may also be suppressed by a base-induced 1,3-migration of a silyl group of these compounds from carbon to oxygen, the migration being referred to as the homo-Brook rearrangement.²⁾ The latter protodesilylation must take place via a postulated four-membered transition state, the very one for the syn-elimination in the absence of any proton source (Scheme 1).



We have found that four diastereomerically pure 7,8-epoxy-7-(trimethylsilyl)-6-tridecanols, which are key intermediates for the preparation of substrates of the competitive eliminations mentioned above, undergo easily the homo-Brook rearrangement (eq 1, vide infra).

The aptitude for the migration differs markedly from one isomer to the other, and we wish to report here a semi-quantitative rate measurement of a novel homo-Brook rearrangement of these compounds.



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

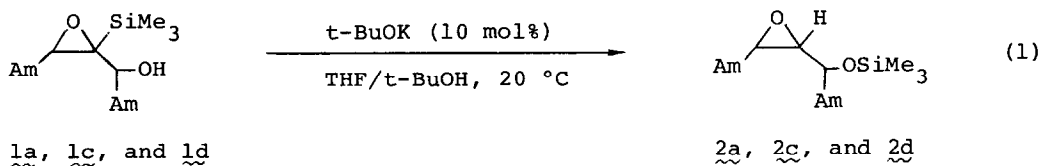
Scheme 2 ($\text{Am} = \text{C}_5\text{H}_{11}$)

The requisite 7,8-epoxy-7-(trimethylsilyl)-6-tridecanols (1a-1d) were selectively prepared using 1-(trimethylsilyl)-1-heptyne by known procedures³⁻⁵ as depicted in Scheme 2, and purified by column chromatography.

Attempted methylation of diastereomerically pure 1b by using KH (2 equiv) and MeI (10 equiv) in THF at 0°C failed due to exclusive silyl group migration. While 1a gave the corresponding methyl ether and rearranged silyl ether in a ratio of ca. 1 : 1, 1c and 1d afforded satisfactorily the respective methyl ether under the same conditions.⁶ These results indicate significant difference in rates of the silyl group migration among the four diastereomers.

Thus, a rate measurement of the base-catalyzed 1,3-trimethylsilyl migration of three diastereomers was undertaken except 1b which rearranged most rapidly. After trials in adjusting reaction conditions, it was found that 10 mol% of $t\text{-BuOK}$ in $t\text{-BuOH}$ (1M solution) added to a THF solution of the substrate (initial concentration 0.10M) at 20°C catalyzed the migration to proceed most smoothly (eq 1).

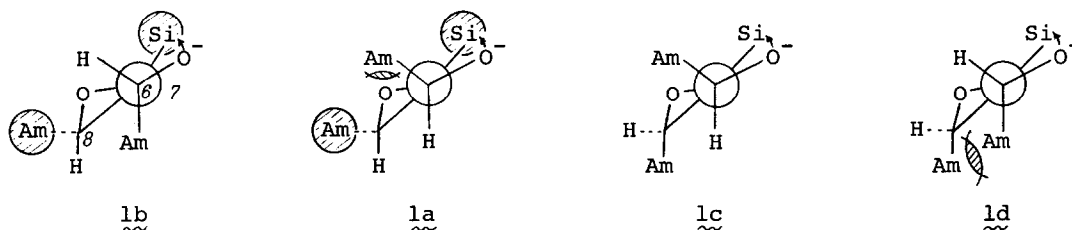
The conversion could be conveniently monitored with GLC by an internal standard method. The initial reaction rates of duplicated runs were estimated to be as follows: 1a, 3×10^{-3} ; 1c, 1×10^{-4} ; and 1d, 4×10^{-5} $\text{mol L}^{-1} \text{sec}^{-1}$. The ease of the silyl group migration were found to be in the order of (1b)1a>1c>1d. The rate difference between 1a and 1c is given by a factor of 30.



Stereochemistry of the migration products (2a-2d) were readily determined by ^1H NMR,⁷⁾ where the coupling constant of the C-7 proton newly introduced in the resulting 7,8-cis-epoxides of 2c and 2d ($J=4.1$ and 4.4 Hz) was larger than that in the 7,8-trans-epoxides of 2a and 2b ($J=2.2$ Hz), indicating that the protodesilylation at C-7 took place with retention of configuration in every case.

