A novel stereoselective synthesis of trisubstituted 1,3-dienes by a hydrostannylation-Stille tandem reaction of alkylarylacetylenes with alkenyl halides

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Trisubstituted 1,3-dienes can be stereoselectively synthesised in one pot under mild conditions, in good yields, by the hydrostannylation of alkylarylacetylenes, followed by the Stille cross-coupling with alkenyl halides.

Keywords: hydrostannylation, 1,3-diene, alkylarylacetylene, Stille coupling, tandem reaction

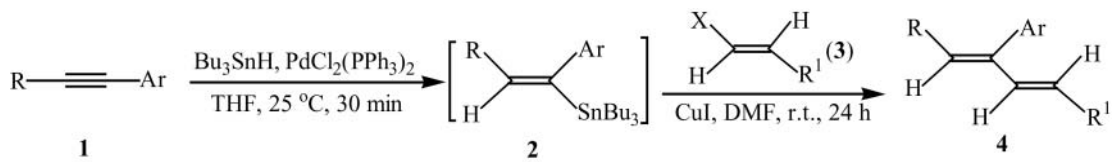
The stereocontrolled synthesis of conjugated dienes has attracted considerable interest in organic chemistry because of their appearance in a wide variety of biologically active molecules and their key synthetic intermediates.[1–3] The synthesis of 1,3-dienes for use in the Diels-Alder reaction is still an important challenge in organic synthesis[4,5] although other elegant uses of these compounds have been developed.[6] Conjugated dienes are usually prepared by utilising either a Wittig type approach[7,8] or through transition-metal-catalysed coupling reactions of stereodefined vinyl halides with vinyl organometallic compounds.[9,10] Kasatkin and Whitby reported the insertion of 1-lithio-1-halo-buta-1,3-diene into organozirconocenes providing a stereocontrolled synthesis of (1*E*,3*Z*)-1,3-dienes.[11] Recently, Molander and Yokoyama reported one-pot stereoselective synthesis of trisubstituted 1,3-dienes via sequential Suzuki-Miyaura cross-coupling with alkenyl- and alkyltrifluoroborates.[12] Tanaka *et al.* reported rhodium-catalysed regio- and stereoselective codimerisation of alkenes and electron-deficient internal alkynes leading to trisubstituted 1,3-dienes.[13]

The tandem reaction has recently been of interest for organic synthesis because it offers a convenient and economical method with which to prepare target organic molecules.[14–17] The palladium-catalysed hydrostannylation of alkynes and the Stille coupling reaction are acknowledged as useful tools for constructing complex organic molecules. However, to the best of our knowledge, there have been no reports on palladium-catalysed tandem hydrostannylation-Stille coupling reaction of tributyltin hydride with alkylarylacetylenes and alkenyl halides to date. Herein we wish to report that trisubstituted 1,3-dienes can be stereoselectively synthesised in one pot under mild conditions, in good yields, by the hydrostannylation of alkylarylacetylenes, followed by the Stille cross-coupling with alkenyl halides.

Palladium-catalysed hydrostannylation of alkynes provides a simple, general route for the synthesis of vinylstannanes.[18] Alami *et al.*[19] reported that the palladium-catalysed hydrostannylation of alkylarylacetylenes with Bu_3SnH in THF at room temperature was highly regio- and stereoselective, giving (*E*)-α-arylvinylstannanes in high yields. It is well known that vinylstannanes can undergo the palladium-catalysed cross-coupling reaction with organic halides.[20,21] Stille and Groh reported[22] stereospecific cross-coupling of vinyl halides with vinyl tin reagents catalysed by palladium. Considering the fact that both the hydrostannylation and Stille reactions were catalysed by palladium complexes, we tried to combine the two reactions, in one pot, to synthesise stereoselectively trisubstituted 1,3-dienes (Scheme 1).

