

$\alpha$ -BROMOALLYLSTANNANES AS SYNTHETIC TOOLS: PREPARATIONS AND REACTIVITIESMasakatsu SHIBASAKI,<sup>†</sup> Hideyuki SUZUKI, Yasuhiro TORISAWA, and Shiro IKEGAMI<sup>\*</sup>

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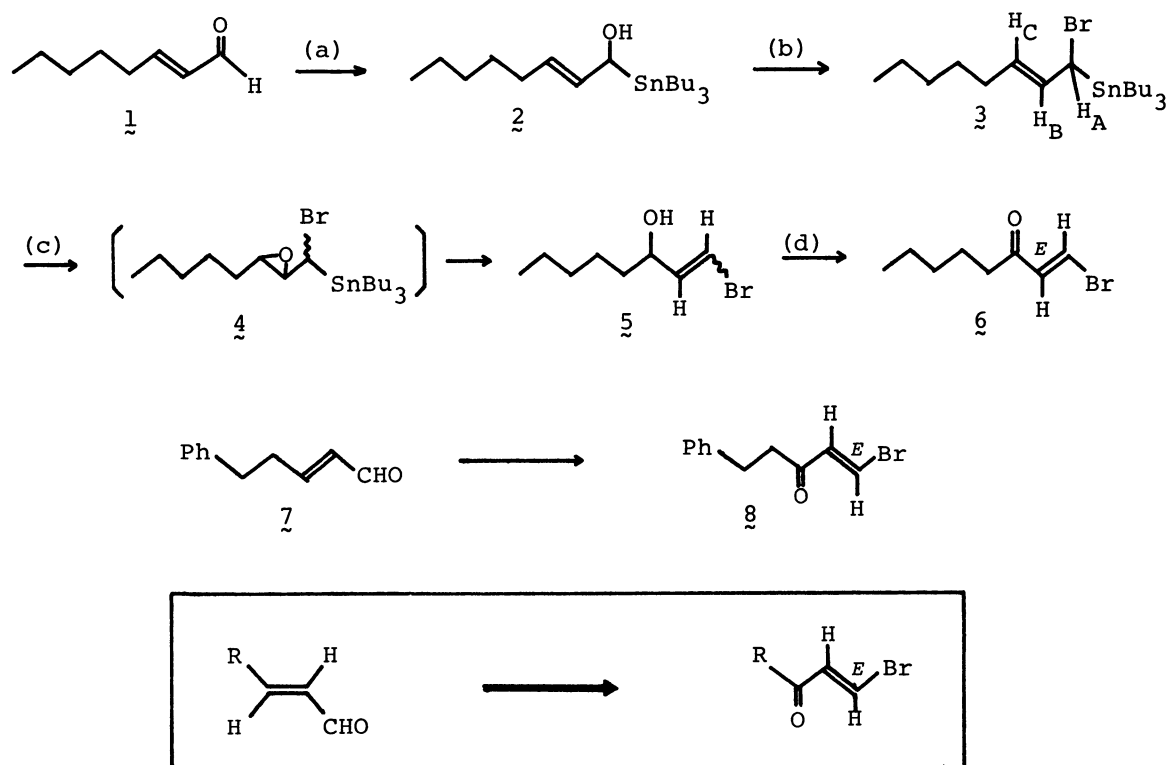
*A couple of useful compounds such as E-1-bromo-3-oxo-1-alkenes, E-1-substituted-1,3-dienes and 3-hydroxy-1-alkynes are prepared from  $\alpha$ -bromoallylstannanes derived from the corresponding  $\alpha,\beta$ -unsaturated aldehydes.*

In the course of our synthetic studies on biologically active compounds, we have recently established a general method for the preparation of  $\alpha$ -haloalkylstannanes from aldehyde,<sup>1)</sup> and have investigated their chemical reactivities in detail.<sup>1,2)</sup> As a result, these studies provided us with several new synthetic tools including the transformation of aldehydes to terminal acetylenes via 1-alkenylstannanes (  $RCH_2CHO \longrightarrow RCH_2CHBrSnBu_3 \longrightarrow RCH=CHSnBu_3 \longrightarrow RC\equiv CH$  ). As an extension of this research we have also attempted the preparation of  $\alpha$ -haloallylstannanes from  $\alpha,\beta$ -unsaturated aldehydes in order to investigate their chemical reactivities. In this communication we wish to report a general method for the preparation of  $\alpha$ -bromoallylstannanes from  $\alpha,\beta$ -unsaturated aldehydes and their transformations to a couple of synthetically useful compounds.

