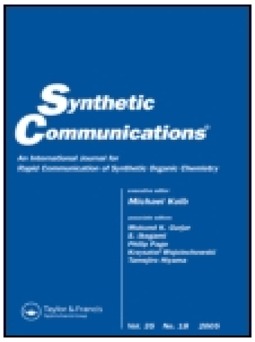

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PALLADIUM-CATALYZED COUPLING REACTION OF VINYL EPOXIDES, DIOL ACETONIDES, AND DIOL CARBONATES WITH ORGANOBISMUTH COMPOUNDS

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ABSTRACT

The palladium-catalyzed arylation reaction of vinyl epoxides with organobismuth compounds afforded the aryl-substituted (*E*)-allylic alcohols *via* ring opening of epoxides. Alternatively, the palladium-catalyzed reaction of diol acetonides and carbonates with bismuth derivatives afforded the aryl-substituted diol acetonides and carbonates without ring opening.

The use of bismuth salts as Lewis acid catalyst or reagent is reported.[1] The application of organobismuth compounds to carbon-carbon bond formation is rather limited. In the literature a self-coupling of Ar_3Bi to form biaryl,[2] aryl ketones from heterocyclic bismuth (III) compounds with aryl halides,[3] esters form Ar_3Bi and MeOH under CO,[4] and the cross-coupling of

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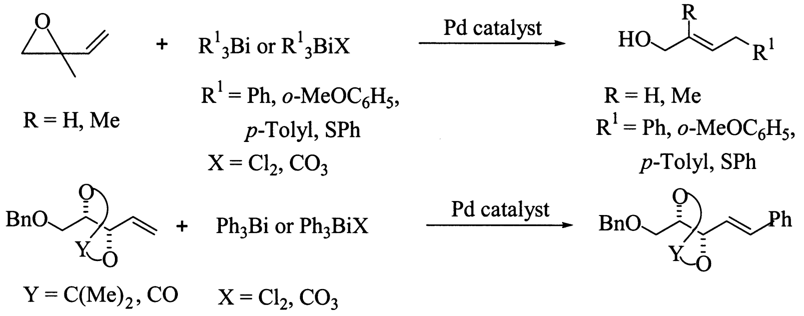
*Corresponding author.

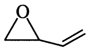
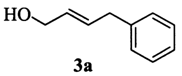
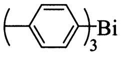
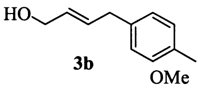
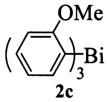
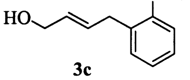
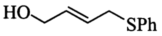
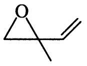
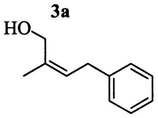
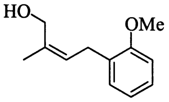
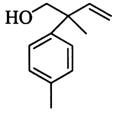
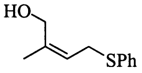
organobismuth compounds with aryl was triflate was known.[5] The Heck type reaction of Ph_3Bi with alkenes afforded the coupled products along with biphenyl in a low yield.[6] In our efforts to utilize organobismuth compounds in organic synthesis,[7] we have investigated the palladium-catalyzed aryl substitution reaction of organobismuth compounds with vinyl epoxides, diol acetonides, and diol carbonates, which is shown in Scheme 1.[8]

The results of the palladium-catalyzed coupling of organobismuth compounds with vinyl epoxides are summarized in Table 1. The vinyl epoxide **1a** reacted with triphenylbismuthine **2a** in the presence of $PdCl_2$ (5 mol%) in DMF/H_2O (5:1) at room temperature for 12 h to afford the phenyl-substituted (*E*)-allylic alcohol **3a** as the sole product in 74% yield (entry 1 in Table 1). Of the solvents tested DMF/H_2O, DMF, toluene, CH_3CN, DMF/H_2O (5:1) is the best of choice. Under the same conditions, tri(*p*-tolyl)bismuth(III) compound **2b** was treated with vinyl epoxide **1a** to give the *p*-tolyl-substituted (*E*)-allylic alcohol **3b** in 71% yield (entry 2). For the tri(*o*-methoxyphenyl)bismuthine **2c**, **1a** was readily coupled to give the aryl-substituted (*E*)-allylic alcohol **3c** in 75% yield (entry 3). When tri(thiophenoxy)bismuthine **2d**[9] was reacted with **1a** in the presence of $PdCl_2$ the thiophenyl-substituted (*E*)-allylic alcohol **3d** was provided in 70% yield (entry 4). This coupling method was extended to the pentavalent bismuth(V) compounds **2e** and **2f**. The reaction of the compounds **2e** and **2f** with **1a** furnished the phenyl-substituted alcohol **3a** in 69 and 75% yields, respectively (entries 5 and 6). We also examined the coupling of methyl-substituted vinyl epoxide **1b** as a substrate for the coupling. The reaction of **1b** with Ph_3Bi (**2a**) afforded (*Z*)-and (*E*)-allylic alcohol **3e** in the ratio of 2:5 in 91% combined yield (entry 7). Under the same conditions for **2c** in the presence of $PdCl_2(dppf)$ at 70°C the coupling gave the substituted alcohol **3f** in the ratio of 1:2 (*Z*:*E*) in 85% yield (entry 8). However when **1b** was



