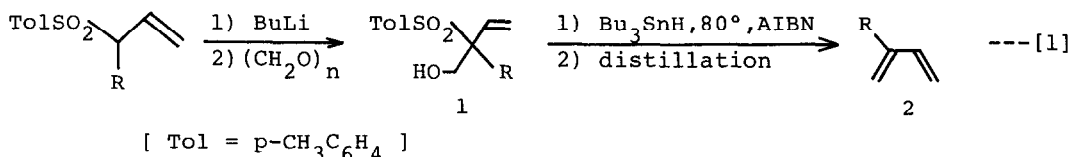


STANNANES IN SYNTHESIS: A NEW ROUTE TO 2-SUBSTITUTED-1,3-BUTADIENES  
VIA STEREOSELECTIVE ALLYL TIN FORMATION UNDER HOMOLYTIC CONDITIONS<sup>1</sup>

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Summary;  $\alpha$ -(Hydroxymethyl)allyl tolylsulfones reacted with tributyltin hydride in the presence of azobisisobutyronitrile(AIBN) in refluxing benzene to give a allyltin derivatives which subsequently gave 2-substituted-1,3-butadienes upon distillation in good yield.

In general, radical reactions are not so effective to achieve stereo-controlled transformations. During our studies on the desulfurizative stannylation,<sup>2</sup> we found a highly stereoselective allyltin formation under homolytic conditions. We wish to report here a new efficient route to 2-substituted-1,3-butadienes(2), and provide a first clear-cut example for the stereoselective allyltin formation under homolytic conditions.



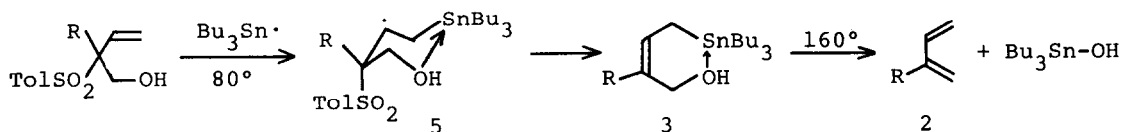
First, we observed that  $\alpha$ -(hydroxymethyl)allyl sulfones(1), easily prepared by alkylation<sup>2d</sup> of anion of allyl tolyl sulfone with alkyl halides(RX) followed by hydroxymethylation with paraformaldehyde (Table 1), reacted with tri-n-butyltin hydride in the presence of catalytic amount of azobisisobutyronitrile(AIBN) as a radical initiator in refluxing benzene for 2h. Direct distillation from the reaction mixture afforded 2-substituted-1,3-butadienes(2) in good yield (Table 1). Related olefin synthesis from  $\beta$ -hydroxy sulfone has been carried out by electrochemical or sodium-amalgam reduction.<sup>3</sup>

Careful isolation of the intermediate before distillation revealed the stereoselective allyltin formation, i.e., Z-isomer(3) was formed predominantly.<sup>4</sup>



Differential thermal analysis (DTA) study revealed the clean fragmentation of the above allyltins occurred at about 160°C to result in the formation of butadienes(2).

These results suggest the following reaction scheme.



Thus, the co-ordination from the oxygen lone-pair to tin atom in the initial adduct(5) seems to fix the conformation to result in the formation of predominant Z-isomers(3).

Z-Isomer(3) should be a precursor to the butadiene(2). That is, a new type of fragmentation from Z-isomer might be taken place at  $160^\circ\text{C}$  by concerted mechanism with elimination of tributyltin hydroxide. In fact, bis(tributyltin)oxide was isolated from the reaction mixture.<sup>10</sup> It seems to be highly difficult that E-isomer(4) cleaves concertedly or through the intermolecular co-ordination to butadienes, since usual allyltins resist alcoholysis.<sup>11</sup>

Somewhat lower stereoselectivity in the case of 1b as a starting sulfone corresponds to the lower yield of the resulting butadiene(2b). In some cases, small amounts of stable allyltins having hydroxymethyl group, presumably E-isomers, were isolated by high temperature distillation ( $>200^\circ\text{C}$ ) without fragmentation to butadienes.

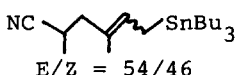

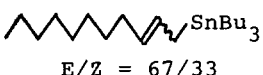

A typical procedure is as follows. To a solution of 3-tolylsulfonylundeca-1-ene (1.0g, 3.24mmol) and TMEDA (0.49ml, 3.24mmol) in THF (15ml), a solution of n-butyllithium (2.1ml, 3.24mmol) in hexane was added at  $-70^\circ\text{C}$  under a nitrogen atmosphere. After 1h, paraformaldehyde (0.12g, 3.24mmol, 85% purity) was added and stirring was continued for additional 1h at  $-70^\circ\text{C}$ , then at room temperature for 3h. After usual workup, purification by column chromatography gave pure 3-hydroxymethyl-3-tolylsulfonylundeca-1-ene (1a) in 95% yield.

A mixture of 1a (0.75g, 2.23mmol), tri-n-butyltin hydride (1.30g, 4.46mmol), and AIBN (~10mg) in dry benzene (3ml) was refluxed for 2h. Direct Kugelrohr distillation gave 2-octyl-1,3-butadiene (2a) in 92% yield.

bp. 160-162°C (15mmHg) ;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ,  $\delta$ ) 0.65-1.85(m,15H), 2.00-2.50(m,2H), 4.85-5.45(m,4H), and 5.95-6.56(m,1H).

#### References and footnotes

- 1) Synthetic Reactions using Organotin and Sulfur Compounds. Part 7.  
For part 6. Y.Ueno, H.Sano, M.Okawara, *Synthesis*, 1011 (1980).
- 2) (a) Y.Ueno, M. Ohta, M. Okawara, *J. Organometal. Chem.*, 197, C 1 (1980);  
(b) Y.Ueno, S. Aoki, M. Okawara, *J. Chem. Soc., Chem. Commun.*, 683 (1980);  
(c) Y.Ueno, H. Sano, M. Okawara, *Tetrahedron Lett.*, 21, 1767 (1980);  
(d) Y.Ueno, S. Aoki, M. Okawara, *J. Am. Chem. Soc.*, 101, 5414 (1979).
- 3) T. Shono, Y. Matsumura, S. Kashima, *Chem. Lett.*, 1978 69, and references cited therein.
- 4) Allyltins were isolated by column chromatography (silica gel, eluted with dry benzene); 1-Tributylstannyl-3-hydroxymethylundeca-2-ene (3a+4a) (41%), 1-Tributylstannyl-3-hydroxymethylnona-2-ene (61%).
- 5) All new compounds obtained here had satisfactory spectral and analytical data.
- 6)  $^1\text{H-NMR}$  was measured in the presence of  $[\text{Eu}(\text{fod})_3]$ .
- 7) The high stability of allyltin derivatives having longer alkyl chain except crotyltrimethyltin is reported.  
H. Yatagai, Y. Yamamoto, K. Maruyama, *J. Am. Chem. Soc.*, 102, 4548 (1980).
- 8) For example, poor E/Z ratios were observed in the following compounds;
 

 <p>NC  SnBu<sub>3</sub> E/Z = 54/46</p>	 <p> SnBu<sub>3</sub> E/Z = 67/33</p>
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See, ref. 2a and 2d.
- 9) Stereoselective allyltin formation in polar reaction, see ref. 7.
- 10) Tributyltin hydroxide is easily dehydrated to bis(tributyltin)oxide.  
R. C. Poller, "The Chemistry of Organotin Compounds", Logos Press, London, England, 1970, p. 69.
- 11) For example, allyltributyltin is stable in refluxing ethanol.

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