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A NEW METHOD FOR REGIOSELECTIVE SYNTHESIS OF α-SUBSTITUTED ALLYLSILANES AND ITS APPLICATION TO THE SYNTHESIS OF *E*- AND *Z*-TAGETONES

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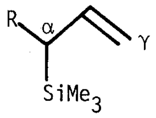
Sequential addition of lithium salt of carbanion and tributylstannylmethyl iodide (3) to vinyl sulfone 2 afforded β-tributylstannyl sulfones 5, which gave substituted allylsilanes 1 in a regioselective manner by the smooth destannylsulfonation. Allylsilane 8 prepared by Michael type addition of isopropenyllithium to 2 was converted into tagetones (10).

KEYWORDS —— allylsilane; β-trimethylsilylvinyl sulfone; destannylsulfonation; tributylstannylmethyl iodide; tagetone; Michael addition

Allylsilane is an important class of compounds for organic synthesis.[1)] The most valuable feature of the reactions of substituted allylsilanes with various kinds of electrophiles is their high regioselectivity for the γ-substitution reaction.[1a)] Hence it became very important to develop the methods for the regioselective synthesis of the α-substituted allylsilanes, and some methods have been reported.[2)] Here we report a new method for the regioselective synthesis



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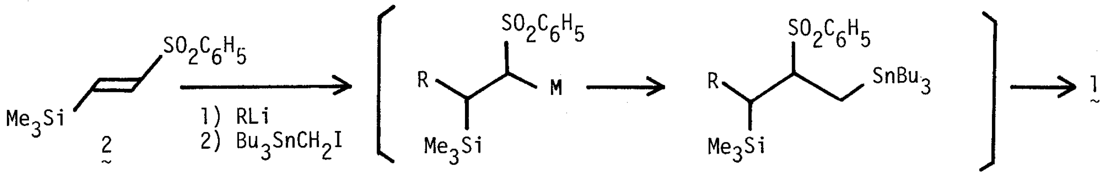
a: R=C_6H_5
b: R=p-MeOC_6H_4
c: R=p-MeC_6H_4
d: R=p-ClC_6H_4
e: R=$C_6H_5SO_2CH_2$

of α-substituted allylsilanes 1, which consists of a sequential addition of nucleophiles (RLi) and tributylstannylmethyl iodide (3) to *E*-1-phenylsulfonyl-2-(trimethylsilyl)ethylene (2) followed by β-elimination of the resulting β-tributylstannyl sulfone 5 as shown in Chart 1.[3)]



3 4 5

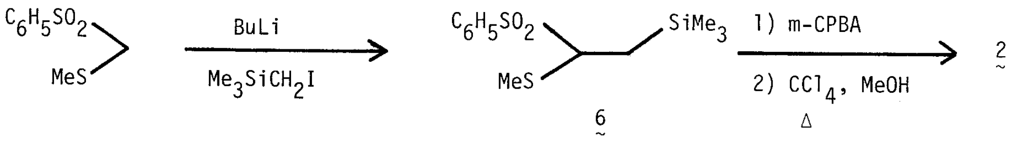
Chart 1

Vinyl sulfone 2 is accessible through the procedure developed by Calas[4)] or Paquette.[5)] We also found a simple method for the synthesis of 2: treatment of the lithium salt of the anion of methylthiomethyl phenyl sulfone with trimethylsilylmethyl iodide[6)] in tetrahydrofuran (THF) at -78°C to room temperature afforded β-trimethylsilyl sulfide 6 in 66% yield, which was oxidized with m-CPBA in dichloromethane at 0°C to the corresponding sulfoxide. Its subsequent silicon-assisted thermolysis[7)] in carbon tetrachloride containing a small amount of methanol yielded the desired sulfone 2 (91%).

Table. Synthesis of Allylsilane 1 from Vinyl Sulfone 2 by a Successive Addition of RLi and Iodide 3 Followed by β-Elimination[a)]

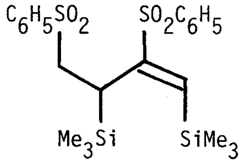
Entry	RLi	Reaction Conditions	Product	Yield, %[b)]
1	C_6H_5Li[c)]	-78°C, 1h[d)]	1a	(6)
2	C_6H_5Li[e)]	-78°C, 2h[d)]	1a	(47)
3	C_6H_5Li	-78°C, 1h[d)]	1a	70 (82)
4	p-$MeOC_6H_4Li$	-20°C, 1h	1b	80
5	p-MeC_6H_4Li	-20°C, 1h	1c	82
6	p-ClC_6H_4Li	-20°C, 2h	1d	51 (69)
7	$C_6H_5SO_2CH_2Li$[f)]	-20°C, 0.3h	1e	53

a) Reactions were performed as described in the text unless otherwise noted. b) Isolated yield (GLC yield). c) 1.1 Equiv. of phenyllithium and 1.1 equiv. of iodide 3 were used. d) Iodide 3 was added very slowly at -78°C. e) 2.1 Equiv. of phenyllithium and 1.1 equiv. of iodide 3 were used. f) After the addition of 1.2 equiv. of lithium salt of methyl phenyl sulfone (-78°C, 1.3 h), 2 equiv. of phenyllithium were added (-78°C, 1.3 h).



