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α-BROMOALLYLSTANNANES AS SYNTHETIC TOOLS: PREPARATIONS AND REACTIVITIES

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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 α-bromoallylstannanes derived from the corresponding α,β-unsaturated aldehydes.

In the course of our synthetic studies on biologically active compounds, we have recently established a general method for the preparation of α-haloalkylstannanes from aldehyde,[1] and have investigated their chemical reactivities in detail.[1,2] 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 extention of this research we have also attempted the preparation of α-haloallylstannanes from α,β-unsaturated aldehydes in order to investigate their chemical reactivities. In this communication we wish to report a general method for the preparation of α-bromoallylstannanes from α,β-unsaturated aldehydes and their transformations to a couple of synthetically useful compounds.

Treatment of 2-octenal (1) with tributylstannyllithium (1.2 equiv.) in THF at -78°C[3] afforded the fairly unstable α-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°C, 0.5 h).[4] The PMR spectrum of 3 displayed one proton doublet (δ4.16, J=8 Hz, H_A) together with two olefinic protons (δ5.80, dd, J=14 Hz, 8 Hz, H_B; δ5.52, 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 α,β-unsaturated ketones,[5] reaction of tributylstannyllithium in THF with the α,β-unsaturated

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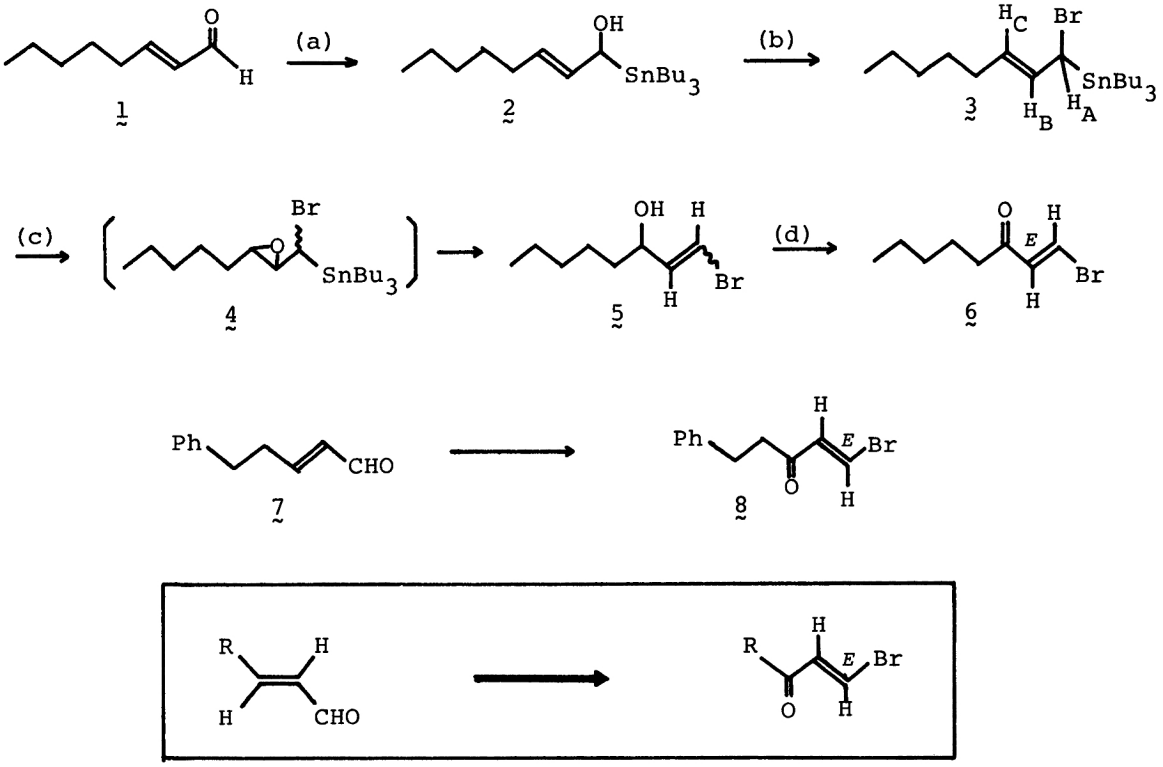
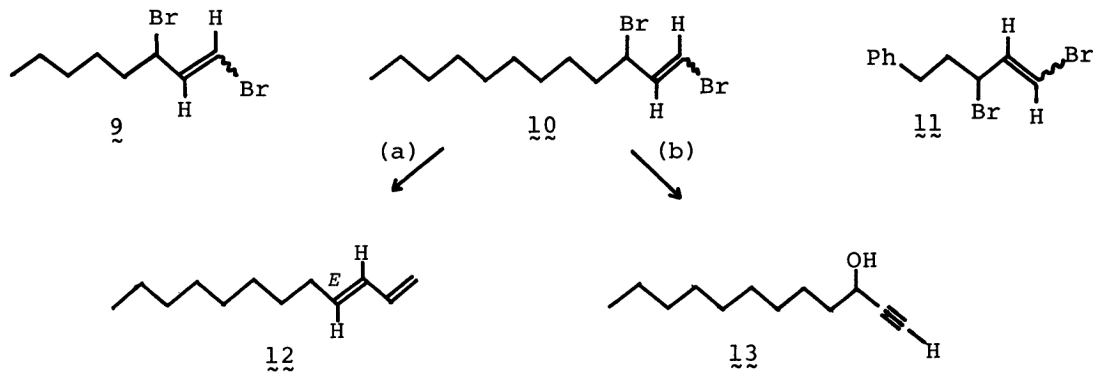
Scheme 1.