Scheme 1.

Table 1. Palladium-Catalyzed Reaction of Vinyl Epoxides with Organobismuth Compounds[a]

Entry	Vinyl Epoxide	Organobismuth Compounds	Catalyst[b]	Temp.	Products	Isolated Yield (%)
1	 **1a**	Ph_3Bi **2a**	$PdCl_2$	rt	 **3a**	74
2	**1a**	 **2b**	$PdCl_2(dppf)$	40 °C	 **3b**	71
3	**1a**	 **2c**	$Pd_2(dba)_3{\cdot}CHCl_3$	rt	 **3c**	75
4	**1a**	$(PhS)_3Bi$ **2d**	$PdCl_2$	rt	 **3d**	70
5	**1a**	Ph_3BiCO_3 **2e**	$Pd_2(dba)_3{\cdot}CHCl_3$	rt	**3a**	69
6	**1a**	Ph_3BiCl_2 **2f**	$Pd_2(dba)_3{\cdot}CHCl_3$	rt	**3a**	75
7	 **1b**	**2a**	$PdCl_2$	0 °C	 **3e** (Z : E = 2 : 5)	91
8	**1b**	**2c**	$PdCl_2(dppf)$	70 °C	 **3f** (Z : E = 1 : 2)	85
9	**1b**	**2b**	$PdCl_2(dppf)$	70 °C	 **3g**	68
10	**1b**	**2b**	$PdCl_2$	rt	**3c** (Z : E = 3 : 1)	90
11	**1b**	**2d**	$Pd_2(dba)_3{\cdot}CHCl_3$	rt	 **3h** (Z : E = 7 : 5)	64

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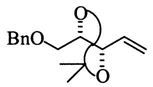
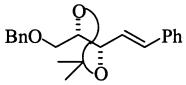
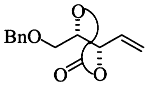
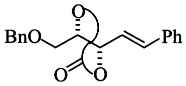
[a]All the reactions were in run in DMF/H_2O (5:1) for 12 h. [b]The catalysts were chosen which gave the best results.

treated with tri(*p*-tolyl)bismuthine (**2b**) in the presence of $PdCl_2$(dppf) at 70°C 2-methyl-2-*p*-tolyl substituted homoallylic alcohol **3g** was afforded in 68% yield (entry 9). Instead of $PdCl_2$(dppf), with $PdCl_2$ as a catalyst at room temperature for 12 h (*Z*)- and (*E*)-allylic alcohol **3c** (3:1) was obtained in 90% yield (entry 10). For tri(thiophenoxy)bismuthine **2d** the coupling with **1b** afforded thiophenyl-substituted alcohol **3h** in 64% yield (entry 11).

The arylation reaction was applied to 1,2-diol acetonides **1c**[10] and 1,2-diol carbonates **1d**[9], which the results were summarized in Table 2. The diol acetonide **1c** reacted with Ph_3Bi (**2a**) in the presence of $PdCl_2$ (5 mol%) at room temperature for 12 h to afford the phenyl-substituted diol acetonide in 38% yield (entry 1). By changing the bismuth compounds to **2e** and **2f** the yields became higher and **5a** was obtained in 64 and 52% yields, respectively (entries 2 and 3). Under the same mild conditions phenyl substitution reaction was carried out without opening of the diol cyclic carbonate **1d** to afford the phenyl-substituted carbonate **5b** in moderate yields (entries 4–6).[8]

In summary the palladium-catalyzed arylation reaction of vinyl epoxides with organobismuth compounds afforded (*E*)-allylic alcohols *via* ring opening of epoxides. Alternatively, the palladium-catalyzed reaction of 1,2-diol acetonides and carbonates with bismuth derivatives afforded the aryl-substituted diol acetonides and carbonates without ring opening.

