Electronic Supplementary Material (ESI) for ChemComm.

EPR Evidence for α-Triphenylstannylvinyl Radicals in the O-Directed Hydrostannation of Dialkylacetylenes with Ph_3SnH/cat. Et_3B/O_2

Hamish A. Watson,[a] Alistair J. Fielding*[b] and Karl J. Hale*[a]

[a]*The School of Chemistry & Chemical Engineering,*

Queen's University Belfast,

Stranmillis Road, Belfast BT9 5AG,

Northern Ireland, United Kingdom

and

[b]*The School of Pharmacy and Biomolecular Sciences,*

Liverpool John Moores University,

Byrom Street, Liverpool L3 3AF,

United Kingdom.

Supporting Information

(3 Pages Inclusive of Cover Pages)

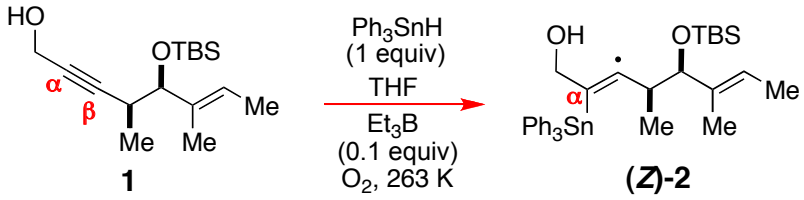
Index

General Information

Unless stated otherwise, all reactions were run in dry solvents under an Ar atmosphere. Dry THF was distilled from CaH_2 under a N_2 atmosphere and dry PhMe was used as supplied by Sigma-Aldrich. Both dry solvents were taken out by dry syringe under an Ar atmosphere. Ph_3SnH was purchased from Sigma-Aldrich and used as supplied because of its high quality; it was always handled inside a glove-bag under Ar. EPR experiments were carried out using a Bruker MicroEMX spectrometer with a super high Q cavity at 9.4 GHz, microwave power of 2-20 mW, field modulation of 100 kHz and modulation amplitude of 2-4 G. Field calibration was carried out using 2,2-diphenyl-1-picrylhydrazyl (DPPH). All samples were analyzed in either quartz capillary or 4 mm quartz EPR tubes.

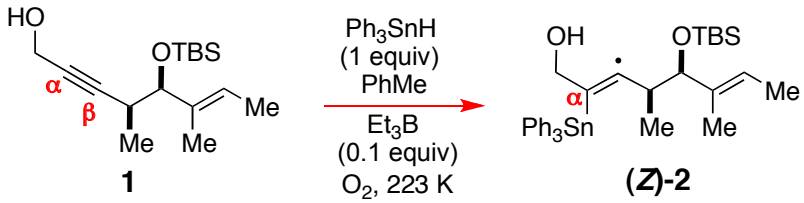
Experimental Procedures For Generating the α-Stannylvinyl Radicals (*Z*)-2 and (*Z*)-9

Optimized Experimental Procedure For Generating the α-Stannylvinyl Radical (*Z*)-2 in THF



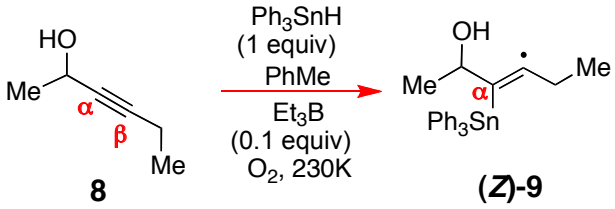
A solution of **1** (1M in THF) was prepared by dissolving **1** (0.2847 g, 1.0 mmol) in dry THF (1 mL) under Ar. A separate solution of Ph_3SnH (1M in THF) was prepared by weighing out Ph_3SnH (0.8134 g, 2.32 mmol) inside an argon-filled glove bag and then dissolving in dry THF (2.32 mL) under Ar. To a round-bottom flask containing a solution of alkynol **1** (0.1 mL, 1 M in THF, 0.1 mmol) under Ar was added a solution of Ph_3SnH (0.1 mL, 1 M in THF, 0.1 mmol) by syringe under Ar. To this resulting stirred mixture was then added Et_3B (0.01 mL, 1 M in Hex, 0.01 mmol) by syringe under Ar. Air (5 mL) was then bubbled through the solution via syringe before the solution was transferred via glass pipette to a quartz EPR tube, which was then introduced into the EPR spectrometer resonator, which had been precooled to -10 ^{o}C. The EPR spectra of **(*Z*)-2** were then recorded at -10 ^{o}C (263 K).

Optimized Experimental Procedure For Generating the α-Stannylvinyl Radical (*Z*)-2 in PhMe



A solution of **1** (1M in PhMe) was prepared by dissolving **1** (0.2777 g, 0.983 mmol) in dry PhMe (1 mL) under Ar. A separate solution of Ph_3SnH (1 M in PhMe) was prepared by weighing out Ph_3SnH (0.5450 g, 1.55 mmol) inside an argon-filled glove bag and then dissolving in dry PhMe (1.6 mL) under Ar. To a round-bottom flask containing a solution of alkynol **1** (0.5 mL, 1M in PhMe, 0.5 mmol) under Ar was added a solution of Ph_3SnH (0.5 mL, 1 M in PhMe, 0.5 mmol) by syringe under Ar. To this resulting stirred mixture was then added Et_3B (0.05 mL, 1 M in Hex, 0.05 mmol) by syringe under Ar, air (5mL) was then bubbled through the solution via syringe before the solution was transferred via glass pipette to a quartz EPR tube, which was then introduced into the EPR spectrometer resonator which had been precooled to -50 ^{o}C. The EPR spectra of **(*Z*)-2** were then recorded at -50 ^{o}C (223 K).

Optimized Experimental Procedure For Generating the α-Stannylvinyl Radical (*Z*)-9 in PhMe



A solution of 3-hexyn-2-ol **8** (1 M in PhMe) was prepared by dissolving 3-hexyn-2-ol **8** (0.098 g, 1.00 mmol) in dry PhMe (1 mL) under Ar. A separate solution of Ph_3SnH (1 M in PhMe) was prepared by weighing out Ph_3SnH (0.4353 g, 1.24 mmol) inside an argon filled glove bag and then dissolving in dry PhMe (1.24 mL) under Ar. To a round-bottom flask containing a solution of 3-hexyn-2-ol **8** (0.25 mL, 1 M in PhMe, 0.25 mmol) under Ar was added a solution of Ph_3SnH (0.25 mL, 1 M in PhMe, 0.25 mmol) by syringe under Ar. To this resulting stirred mixture was then added Et_3B (0.025 mL, 1 M in Hex, 0.025 mmol) by syringe under Ar. Air (5 mL) was then bubbled through the solution via syringe before the solution was transferred via glass pipette to a quartz EPR tube which was then placed inside the EPR resonator which had been precooled to -43 ^{o}C (230 K). The EPR spectra of **(*Z*)-9** were then recorded at -43 ^{o}C (230 K).