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A New Facile Synthesis of 2-Substituted 1,3-Butadiene Derivatives *via* Palladium-Catalyzed Cross-Coupling Reaction of 2,3-Alkadienyl Carbonates with Organoboron Compounds

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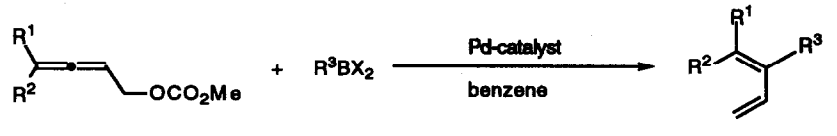
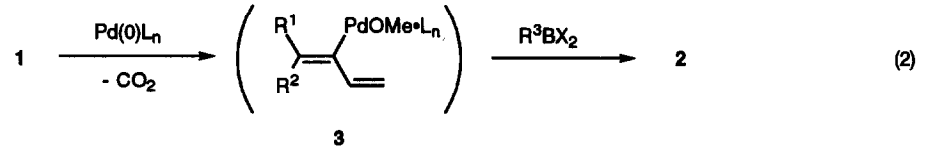
Abstract: A synthesis of 2-aryl-, 2-(1-alkenyl)-, and 2-alkyl-1,3-butadiene derivatives (**2**) by the palladium-catalyzed cross-coupling reaction of 2,3-butadienyl carbonates (**1**) with 9-alkyl-9-bicyclo[3.3.1]nonanes (9-alkyl-9-BBN), 1-alkenylboronic acids, or arylboronic acids is described. The reaction proceeded regioselectively with the palladium-phosphine complexes under neutral conditions.

The palladium-catalyzed carbonylation and coupling reactions of allylic, propargylic, and 2,3-alkadienyl carbonates have been extensively studied by Tsuji and Mandai.[1] The reaction provides an efficient method for *in situ* generation of an (alkoxo)palladium(II) species by oxidative addition of the carbonates to Pd(0) complex, and their addition and coupling with electrophiles have enabled various synthetic transformations which are not accessible by the conventional methods. Although these carbonates are also attractive as a substrate for the cross-coupling reaction with organometallic reagents, such reaction has not been reported to date.



1 **2** (1)

Herein, we describe that 2-substituted 1,3-butadiene derivatives (**2**), which are useful precursor for the inter- and intramolecular Diels-Alder reactions, are easily obtained in high yields by the cross-coupling reaction of 2,3-alkadienyl carbonates (**1**) with organoboron compounds. Although they have been prepared most frequently by addition or coupling reactions of 1,3-butadien-2-yllithium or magnesium halides with electrophiles,[2] this route may require the synthesis of labile 2-halo-1,3-butadiene derivatives which cannot always be obtained with regioselectively.[3] The coupling with **1** proceeds through the



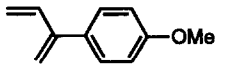
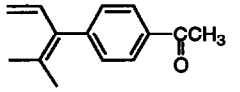
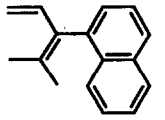
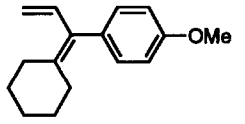
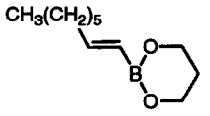
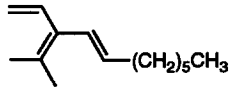
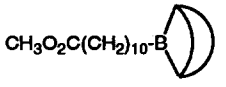
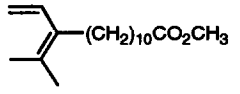
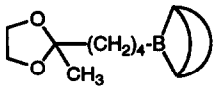
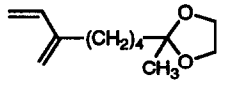
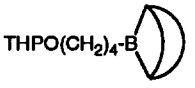
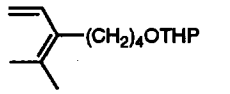
(2)

sequence of oxidative addition by the S_N2' type displacement of **1** with Pd(0) complex to produce **3**,[1,4] displacement of an alkoxy group with organic group on boron, and reductive elimination of **2** to regenerate Pd(0) complex. The palladium-catalyzed cross-coupling reaction of organoboron compounds with organic halides and triflates have been carried out in the presence of bases;[5] however, the mechanistic consideration suggested that the reaction may occur under neutral conditions with the intermediacy of (alkoxo)palladium(II) complexes formed by oxidative addition of some of β,γ-unsaturated ethers or carbonates.[6] Indeed, the present reaction with carbonates easily proceeded under neutral conditions.