Table 2. Palladium-Catalyzed Coupling Reaction of Diol Acetonides and Carbonates[a]

Entry	Vinyl Epoxide	Organobismuth Compounds	Products	Isolated Yield (%)
1	 **1c**	Ph_3Bi **2a**	 **5a**	38
2	**1c**	Ph_3BiCO_3 **2e**	**5a**	64
3	**1c**	Ph_3BiCl_2 **2f**	**5a**	52
4	 **1d**	**2a**	 **5b**	47
5	**1d**	**2e**	**5b**	54
6	**1d**	**2f**	**5b**	55

[a] All the reactions were run in the presence of $PdCl_2$ (5 mol%) in DMF/H_2O (5:1) for 12 h at room temperature.

EXPERIMENTAL SECTION

Typical Procedure

Preparation of (*E*)-4-Phenyl-but-2-en-1-ol (**3a**)

To a stirred solution of butadiene monoxide (**1a**) (34.8 mg, 0.50 mmol), and triphenylbismuth (**2a**) (220 mg, 0.50 mmol) in DMF/H_2O (5:1, 5 mL) was added $PdCl_2$ (4.50 mg, 5 mol%) and stirred at room temperature for 12 h. The reaction mixture was extracted with diethyl ether (20 mL × 3) and washed with water. The organic layer was dried over anhydrous $MgSO_4$ and evaporated *in vacuo***.** The crude product was separated by SiO_2 column chromatography (EtOAc/Hexanes 1:1, $R_f = 0.36$) to afford 4-phenylbut-2-en-1-ol (**3a**) (54.4 mg, 74%): TLC, SiO_2, EtOAc/hexanes 1:1, $R_f = 0.36$. ^{1}H NMR (500 MHz, DMSO) δ 3.40 (m, 2H), 3.90 (m, 2H), 4.64 (t, 1H, $J = 5.5$ Hz) 5.57 (m, 1H), 5.72 (m, 1H), 7.18 (m, 2H), 7.30 (m, 3H). MS (EI): m/e (relative intensity) = 149 (4), 148 (54), 130 (53), 129 (63), 117 (100), 92 (64), 91 (91), 57 (43).

4-*p*-Tolyl-but-2-en-1-ol (**3b**): TLC, SiO_2, EtOAc/hexanes 1:1, $R_f = 0.34$. ^{1}H NMR (500 MHz, DMSO) δ 2.34 (s, 3H), 3.26 (m, 2H), 3.90 (m, 2H), 4.62 (t, 1H, $J = 5.5$ Hz), 5.57 (m, 1H), 5.71 (m, 1H), 7.07 (m, 4H). MS (EI): m/e (relative intensity) = 163 (4), 162 (42), 144 (15), 131 (100), 129 (60), 105 (41), 91 (26).

4-(2-Methoxyphenyl)-but-2-en-1-ol (**3c**): TLC, SiO_2, EtOAc/hexanes 1:1, $R_f = 0.25$. ^{1}H NMR (500 MHz, DMSO) δ 3.29 (m, 2H), 3.79 (s, 3H), 3.90 (m, 2H), 4.62 (t, 1H, $J = 5.5$ Hz), 5.55 (m, 1H), 5.73 (m, 1H), 6.88 (m, 1H), 6.97 (m, 1H), 7.18 (m, 1H), 7.21 (m, 1H).

4-Phenylsulfanyl-but-2-en-1-ol (**3d**): TLC, SiO_2, EtOAc/hexanes 1:1, $R_f = 0.32$. ^{1}H NMR (500 MHz, DMSO) δ 3.56 (m, 2H), 3.84 (m, 1H), 5.00~5.12 (m, 3H), 5.77 (m, 1H), 7.21 (m, 1H), 7.30 (m, 2H), 7.36 (m, 2H). MS (EI): m/e (relative intensity) = 179 (23), 149 (79), 134 (16), 116 (37), 110 (100), 70 (25), 69 (13).

(Z)-2-Methyl-4-phenyl-but-2-en-1-ol (**3e**): TLC, SiO_2, EtOAc/hexanes 1:1, $R_f = 0.34$. ^{1}H NMR (500 MHz, DMSO) δ 1.74 (s, 3H), 3.38 (m, 2H), 4.04 (m, 2H), 4.68 (m, 1H), 5.33 (m, 1H), 7.27 (m, 5H).

