Regioselective β-Addition of Sulfonyl Anions to an α,β-Epoxysilane. Use of Triphenylsilyloxirane for Synthesis of Stable Cyclopropene Derivatives

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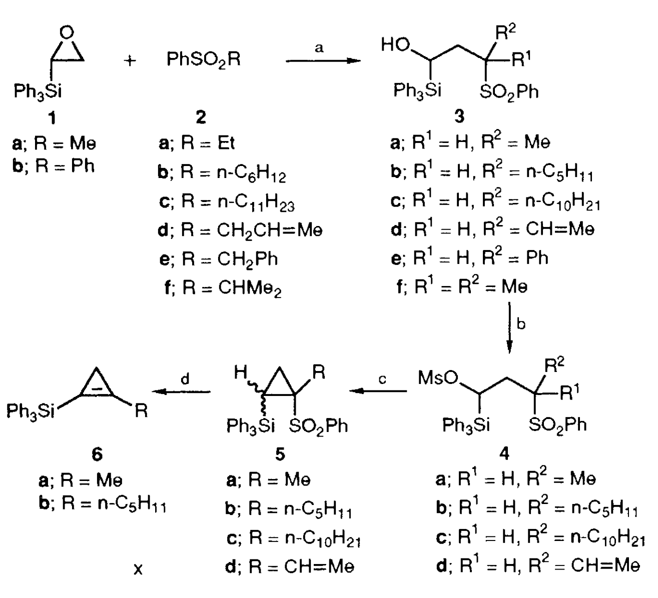
Anions generated from primary alkyl phenyl sulfones react with triphenylsilyloxirane to yield products of addition in the β-position, which were used for synthesis of stable cyclopropene derivatives.

Our recent observation[1] regarding the effect of the bulk of an anion on the regioselectivity of its additions to trimethylsilyloxirane **1a** have prompted us to examine the reaction of triphenylsilyloxirane **1b** with anions generated from primary alkyl phenyl sulfones. We expected that the bulky triphenylsilyl group will direct the nucleophile to attack the β-carbon atom, in contrast to the trimethylsilyl group for which the α-directing effect is well documented.[2] Products of such 'β-addition' appeared to be of interest as versatile synthetic intermediates. Now we report that anions generated from a range of sulfones **2a–f** react with the oxirane **1b** to afford products **3a–f** of β-addition (Scheme 1, Table 1), and that these adducts may be used for synthesis of cyclopropene derivatives which are difficult to obtain by other routes.[3]

Treatment of triphenylsilyloxirane **1b** in tetrahydrofuran (THF) with anions generated from sulfones **2a–f** and butyllithium afforded adducts **3a–f**, respectively, as diastereoisomeric mixtures. All reactions were carried out for 18 h at room temperature, except for that of sulfone **2a** for which the reaction time was 3 h. The results are presented in Table 1.

Extension of the reaction time of sulfone **2a** with the oxirane **1b** (Table 1, entry 1) to 18 h resulted in a drastic decrease in the adduct yield (13%). Instead, the triphenylsilyl ether **7** and triphenylsilanol were isolated as the major products (23 and 36% yield, respectively), this indicating that the primary adduct undergoes the Brook rearrangement.[4] It should be noted that small amounts of triphenylsilanol could be detected in crude products of all the other reactions studied.

Separated diastereoisomers of alcohols **3a–d** were esterified with methanesulfonyl chloride in pyridine to give mesyl esters **4a–d**, respectively. The latter products were treated with sodium bis(trimethylsilyl)amide in THF at −20 °C to give cyclopropane derivatives **5a–d** in excellent overall yields. The results are shown in Table 1. It is noteworthy that in each case from both diastereoisomeric mesylates the same diastereoisomerically pure cyclopropane derivative was formed. It was tentatively assumed that the cyclopropane derivatives are diastereoisomers with triphenylsilyl and benzenesulfonyl groups in *trans* configuration.[5]



Scheme 1 *Reagents* (all reactions at room temperature): a, Bu^{n}Li, THF; b, MeSO$_2$Cl, pyridine; c, NaN(SiMe$_3$)$_2$; d, Bu^{n}Li, THF

The triphenylsilyl and benzenesulfonyl groups may act as efficient carbanion-stabilizing[6] and leaving groups, respectively. Their arrangement in compounds **5** appeared favourable for generation of a highly strained double bond within the three-membered ring. Treatment of compound **5a** in THF with 1 equiv. of n-butyllithium in hexane at room temperature gave the cyclopropene derivative **6a**, m.p. 95–97 °C (pentane) in 77% yield. Likewise, compound **5b** afforded the derivative **6b**, m.p. 30–32 °C, in 90% yield.† It is noteworthy that compounds **6a** and **6b** may be stored at room temperature for several days without noticeable decomposition, whereas the corresponding trimethylsilylcyclopropenes could be handled only in dilute solution in diethyl ether.[3a,c]

Only few previous studies on the reaction of triphenylsilyloxirane **1b** with nucleophiles have been reported.[2b,7] They seem to suggest that the regioselectivity of the oxirane ring

Table 1 Reaction of triphenylsilyloxirane **1b** with anions generated from sulfones and Bu^{n}Li, and subsequent transformations of the adducts (Scheme 1)

	Adduct	Mesylate	Cyclopropane
Sulphone	Yield (%) Diastereoisomer ratio[a]	Yield (%)[b]	Yield (%)[b]
2a	**3a** 71 1 : 1.3	**4a** 90, 94	**5a** 81, 90
2b	**3b** 68 1 : 1.8	**4b** 90, 96	**5b** 90, 98
2c	**3c** 69 1 : 1.2	**4c** 91, 92	**5c** 77, 82
2d	**3d** 52 1 : 1.1	**4d** 95, 97	**5d** 90, 93
2e	**3e** 48 1 : 1.7	—	—
2f	**3f** 80 —	—	—

[a] Diastereoisomers were separated by chromatography. [b] Yields are given for separated diastereoisomers.

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† The cyclopropene derivatives show the following properties: **6a**, IR (CHCl$_3$) ν/cm^{-1} 1815, 1500 and 1440; NMR δ_H (200 MHz) 1.15 (2H, s, 3-H), 2.40 (3H, s, Me) and 7.41–7.65 (15H, m, ArH); δ_C (50 MHz) 8.23 (C–3), 14.43 (Me), 102.11 (C-1), 127.89 (*m*-ArC), 129.62 (*p*-ArC), 134.50 (ArC), 135.58 (*o*-ArC) and 137.15 (C-2). Satisfactory elemental analyses were obtained.

6b, IR (CHCl$_3$) ν/cm^{-1} 2960, 2940, 2880, 1800 and 1430 cm^{-1}; NMR δ_H (200 MHz) 0.87 (3H, t, *J* 6.6 Hz, Me), 1.15 (2H, s, 3-H), 1.23–1.32 (4H, m, 3′- and 4′-H), 1.48–1.63 (2H, m, 2′-H), 2.70 (2H, t, *J* 7.2 Hz, 1′-H) and 7.41–7.65 (15 H, m, ArH); δ_C (50 MHz) 7.71 (C-3), 13.95 (Me), 22.33 (C-4′), 26.63 (C-2′), 28.47 (C-1′), 31.55 (C-3′), 101.11 (C-1), 127.84 (*m*-ArC); 129.58 (*p*-ArC), 134.54 (ArC), 135.63 (*o*-ArC) and 140.31 (2-C); high resolution mass spectrum consistent with formula.

opening in triphenylsilyloxirane **1b** does not differ from that observed for its trimethylsilyl analogue **1a**.

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