A Novel Stereoselective Synthesis of Symmetrical (1*E*,3*E*)-1,4-Diarylbuta-1,3-dienes

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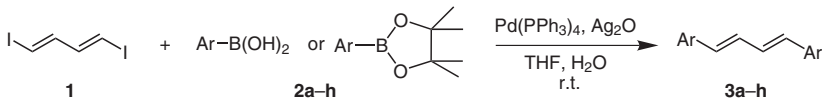
Abstract: A convenient methodology for the stereoselective synthesis of symmetrical (1*E*,3*E*)-1,4-diarylbuta-1,3-dienes based on palladium-catalyzed Suzuki–Miyaura cross-coupling reaction of (1*E*,3*E*)-1,4-diiodobuta-1,3-diene with arylboronic reagents is reported.

Key words: diene, Suzuki cross-coupling reaction, stereoselective synthesis, palladium



Scheme 1

Introduction

The synthesis of stereodefined conjugated dienes is a topic of considerable interest because this structural motif is frequently met in biologically active compounds such as, for example, pheromones,[1] and in organic materials used as fluorescent probes,[2] dopant emitters in electroluminescent devices,[3] or nonlinear optical chromophores.[4] Moreover, these molecules are useful substrates in various reactions, the most common being Diels–Alder cyclizations.[5]

Several synthetic routes to functionalized conjugated dienes have been developed. Among them, methodologies based on the Wittig alkenation of aldehydes,[6] the rearrangement of cyclopropylcarbinyl derivatives,[7] intermolecular enyne metathesis,[8] and anil synthesis with Schiff bases and propenyl substrates[9] have found various applications. However, many of these strategies suffer from poor stereocontrol on formation of the conjugated double bonds.

Alternative synthetic approaches involve transition-metal-catalyzed coupling reactions[10] of vinyl organometallic compounds and/or alkenyl electrophiles. The homocoupling of alkenylstannanes,[11] vinylboronic acids[12] or unsaturated silanes,[13] as well as the metal-promoted reductive dimerization of vinyl halides[14] have been used as synthetic tools for the synthesis of symmetrically functionalized buta-1,3-dienes. A number of methodologies for the preparation of unsymmetrically functionalized buta-1,3-dienes have also been developed based on cross-coupling reactions of vinyl halides or triflates with alkenyl-substituted organometallic compounds such as vinylboron,[15] -tin,[16] -zinc,[17] -germanium,[18] -zirconium,[19] or -magnesium[20] derivatives. In many cases these homocoupling and cross-coupling processes are highly stereoselective.

High stereoselectivity has been also achieved in synthetic methods involving coupling reactions of preformed dienyl moieties bearing nucleophilic or electrophilic reactive sites.

Examples involving nucleophilic dienyl building blocks are represented by the cross-coupling of aryl halides with mono- or bis-metalated buta-1,3-dienyl reagents such as 2-aryl-3-silyl-,[21] 1,4-bis-silyl-,[22] or 1-boryl-4-stannylbuta-1,3-dienes.[23] 1,4-Bis-silylated dienes have also been used in acylation reactions with carboxylic acid chloride–aluminum trichloride complexes.[24]

The complementary approach based on cross-coupling reactions of organometallic reagents with bis-electrophilic buta-1,3-dienes has not been extensively investigated, with the exception of a few examples including cross-coupling processes of Grignard reagents with 2,3-dichlorobuta-1,3-diene,[25] (1*E*,3*E*)-1,4-diiodobuta-1,3-diene (**1**),[26] and (1*E*,3*E*)-1-bromo-4-(phenylthio)buta-1,3-diene,[27] the latter two proceed with complete retention of double bond configuration.