We found that, after the hydrostannylation reaction of alkylarylacetylenes **1** with Bu_3SnH using 3 mol% $PdCl_2(PPh_3)_2$ in THF at 25 °C for 30 min, solvent removal under reduced pressure and stirring of the residue with DMF, alkenyl iodides **3** and 75 mol% CuI at room temperature for 24 h, the trisubstituted 1,3-dienes **4** were obtained in good yields. The experimental results are summarised in Table 1. As shown in Table 1, the hydrostannylation-Stille tandem reaction of Bu_3SnH with a variety of alkylarylacetylenes and alkenyl iodides proceeded smoothly under very mild conditions to afford stereoselectively the corresponding trisubstituted 1,3-dienes **4**. The Stille-coupling reaction of the intermediates **2** with alkenyl bromides also proceeded smoothly under the same reaction conditions, giving the corresponding coupled products in good yields after 24 h of reaction time. However, the Stille coupling reaction of the intermediates **2** with alkenyl chlorides did not occur at all.

Investigation of the crude products **4** by ^{1}H NMR spectroscopy (400 MHz) showed their isomeric purities of more than 98%. One olefinic proton signal of compounds **4a–j**, except **4h**, splits characteristically into one triplet at $\delta = 5.51–5.93$ with coupling constant $J = 6.4–7.6$ Hz, which indicated that the hydrostannylation to the alkylarylacetylenes had taken place with strong preference for the addition of the tin atom at the carbon adjacent to the aryl group. It is well documented that the Stille cross-coupling reaction of vinylstannanes with organic halides in the presence of a palladium catalyst occurs with retention of configuration.[20,21] The (*E*)-configuration of the compounds **4a–j** at the double bond originating from the alkenyl halide has been confirmed by their ^{1}H NMR spectra which show a doublet at $\delta = 6.20–7.01$ with a coupling constant of 15.6–16.0 Hz, giving evidence of the retention of the *E*-configuration of the starting alkenyl halides. In addition, the (*Z*)-configuration at the double bond originating from the vinylstannane [C(4) = C(5)] of compound **4c** was confirmed by the NOESY in the ^{1}H NMR spectrum. An enhancement of the allylic protons was observed as the vinylic proton ($\delta = 5.72$)



1 **2** **4**

Scheme 1

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Table 1 Synthesis of trisubstituted 1,3-dienes (**4a–j**)

Entry	R	Ar	R^1	X	Product	Yield[a]/%
1	n-C_6H_{13}	Ph	Ph	I	**4a**	78
2	n-C_6H_{13}	Ph	n-C_4H_9	I	**4b**	75
3	n-C_6H_{13}	Ph	$MeOCH_2$	I	**4c**	69
4	n-C_6H_{13}	4-MeC_6H_4	n-C_6H_{13}	I	**4d**	80
5	n-C_4H_9	Ph	$MeOCH_2$	I	**4e**	70
6	n-C_4H_9	Ph	Ph	I	**4f**	77
7	n-C_4H_9	Ph	n-C_4H_9	I	**4g**	74
8	Me	Ph	Ph	I	**4h**	64
9	MeO-CH_2CH_2	4-ClC_6H_4	Ph	I	**4i**	67
10	$MeOCH_2$	2-$MeOC_6H_4$	n-C_4H_9	I	**4j**	62
11	n-C_6H_{13}	Ph	Ph	Br	**4a**	79
12	n-C_6H_{13}	Ph	$MeOCH_2$	Br	**4c**	72
13	n-C_4H_9	Ph	n-C_4H_9	Br	**4g**	68

[a] Isolated yield based on alkylarylacetylene **1** used.

of **4c** was irradiated. There was no correlation between the vinylic proton (δ = 5.72) and aromatic protons. Correlation between the allylic protons and aromatic protons was observed. Correlation between the vinylic proton (δ = 5.72) and another vinylic proton (δ = 6.45) was also observed. The NOE results indicate that the compound **4c** has the expected (*Z*)-configuration at C(4) = C(5) and the Pd-catalysed cross-coupling reaction of (*E*)-α-arylvinylstannanes **2** with alkenyl halides occurs with configuration retention of both the starting intermediates **2** and the alkenyl halides.

In summary, we have developed an efficient and stereoselective one-pot method for the synthesis of trisubstituted 1,3-dienes via the hydrostannylation-Stille coupling tandem reaction of alkylarylacetylenes with alkenyl halides. The present method has the advantages of readily available starting materials, straightforward and simple procedures, mild reaction conditions and good yields. The procedure should find wide application to the synthesis of a large array of naturally occurring substances having the trisubstituted 1,3-diene system.

