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ONE-POT, STEREOSELECTIVE SYNTHESIS OF TRISUBSTITUTED 1,3-DIENES BY HYDROMAGNESIATION–CROSS-COUPLING TANDEM REACTION OF ALKYLARYLACETYLENES WITH ALKENYL IODIDES

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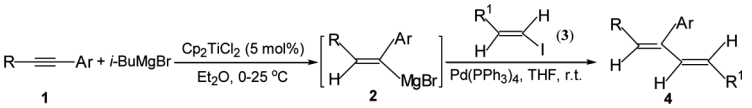
GRAPHICAL ABSTRACT



Abstract *Trisubstituted 1,3-dienes can be stereoselectively synthesized in one pot under mild conditions, in good yields, by hydromagnesiation of alkylarylacetylenes, followed by the palladium-catalyzed cross-coupling with alkenyl iodides.*

Keywords Alkylarylacetylene; cross-coupling; 1,3-diene; hydromagnesiation; tandem reaction

INTRODUCTION

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] The synthesis of 1,3-dienes for use in the Diels–Alder reaction is still an important challenge in organic synthesis,[2] although other elegant uses of these compounds have been developed.[3] Conjugated dienes are usually prepared by utilizing either a Wittig-type approach[4] or through transition-metal-catalyzed coupling reactions of stereodefined vinyl halides with vinyl organometallic compounds.[5] Whitby et al. reported the insertion of 1-lithio-1-halo-butadiene into organozirconocenes derived from the hydrozirconation of alkynes, providing a stereocontrolled synthesis of (1*E*,3*Z*)-1,3-dienes.[6] Recently, Molander and Yokoyama reported a one-pot stereoselective

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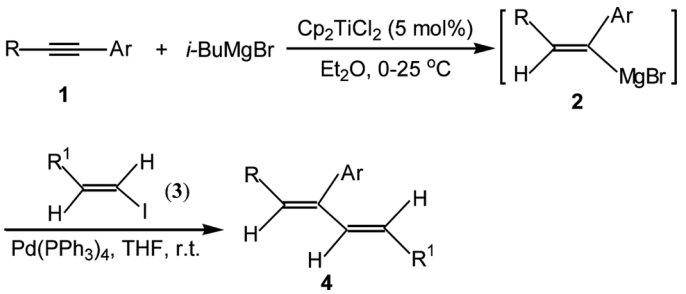
synthesis of trisubstituted 1,3-dienes via sequential Suzuki–Miyaura cross-coupling of 1,1-dibromoalkenes with alkenyl- and alkyltrifluoroborates.[7]

The transition-metal-catalyzed cross-coupling reaction is a highly versatile method for carbon–carbon bond formation and has been widely used as a synthetic tool.[8] Hydromagnesiation has emerged as a unique hydrometallation with some attractive features such as the high regioselectivity and stereoselectivity observed with alkylarylacetylenes[9] and alkynylsilanes.[10] Recently, we reported the stereoselective synthesis of (*E*)-1,2-disubstituted vinylstannanes[11] and (*E*)-1,2-disubstituted vinylic selenides[12] via the hydromagnesiation of alkylarylacetylenes. Herein we report that trisubstituted 1,3-dienes could be stereoselectively synthesized in one pot under mild conditions, in good yields, by hydromagnesiation of alkylarylacetylenes, followed by the palladium-catalyzed cross-coupling with alkenyl iodides.

RESULTS AND DISCUSSION

Alkylarylacetylenes **1** were prepared according to the literature procedure.[13] It is well known that the hydromagnesiation of alkylarylacetylenes **1** with *i*-BuMgBr in diethyl ether proceeds highly regio- and stereoselectively to generate (*E*)-α-arylvinyl Grignard reagents **2**, and the addition of H-Mg to alkylarylacetylenes is in pure *syn*-fashion.[9] To extend the application of the hydromagnesiation reaction of alkylarylacetylenes, considering the fact that alkenyl halides are efficient electrophiles and can undergo cross-coupling reaction with vinyl Grignard reagents in the presence of transition-metal catalysts, we investigated the palladium-catalyzed cross-coupling reaction of alkenyl halides with (*E*)-α-arylvinyl Grignard reagents **2** obtained by hydromagnesiation of alkylarylacetylenes **1** (Scheme 1).