The representative results are summarized in Table 1. When one equivalent of carbonates **1** was stirred and refluxed in benzene for 6 h with slightly excess of arylboronic acids or their esters in the presence of 3 mol% of $Pd(PPh_3)_4$, the 2-aryl-1,3-butadiene derivatives were obtained in high yields (**2a-d**). Using the same conditions, the triene **2e** was prepared in a high yield by the reaction of **1** (R^1, R^2=Me) with (E)-1-octenylboronic ester. The reaction of 9-alkyl-9-BBN derivatives, obtained *in situ* by hydroboration of alkenes with 9-BBN, also proceeded under neutral conditions in 30-60% yields (**2f-h**). However, the addition of K_3PO_4 (1.2 equivs) definitely demonstrated to accelrate the reaction with a $Pd(OAc)_2$ / 4 PPh_3 catalyst and the yields could improve to 70% or above. The 1,3-dienes **2a-h** thus obtained were indicated to be a single isomer in each cases without formation of any noticeable quantities of regioisomers such as coupling product at the allylic carbon. The mildness of present procedure was demonstrated in the synthesis of functionalized dienes having acetyl, carbomethoxy and THP groups, e.g., **2b,f,h**.

The utility of the present reaction is demonstrated by the following simple short step preparation of bicyclic bridgehead alkene (**6**), as shown in Eq. 3. The hydroboration of 4-bromo-1-butene with 9-BBN was followed by the cross-coupling with **1** (R^1, R^2=H) at room temperature in the presence of 3 mol% of $Pd(OAc)_2$ and 12 mol% of PPh_3 to produce a 67% yield of **4**. It was then treated with lithium methoxyallene[7] to elaborate a 63% yield of desired α,β-unsaturated ketone (**5**) which was reported to

Table 1. Synthesis of 2-Substituted 1,3-Butadienes[a]

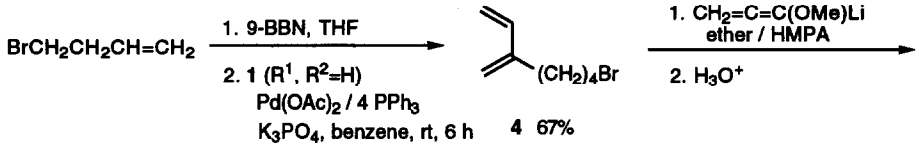
1		R^3BX_2	Product **2**		Yield (%)[b]
R^1=	R^2=				
H	H	4-$MeOC_6H_4B(OH)_2$		**2a**	88
Me	Me	4- $MeCOC_6H_4$-B(O,O)		**2b**	91
Me	Me	1-naphthylB(OH)$_2$		**2c**	92
-$(CH_2)_5$-		4-$MeOC_6H_4B(OH)_2$		**2d**	97
Me	Me			**2e**	92
Me	Me			**2f**	60 (79)[c]
H	H			**2g**	(71)[c]
Me	Me			**2h**	31 (69)[c]

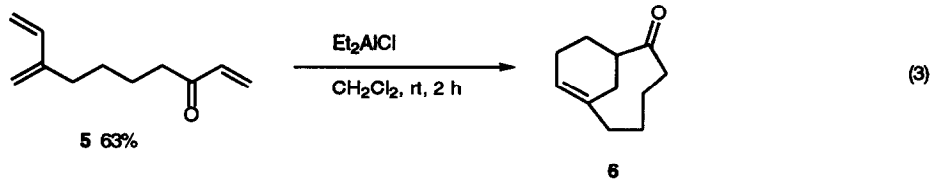
[a] A mixture of carbonate 1 (1 equiv), organoboron compound (1.1-1.5 equivs), and Pd-catalyst ($Pd(PPh_3)_4$ or $Pd(OAc)_2$ / 4 PPh_3, 3 mol%) in benzene was refluxed, unless otherwise noted.

[b] Isolated yields based on carbonates 1.

[c] The reaction was carried out in the presence of K_3PO_4 (1.2 equivs).

provide the intramolecular Diels-Alder adduct (**6**) in a 75% yield in the presence of 1 equivalent of diethylaluminum chloride.[8]





(3)

EXPERIMENTAL SECTION

All 2,3-butadienols were prepared by reported method[9] and converted to the corresponding methyl carbonates by treatment with pyridine and methyl chloroformate.[1] 4-Methoxy-, 4-acetyl-, and 1-naphthylboronic acids were prepared from the corresponding Grignard reagents and trimethyl borate.[10] $Pd(PPh_3)_4$[11] and $Pd(OAc)_2$[12] were prepared by the reported procedures. A 9-borabicyclo[3.3.1]nonane (9-BBN) solution in THF were commercial product from Aldrich Chemical Co. Kieselgel 60 (70-230 mesh) from Merck was used for chromatography. Mass spectra were recorded on a JEOL JMS-D 300 for high resolution analysis and a Finnigan ITD 800 for GC-mass analysis. The ^1H NMR were measured with a Bruker MSL-300 (300 MHz) spectrometers.

