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THE REACTION OF α,β-EPOXYSILANES WITH METALLATED ALKYLARYL SULPHONES. A NOVEL APPROACH TO ALLYLIC ALCOHOLS

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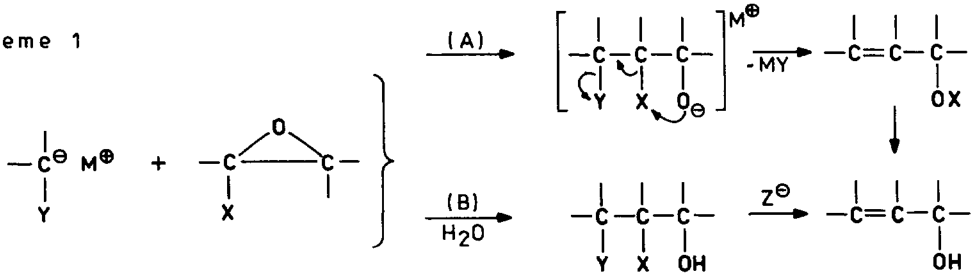
Summary: Lithiated alkylaryl sulphones (2a-c) react with α,β-epoxysilane (1) to yield O-trimethylsilyl allylic alcohols (3a-c), predominantly as Z isomers. The BF_3-assisted reaction followed by treatment of the adduct with nBu_4NF affords allylic alcohols.

The methodology for constructing the allylic alcohol moiety from saturated precursors has attracted a great deal of attention, particularly in connection with the synthesis of natural products such as prostaglandins, pheromones and macrolides[1]. Recently, a procedure has been developed in our laboratory for preparation of allylic alcohols, starting from addition of an alkylaryl sulphone to an oxirane and involving some additional transformations[2]. It occurred to us that the use of a sulphone and an oxirane, the latter having at its electrophilic centre a substituent (such as the trialkylsilyl group) capable of migration from carbon to oxygen, would provide a direct approach to allylic alcohols. This concept is illustrated in Scheme 1, route A, where Y = leaving group, X = group capable of migration from C to O, and M = metal. Alternatively, X could be a group with an affinity to the external ion Z^- (route B) which would initiate elimination of substituents X and Y. Now, we report a practical realization of the reaction according to the above general scheme for the case when Y = phenylsulphonyl group, X = trimethylsilyl group, and M = lithium, this representing the reaction of alkylphenyl sulphones with α,β-epoxysilane. Both reaction components are readily available[3]. The selectivity of nucleophilic attack on the carbon atom bearing the silicon substituent in α,β-epoxysilanes is well documented[4].

Scheme 1



The treatment of α,β-epoxysilane 1[5] with lithium derivative of sulphone 2a (2 equivalents), in a tetrahydrofuran (THF) solution, with the temperature rising from -78° to 20°C, resulted in complete consumption of oxirane and gave 3-(trimethylsilyloxy)hept-1-ene 3a as the only product (Table 1). Under the analogous conditions, the reaction of sulphone 2b with epoxysilane 1 afforded quantitatively 4-(trimethylsilyloxy)-oct-2-ene 3b as a mixture of E and Z isomers at the 15:85 ratio. The reaction of 1 with lithiated n-butylphenyl sulphone 2c furnished 6-(trimethylsilyloxy)-dec-4-ene 3c as a pure isomer Z. Since the E isomer of 3c could not be detected by GLC and NMR, we estimate that the product is at least 95% isomerically pure.

Silyl ethers 3a, 3b and 3c were hydrolyzed upon heating in a methanol solution with traces of perchloric acid. Alcohols 4a, 4b and 4c were isolated, respectively, and their structures were confirmed by NMR and mass spectra. The results are compiled in Table 1.