Although exact nature of retention stereochemistry as to the protodesilylation at C-7 is not clear at present,⁸⁾ there have been recent examples for the similar retentive protodesilylation mediated by fluoride ion,⁹⁾ originally reported by Chan and coworkers.¹⁰⁾

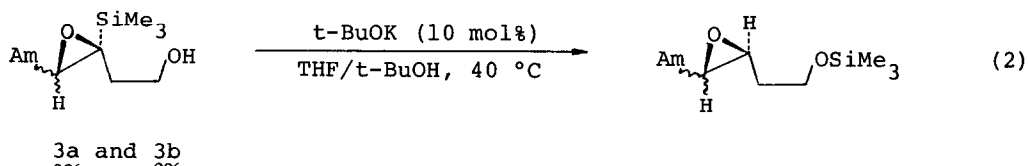
The observed rate differences may be rationalized in terms of three distinct factors of configurational environment around the trimethylsilyl group of the respective substrate: 1) Steric conjection by mutual cis configuration between the trimethylsilyl group and an amyl group on C-8 must play a crucial role in a rapid 1,3-migration of the silyl group from C-7 to oxygen. 2) In the postulated four-membered transition state for the attack of a β -oxide ion onto the silyl group as depicted in Scheme 3, steric hindrance between an epoxide oxygen and amyl group on C-6 may retard such migration in 1a as compared with



Scheme 3 (rel. rate: 1b>1a>1c>1d)

1b. 3) In addition to these factors, serious conjection between both amyl groups on C-6 and C-8 present in eclipsed transition state for 1d imposes another factor for slower migration just observed.

Finally, that the steric conjection around the trimethylsilyl group cis to an amyl group fixed by an epoxy moiety is of primary importance for a rapid migration was found also to be the case in homologous 1,4-migration of the trimethylsilyl group.¹¹⁾ Thus, cis and trans-3,4-epoxy-3-(trimethylsilyl)-nonanol (3a and 3b) were prepared and subjected to the base-catalyzed migration



under exactly the same conditions employed as above but at slightly high temperature (40 °C). The observed initial rates were 1.7×10^{-4} for 3a and 1.5×10^{-6} mol L⁻¹ sec⁻¹ for 3b, respectively. Again the rate difference is shown to be by a factor of ca. 110. In addition, it should be pointed out that 1,3-migration is much faster than 1,4-migration, reaction temperature employed being taken into account (eq 2).

Base-catalyzed cyclization of 4,5-epoxy-4-(trimethylsilyl)-decanol, further homolog of 3, has been reported by Negishi¹²⁾ to result in exclusive epoxide opening followed by the Peterson olefination.

References

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- 6) It was confirmed that possible intramolecular transepoxydation did not participate in the reactions, because 1b must be transformed into 1c in such a process and the latter gave the corresponding methyl ether selectively.
- 7) ¹H NMR (90 MHz, CDCl₃, TMS) 2a: 0.10 (s, 9H), 0.89 (br t, 6H), 1.30 (centered m, 16H), 2.62 (dd, J=2.2 and 5.3 Hz, 1H), 2.7-2.9 (m, 1H), 3.46 (q, J=5 Hz, 1H). 2b: 0.14 (s, 9H), 0.89 (br t, 6H), 1.30 (m, 16H), 2.67 (dd, J=2.2 and 6.2 Hz, 1H), 2.5-2.8 (m, 1H), 3.30 (q, J=6 Hz, 1H). 2c: 0.12 (s, 9H), 0.90 (br t, 6H), 1.34 (m, 16H), 2.84 (dd, J=4.2 and 7.3 Hz, 1H), 2.8-2.9 (m, 1H), 3.49 (dt, J=5.2 and 7.2 Hz, 1H). 2d: 0.15 (s, 9H), 0.91 (br t, 6H), 1.38 (m, 16H), 2.83 (dd, J=4.4 and 7.7 Hz, 1H), 2.7-3.1 (m, 1H), 3.2-3.6 (m, 1H).
- 8) A probable source of the proton is unrearranged alcohol present in the reaction mixture unless t-BuOH is added; A. G. Brook, and J. J. Chrusciel, Organometallics, 3, 1317 (1984).
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