Typical Procedure for 2a-e: 1-Naphthylboronic acid (206 mg, 1.2 mmol) and $Pd(PPh_3)_4$ (39 mg, 0.034 mmol) were placed in a flask and flushed with nitrogen. Benzene (10 ml) and 4-methyl-2,3-pentadienyl methyl carbonate **1** (R^1=Me, R^2=Me) (157 mg, 1 mmol) were then added. The mixture was stirred and refluxed for 6 h. After cooling to room temperature, the reaction mixture was diluted with benzene (ca 50 ml), washed with water, and dried over $MgSO_4$. The product was isolated by column chromatography over silica gel with hexane to give 193 mg (92%) of **2c**. IR (nujor) 990, 915, 800, 780 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.44 (s, 3H), 2.09 (s, 3H), 4.32 (d, 1H, J=17.0 Hz), 4.93 (d, 1H, J= 10.7

Hz), 7.11 (dd, 1H, J=10.7 and 17.0 Hz), 7.18 (dd, 1H, J=1.2 and 7.1 Hz), 7.37-7.48 (m, 3H), 7.70 (d, 1H, J=7.8 Hz), 7.7 (d, 1H, J=8.3 Hz), 7.84 (d, 1H, J=8.1 Hz); ^{13}C NMR ($CDCl_3$) 138.2, 135.2, 134.3, 133.7, 133.5, 132.2, 128.1, 127.3, 126.8, 125.9, 125.6, 125.4, 115.0, 23.1, 19.9; MS (EI) *m/e* 165 (100), 178 (37), 193 (34), 208 (M^+, 28); exact mass calcd for $C_{16}H_{16}$ 208.1252, found 208.1252.

The following compounds were prepared by the above general procedures, unless otherwise noted.

2a: IR (film) 1610, 990, 900, 830 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.82 (s, 3H), 5.17 (d, 1H, J = 11.2 Hz), 5.19 (d, 1H, J = 16.9 Hz), 5.24 (s, 2H), 6.60 (dd, 1H, J = 16.9 and 11.2 Hz), 6.88 (d, 2H, J = 8.8 Hz), 7.26 (d, 2H, J = 8.8 Hz); ^{13}C NMR ($CDCl_3$) 159.0, 147.5, 138.3, 132.0, 129.1, 116.8, 115.7, 113.4, 55.1; MS(EI) *m/e* 51 (29), 63 (32), 77 (13), 91 (30), 115 (80), 128 (54), 145 (36), 160 (M^+, 100); exact mass calcd for $C_{11}H_{12}O$ 160.0888, found 160.0877.

2b: IR (film) 1685, 1610, 1270, 960, 905, 845 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.56 (s, 3H), 1.97 (s, 3H), 2.62 (s, 3H), 4.46 (d, 1H, J = 17.1 Hz), 5.01 (d, 1H, J = 10.8 Hz), 6.96 (dd, 1H, J = 17.1 and 10.8 Hz), 7.17 (d, 2H, J = 8.1 Hz), 7.95 (d, 2H, J = 8.1 Hz); ^{13}C NMR ($CDCl_3$) 196.9, 145.5, 135.0, 134.7, 134.5, 132.9, 130.0, 127.8, 114.8, 26.2, 22.7, 19.6; MS(EI) *m/e* 115 (51), 129 (40), 142 (100), 157 (81), 185 (10), 200 (M^{+1}, 19); exact mass calcd for $C_{14}H_{16}O$ 200.1201, found 200.1200.

