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REACTION OF TRI-n-BUTYLTIN FORMATE. III.
SYNTHESIS OF ALLYLIC TRI-n-BUTYLTIN BY THE REACTION OF TRI-n-BUTYLTIN FORMATE WITH ALLYLIC SULFONES AND SULFIDES

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Summary: Allylic tri-n-butyltins can be prepared easily by the treatment of allylic sulfones or sulfides with tri-n-butyltin formate in refluxing xylene.

Tri-n-butyltin hydride has often been employed for the synthesis of allylic$^{1)}$ or vinylic$^{2)}$ tri-n-butyltins which are useful for allylating or vinylating reagents.$^{3)}$ However, the hydride is not only unstable thermally but also unstable toward light,$^{2a)}$ therefore it should be treated carefully to avoid decomposition.

It has been known$^{4)}$ that the hydride can be obtained by continuous pyrolytic distillation of tri-n-butyltin formate under appropriate reduced pressure. In the case of pyrolysis without simultaneous distillation, it has been confirmed that the sole product obtained was hexa-n-butylditin. Moreover, electrosynthetic study$^{5)}$ showed that the triorganotin formate can be converted effectively to the corresponding hexaorganoditins by the electrolysis in dimethylacetamide. Thus the formate, which is easily available and can handle without special precaution, could be used as a precursor of the hydride in some organic reactions. We describe an example of this reaction in the case of synthesis of allylic tri-n-butyltins which are obtained by the reaction of allylic sulfones or sulfides with tri-n-butyltin hydride.$^{1)}$

Allyl p-tolyl sulfone **2** (7 mmol), tri-n-butyltin formate **1** (15 mmol), and catalytic amount of azobisisobutyronitrile (AIBN) in dry xylene were heated at 165-170°C (oil bath) with stirring for 5.5 hr. Allyltri-n-butyltin **3** was isolated by Kugelrohr distillation from the reaction mixture in 60% yield$^{6)}$ (Table 1) and tri-n-butyltin p-toluenesulfinate **4** was remained as the residue. Treatment of the residue with allyl bromide at 80°C without solvent gave **2** and tri-n-butyltin bromide quantitatively. The bromide (as well known in the organotin chemistry)$^{2a)}$ can be easily converted to **1** by the reaction with sodium formate. These reactions are schematically shown below.

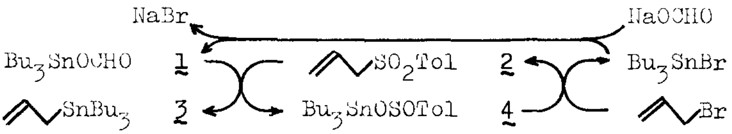
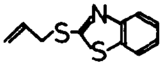
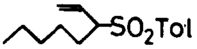
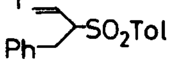


Table 1. Reaction of allylic sulfones and sulfides with tri-n-butyltin formate in the presence of AIBN at 165-170°C

allylic sulfone and sulfide[a)]	(mmol)	xylene (ml)	reaction time (hr)	Product[b)]	yield (%)
	7.0	3.0	5.5		60
	10.2	0.6	16.0[c)]		72
	9.7	0.8	5.0		50
	1.8	0.5	1.3		60
	2.1	0.5	1.5		42
	2.0	0.6	1.9		59
	2.6	0.5	1.5		40
	1.6	1.3	2.8		67
	1.8	1.4	3.4[d)]		58

a) Tol=p-$CH_3C_6H_4$, Ph=C_6H_5. b) E/Z=ca. 5/2. c) at 150°C. d) at 175°C

References and Notes

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3) For a review of the reactions, see M. Kosugi and T. Migita, J. Syn. Org. Chem. Jpn., **38**, 1142(1980).

4) M. Ohara and R. Okawara, J. Organometal. Chem., **3**(1965)484.

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6) Allylic tri-n-butyltins were purified by silica gel column chromatography eluted with n-hexane.

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