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# THE REACTION OF β-(TRIMETHYLSILYL)ALKYL PHENYL SULFONES WITH OXIRANES. A METHOD FOR STEREOCONTROLLED SYNTHESIS OF HOMOALLYLIC ALCOHOLS

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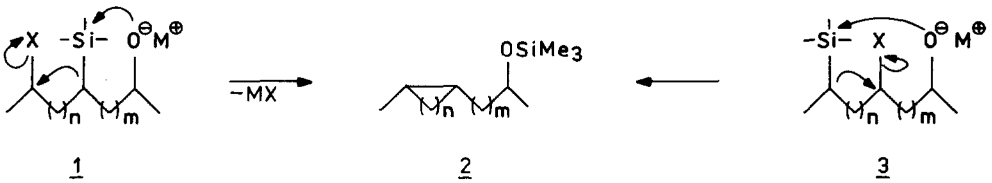
Abstract: The reaction of β-trimethylsilylalkyl sulfones (4a-4b) with oxirane derivatives (5a - 5d, 9) followed by treatment of the immediate adducts with sodium hydride, affords O-trimethylsilyl homoallylic alcohols (7a - 7e, 11), mainly (Z) isomers.

Recently we have demonstrated that the reaction of α-sulfonyl carbanions with α,β-epoxyalkylsilanes affords O-silylated allylic alcohols *via* nucleophilic addition followed by 1,3-migration of the silyl group from carbon to oxygen and elimination of the sulfonyl group[1]. Our experience with transformations of epoxysilanes prompted us to examine a more general reaction scheme which involves generation of an anionic species 1 or 3 (Scheme 1, X= leaving group, M = metal), with subsequent oxyanion to carbanion rearrangement [2] and elimination of the leaving group. Such a process would provide an approach to a variety of unsaturated alcohols (2, n=0) and possibly to cyclopropane derivatives (2, n=1)[3] or to some other cyclic alcohols. In particular, we were interested in the reaction of an anion generated from β-trimethylsilylalkyl phenyl sulfones 4 with oxiranes 5, which would give intermediate adducts 6 and then O-silylated homoallylic alcohols 7 (Scheme 2)[4]. We now report a practical realization of the reaction illustrated in Scheme 2 as well as some observations regarding further transformation of homoallylic alcohols into 1,3-diols and polyols comprising repeated 1,3-diol units.

Scheme 1



The treatment of 1,2-epoxyhexane (5a, $R^2$=H, $R^3$=nBu) with the lithium derivative of silyl sulfone 4a[5,6] (1.2 molequivalents), in a dimethoxyethane (DME) solution, with temperature rising from -78 to 20°C, resulted in consumption of oxirane within 2 h. Sodium hydride (1.5-3 molequivalents) was then added and the mixture was briefly heated at reflux temperature. Conventional workup gave O-trimethylsilyl oct-1-en-4-ol (7a). Under analogous conditions the reaction of sulfones 4a and 4b with oxiranes 5a-5c afforded O-trimethylsilyl derivatives of the corresponding allylic alcohols 7a - 7e; the results are presented in Table 1. It is noteworthy that the reaction of the carbanion derived from sulfone bearing the silyl group at the secondary carbon atom 4b with epoxides 5a and 5b afforded O-silylated homoallylic alcohols 7d and 7e, respectively, in a high yield and with high selectivity with respect to the (Z) isomer (Table 1, entries 4 and 5).

From the standpoint of the synthesis of natural products consisting the repeated structural unit of 1,3-diol, as some ionophoric antibiotics[7], we have prepared (S) epoxide 9 (Scheme 3) starting from (S) malic acid[8]. Treatment of 9 with lithiated silyl sulfone 4a and then with sodium hydride gave O-trimethylsilyl homoallylic alcohol 10 in 80% yield {$[\alpha]_D^{22}$=-16.1°(c=1.1, $CHCl_3$)}. The latter product was selectively hydrolyzed to homoallylic alcohol 11 {$[\alpha]_D^{22}$=+3.51° (c=1.2, $CHCl_3$)} using a trace of pyridinium p-toluenesulfonate in methanol[9] (93% yield). Oxidation of unsaturated alcohol 11 with t-butylhydroperoxide in toluene in the presence of vanadyl catalyst[10] afforded epoxide 12 in a 70% yield (62% of conversion) as a mixture of diastereomers in a 1:1.8 ratio. The similarity in structure of epoxides 9 and 12 suggests that the present method for homoallylic alcohol synthesis may be applied to construct polyhydroxylated chains.