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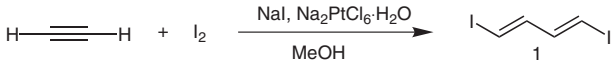
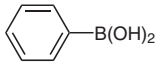
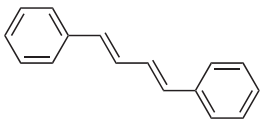
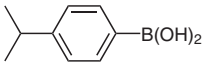
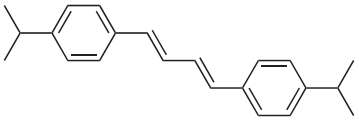
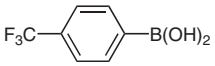
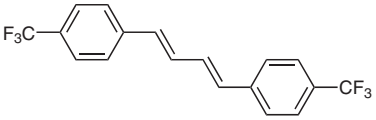
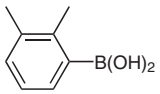
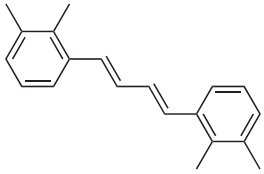
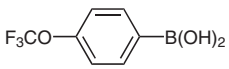
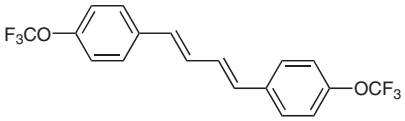
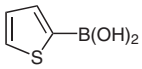
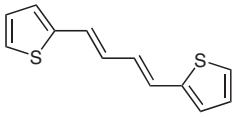
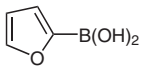
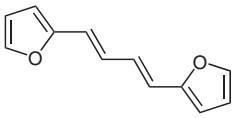
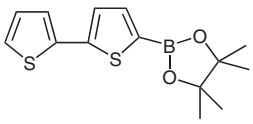
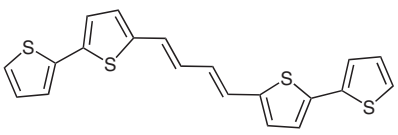
Scope and Limitations

In the framework of our studies on the stereoselective synthesis of polyconjugated organic compounds,[28] we have developed a convenient protocol for the preparation of all-*E* symmetrical 1,4-diarylbuta-1,3-dienes that is based on the palladium-catalyzed Suzuki–Miyaura cross-coupling reaction of aromatic boronic derivatives with (1*E*,3*E*)-1,4-diiodobuta-1,3-diene (**1**) (Scheme 1). As reported by Beletskaya et al.,[29] diiodobutadiene **1** can be easily prepared by dimerization of acetylene accompanied by addition of iodine in the presence of a platinum(IV) catalyst and sodium iodide (Scheme 2) and it can be isolated by crystallization (H_2O–MeOH).



Scheme 2 Synthesis of (1*E*,3*E*)-1,4-diiodobuta-1,3-diene

Table 1 Suzuki–Miyaura Cross-Coupling Reaction between the (1*E*,3*E*)-1,4-Diiodobuta-1,3-diene (**1**) and Boronic Reagents

Entry	Boronic reagent	Diene	Yield[a] (%)
1	 **2a**	 **3a**	95
2	 **2b**	 **3b**	80
3	 **2c**	 **3c**	45
4	 **2d**	 **3d**	67
5	 **2e**	 **3e**	84
6	 **2f**	 **3f**	90
7	 **2g**	 **3g**	86
8	 **2h**	 **3h**	87

[a] Yields refer to pure isolated products.

The simple synthesis of **1** made it particularly attractive in our search for an electrophilic butadienyl building block for cross-coupling reactions with organometallic reagents, especially if compared with the corresponding chloro derivative (1*E*,3*E*)-1,4-dichlorobuta-1,3-diene[30] or with the all-*Z* counterparts (1*Z*,3*Z*)-1,4-diiodo-[31] and (1*Z*,3*Z*)-1,4-dibromobuta-1,3-diene,[32] whose syntheses appear complicated.

Although one example of the cross-coupling of butadiene **1** with phenylmagnesium bromide was described by Beletskaya et al.,[26] we preferred to investigate the Suzuki–Miyaura reaction, which appears more convenient, both in terms of organometallic substrate availability and experimental conditions, as a general approach to convert stereoselectively **1** into diaryl-functionalized butadienes.