We found that the trisubstituted 1,3-dienes **4** were obtained in good yields after the hydromagnesiation reaction of alkylarylacetylenes **1** with *i*-BuMgBr using 5 mol% Cp_2TiCl_2 in diethyl ether at 25 °C for 1 h, solvent removal under reduced pressure, and stirring of the residue with tetrahydrofuran (THF), alkenyl iodides (**3**), and 5 mol% $Pd(PPh_3)_4$ at room temperature for 8 h. The experimental results are summarized in Table 1. As shown in Table 1, the hydromagnesiation–cross-coupling tandem reaction of *i*-BuMgBr 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 cross-coupling reaction



Scheme 1. Synthesis of trisubstituted 1,3-dienes.

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

Entry	R	Ar	R^1	Product	Yield[a] (%)
1	n-C_6H_{13}	Ph	n-C_4H_9	**4a**	86
2	n-C_6H_{13}	Ph	Ph	**4b**	82
3	n-C_6H_{13}	Ph	CH_3OCH_2	**4c**	85
4	n-C_6H_{13}	4-$CH_3C_6H_4$	n-C_6H_{13}	**4d**	88
5	n-C_4H_9	Ph	CH_3OCH_2	**4e**	83
6	n-C_4H_9	Ph	Ph	**4f**	80
7	n-C_4H_9	Ph	n-C_4H_9	**4g**	87
8	CH_3	Ph	Ph	**4h**	84
9	$CH_3OCH_2CH_2$	4-ClC_6H_4	Ph	**4i**	79

[a]Isolated yield based on alkenyl iodide **3**.

of the intermediates **2** with alkenyl bromides was very slow under the same reaction conditions, and only traces of coupled products were obtained after 24 h of reaction time.

Investigation of the crude products **4** by ^{1}H NMR spectroscopy (400 MHz) showed isomeric purities of more than 97%. One olefinic proton signal of compounds **4a–i** except for **4h** splits characteristically into one triplet at $\delta = 5.51$–5.91 with coupling constant $J = 7.2$–7.6 Hz, which indicated that the hydromagnesiation to the alkylarylacetylenes had taken place with strong preference for the addition of the magnesium atom at the carbon adjacent to the aryl group. It is well documented that the cross-coupling reaction of vinyl Grignard reagents with alkenyl halides occurs with the configuration retention of both the starting vinyl Grignard reagents and the alkenyl halides.[14] The (*E*)-configuration of the compounds **4a–i** has been proved 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, and this is also the evidence of the retention of the (*E*)-configuration of the starting alkenyl iodides. In addition, the (*Z*)-configuration of the compound **4c** was confirmed by nuclear overhauser effect spectroscopy (NOESY) in the ^{1}H NMR spectrum (Fig. 1). An enhancement of the allylic protons was observed as the vinylic proton ($\delta = 5.72$) of **4c** was irradiated. There was no correlation between the vinylic proton ($\delta = 5.72$) and aromatic protons. The correlation between the allylic protons and aromatic protons was observed. The correlation between the vinylic proton ($\delta = 5.72$) and another vinylic proton ($\delta = 6.45$) was also observed. The NOE results indicate that the compound **4c** has the expected (*Z*)-configuration and the Pd-catalyzed cross-coupling reaction of (*E*)-α-arylvinyl Grignard reagents **2** with alkenyl iodides occurs with the configuration retention of both the starting intermediates **2** and the alkenyl iodides.

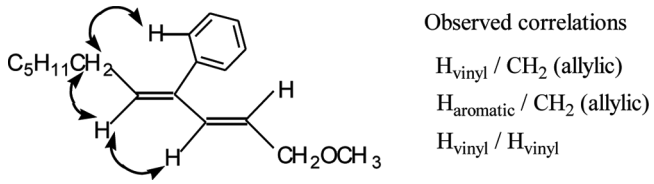


Figure 1. NOESY spectrum of compound **4c**.