Scheme 2

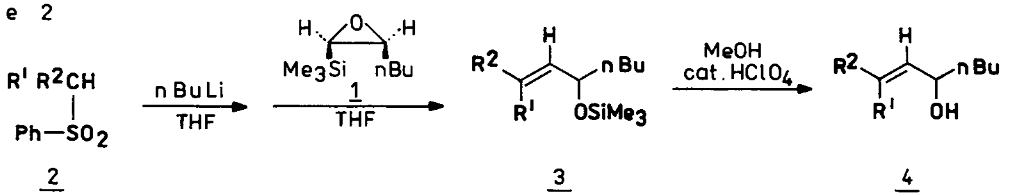


Table 1. Reactions of sulphones with oxirane 1 according to Scheme 2

	R^1,R^2	Sulphone	Silyl ethers			Allylic alcohols
				Yield%	E:Z Ratio	
1	H ,H	2a	3a	quant.^{a}	—	4a
2	H ,Me	2b	3b	quant.^{a}	15:85	4b
3	H ,nPr	2c	3c	$70^{b,c}$	95%Z	4c

Reactions were performed on a 1-2 mmol scale; yields are calculated against oxirane;a) determined by GLC; b) isolated product; c) yields not optimalized

The above examples of alkenylation via the reaction of sulphones with a representative α,β-epoxysilane are most encouraging because of their efficiency and preparative simplicity. The high selectivity regarding Z isomers is an additional and important asset. It was of interest to examine some sterically hindered, less reactive sulphones. In the light of previous experience with the reaction of such sulphones with oxiranes[2,7] we were conscious that the reaction might fail to afford the required products. Indeed, the lithium derivative of isobutylphenyl sulphone (2d) did not react with epoxysilane 1 under the conditions indicated in Scheme 2. Therefore, we had to resort to the Lewis-acid-assisted reaction[8] and we started by using the investigated sulphones 2a and 2b.

When lithiated sulphone 2a in a THF solution, at -20°C, was treated with epoxysilane 1 (0.5 equivalent) and BF_3 Et_2O (1 equivalent) a single product was formed rapidly. After chromatography, the adduct 5a was isolated in 90% yield (Scheme 3, Table 2). The ^1H NMR spectrum indicated that 5a consisted of one diastereomer, as expected for the addition with inversion of configuration at C_1. The adduct 5a was treated with nBu_4NF $3H_2O$ in a THF solution to yield quantitatively allylic alcohol 4a. In further experiments, the adducts were - after water workup and drying, without any purification - reacted with nBu_4NF $3H_2O$ in THF to give allylic alcohols. The results are compiled in Table 2.

Starting from ethylphenyl sulphone 2b and silyloxirane 1, upon use of BF_3-assisted reaction followed by treatment of the adduct with fluoride, allylic alcohol 4b was obtained. In contrast to the noncatalyzed reaction, this product consisted of a mixture of E and Z isomers in almost equal amounts (Table 2, Entry 2). Reactions of sulphones 2d, 2e and 2f with oxirane 1 followed by treatment of the adducts with nBu$_4$NF 3H$_2$O gave alcohols 4d, 4e and 4f, respectively (Table 2). Similarly as in case of 2d, lithiated sulphones 2e and 2f did not react with epoxysilane 1 in the absence of BF$_3$.