To check both scope and limitations of the methodology proposed, **1** was coupled with commercially available arylboronic acids **2a**–**g** (Scheme 1). The coupling reactions were performed in tetrahydrofuran/water using tetrakis(triphenylphosphine)palladium(0) [$Pd(PPh_3)_4$] as the catalyst, in the presence of silver oxide as the base, and at room temperature. Due to the mild experimental conditions, the process tolerates the presence of various substituents in the arylboronic acid reagent, affording functionalized 1,4-diarylbuta-1,3-dienes (Table 1) in good to excellent yields, with the exception of the arylboronic acid **2c**, functionalized with the strongly electron-withdrawing trifluoromethyl group (entry 3), which gave diene **3c** in only 45% yield. The coupling reaction appears to be slightly sensitive to sterical hindrance by the methyl group *ortho* to the boronic functionality in **2d**, as shown by the decrease in yield to 67% (entry 4). The process is also very efficient with heteroarylboronic acids, such as thienyl and furyl reagents (entries 6 and 7). A boronic ester can be used in place of the corresponding acid, as in the case of 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2′-bithiophene (**2h**) (Scheme 1 and Table 1, entry 8). This example also shows the versatility of our approach for the synthesis of extended conjugated systems of potential interest as organic molecular semiconductors and materials for nonlinear optics.

The stereochemistry of dienes **3a**–**h** can not be directly derived from the ^{1}H NMR spectra on the basis of the coupling constants of the protons of the diene moiety, because they appear as a second order AA′BB′ spin system. However, the analysis of this spin system by means of MestReC NMR software allowed us to define the coupling constant values J(AB) = J(A′B′) ~ 16 Hz, J(BB′) = 9–11 Hz, J(AB′) = 0–2 Hz, J(AA′) ~ 0 Hz for **3a**–**h**, which are characteristic of a (1*E*,3*E*)-diene structure.

Therefore, the spectral analysis shows that the reaction proceeds with complete retention of configuration of the 1,3-dienyl moiety of **1**, thus leading only to stereodefined (1*E*,3*E*)-1,4-diarylbuta-1,3-dienes.

In summary, a simple highly stereoselective route to all-*E* symmetrical 1,4-diaryl dienes has been described that starts from easily available reagents and that can be also used for the synthesis of extended conjugated systems.

Arylboronic reagents **2a**–**h**, $Pd(PPh_3)_4$, and Ag_2O (Lancaster and Aldrich) were used without further purification. THF was distilled from Na/benzophenone under N_2 immediately prior to use. H_2O–THF mixture used as the reaction solvent was carefully degassed by bubbling N_2. The diiodobutadiene **1** was prepared according to the literature[29] and it was stored at 4 °C. Column chromatography was performed using silica gel 60, 40–63 μm from Merck. FT-IR spectra were measured on a Perkin Elmer Spectrum BX spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker AM 500 spectrometer. For peak multiplicity, standard abbreviations are used; in addition, 'd like' is used to describe pattern which rigorously cannot be a doublet but experimentally appear like broad doublets because of the presence of longe-range low coupling constants. MS spectra were recorded on a Polaris Q Thermo Electron Corporation spectrometer. Elemental analyses were performed on a Carlo Erba CHNS-O EA1108-Elemental Analyzer.

(1*E*,3*E*)-1,4-Diarylbuta-1,3-dienes 3a–h; General Procedure

A mixture of (1*E*,3*E*)-1,4-diiodobuta-1,3-diene (**1**, 306 mg, 1 mmol), arylboronic acid **2a**–**g** or ester **2h** (2.5 mmol), catalyst $Pd(PPh_3)_4$ (23 mg, 0.02 mmol), and Ag_2O (695 mg, 3 mmol) in THF (12 mL) and H_2O (3 mL) was stirred at r.t. for 12 h. The mixture was subsequently filtered to remove Ag_2O. The organic soln was extracted with hexane (3 × 15 mL) [CH_2Cl_2 (3 × 25 mL) was used for **3h**] and the organic extracts were dried (anhyd Na_2SO_4). After distillation of the solvent at reduced pressure, the crude product was purified by column chromatography (silica gel, petroleum ether or, in the case of **3d** and **3h**, petroleum ether–CH_2Cl_2, 9.5:0.5 or 8:2, respectively).