(a) Bu_3SnLi, THF, -78°C. (b) Ph_3P, CBr_4, Na_2SO_3, CH_2Cl_2, -25°C.
(c) m-CPBA, CH_2Cl_2, 0°C. (d) i)PCC, CH_2Cl_2, ii)TsOH, benzene, 50°C.

Scheme 2.



(a) i)DBU, toluene, r.t., ii)t-BuLi, THF-pentane, -78°C. (b) KO_2, 18-crown-6, DMSO, r.t.

aldehyde (1) provided the 1,2-addition product (2) exclusively.[6] Furthermore it was shown that no allylic migration took place at the bromination stage. Since the α-bromoallylstannane (3) was found to be rather unstable in contrast to α-bromoalkylstannanes derived from saturated aldehydes, after rapid purification by silica gel column chromatography,[7] 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.[8] 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 α,β-unsaturated aldehydes to stereochemically pure E-1-bromo-1-alken-3-ones was realized as shown in Scheme 1.

On the other hand, the α-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.[9] 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 α,β-unsaturated aldehydes. 1,3-Dibromo-1-dodecene (10) was then transformed to the nearly homogeneous (E:Z=10:1) terminal diene (12)[10] 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)[11] provided 1-dodecyn-3-ol (13) (31%)(Scheme 2).

In this way it has been shown that α-bromoallylstannanes prepared from α,β-unsaturated aldehydes are synthetically useful intermediates for the transformation of α,β-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 trialkylstannyllithium in THF with α,β-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 tributylstannyllithium in THF at -78°C, see J. Chem. Soc., Chem. Commun., 1982, 1115.
7) Before the reaction with m-CPBA, the α-bromoallylstannane (3) was purified as follows. After the addition of ether to the reaction mixture, the organic layer was washed with saturated $Na_2S_2O_3$ aq. for 5 times. Evaporation of the dried solvent ($MgSO_4$) afforded crude 3, which was rapidly purified by silica gel column chromatography (petr.ether containing 0.1% Et_3N) to give nearly pure 3. Ethereal solution of 3 was again washed with saturated $Na_2S_2O_3$ aq. for 5 times, and dried over $MgSO_4$. It should be noticed that this repeated washing of the crude product (3) with saturated $Na_2S_2O_3$ 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 CH_2Cl_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.
11) E.J.Corey, K.C.Nicolaou, M.Shibasaki, Y.Machida, and C.S.Shiner, Tetrahedron Lett., 1975, 3183.

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