Experimental

^{1}H NMR spectra were recorded on a Bruker AC-P400 (400 MHz) spectrometer with TMS as an internal standard using $CDCl_3$ as the solvent. ^{13}C NMR (100 MHz) spectra were recorded on a Bruker AC-P400 (400 MHz) spectrometer using $CDCl_3$ as the solvent. IR spectra were determined on an FTS-185 instrument as neat films. Mass spectra were obtained on a Finnigan 8239 mass spectrometer. Microanalyses were measured using a Yanaco MT-3 CHN microelemental analyser. All reactions were carried out in pre-dried glassware (150 °C, 4 h) and cooled under a stream of dry Ar. THF was freshly distilled from sodium-benzophenone prior to use. DMF was dried by distillation over calcium hydride. Alkylarylacetylenes were prepared according to the literature procedure.[23]

*General procedure for the synthesis of trisubstituted 1,3-dienes (**4a–j**)*

A 25 mL, two-necked, round-bottom flask equipped with a magnetic stir bar and argon was charged sequentially with the alkylarylacetylene (1.0 mmol), THF (2 mL), $PdCl_2(PPh_3)_2$ (0.03 mmol) and Bu_3SnH (1.1 mmol). The mixture was stirred at 25 °C for 30 min. Then the solvent was removed under reduced pressure and the residue was dissolved in DMF (8 mL). The alkenyl halide (1.1 mmol) and CuI (0.75 mmol) were added and the mixture was stirred for 24 h at room temperature and monitored by TLC (SiO_2) for the disappearance of the intermediate **2**. The reaction mixture was diluted with diethyl ether (30 mL), filtered and then treated with 20% aqueous KF (10 mL) for 30 min before being dried and concentrated. The residue was purified by column chromatography on silica gel, eluting either with a mixture of diethyl ether and petroleum ether or just petroleum ether.

(1E,3Z)-1,3-Diphenyldeca-1,3-diene (**4a**): Oil. IR (neat): ν (cm^{-1}) 3059, 3027, 2927, 2854, 1708, 1598, 1494, 1456, 1377, 962, 750, 702; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43–7.39 (m, 2H), 7.35–7.24 (m, 5H), 7.19–7.16 (m, 3H), 7.01 (d, *J* = 16.0 Hz, 1H), 5.98 (d, *J* = 16.0 Hz, 1H), 5.86 (t, *J* = 7.6 Hz, 1H), 1.98–1.94 (m, 2H), 1.36–1.20 (m, 8H), 0.85 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.2, 138.2, 137.7, 135.1, 133.4, 129.6, 129.0, 128.5 128.2, 127.0, 126.8, 126.2, 31.7, 29.7, 29.3, 28.9, 22.6, 14.1; MS (EI, 70 eV): *m/z* 290 (M$^+$, 12), 219 (29), 205 (39), 105 (90), 57 (100). Anal. Calcd for $C_{22}H_{26}$: C, 90.98; H, 9.02. Found: C, 90.71; H, 9.25%.

(5E,7Z)-7-Phenyltetradeca-5,7-diene (**4b**): Oil. IR (neat): ν (cm^{-1}) 3058, 2932, 2860, 1724, 1600, 1493, 1465, 1379, 963, 703; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37–7.27 (m, 3H), 7.10 (d, *J* = 7.2 Hz, 2H), 6.23 (d, *J* = 15.6 Hz, 1H), 5.58 (t, *J* = 7.6 Hz, 1H), 5.10 (dt, *J* = 15.6, 7.6 Hz, 1H), 2.05–2.00 (m, 2H), 1.90–1.85 (m, 2H), 1.34–1.16 (m, 12H), 0.89–0.84 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.1, 139.0, 134.2, 131.6, 131.3, 129.6, 127.9, 126.5, 32.5, 31.7, 31.6, 29.8, 28.9, 28. 9, 22.6, 22.3, 14.06, 13.9; MS (EI, 70 eV): *m/z* 270 (M$^+$, 1.1), 159 (24), 105 (100), 77 (41). Anal. Calcd for $C_{20}H_{30}$: C, 88.82; H, 11.18. Found: C, 88.59; H, 11.37%.