(1*E*,3*E*)-1,4-Diphenylbuta-1,3-diene (3a)[9a]

Pale yellow solid; yield: 196 mg (95%); mp 149–150 °C (Lit.[9a] 150–153 °C).

IR (KBr): 3015, 1491, 1444, 1269, 990, 740, 690 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.64–6.73 (m, 2 H), 6.93–7.01 (m, 2 H), 7.21–7.27 (m, 2 H), 7.31–7.37 (m, 4 H), 7.43–7.47 (m, 4 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 126.34, 127.52, 128.61, 129.19, 132.77, 137.28.

GC-MS (EI, 70 eV): *m*/*z* (%) = 206 (100) [M]$^+$, 205 (44), 191 (46), 129 (13), 128 (36), 91 (44).

Anal. Calcd for $C_{16}H_{14}$: C, 93.16; H, 6.84. Found: C, 93.25; H, 6.90.

(1*E*,3*E*)-1,4-Bis(4-isopropylphenyl)buta-1,3-diene (3b)

Pale yellow solid; yield: 232 mg (80%); mp 139–141 °C.

IR (KBr): 3015, 2957, 1509, 1456, 992, 853, 805 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.26 (d, J = 6.9 Hz, 12 H), 2.90 (sept., J = 6.9 Hz, 2 H), 6.58–6.69 (m, 2 H), 6.86–6.96 (m, 2 H), 7.20 (d, J = 8.1 Hz, 4 H), 7.37 (d, J = 8.1 Hz, 4 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 23.90, 33.87, 126.30, 126.69, 128.61, 132.22, 135.08, 148.32.

GC-MS (EI, 70 eV): *m*/*z* (%) = 290 (29) [M]$^+$, 247 (32), 205 (100).

Anal. Calcd for $C_{22}H_{26}$: C, 90.98; H, 9.02. Found: C, 90.85; H, 8.93.

(1*E*,3*E*)-1,4-Bis[4-(trifluoromethyl)phenyl]buta-1,3-diene (3c)

Pale yellow solid; yield: 154 mg (45%); mp 145–147 °C.

IR (KBr): 1612, 1413, 1321, 1179, 1127, 1109, 1066, 1012, 989, 862, 807 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.71–6.79 (m, 2 H), 6.99–7.08 (m, 2 H), 7.54 (d, J = 8.3 Hz, 4 H), 7.60 (d, J = 8.3 Hz, 4 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 124.13 (q, $^1J_{C-F}$ = 271.7 Hz), 125.63 (q, $^3J_{C-F}$ = 3.7 Hz), 126.56, 129.45 (q, $^2J_{C-F}$ = 32.4 Hz), 130.92, 132.66, 140.37.

GC-MS (EI, 70 eV): *m*/*z* (%) = 342 (58) $[M]^+$, 323 (12), 273 (100), 233 (78), 204 (18), 159 (24).

Anal. Calcd for $C_{18}H_{12}F_6$: C, 63.16; H, 3.53. Found: C, 63.22; H, 3.57.

(1*E*,3*E*)-1,4-Bis(2,3-dimethylphenyl)buta-1,3-diene (3d)
Yellow solid; yield: 176 mg (67%); mp 180–182 °C.

IR(KBr): 3030, 2921, 1574, 1456, 1380, 1262, 1091, 988, 773, 734, 707 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.31 (s, 6 H), 2.32 (s, 6 H), 6.83–6.92 (m, 2 H), 6.93–7.02 (m, 2 H), 7.05–7.15 (m, 4 H), 7.42 (d like, *J* = ~7 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 15.30, 20.73, 123.36, 125.51, 129.13, 130.97, 131.13, 134.13, 136.52, 136.88.

GC-MS (EI, 70 eV): *m*/*z* (%) = 262 (25) $[M]^+$, 247 (100), 232 (48), 217 (18), 119 (10).