Scheme 3

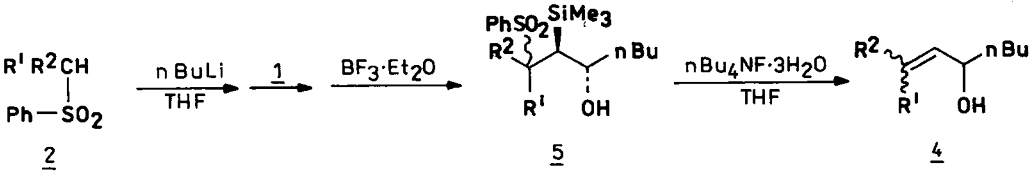


Table 2. Reactions of sulphones with oxirane 1 according to Scheme 3

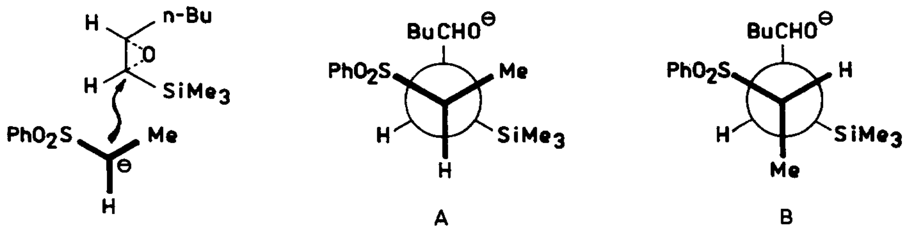
	R^1, R^2	Sulphone	Adduct		Allylic alcohol		
				Yield%		Yield %	E:Z Ratio
1	H ,H	2a	5a	90[b]	4a	100[a] 50[b]	—
2	H ,Me	2b	5b	70[b]	4b	67[b]	3 : 2
3	H, iPr	2d	5d	d	4d	66[b]	3 : 2
4	H, Ph	2e	5e	d	4e	88[b]	2 : 3
5	Me,Me	2f	5f	48[c]	4f	40[b,c]	—

a,b,c - for explanations, see Table 1; d) product not isolated

In order to get insight into the steric course of the BF$_3$-assisted reaction, the following experiments were carried out. (a) The adduct 5b in a THF solution was treated with nBuLi (1.2 M, in hexane, 1 equivalent), whereupon the product (a silyl ether) was heated in a methanol solution with a trace of perchloric acid. Allylic alcohol 4b was obtained as a mixture of isomers E and Z at ca. 3:2 ratio. (b) The adduct 5b was isolated and analyzed by TLC. It was found that it consists of two isomers (3:2) which were subsequently resolved by column chromatography. The NMR spectra confirmed the purity of these isomers (5b' and 5b''). We conclude that formation of a mixture of epimers of adduct 5b at the carbon atom bearing the sulphonyl group is responsible for the low selectivity in formation of double bond isomers 4bE and 4bZ.

The preference in formation of Z isomers of alkenes in the noncatalyzed reaction deserves a comment. It appears reasonable to assume that the phenylsulphonyl group is eliminated

Figure 1



in the adduct when the C-Si and C-SO$_2$ bonds are in anti-periplanar alignment. In this case upon addition of the anion and oxirane, epimer A would be formed in an excess, whereas the unbonding interactions are weakest in epimer B (Fig. 1).

In the BF_3-assisted reaction, the formation of a complex including lithiated sulphone, oxirane and BF_3 is likely to be the rate-determining step. Reorganization of bonds within the complex could be relatively fast process devoid of sterical bias.

Further investigations on the reactions of heteroatom-stabilized carbanions with oxiranes substituted with groups capable of migration from carbon to oxygen are in progress at this laboratory.