(2E,4Z)-1-Methoxy-4-phenylundeca-2,4-diene (**4c**): Oil. IR (neat): ν (cm^{-1}) 3058, 2927, 2854, 1729, 1595, 1493, 1449, 1122, 960, 703; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (t, *J* = 7.4 Hz, 2H), 7.27 (m, 1H), 7.12 (d, *J* = 6.8 Hz, 2H), 6.45 (d, *J* = 15.6 Hz, 1H), 5.72 (t, *J* = 7.6 Hz, 1H), 5.21 (dt, *J* = 15.6, 6.4 Hz, 1H), 3.91 (d, *J* = 6.4 Hz, 2H), 3.30 (s, 3H), 1.94–1.88 (m, 2H), 1.34–1.16 (m, 8H), 0.84 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.3, 138.2, 137.1, 134.4, 129.5, 128.1, 126.8, 126.1, 73.1, 58.0, 31.7, 29.6, 29.1, 28.9, 22.6, 14.10; MS (EI, 70 eV): *m/z* 258 (M$^+$, 1.5), 120 (35), 105 (100), 77 (57). Anal. Calcd for $C_{18}H_{26}O$: C, 83.67; H, 10.14. Found: C, 83.43; H, 9.97%.

(7Z,9E)-8-Tolylhexadeca-7,9-diene (**4d**): Oil. IR (neat): ν (cm^{-1}) 3057, 2926, 2858, 1712, 1600, 1493, 1456, 1378, 961, 702; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.20 (d, *J* = 15.6 Hz, 1H), 5.51 (t, *J* = 7.6 Hz, 1H), 5.06 (dt, *J* = 15.6, 7.6 Hz, 1H), 2.35 (s, 3H), 2.02–1.97 (m, 2H), 1.90–1.84 (m, 2H), 1.35–1.15 (m, 16H), 0.90–0.85 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.3, 139.4, 134.4, 132.2, 131.8, 130.2, 126.8, 125.2, 32.9, 31.7, 31.7, 29.9, 29.8, 29.4, 28.9, 28.9, 22.6, 21.6, 14.1, 14.0; MS (EI, 70 eV): *m/z* 312 (M$^+$, 1.8), 91 (45), 57 (100). Anal. Calcd for $C_{23}H_{36}$: C, 88.39; H, 11.61. Found: C, 88.13; H, 11.84%.

(2E,4Z)-1-Methoxy-4-phenyl-2,4-nonadiene (**4e**): Oil. IR (neat): ν (cm^{-1}) 2957, 2926, 1597, 1464, 1379, 1122, 968, 703; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34–7.26 (m, 3H), 7.12–7.10 (m, 2H), 6.45 (d, *J* = 15.6 Hz, 1H), 5.72 (t, *J* = 7.2 Hz, 1H), 5.20 (dt, *J* = 15.6, 6.0 Hz, 1H), 3.91 (d, *J* = 6.0 Hz, 2H), 3.30 (s, 3H), 1.95–1.89 (m, 2H), 1.33–1.19 (m, 4H), 0.85 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.3, 138.2, 137.1, 134.4, 129.5, 128.1, 126.8, 126.1, 73.1, 57.9, 31.9, 28.8, 22.3, 14.0; MS (EI, 70 eV): *m/z* 230 (M$^+$, 6), 105 (100), 77 (54), 57 (65). Anal. Calcd for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.20; H, 9.82%.

(1E,3Z)-1,3-Diphenylocta-1,3-diene (**4f**): Oil. IR (neat): ν (cm^{-1}) 3060, 3029, 2956, 2871, 1705, 1599, 1494, 1455, 1379, 965, 754, 700; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43–7.39 (m, 2H), 7.35–7.24 (m, 5H), 7.21–7.14 (m, 3H), 6.99 (d, *J* = 16.0 Hz, 1H), 5.98 (d, *J* = 16.0 Hz, 1H), 5.86 (t, *J* = 7.6 Hz, 1H), 2.00–1.94 (m, 2H), 1.39–1.31 (m, 2H), 1.29–1.22 (m, 2H), 0.83 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.2, 138.2, 137.7, 135.1, 133.4, 129.6, 129.1, 128.5, 128.1, 127.0, 126.8, 126.2, 31.9, 29.0, 22.3, 13.9; MS (EI, 70 eV): *m/z* 262 (M$^+$, 8.5), 105 (100), 77 (56), 57 (87). Anal. Calcd for $C_{20}H_{22}$: C, 91.55; H, 8.45. Found: C, 91.28; H, 8.67%.

