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Preliminary communication

A NEW METHOD FOR THE PREPARATION OF ALLYLSTANNANES CONTAINING FUNCTIONAL GROUPS

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Summary

Allylstannanes containing functional groups such as cyano, ester, or sulfonyl groups were prepared by the hydrostannolysis of the corresponding allylic sulfones with tri-n-butyltin hydride under neutral conditions.

Recently, allylstannanes [1] as well as allylsilanes [2] have been of interest since they react with various electrophiles in a highly regiospecific manner. In general, the allylstannanes hitherto used in synthetically useful reactions have been limited to very simple derivatives without further functional substitution (i.e., allylstannanes having only alkyl (R′) groups as substituents on the allyl function, $R_3SnCH_2CH{=}CHR'$). Such allylstannanes generally have been prepared by polar processes involving allyl Grignard reagents or organostannyllithium species, and the preparation of derivatives containing functional groups such as carbonyl or cyano groups would be very difficult by such methods.

We report here a new approach to such allylstannanes starting from allylic sulfones. Our method is based upon regiospecific allyl transfer from sulfur to tin [3] as formulated below, in which carbon—tin bond formation is achieved by a homolytic process.

Most of allylic sulfones containing functional groups [2] can be prepared easily by Michael addition of α-methylallyl tolyl sulfone to electrophilic olefins such as acrylonitrile (eq. 1)*.

The hydrostannolysis of the resulting allylic sulfones (eq. 2) was found to proceed under mild conditions (in refluxing benzene for 2—5 h) using two molar equivalents of tri-n-butyltin hydride in the presence of catalytic amount (4 mol%) of azobisisobutyronitrile (AIBN). The products were isolated by Kugelrohr distillation under reduced pressure. All new compounds obtained were identified by spectroscopy and by analysis. The functional groups such as ester, nitrile, or

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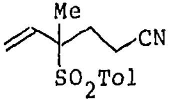
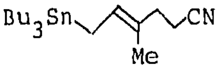
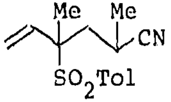
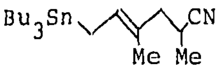
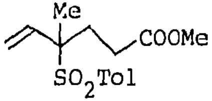
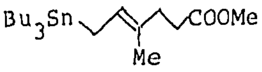
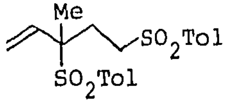
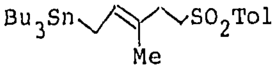
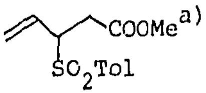
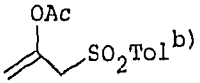
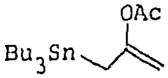
*For similar Michael addition of allyl toluyl sulfone see ref. 4.

Table 1

ALLYLSULFONES AND ALLYLSTANNANES

Sulfones		Yield (%)	M.P. (°C)	Stannanes[d]		Yield (%)	B.P. (°C/mmHg)[e]
1a		83[c]	93.0-93.5 (EtOH-Hexane)	2a		85	150-154/0.1-0.2
1b		66[c]	121.0-122.0 (EtOH-Hexane)	2b		85	142-155/0.1-0.2
1c		100	oil	2c		100	oil
1d		89[c]	127.5-128.0 (EtOH)	2d		82	oil
1e		76[c]	60.5-61.5 (Et$_2$O-Hexane)	2e		94	135-142/0.1
1f		89[c]	89.0-90.0 (EtOH-MeOH)	2f		82	98-107/0.08

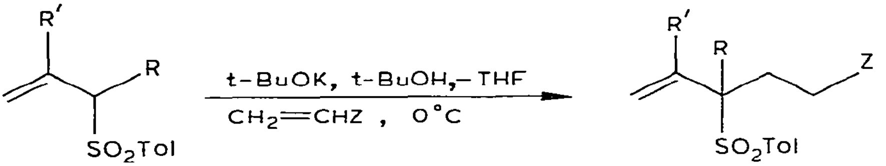
a) See Experimental.

b) See ref. [5].

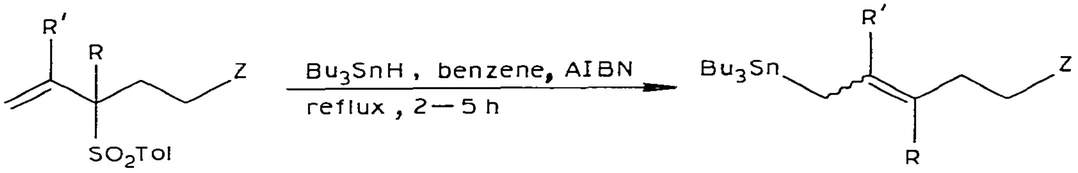
c) Yield after recrystallization from the indicated solvents.

d) For convenience, only the major E-stereoisomers are shown.

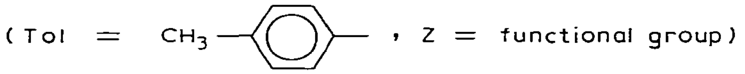
e) Kugelrohr distillation.