EXPERIMENTAL

^{1}H NMR spectra were recorded on a Bruker AC-P400 (400-MHz) spectrometer with tetramethylsilene (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. Infrared (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 analyzer. All reactions were carried out in predried glassware (150 °C, 4 h) and cooled under a stream of dry Ar. Diethyl ether was treated with lithium aluminum hydride and distilled before use. Tetrahydrofuran (THF) was freshly distilled from sodium-benzophenone prior to use.

General Procedure for the Synthesis of Trisubstituted 1,3-Dienes (4a–i)

Cp_2TiCl_2 (25 mg, 0.1 mmol) was added to a solution of isobutylmagnesium bromide (2.5 mmol) in diethyl ether (4 mL) at 0 °C under Ar, and the mixture was stirred for 30 min at that temperature. Alkylarylacetylene **1** (2.0 mmol) was added to this solution, and the mixture was stirred for 1 h at 25 °C. After removal of the ether under reduced pressure (2 h, rt/2 Torr), the residue was dissolved in THF (4 mL) and cooled to 0 °C, and $Pd(PPh_3)_4$ (0.116 g, 0.1 mmol) and alkenyl iodide **3** (1.8 mmol) were added with stirring. The reaction mixture was brought to 30 °C gradually, stirred for 8 h, quenched with saturated aqueous NH_4Cl (15 mL), and extracted with Et_2O (2×30 mL). The organic layer was washed with saturated aqueous NH_4Cl (20 mL) and water (2×20 mL) and dried ($MgSO_4$). Removal of solvent under reduced pressure gave an oil, which was purified by column chromatography on silica gel using light petroleum as eluent.

Selected Data

(5*E*,7*Z*)-7-Phenyl-5,7-tetradecadiene (4a). Oil. ^{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 141.06, 138.98, 134.19, 131.59, 131.33, 129.55, 127.93, 126.48, 32.49, 31.68, 31.56, 29.82, 28.93, 28.89, 22.59, 22.28, 14.06, 13.94; IR (neat): ν (cm^{-1}) 3058, 2932, 2860, 1724, 1600, 1493, 1465, 1379, 963, 703; MS (EI, 70 eV): m/z 270 (M^+, 1.1), 159 (24), 105 (100), 77 (41). Anal. calc. for $C_{20}H_{30}$: C, 88.82; H, 11.18. Found: C, 88.59; H, 11.37%.

(1*E*,3*Z*)-1,3-Diphenyl-1,3-decadiene (4b). Oil. ^{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 141.24, 138.23, 137.72, 135.14, 133.39, 129.62, 129.04, 128.47, 128.16, 126.97, 126.84, 126.19, 31.66, 29.69, 29.29, 28.89, 22.59, 14.08; IR (neat): ν (cm^{-1}) 3059, 3027, 2927, 2854, 1708, 1598, 1494, 1456, 1377, 962, 750, 702; MS (EI, 70 eV): m/z 290 (M^+, 12), 219

(29), 205 (39), 105 (90), 77 (62), 57 (100). Anal. calc. for $C_{22}H_{26}$: C, 90.98; H, 9.02. Found: C, 90.71; H, 9.25%.

(2*E*,4*Z*)-1-Methoxy-4-phenyl-2,4-undecadiene (4c). Oil. ^{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 140.32, 138.19, 137.09, 134.44, 129.49, 128.09, 126.75, 126.06, 73.10, 57.95, 31.66, 29.62, 29.06, 28.86, 22.60, 14.10; IR (neat): ν (cm^{-1}) 3058, 2927, 2854, 1729, 1595, 1493, 1449, 1122, 960, 703; MS (EI, 70 eV): m/z 258 (M^+, 1.5), 120 (35), 105 (100), 77 (57). Anal. calc. for $C_{18}H_{26}O$: C, 83.67; H, 10.14. Found: C, 83.43; H, 9.97%.