Treatment of 2-octenal (1) with tributylstannyl lithium (1.2 equiv.) in THF at  $-78^\circ C$ <sup>3)</sup> afforded the fairly unstable  $\alpha$ -hydroxyallylstannane (2). Without purification, 2 was directly transformed to the corresponding bromide (3) by treatment with triphenylphosphine (1.2 equiv.), carbon tetrabromide (1.2 equiv.) and sodium sulfite (2.4 equiv.) in methylene chloride ( $-25^\circ C$ , 0.5 h).<sup>4)</sup> The PMR spectrum of 3 displayed one proton doublet ( $\delta 4.16$ ,  $J=8$  Hz,  $H_A$ ) together with two olefinic protons ( $\delta 5.80$ , dd,  $J=14$  Hz, 8 Hz,  $H_B$ ;  $\delta 5.52$ , dt,  $J=14$  Hz, 6 Hz,  $H_C$ ), providing the unequivocal proof of the structure of 3. From the above result the following facts were also indicated. In contrast to the case of  $\alpha,\beta$ -unsaturated ketones,<sup>5)</sup> reaction of tributylstannyl lithium in THF with the  $\alpha,\beta$ -unsaturated

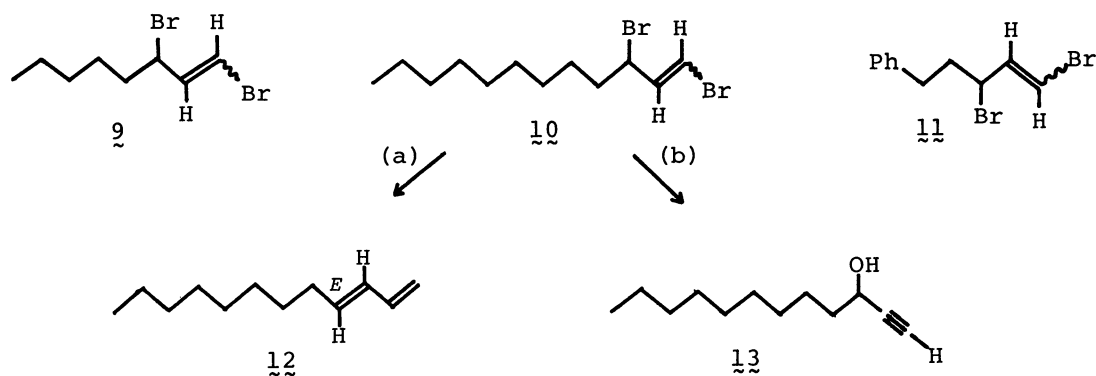
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Scheme 1.



(a)  $\text{Bu}_3\text{SnLi}$ , THF,  $-78^\circ\text{C}$ . (b)  $\text{Ph}_3\text{P}$ ,  $\text{CBr}_4$ ,  $\text{Na}_2\text{SO}_3$ ,  $\text{CH}_2\text{Cl}_2$ ,  $-25^\circ\text{C}$ .  
 (c)  $\underline{m}$ -CPBA,  $\text{CH}_2\text{Cl}_2$ ,  $0^\circ\text{C}$ . (d) i) PCC,  $\text{CH}_2\text{Cl}_2$ , ii) TsOH, benzene,  $50^\circ\text{C}$ .

Scheme 2.



(a) i) DBU, toluene, r.t., ii)  $\underline{t}$ -BuLi, THF-pentane,  $-78^\circ\text{C}$ . (b)  $\text{KO}_2$ , 18-crown-6, DMSO, r.t.

aldehyde (1) provided the 1,2-addition product (2) exclusively.<sup>6)</sup> Furthermore it was shown that no allylic migration took place at the bromination stage. Since the  $\alpha$ -bromoallylstannane (3) was found to be rather unstable in contrast to  $\alpha$ -bromoalkylstannanes derived from saturated aldehydes, after rapid purification by silica gel column chromatography,<sup>7)</sup> it was treated with m-CPBA (3 equiv.) in methylene chloride at 0°C~r.t. for 0.5 h. Under these conditions none of the corresponding epoxide (4) was detected from the TLC analysis. Instead, 1-bromo-1-octen-3-ol (5) was formed as the major product (56% overall yield from 1) possibly via 4.<sup>8)</sup> Since the allyl alcohol (5) was found to be a mixture of the stereoisomers, 5 was oxidized with PCC in methylene chloride followed by the treatment with p-TsOH in benzene (50°C, 3 h), leading to the stereochemically pure E-1-bromo-1-octen-3-one (6) (73% yield from 5). Likewise, 5-phenyl-2-pentenal (7) was converted to the stereochemically pure enone (8) (43% overall yield from the aldehyde). Thus, the general method for the transformation of  $\alpha,\beta$ -unsaturated aldehydes to stereochemically pure E-1-bromo-1-alken-3-ones was realized as shown in Scheme 1.