2d: The coupling of **1** (R^1, R^2= $(CH_2)_5$) with 4-methoxyphenylboronic acid to give **2d** was not completed within 6 h, thus the refluxing was continued for overnight (14 h). IR (film) 1610, 1510, 1245, 1040, 900, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.44-1.68 (m, 6H), 1.95 (t, 2H, J=5.9 Hz), 2.46 (t, 2H, J=5.9 Hz), 3.82 (s, 3H), 4.55 (dd, 1H, J=1.9 and 17.0 Hz), 5.00 (dd, 1H, J=10.6 and 1.9 Hz), 6.88 (d, 2H, J=8.1 Hz), 6.98 (d, 2H, J=8.1 Hz), 7.03 (dd, 1H, J=17.0 and 10.6 Hz); ^{13}C NMR ($CDCl_3$) 157.9, 141.2, 135.2, 132.5, 132.2, 130.9, 115.2, 113.3, 55.1, 33.2, 30.2, 28.6, 28.4, 27.0; MS (EI) *m/e* 115 (50), 121 (70), 129 (75), 171 (45), 172 (45), 185 (45), 199 (24), 213 (40), 228 (M^+, 100); exact mass calcd for $C_{16}H_{20}O$ 228.1514, found 228.1486.

2e: IR (film) 1640, 1605, 975, 910 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, 3H, J = 6.8 Hz), 1.43-1.29 (m, 8H), 1.83 (s, 6H), 2.13 (dt, 2H, J = 6.7 and 6.7 Hz), 5.12 (dd, 1H, J = 17.3 and 2.2 Hz), 5.14 (dd, 1H, J = 11.1 and 2.2 Hz), 5.56 (dt, 1H, J = 15.8 and 6.7 Hz), 6.10 (d, 1H, J = 15.8 Hz), 6.54 (dd, 1H, J = 17.3 and 11.1 Hz); ^{13}C NMR ($CDCl_3$) 135.0, 133.5, 131.8, 130.7, 127.0, 115.5, 33.3, 31.9, 29.7, 29.0, 22.8, 21.6, 21.2, 14.1; MS (EI) *m/e* 79 (14), 91 (25), 93 (18), 105 (21), 107 (100), 121 (8), 192 (13); exact mass calcd for $C_{14}H_{24}$ 192.1878, found 192.1861.

Typical Procedure for 2f-h: To a solution of methyl 10-undecenoate (1 g, 5.05 mmol) in THF (2.5 ml) was added 9-BBN (0.5 M in THF, 11 ml, 5.5 mmol) at 0 °C, and the mixture was stirred for 16 h at room temperature. Benzene (50 ml), **1** (R^1, R^2=Me) (0.94 g, 6.03 mmol), PPh_3 (146 mg, 0.56 mmol), $Pd(OAc)_2$ (31 mg, 0.14 mmol), K_3PO_4 (1.27 g, 6 mmol) were added to the above borane solution. After being stirred and reflexed for 6 h, the reaction mixture was diluted with benzene (ca 50 ml), washed with water, and dried over $MgSO_4$. Chromatography over silica gel gave 1.14 g (79%) of **2f**: IR (film) 1760, 1640, 995, 895 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.28 (m, 14H), 1.59 (m, 2H), 1.78 (s, 3H), 1.80

(s, 3H), 2.22 (t, 2H, J = 7.8 Hz), 2.30 (t, 2H, J = 7.4 Hz), 3.66 (s, 3H), 4.95 (d, 1H, J = 11.0 Hz), 5.10 (d, 1H, J = 17.3 Hz), 6.73 (dd, 1H, J = 11.0 and 17.3 Hz); ^{13}C NMR ($CDCl_3$) 173.2, 134.3, 131.5, 130.2, 110.2, 50.8, 33.7, 29.7, 29.3, 29.2, 29.0, 28.9, 28.6, 27.6, 24.7, 21.1, 19.8; MS (EI) *m/e* 81 (73), 95 (27), 107 (98), 123 (100), 280 (0.1); exact mass calcd for $C_{18}H_{32}O_2$ 280.2402, found 280.2431.

The following compounds were synthesized by the above general procedures.

2g: IR (film) 1603, 1380, 900, 860 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.32 (s, 3H), 1.40-1.55 (m, 4H), 1.66 (t, 2H, J=7.8 Hz), 2.22 (t, 2H, J=7.8Hz), 3.92-3.96 (m, 4H), 4.98 (s, 1H), 5.00 (s, 1H), 5.05 (s, 1H), 5.22 (d, 1H, J=17.6 Hz), 6.36 (dd, 1H, J= 10.7 and 17.6 Hz); ^{13}C NMR ($CDCl_3$) 145.7, 138.4, 114.8, 112.3, 109.3, 64.0, 38.6, 30.9, 28.0, 23.6, 23.2; MS (EI) *m/e* 87 (100), 99 (4), 107 (2), 119 (17), 135 (9), 147 (0.3), 158 (0.5), 181 (2), 196 (0.2); exact mass calcd for $C_{12}H_{20}O_2$ 196.1464, found 196.1478.