(7*Z*,9*E*)-8-Tolyl-7,9-hexadecadiene (4d). Oil. ^{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 141.25, 139.38, 134.35, 132.19, 131.84, 130.23, 126.83, 125.19, 32.86, 31.74, 31.68, 29.85, 29.75, 29.36, 28.94, 28.89, 22.62, 21.56, 14.08, 14.04; IR (neat): ν (cm^{-1}) 3057, 2926, 2858, 1712, 1600, 1493, 1456, 1378, 961, 702; MS (EI, 70 eV): m/z 312 (M^+, 1.8), 91 (45), 57 (100). Anal. calc. for $C_{23}H_{36}$: C, 88.39; H, 11.61. Found: C, 88.13; H, 11.84%.

(2*E*,4*Z*)-1-Methoxy-4-phenyl-2,4-nonadiene (4e). Oil. ^{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 140.34, 138.18, 137.09, 134.39, 129.49, 128.10, 126.75, 126.08, 73.10, 57.93, 31.85, 28.80, 22.26, 13.95; IR (neat): ν (cm^{-1}) 2957, 2926, 1597, 1464, 1379, 1122, 968, 703; MS (EI, 70 eV): m/z 230 (M^+, 6), 105 (100), 77 (54), 57 (65). Anal. calc. for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.20; H, 9.82%.

(1*E*,3*Z*)-1,3-Diphenyl-1,3-octadiene (4f). Oil. ^{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 141.24, 138.21, 137.71, 135.07, 133.36, 129.60, 129.05, 128.46, 128.14, 126.95, 126.83, 126.18, 31.90, 29.00, 22.27, 13.91; IR (neat): ν (cm^{-1}) 3060, 3029, 2956, 2871, 1705, 1599, 1494, 1455, 1379, 965, 754, 700; MS (EI, 70 eV): m/z 262 (M^+, 8.5), 105 (100), 77 (56), 57 (87). Anal. calc. for $C_{20}H_{22}$: C, 91.55; H, 8.45. Found: C, 91.28; H, 8.67%.

(5*Z*,7*E*)-6-Phenyl-5,7-dodecadiene (4g). Oil. ^{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 141.06, 138.97, 134.17, 131.60, 131.28, 129.54, 127.93, 126.48, 32.48, 32.05, 31.55, 28.65, 22.27, 22.26, 13.94, 13.92; IR (neat): ν (cm^{-1}) 3058, 3023, 2958, 2872, 1723,

1600, 1494, 1466, 1379, 983, 703; MS (EI, 70 eV): m/z 242 (M^+, 1.3), 105 (100), 77 (47). Anal. calc. for $C_{18}H_{26}$: C, 89.19; H, 10.81. Found: C, 88.97; H, 10.97%.

(1*E*,3*Z*)-1,3-Diphenyl-1,3-pentadiene (4h). Oil. ^{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 142.28, 142.18, 140.53, 137.96, 137.73, 129.73, 128.89, 128.48, 127.69, 126.95, 126.78, 126.19, 15.18; IR (neat): ν (cm^{-1}) 3058, 3026, 1625, 1598, 1494, 962, 702; MS (EI, 70 eV): m/z 220 (M^+, 4.7), 105 (100), 77 (67). Anal. calc. for $C_{17}H_{16}$: C, 92.68; H, 7.32. Found: C, 92.41; H, 7.53%.

(1*E*,3*Z*)-1-Phenyl-3-(4-chlorophenyl)-6-methoxy-1,3-hexadiene (4i). Oil. ^{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 141.76, 139.05, 137.84, 135.69, 134.78, 129.75, 129.55, 128.82, 128.57, 127.25, 126.96, 126.34, 69.36, 58.13, 31.21; IR (neat): ν (cm^{-1}) 3057, 3032, 2958, 1703, 1601, 1496, 1179, 1123, 962, 753, 702; MS (EI, 70 eV): m/z 298 (M^+, ^{35}Cl, 2.1), 105 (100), 77 (51). Anal. calc. for $C_{19}H_{19}OCl$: C, 76.36; H, 6.41. Found: C, 76.11; H, 6.23%.

CONCLUSION

In summary, we have developed an efficient and stereoselective one-pot method for the synthesis of trisubstituted 1,3-dienes via the hydromagnesiation–cross-coupling tandem reaction of alkylarylacetylenes with *i*-BuMgBr and alkenyl iodides. 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.

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