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β-STANNYLPROPIONALDEHYDE. A VERSATILE CYCLOPROPANE BUILDING-BLOCK

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Summary; Various functional group-substituted cyclopropanes were prepared in good yield starting from β-tributylstannylpropionaldehyde via homoallylstannanes or γ-hydroxypropylstannanes.

Cyclopropanes are interesting synthetic intermediates, which are capable of various types of ring opening or ring expansions.[1] These cyclopropanes are generally prepared by the addition of carbene or carbenoid to olefins.[2] Although simple homoallylstannanes such as 3-butenyltributylstannane are known to react with various electrophiles to give cyclopropanes,[3] the method seems to draw little attention, presumably due to the less availability of the functionalized homoallylstannanes.

We wish to report here the first preparation of β-tributylstannylpropionaldehyde (2) and its potential use for the construction of cyclopropane rings.

Preparation of β-tributylstannylpropionaldehyde (2).

Oxidation of 3-tributylstannylpropanol (1), easily accessible from tributylstannane and allylalcohol in 98% yield,[4] was examined using four different oxidizing reagents (vide infra). Among them, N-chlorosuccinimide (NCS)-Me_2S[5] gave the best results.

$$Bu_3SnCH_2CH_2CH_2OH \xrightarrow[2)\ NEt_3]{1)\ NCS\text{-}Me_2S} Bu_3SnCH_2CH_2CHO \quad 81\%$$

1 2

Other reagents, CrO_3PyHCl,[6] $CrO_3 2Py$,[7] and EtMgBr/t-BuLi/NCS[8] gave the aldehyde 2 in 55, 50, and 25% yield, respectively.[9]

To a mixture of NCS (8.03 g, 60.2 mmol) and dimethyl sulfide (5.6 ml, 76.3 mmol) in dry toluene (165 ml), stannylalcohol 1 (10.5 g, 30.1 mmol) was added dropwise (~40 min) at -30°C. After stirring for 3 h, triethylamine (8.4 ml, 60.2 mmol) was added at -30°C (~20 min). After stirring for 20 min, the mixture was treated with a saturated aq. ammonium chloride solution (150 ml) at 0°C. Usual work up and column chromatography (silica gel, n-hexane-ether) gave a colorless oil 2 in 81% yield: bp. 110-115°C/0.1 mmHg, NMR($CDCl_3$), 0.2-2.3 (m, 29H), 2.59 (dt, 2H), 9.74 (t, 1H).[10]

Functionalized homoallylstannanes and cyclopropane formation.

β-Stannylpropionaldehyde was easily converted to homoallylstannanes 4 by the reaction of appropriate Wittig reagents in refluxing benzene (3a-c) or tetrahydrofuran (THF) at room temperature (3d) in good yield (Table 1).[10]

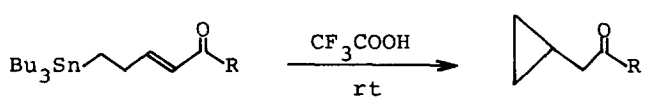
$$\underset{\underline{2}}{Bu_3SnCH_2CH_2CHO} + \underset{\underline{3}}{Ph_3P{=}CHR} \longrightarrow \underset{\underline{4}}{Bu_3SnCH_2CH_2CH{=}CHR}$$

Table 1. Preparation of homoallylstannanes 4.

Phosphorane 3		Homoallylstannanes 4*	Yield (%)
a	$Ph_3P{=}CHCOMe$	$Bu_3SnCH_2CH_2CH{=}CHCOMe$	93
b	$Ph_3P{=}CHCOPh$	$Bu_3SnCH_2CH_2CH{=}CHCOPh$	84
c	$Ph_3P{=}CHCOOMe$	$Bu_3SnCH_2CH_2CH{=}CHCOOMe$	92
d	$Ph_3P{=}CH$-C$_6$H$_4$-NO_2	$Bu_3SnCH_2CH_2CH{=}CH$-C$_6$H$_4$-NO_2	79

* Mainly E-isomers (>90%) were obtained in all cases.

Next, we examined the cyclopropane ring formation via destannylation of 4. When the homoallylstannanes 4a, b were treated with trifluoroacetic acid (1.1 eq.) in THF or dichloromethane at room temperature overnight to afford the desired cyclopropanes 5.