(1)



(2)



sulfonyl groups* were not affected by tri-n-butyltin hydride under the reaction conditions. Allylstannanes were isolated as mixtures of *E*- (major) and *Z*- (minor) stereoisomers**. For example, the *E*/*Z* ratio in stannane 2e was estimated to be 71/29 from ^{13}C NMR spectrum. The results are summarized in Table 1.

These are the first examples of the preparation of such functionally substituted allylstannanes. The present method seems to be capable of considerable modification for the introduction of functionalities. Moreover, resulting allylstannanes are potentially interesting reactive intermediates for the synthesis of more complex molecules. Work along these lines is in progress in our laboratory.

Experimental

All reactions were carried out under a nitrogen atmosphere.

Typical procedure for the allylic sulfones: into a cooled (0°C) solution of potassium t-butoxide (10 mmol) in t-butyl alcohol (20 ml) and tetrahydrofuran (THF) (30 ml) was added dropwise a solution of 3-*p*-toluenesulfonyl-1-butene (10 mmol) in THF (20 ml) (15 min). The mixture was stirred for an additional hour at 0°C. Acrylonitrile (10 mmol) in THF (10 ml) was added dropwise to the above mixture (10 min) and stirring was continued for 1.5 h at 0°C. The mixture was poured into cooled aqueous saturated ammonium chloride (50 ml) and was extracted with ether (50 ml × 3). The combined organic layer was washed with water (100 ml × 3), aqueous saturated sodium chloride (100 ml), and dried over magnesium sulfate. Removal of solvent followed by recrystallization from ethanol/hexane gave 4-methyl-4-*p*-toluenesulfonyl-5-hexenenitrile (1a) in 83% yield: m.p. 93.0—93.5°C. IR (KBr), 2240, 1280, 1140 cm^{-1}; NMR (CDCl$_3$) (ppm) δ 1.40 (s, 3H, Me), 2.30—2.60 (m, 4H, CH$_2$CH$_2$), 2.48 (s, 3H, Me), 5.12

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*A sulfonyl group located other than at the allylic position does not react with tri-n-butyltin hydride; see compound 1d.

**The structures of *E*-stereoisomers are shown in Table 1.

(dd, 1H), 5.45 (dd, 1H), 5.99 (dd, 1H) (J_{gem} 1.0 Hz, J_{cis} 10.0 Hz, J_{trans} 17.0 Hz), 7.38, 7.77 (d, J 8.0 Hz, 4H, Ar); Found: C, 63.69; H, 6.41; N, 5.36. $C_{14}H_{17}NO_2S$ calcd.: C, 63.85; H, 6.51; N, 5.32%.

Methyl 3-*p*-toluenesulfonyl-4-pentenoate (1a). To a mixture of allyl tosyl sulfone (10 mmol) and tetramethylethylenediamine (TMEDA) (10 mmol) in dry THF (40 ml) was added dropwise a solution of n-butyllithium in hexane (10.1 mmol) at −78°C (15 min). After stirring for 1 h, methyl bromoacetate (10.4 mmol) dissolved in THF (5 ml) was added to the above mixture (10 min). Stirring was continued for 3 h at −78°C. Usual work-up followed by recrystallization from ether/hexane gave the pure ester (1e) in 76% yield, m.p. 60.5—61.5°C; IR (KBr) 1740, 1300, 1140 cm^{-1}; NMR ($CDCl_3$) (ppm) δ 2.48 (s, 3H, Me), 2.60—3.35 (m, 2H, CH_2), 3.68 (s, 3H, OMe), 3.80—4.45 (m, 1H, CH), 4.95—6.10 (m, 3H, $CH_2{=}CH$), 7.40, 7.77 (d, J 9.0 Hz, 4H, Ar). Found: C, 58.41; H, 6.10. $C_{13}H_{16}O_4S$ calcd.: C, 58.19; H, 6.01%.

The typical procedure for the preparation of the allylstannane is as follows: Methyl 5-tributylstannyl-3-pentenoate (2e). A mixture of tributyltin hydride (2 mmol), the allylic sulfone (1e) (1 mmol) and a catalytic amount (0.04 mmol, 4 mol% for 1e) of AIBN in dry benzene (10 ml) was refluxed for 5 h. Removal of solvent and distillation of the residue under reduced pressure gave the allylstannane 2e in 94% yield, b.p. 135—142°C/0.1 mmHg, IR (film), 1745 cm^{-1}; NMR ($CDCl_3$) (ppm) δ 0.52—1.68 (m, 27H), 1.68—1.84 (m, 2H, CH_2), 2.96—3.16 (m, 2H, CH_2), 3.67 (s, 3H, Me), 5.10—5.90 (m, 2H, CH=CH); Mass *m/e* 404 (M^+); Found: C, 53.66; H, 8.96. $C_{18}H_{36}O_2Sn$ calcd.: C, 53.62; H, 9.00%.

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