(5Z,7E)-6-Phenyldodeca-5,7-diene (**4g**): Oil. IR (neat): ν (cm^{-1}) 3058, 3023, 2958, 2872, 1723, 1600, 1494, 1466, 1379, 983, 703; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37–7.27 (m, 3H), 7.10 (d, *J* = 7.6 Hz, 2H), 6.23 (d, *J* = 15.6 Hz, 1H), 5.58 (t, *J* = 7.6 Hz, 1H), 5.11 (dt, *J* = 15.6, 7.6 Hz, 1H), 2.06–2.00 (m, 2H), 1.93–1.86 (m, 2H), 1.33–1.20 (m, 8H), 0.87–0.79 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.1, 139.0, 134.2, 131.6, 131.3, 129.5, 127.9, 126.5, 32.5, 32.1, 31.6, 28.7, 22.3, 22.3, 13.9, 13.9; MS (EI, 70 eV): *m/z* 242 (M$^+$, 1.3), 105 (100), 77 (47). Anal. Calcd for $C_{18}H_{26}$: C, 89.19; H, 10.81. Found: C, 88.97; H, 10.97%.

(1E,3Z)-1,3-Diphenylpenta-1,3-diene (**4h**): Oil. IR (neat): ν (cm^{-1}) 3058, 3026, 1625, 1598, 1494, 962, 702; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44–7.14 (m, 10H), 6.99 (d, *J* = 16.0 Hz, 1H), 6.01 (d, *J* = 16.0 Hz, 1H), 5.95 (q, *J* = 6.8 Hz, 1H), 1.63 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.3, 142.2, 140.5, 138.0, 137.7, 129.7, 128.9, 128.5, 127.7, 127.0, 126.8, 126.2, 15.18; MS (EI, 70 eV): *m/z* 220 (M$^+$, 4.7), 105 (100), 77 (67). Anal. Calcd for $C_{17}H_{16}$: C, 92.68; H, 7.32. Found: C, 92.41; H, 7.53%.

(1E,3Z)-1-Phenyl-3-(4-chlorophenyl)-6-methoxyhexa-1,3-diene (**4i**): Oil. IR (neat): ν (cm^{-1}) 3057, 3032, 2958, 1703, 1601, 1496, 1179, 1123, 962, 753, 702; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43–7.15 (m, 9H), 7.01 (d, *J* = 16.0 Hz, 1H), 6.02 (d, *J* = 16.0 Hz, 1H), 5.91

(t, J = 7.6 Hz, 1H), 3.51 (t, J = 6.4 Hz, 2H), 3.29 (s, 3H), 2.97–2.91 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.8, 139.1, 137.8, 135.7, 134.8, 129.8, 129.6, 128.8, 128.57, 127.3, 127.0, 126.3, 69.4, 58.1, 31.2; MS (EI, 70 eV): *m/z* 298 (M^+, ^{35}Cl, 2.1), 105 (100), 77 (51). Anal. Calcd for $C_{19}H_{19}OCl$: C, 76.36; H, 6.41. Found: C, 76.11; H, 6.23%.

(2Z,4E)-1-Methoxy-3-(2-methoxyphenyl)-2,4-nonadiene (**4j**): Oil. IR (neat): v (cm^{-1}) 3058, 2957, 2925, 1721, 1597, 1490, 1465, 1240, 1113, 967, 749; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21–7.17 (m, 1H), 6.91–6.86 (m, 2H), 6.82 (d, J = 8.4 Hz, 1H), 6.25 (d, J = 15.6 Hz, 1H), 5.93 (t, J = 6.4 Hz, 1H), 5.19 (dt, J = 15.6, 7.6 Hz, 1H), 4.00–3.97 (m, 2H), 3.79 (s, 3H), 3.30 (s, 3H), 2.05–2.00 (m, 2H), 1.27–1.16 (m, 4H), 0.84 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.4 146.5, 137. 6, 134.2, 132.7, 131.3, 128.4, 127.1, 120.4, 110.0, 70.4, 57.8, 55.1, 32.2, 31.2, 22.3, 14.0; MS (EI, 70 eV): *m/z* 260 (M^+, 4.1), 57 (100), 45 (52). Anal. Calcd for $C_{17}H_{24}O_2$: C, 78.42; H, 9.29. Found: C, 78.17; H, 9.38%.

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