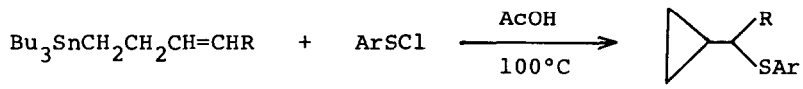


4a,b

5a,R=Me 90%

5b,R=Ph 89%

Arylsulfenyl chloride also reacted with homoallylstannanes 4 in acetic acid at 100°C for 2 h furnishing the sulfur-substituted cycloprapanes 6.[10]



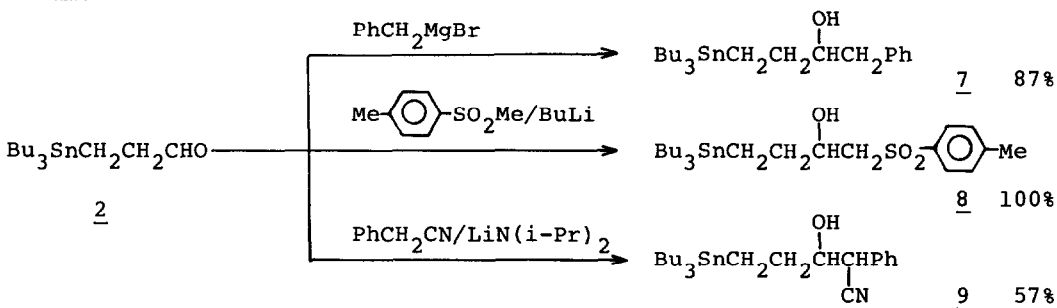
(Ar=2,4-dinitrophenyl)

6a R=Ph 75%

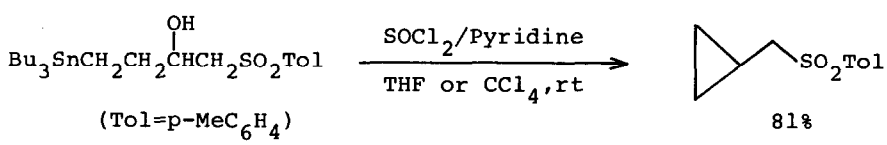
6b R=p-$NO_2C_6H_4$ 93%

Cyclopropanes via γ-hydroxypropylstannanes.

Utility of β-stannylpropionaldehyde 2 was further enhanced by the facile conversion to γ-hydroxypropylstannanes. Thus, 2 reacted with a Grignard reagent or relatively stabilized carbanions such as toluenesulfonylmethylide to produce the γ-hydroxypropylstannanes 7-9 without metal exchange reaction, which was a well established reaction between organostannanes and organolithium.[11]



Cyclopropanes were easily obtained by simple treatment of stannyl alcohols (7-9) with thionylchloride[12] in THF or carbon tetrachloride at room temperature overnight (Table 2).



All these cyclopropane ring formations are best explained by the generation of carbocations at γ-position followed by the simultaneous destannylation.

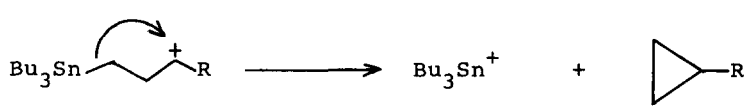
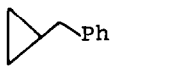
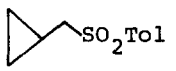
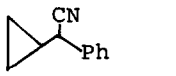


Table 2. Cyclopropanes from γ-hydroxypropylstannanes.[10]

Hydroxystannanes	Cyclopropanes	Yield(%)
$Bu_3SnCH_2CH_2\underset{\displaystyle OH}{\underset{\vert}{C}}HCH_2Ph$	 10	77
$Bu_3SnCH_2CH_2\underset{\displaystyle OH}{\underset{\vert}{C}}HCH_2SO_2Tol$	 11	81
$Bu_3SnCH_2CH_2\underset{\displaystyle OH}{\underset{\vert}{C}}H\underset{\displaystyle CN}{\underset{\vert}{C}}HPh$	 12	77

Stannylpropionaldehyde 2 is a unique reagent, in which the aldehyde part is attacked by nucleophiles and the stannyl group is attacked by electrophiles intramolecularly furnishing the highly functionalized cyclopropanes as demonstrated as above. This property may enable β-stannylpropionaldehyde 2 to be a synthetically useful reagent.

References and notes

1) For example, see S. Danishefsky, Acc. Chem. Res., 12, 66 (1979).
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9) Tributylchlorostannane was also isolated in the case of CrO_3PyHCl.
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11) D. Seyferth, M. A. Weiner, J. Org. Chem., 24, 1395 (1959).
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