The reaction of 1,2-epoxyhexane (5a) with lithiated sulfone 4a in THF or DME solution (under conditions indicated in Scheme 1 but without adding sodium hydride) gave adduct 8a[6]. Likewise, the reaction of other sulfones with oxiranes afforded the respective adducts; yields and isomer ratios are given in Table 1. An example of application of such compounds to natural product synthesis is given in the accompanying communication.

It should be noted that the reaction of β-silyl sulfones (as lithium derivative) with aldehydes, followed by sodium hydride treatment of the immediate product, affords O-trimethylsilyl derivatives of allylic alcohols. For example, the reaction of sulfone 4a with decanal gave O-trimethylsilyl dodec-1-en-3-ol in a 87% yield.

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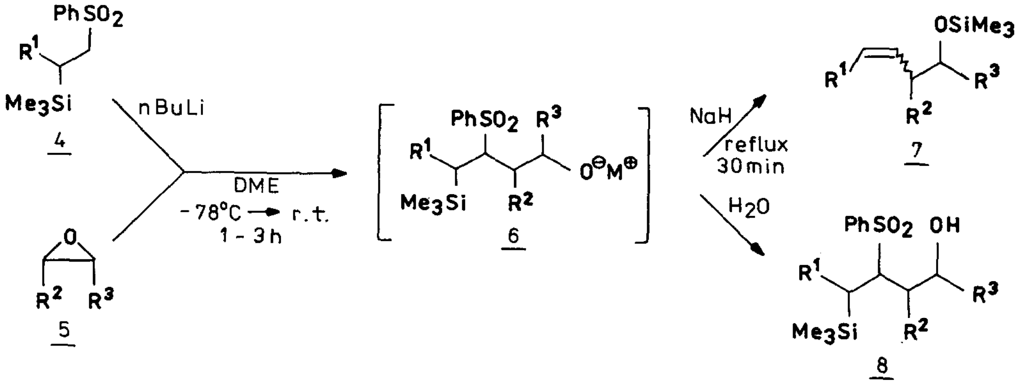
Scheme 2



| 4 | $R^1$ |
|---|---|
| a | H |
| b | $nC_5H_{11}$ |

| 5 | $R^2$ | $R^3$ |
|---|---|---|
| a | H | nBu |
| b | H | Ph |
| c | $-(CH_2)_4-$ | |

| 7 and 8 | $R^1$ | $R^2$ | $R^3$ |
|---|---|---|---|
| a | H | H | nBu |
| b | H | H | Ph |
| c | H | $-(CH_2)_4-$ | |
| d | $C_5H_{11}$ | H | nBu |
| e | $C_5H_{11}$ | H | Ph |

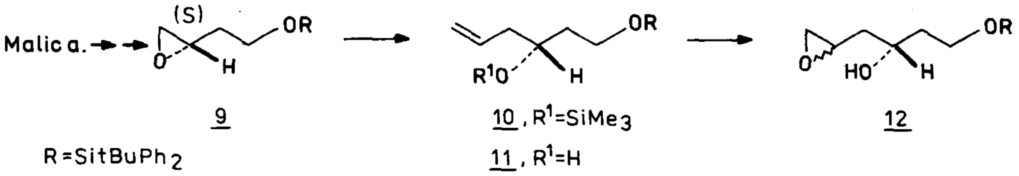
Table 1

The reactions of sulfones 4 with oxiranes 5 according to Scheme 2

| Entry | Sulfone | Oxirane | O-TMS-alcohol | | | Adduct | | |
|---|---|---|---|---|---|---|---|---|
| | | | (No) | Yield(%) | E:Z ratio | (No) | Yield(%) | Isomer ratio |
| 1 | 4a | 5a | 7a | 90 | - | 8a | 90 | 1:2$^{a}$ |
| 2 | 4a | 5b | 7b | 87$^{b}$ | - | 8b | 89 | 1:2$^{a}$ |
| 3 | 4a | 5c | 7c | 85$^{b}$ | - | 8c | 83 | 1:1.4$^{a}$ |
| 4 | 4b | 5a | 7d | 92 | 1:10 | 8d | 80 | 3:3:1$^{c}$ |
| 5 | 4b | 5b | 7e | 87 | 1:13 | - | - | - |

a) isomers were separated by chromatography; b) isolated as free alcohols; c) determined by $^1$H NMR measurements of a mixture of the respective acetates

Scheme 3



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