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REFERENCES AND NOTES

1. For leading references, see: A.Mitra, "Synthesis of Prostaglandins", Wiley, New York,1977; P. Kocieński, Phosphorus Sulphur, 24, 97 (1985). 2. B.Achmatowicz, S.Marczak, J.Wicha, JCS, Chem.Comm., 1987, 1226. 3. For leading references on sulphones, see: P.D.Magnus, Tetrahedron, 33, 2019 (1977); T.Durst in "Comprehensive Organic Chemistry" Eds D.H.R.Barton, W.D.Ollis, Pergamon, Oxford, 1979, vol. 3; for preparation of α,β-epoxysilanes, see: J.J.Eisch, J.T.Trainor, J.Org.Chem., 28, 487 (1963); P.F.Hudrlik, C.N.Wan, Synth.Comm., 9, 333(1979); C.Burford F.Cooke, G.Roy, P.Magnus, Tetrahedron, 39, 867 (1983); T.Katsuki, Tetrahedron Lett., 25, 2821 (1984); Y.Kitano, T.Matsumoto, F.Sato, J.C.S.Chem.Comm., 1986, 1323; M.Kusakabe, H.Kato, F. Sato,Chem.Lett., 1987, 2163. 4. J.J.Eisch, J.E.Galle, J.Org.Chem., 41, 2615 (1976); T.H.Chan, Acc.Chem.Res., 10, 442 (1977); I.Fleming in "Comprehensive Organic Chemistry"; E.W.Colvin, "Silicon in Organic Chemistry", Butterworth, London, 1981. 5. For racemates only one enantiomer is presented; this compound was prepared from Z-1-trimethylsilyl-1-hexene[6] and m-chloroperbenzoic acid. 6. R.B.Miller, T.Reichenbach, Tetrahedron Lett., 1974, 543. 7. T.Nakata, K. Saito, T.Oishi, Tetrahedron Lett., 27, 6345 (1986); S.Marczak, J.Wicha, unpublished results. 8. For a review, see: Y.Yamamoto, Angew.Chem.Intern.Ed., 25, 947 (1986); see also, S.Tomoda, Y.Matsumoto, Y.Takeuchi, Y.Nomura, Chem. Lett., 1986, 1193.

Diagnostic ^1H NMR data (Bruker AM 500) for representative compounds: 4a, δ (ppm) 5.86 (d,d,d, 1H, J_1= 6.2 Hz, J_2= 10.3 Hz, J_3= 17.2 Hz, C_2-$\underline{H}$); 5.23 (d,t, 1H, J_1= 17.2 Hz, J_2= 1.4 Hz, C_1-$\underline{H}$), 5.11(d,t, 1H, J_1= 10.3 Hz, J_2= 1.2 Hz, C_1-H_b), 4.10 (br q, 1H, J= 6.2 Hz, C_3-$\underline{H}$); 4b E δ (ppm) 5.65 (d,q,d, 1H, J_1= 15.3 Hz, J_2= 6.5 Hz, J_3= 0.3 Hz, C_2-$\underline{H}$), 5.48 (d,d,q, 1H, J_1= 15.3 Hz, J_2 =7.2 Hz, J_3= 1.5 Hz, C_3-$\underline{H}$), 4.02 (br q, 1H, J= 6.7 Hz, C_4-$\underline{H}$); 4b Z δ (ppm) 5.55 (d,q,d, 1H, J_1= 10.9 Hz, J_2= 6.9 Hz, J_3= 1.0 Hz, C_2-$\underline{H}$), 5.40(d,d,q, 1H, J_1=10.9 Hz, J_2= 8.8 Hz, J_3= 1.7 Hz, C_3-$\underline{H}$), 4.47 (d,t,d, 1H, J_1=8.7 Hz, J_2= 6.6 Hz, J_3= 0.9 Hz, C_4-$\underline{H}$); 5a δ (ppm) 3.69 (m, 1H, C_3-$\underline{H}$), 3.50 (d,d, 1H, J_1= 14.4 Hz, J_2= 8.0 Hz, C_1-Ha), 3.02(d,d, 1H, J_1= 14.4 Hz, J_2= 2.7 Hz, C_1-Hb); 0.03 (s, 9H, $SiC\underline{H}_3$); 5b' δ (ppm) 3.55 (q,d, 1H, J_1= 7.1 Hz, J_2= 1.6 Hz, C_2-$\underline{H}$), 1.41 (d, 3H, J= 7.1 Hz, C_1-$\underline{H}$), 0.20 (s, 9H, $SiC\underline{H}_3$); 5b'' δ (ppm) 3.86 (m, 1H, C_4-$\underline{H}$), 3.42(q, 1H, J= 7.2 Hz, C_2-$\underline{H}$), 1.39(d, 3H, J= 7.3 Hz, C_1-$\underline{H}$), 0.09 (s, 9H, $SiC\underline{H}_3$).

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