2h: IR (film) 1640, 1605, 900, 820 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.40-1.78 (m, 6H), 1.79 (s, 3H), 1.81 (s, 3H), 2.27 (t, 2H, J=7.8 Hz), 3.36-3.44 (m, 2H), 3.46-3.54 (m, 2H), 3.71-3.79 (m, 2H), 3.84-3.91 (m, 2H), 4.57-4.59 (m, 1H), 4.96 (d, 1H, J=11.0 Hz), 5.11 (d, 1H, J=17.4 Hz), 6.72 (dd, 1H, J=11.0 and 17.4 Hz); ^{13}C NMR ($CDCl_3$) 134.1, 131.2, 130.3, 110.3, 98.1, 66.8, 61.4, 30.4, 29.6, 27.2, 25.3, 25.2, 21.0, 19.7, 19.2; MS (EI) *m/e* 85 (100), 95 (14), 107 (6), 121 (6), 136 (4), 238 (2); exact mass calcd for $C_{15}H_{26}O_2$ 238.1933, found 238.1948.

Synthesis of 6: To a solution of 4-bromo-1-butene (1 mmol) in THF (0.5 ml) was added 9-BBN (0.5 M in THF, 2.2 ml, 1.1 mmol) at 0 °C, and the mixture was stirred overnight at room temperature. After evaporation of THF in vacuo (10 mmHg), benzene (5 ml), PPh_3 (28 mg), $Pd(OAc)_2$ (6 mg), K_3PO_4 (0.25 g), **1** (R^1, R^2=H) (1.2 mmol) were successively added. The reaction mixture was stirred for 6 h at room temperature. GC analysis using heptadecane as an internal standard indicated the formation of 67% yield of **6**. The reaction mixture was diluted with benzene, washed with brine, and dried over $MgSO_4$. Chromatography over silica gel gave a 51% yield of **6**: IR (film) 3100, 1605, 995, 905 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.61-1.69 (m, 2H), 1.86-1.94 (m, 2H), 2.24 (t, 1H, J = 8.0 Hz), 3.43 (t, 2H, J = 6.8 Hz), 5.00 (s, 1H), 5.03 (s, 1H), 5.07 (d, 1H, J=11.2 Hz), 5.23 (d, 1H, J = 17.6 Hz), 6.36 (dd, 1H, J = 11.2 and 17.6 Hz) Hz); ^{13}C NMR ($CDCl_3$) 145.5, 138.5, 115.7, 113.1, 33.4, 32.5, 30.4, 26.6; MS (EI) *m/e* ; 67 (76), 68 (100), 81 (21), 95 (7), 109 (57), 188 (3), 190 (3); exact mass calcd for $C_8H_{13}Br$ 188.0201, found 188.0209.

To a solution of ^{n}BuLi (1.6M, 1 mmol) were added ether (6 ml) and methoxyallene (1 mmol) at -30 °C. 2-(4-Bromobutyl)-1,3-butadiene (0.93 mmol) and HMPA (1.3 ml) were then added at -35 °C. After being stirred for 10 min below -15 °C, the cooling bath was then removed. The mixture was stirred for additional 1 h. The reaction mixture was treated with aqueous 1M HCl at 0 °C for 0.5 h. The organic phase was washed with brine, 10% aqueous sodium bicarbonate, and dried over $MgSO_4$. Chromatography over silica gel with hexane/ethyl acetate=20/1 gave a 0.103 g (63%) of **5**: IR (film) 3100, 1710, 1690, 1610, 1600, 900 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.45-1.70 (m, 4H), 2.23 (t, 2H, J = 7.7 Hz), 2.61 (t, 2H, J = 7.1

Hz), 4.99 (s, 1H), 5.01 (s, 1H), 5.05 (d, 1H, J = 10.9 Hz), 5.22 (d, 1H, J = 17.6 Hz), 5.82 (dd, 1H, J = 1.3 and 10.3 Hz), 6.22 (dd, 1H, J = 1.3 and 17.7 Hz), 6.32-6.41 (m, 2H); 13C NMR (CDCl3) 213.0, 136.6, 125.8, 47.2, 42.1, 35.2, 26.8, 26.5, 24.6, 22.3, 21.3; MS (EI) *m/e* 55 (100), 68 (37), 79 (81), 83 (21), 94 (56), 105 (8), 120 (6), 131 (4), 135 (3), 146 (3), 149 (4), 164 (2); exact mass calcd for $C_{11}H_{16}O$ 164.1201, found 164.1206.

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