Anal. Calcd for $C_{20}H_{22}$: C, 91.55; H, 8.45. Found: C, 91.67; H, 8.53.

(1*E*,3*E*)-1,4-Bis[4-(trifluoromethoxy)phenyl]buta-1,3-diene (3e)
Pale orange solid; yield: 314 mg (84%); mp 97–99 °C.

IR(KBr): 3013, 1600, 1506, 1274, 1222, 1166, 988, 857 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.63–6.70 (m, 2 H), 6.87–6.94 (m, 2 H), 7.19 (d like, *J* = ~8 Hz, 4 H), 7.45 (d like, *J* = ~8 Hz, 4 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 120.46 (q, $^1J_{C-F}$ = 257.3 Hz), 121.19, 127.58, 129.70, 131.78, 135.89, 148.50 (q, $^3J_{C-F}$ = 1.9 Hz).

GC-MS (EI, 70 eV): *m*/*z* (%) = 374 (100) $[M]^+$, 289 (99), 249 (63), 203 (44), 202 (40), 175 (24).

Anal. Calcd for $C_{18}H_{12}F_6O_2$: C, 57.76; H, 3.23. Found: C, 57.60; H, 3.11.

(1*E*,3*E*)-1,4-Bis(2-thienyl)buta-1,3-diene (3f)[6c]
Pale yellow solid; yield: 197 mg (90%); mp 170–171 °C (Lit.[6c] 170 °C).

IR(KBr): 3098, 1599, 1506, 1421, 1252, 980, 858, 841, 801, 698 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.65–6.73 (m, 2 H), 6.73–6.81 (m, 2 H), 6.94–7.02 (m, 4 H), 7.18 (d like, *J* = ~5 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 124.43, 125.40, 125.91, 127.66, 128.47, 142.84.

GC-MS (EI, 70 eV): *m*/*z* (%) = 218 (100) $[M]^+$, 217 (53), 185 (42), 184 (67), 152 (12), 134 (9).

Anal. Calcd for $C_{12}H_{10}S_2$: C, 66.01; H, 4.62; S, 29.37. Found: C, 65.88; H, 4.54; S, 29.29.

(1*E*,3*E*)-1,4-Bis(2-furyl)buta-1,3-diene (3g)[6c]
Pale yellow solid; yield: 160 mg (86%); mp 90 °C (Lit.[6c] 95 °C).

IR(KBr): 3129, 1463, 1256, 1149, 1014, 988, 922, 883, 791, 736 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.29 (d, *J* = 3.3 Hz, 2 H), 6.40 (dd, *J* = 3.3, 1.8 Hz, 2 H), 6.40–6.48 (m, 2 H), 6.75–6.83 (m, 2 H), 7.38 (d, *J* = 1.8 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 108.57, 111.74, 120.17, 127.37, 142.19, 153.26.

GC/MS (EI, 70 eV): *m*/*z* (%) = 186 (100) $[M]^+$, 157 (46), 129 (39), 128 (47).

Anal. Calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41. Found: C, 77.51; H, 5.49.

(1*E*,3*E*)-1,4-Bis(2,2′-bithiophen-5-yl)buta-1,3-diene (3h)
Red solid; yield: 333 mg (87%); mp 210–212 °C.

IR(KBr): 3100, 3062, 3006, 1600, 1496, 1425, 1233, 1055, 970, 959, 837, 815, 785, 693 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.71–6.80 (m, 2 H), 6.86–6.95 (m, 2 H), 7.06–7.14 (m, 4 H), 7.24 (d, *J* = 3.7 Hz, 2 H), 7.33 (d, *J* = 3.5 Hz, 2 H), 7.53 (d, *J* = 5.0 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 124.15, 124.73, 125.41, 125.68, 127.94, 128.45, 128.57, 135.42, 136.36, 141.20.

Anal. Calcd for $C_{20}H_{14}S_4$: C, 62.79; H, 3.69; S, 33.53. Found: C, 62.90; H, 3.77; S, 33.62.

Acknowledgment

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