On the other hand, the  $\alpha$ -bromoallylstannane (3) was directly converted to 1,3-dibromo-1-octene (9) as a mixture of the stereoisomers (64% from the aldehyde) when the reaction mixture was directly treated with m-CPBA at 0°C~r.t. for 0.5 h.<sup>9)</sup> In the same manner, 1,3-dibromo-5-phenyl-1-pentene (11) (63%) and 1,3-dibromo-1-dodecene (10) (77%) were obtained from the corresponding  $\alpha,\beta$ -unsaturated aldehydes. 1,3-Dibromo-1-dodecene (10) was then transformed to the nearly homogeneous (E:Z=10:1) terminal diene (12)<sup>10)</sup> by successive treatment with DBU (10 equiv.) in toluene (r.t., 2 h) and t-BuLi (2 equiv.) in THF-pentane (1:1, -78°C, 1 h) (47%). On the other hand, reaction of 10 with potassium superoxide (8 equiv.) and 18-crown-6 (3 equiv.) in DMSO (r.t., 1 h)<sup>11)</sup> provided 1-dodecyn-3-ol (13) (31%) (Scheme 2).

In this way it has been shown that  $\alpha$ -bromoallylstannanes prepared from  $\alpha,\beta$ -unsaturated aldehydes are synthetically useful intermediates for the transformation of  $\alpha,\beta$ -unsaturated aldehydes to other useful compounds.

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## References

- 1) Y.Torisawa, M.Shibasaki, and S.Ikegami, *Tetrahedron Lett.*, 22, 2397 (1981).
- 2) M.Shibasaki, Y.Torisawa, and S.Ikegami, *Tetrahedron Lett.*, 23, 4607 (1982).
- 3) W.C.Still, *J. Am. Chem. Soc.*, 100, 1481 (1978).
- 4) Transformation of 2 to the corresponding chloride and the iodide turned out to be unsuccessful.
- 5) In general, reaction of trialkylstannyl lithium in THF with  $\alpha,\beta$ -unsaturated ketones affords 1,4-addition products exclusively, see W.C.Still, *J. Am. Chem. Soc.*, 99, 4836 (1977).
- 6) During our work, A.J.Pratt and E.J.Thomas reported the exclusive formation of the 1,2-addition product when crotonaldehyde was treated with tributylstannyl lithium in THF at  $-78^{\circ}\text{C}$ , see *J. Chem. Soc., Chem. Commun.*, 1982, 1115.
- 7) Before the reaction with m-CPBA, the  $\alpha$ -bromoallylstannane (3) was purified as follows. After the addition of ether to the reaction mixture, the organic layer was washed with saturated  $\text{Na}_2\text{S}_2\text{O}_3$  aq. for 5 times. Evaporation of the dried solvent ( $\text{MgSO}_4$ ) afforded crude 3, which was rapidly purified by silica gel column chromatography (petr.ether containing 0.1%  $\text{Et}_3\text{N}$ ) to give nearly pure 3. Ethereal solution of 3 was again washed with saturated  $\text{Na}_2\text{S}_2\text{O}_3$  aq. for 5 times, and dried over  $\text{MgSO}_4$ . It should be noticed that this repeated washing of the crude product (3) with saturated  $\text{Na}_2\text{S}_2\text{O}_3$  solution was necessary in order to the complete removal of a certain kind of a brominating agent. Concentration of the solution afforded 3 as a pale yellow oil, which was used for the next reaction with m-CPBA.
- 8) For the reaction of allylic stannanes with m-CPBA, see Y.Ueno, H.Sano, and M.Okawara, *Synthesis*, 1980, 1011.
- 9) m-CPBA was directly added to the crude reaction mixture in  $\text{CH}_2\text{Cl}_2$ . In this case, the dibromo derivative (9) would be produced from the bromination of the initially formed allyl alcohol (5) with an excess brominating agent.
- 10) For the discussion concerning the stereochemistry of 1-substituted 1,3-dienes, see L.Crombie, P.Hemesley, and G.Pattenden, *J. Chem. Soc., C*, 1969, 1016.
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