Synthesis of a Stable 2-Tributylstannyl-1,3-butadiene Precursor

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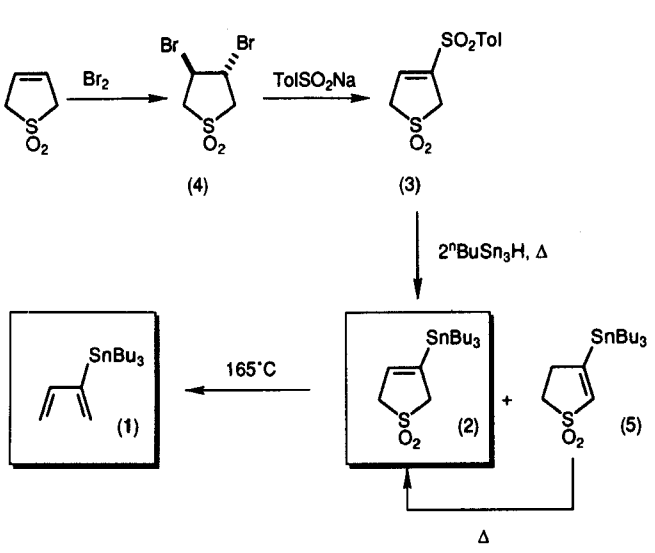
2-Tributylstannyl-1,3-butadiene (**1**) is prepared in 66% yield by retrochelotropic reaction of the corresponding sulfolene **3**.

The utility of stannyldienes in synthesis is recorded.[1] We had need to prepare significant quantities of 2-tributylstannyl-1,3-butadiene (**1**) and found the instability of **1** made repeated preparation tedious.[2] The existing routes to **1** without exception involve use of organometallic reagents (Grignard reagents[3] are most generally used) and this limits the ease of reaction, especially on a large scale. We sought to prepare a more stable stannyldiene equivalent which would allow the preparation of **1** under essentially neutral conditions (thereby allowing easy large-scale preparation) and which itself would be a *stable* precursor to the free stannyldiene – the corresponding (but previously unreported) 3-tributylstannyl-3-sulfolene (**2**) appealed in terms of potential ease of use and flexibility in generation of diene in situ (a variety of methods exist for the extrusion of SO_2 from sulfolenes,[4] with concomitant diene formation). Given our desire for stannylsulfolene **2**, we anticipated that preparation of this compound would be straightforward via application of the radical desulfurative stannylation reaction of Ueno et al to tosylsulfolene **3** (Scheme).[5] Compound **3** is readily prepared from the corresponding 3,4-dibromosulfolane (**4**), which is itself available in very large amounts (ca. 250 g). Since both allylic and vinylic sulfones undergo the Ueno reaction, there was some question as to the regioselectivity upon reaction with **3**; we anticipated that the "external" tolyl sulfone would react more efficiently than the "internal" allylic sulfone.



Compound **3** reacted with two equivalents of tributyltin hydride in boiling benzene to give 3-tributylstannyl-3-sulfolene as a single product in 72% yield after chromatographic purification; the known isomeric instability of sulfolenes[6] occasionally led to a small contamination of **2** with the 2-sulfolene **5** (a contamination level of between 2 and 20% of **5** was observed). This irritation was remedied by use of neutral alumina rather than silica gel in purification.

Distillation of a mixture of **2** gave analytically pure 2-tributylstannyl-1,3-butadiene (**1**) in 66% yield overall from tosylsulfolene **3**. Given the inherent instability of **1**, the complication of some of the previous syntheses of **1**,[7] and our use of two thermally-induced, neutral reaction conditions, we believe that this procedure offers a real improvement in the preparation of this useful compound due to the stability (indefinite at 0°C) and utility of stannylsulfolene **2** as a stable precursor to **1**.

3-Tributylstannyl-3-sulfolene (2) and 2-Tributylstannyl-1,3-butadiene (1):

3-*p*-Toluenesulfonyl-3-sulfolene (8 g, 29.4 mmol), 2,2'-azobisisobutyronitrile (482 mg, 2.904 mmol, 10 mol%) and tributyltin hydride (17.11 g, 58.8 mmol, 2 equiv) were dissolved in benzene (120 mL, distilled and deoxygenated prior to use) and the mixture heated to reflux until no starting material remained (TLC, typically 10 h). The mixture was allowed to cool and then concentrated in vacuo. Petroleum ether (bp 60°C) (100 mL) was added and the resulting white solid removed by filtration. The solid was washed with petroleum ether (25 mL) and the combined petroleum ether fractions were concentrated in vacuo to give crude 3-tributylstannyl-3-sulfolene. This material was immediately distilled under reduced pressure (150°C, 0.01 mm Hg) to yield 2-tributylstannyl-1,3-butadiene (**1**);[7] yield: 6.7 g (66%).

^{1}H NMR ($CDCl_3$/TMS): δ = 6.58 (dd, 1 H, J = 17.2, 10.0 Hz), 5.89 (d, 1 H, J = 2.65 Hz), 5.33 (d, 1 H, J = 2.65 Hz), 5.08 (d, 1 H, J = 10 Hz), 5.07 (d, 1 H, J = 17.3 Hz), 0.83–1.60 (m, 27 H).

Alternatively, **2** could be purified by chromatography on neutral alumina (Brockman grade II) to give 3-tributylstannyl-3-sulfolene as a colourless oil; yield: 8.6 g (72%).

^{1}H NMR ($CDCl_3$/TMS): δ = 6.08 (m, 1 H), 3.78 (br s, 2 H), 3.75 (br s, 1 H), 0.83–1.60 (m, 27 H).

^{13}C NMR ($CDCl_3$): δ = 141.4, 132.0, 61.26, 56.16, 28.85, 27.60, 13.47, 9.46.

IR ($CHCl_3$): ν = 2955, 2923, 2850, 1304, 1123 cm^{-1}.

MS (EI): m/z (%) = 407 (M^+), 177 (100%), 117 (11), 135 (10).

Anal. Calc.: 47.19% C, 7.92% H; Found: 47.55% C 7.95% H.

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(1) See, for instance:
Bates, G.S.; Fryzuk, M.; Stone, C. *Can. J. Chem.* **1987**, *65*, 2612, and references therein.
(2) Chloroprene, the most common precursor to **1**, is not readily commercially available.
(3) 2-Chloromagnesiobutadiene is a frequent precursor to 2-heterodienes, but its preparation from chloroprene is not trivial, often resulting in polymerisation: Aufdermarsh, C.A. *J. Org. Chem.* **1964**, *29*, 1994.
(4) See, for instance:
Chou, T.S.; Chang, S.Y. *J. Org. Chem.* **1992**, *57*, 5015; idem. *J. Chem. Soc., Perkin Trans. 1*, **1992**, 1459.
(5) Ueno, Y.; Ohta, M.; Okawara, M. *J. Organomet. Chem.* **1980**, *197*, C1.
(6) Chou, T.S.; Tso, H.H. *Org. Prep. Proc. Int.* **1989**, *21*, 257.
(7) Fleming, I.; Taddei, M.; Mann, A. *Tetrahedron Lett.* **1986**, *27*, 2913.