Conjugated addition of phenyllithium (1 equiv.) to 2 in THF (-78°C for 1 h) afforded the sulfone 4a (4: R=C_6H_5, M=H) in 84% yield. The sulfone 4a was treated with 1, 2, and 3 equiv. of butyllithium and tributylstannylmethyl iodide (3) to give the desired allylsilane 1a[8)] in 16, 20, and 27% yields, respectively, *via* β-elimination[9)] of the β-tributylstannyl sulfone 5a (5: R=C_6H_5). As contrasted with this stepwise reaction, however, an *in situ* sequential addition of phenyllithium (3 equiv.) and iodide 3 to 2 afforded 1a in much better yield (see Entry 3 in Table). The table summarizes the results of *in situ* reaction. The yield of allylsilane 1a is highly dependent on the amounts of phenyllithium used, and a good result was obtained by using 3 equiv. of phenyllithium[10)] (see Entries 1-3).

A general procedure is as follows. RLi (3 equiv.) was added dropwise to a solution of vinyl sulfone 2 in THF at -78°C under nitrogen and the mixture was stirred for 2 h at the same temperature. A solution of iodide 3 (1.5 equiv.) in THF was added very slowly at -20°C and the mixture was stirred under the conditions described in Table. The mixture was quenched with an aqueous NH_4Cl and extracted with ether. After the usual work-up, the pure product was isolated by preparative TLC.



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In addition to substituted aryllithiums, the lithium salt of the anion of methyl phenyl sulfone was found to act as an effective nucleophile for the Michael type reaction (Entry 7). α-Lithiation of vinyl sulfone 2, however, becomes the major pathway when it is treated with the less nucleophilic base, butyllithium.[11] In this case the dimerization product 7[12] was obtained in 50% yield, which was produced by the Michael type addition of α-vinyllithium compound of 2 to the starting sulfone 2.

Alternatively, if vinyllithium reagents is added to αβ-unsaturated sulfone 2 in a conjugate fashion, it will provide an another approach for the synthesis of α-substituted allylsilanes. We will show one example for such an approach yielding allylsilane 8, which proved to be a valuable synthon for the synthesis of *E*- and *Z*-tagetones 10 as shown in Chart 2. Sulfone 2, on treatment with 2 equiv. of isopropenyllithium in THF at -78°C for 2 h and then -20°C for 1 h, afforded an addition product 8[13] in 65% yield. Regioselective γ-acylation of allylsilane 8 afforded sulfone 9[14] in 81% yield, when 8 was treated with isovaleroyl chloride (1.8 equiv.) and aluminum chloride in dichloromethane at -78°C for 30 min. Elimination of benzensulfinic acid from ε-keto sulfone 9 using aqueous NaOH in ether gave a mixture of *E*- and *Z*-tagetones 10 in a ratio of 1 : 1.9 (92% yield).[14]

The new reactions developed by us provide a very useful method for the synthesis of some specific α-substituted allylsilane.

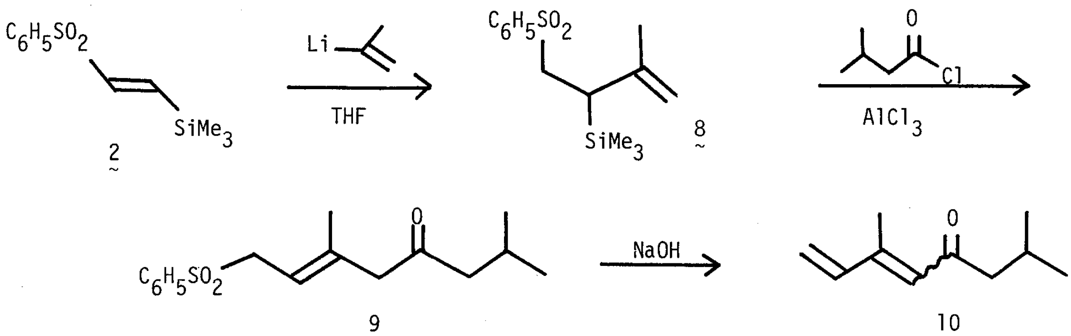

Chart 2

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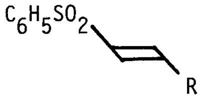

11 R = Me

12 R = C_6H_5

12) The stereochemistry of 7 was tentatively assigned.

13) 8: IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1635, 1305, 1250, 1140, 840, ^{1}H-NMR δ($CDCl_3$): 0.0 (9H, s), 1.58 (3H, s), 2.06 (1H, dd, J=12,3 Hz), 3.09 (1H, dd, J=14,3 Hz), 3.46 (1H, dd, J=14,12 Hz), 4.42 (1H, s), 4.61 (1H, br s), 7.3-8.0 (5H, m), ^{13}C-NMR δ($CDCl_3$): 143.2, 139.8 (each s), 133.4, 129.0, 128.3 (each d), 110.3, 56.5 (each t), 32.2 (d), 22.9, -2.9 (each q).

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