(Z)-4-(2-Methoxyphenyl)-2-methyl-but-2-en-1-ol (**3f**): TLC, SiO_2, EtOAc/hexanes 1:1, $R_f = 0.24$. ^{1}H NMR (500 MHz, DMSO) δ 1.70 (s, 3H), 3.26 (t, 2H, $J = 8.0$ Hz), 3.72 (s, 3H), 4.00 (d, 2H, $J = 6.0$ Hz), 4.57 (t, 1H, $J = 6.0$ Hz), 5.26 (t, 1H, $J = 8.0$ Hz), 7.07 (m, 2H), 7.16 (m, 2H).

2-Methyl-2-*p*-tolyl-but-3-en-l-ol (**3g**): TLC, SiO_2, EtOAc/hexanes 1:1, $R_f = 0.30$. ^{1}H NMR (500 MHz, DMSO) δ 1.35 (s, 3H), 2.25 (s, 3H), 3.53 (m, 2H), 4.66 ((t, 1H, $J = 5.5$ Hz), 5.00 (dd, 1H, $J = 17.5$, 1.5 Hz), 5.06 (dd, 1H, $J = 8.2$, 1.5 Hz), 6.05 (dd, 1H, $J = 17.5$, 8.2 Hz), 7.08 (q, 2H, $J = 2.0$ Hz), 7.20

(q, 2H, $J = 2.0$ Hz). MS (EI): m/e (relative intensity) = 178, 177, 145 (100), 130 (22), 128 (13), 105 (Z)-2-Methyl-4-phenylsulfanyl-but-2-en-1-ol (**3h**): TLC, SiO_2, EtOAc/hexanes 1:1, $R_f = 0.29$. ^1H NMR (500 MHz, DMSO) δ 1.68 (s, 3H), 3.26 (s, 2H), 3.77 (d, 2H, $J = 7.5$ Hz), 4.66 (t, 1H, $J = 5.5$ Hz), 5.36 (t, 1H, $J = 5.5$ Hz), 7.17 (m, 5H).

Preparation of (*2S*, 3S, 4E)-1-*O*-Benzylxoy-5-(4′-phenyl)-4-penten-2,3-diol acetonide (**5a**)

To a stirred solution of (*2S*, 3S)-4-*O*-benzyloxy-2,3-isopropylidenedioxy-4-pentene (**1c**) (28.0 mg, 0.11 mmol) and triphenylbismuth carbonate (**2e**) (56.0 mg, 0.11 mmol) in DMF/H_2O (5:1, 5 mL) was added $PdCl_2$ (1.0 mg, 5 mol%) and stirred at room temperature for 12 h. The reaction mixture was extracted with diethyl ether (20 mL × 3) and washed with water. The organic layer was dried over anhydrous $MgSO_4$ and evaporated *in vacuo***.** The crude product was separated by SiO_2 column chromatography (EtOAc/Hexanes 1:15, $R_f = 0.34$) to afford (*2S*, *3S*, *4E*)-1-*O*-benzylxoy-5-(4′-phenyl)-4-penten-2,3-diol acetonide (**5a**) (23.4 mg, 64%): TLC, SiO_2, EtOAc/hexanes 1:15, $R_f = 0.34$. ^1H NMR (500 MHz, $CDCl_3$) δ 1.35 (m, 6H), 3.59 (m, 2H), 3.95 (m, 1H), 4.36 (m, 1H), 4.50 (m, 2H), 6.29 (dd, 1H, $J = 15.5$, 7.3 Hz), 6.63 (d, 1H, $J = 15.5$ Hz), 7.15 (m, 1H), 7.28 (m, 7H), 7.45 (m, 2H). MS (EI): m/e (relative intensity) = 91 (100), 104 (43), 115 (44), 131 (41), 145 (32), 159 (15), 174 (11), 233 (6), 266 (7), 324 (3).

(*2S*, 3S, 4E)-1-*O*-Benzyloxy-5-(4′-phenyl)-4-penten-2,3-diol cyclic carbonate (**5b**): TLC, SiO_2, EtOAc/hexanes 1:4, $R_f = 0.25$. ^1H NMR (500 MHz, DMSO) δ 3.67 (dd, 1H, $J = 12.0$, 4.0 Hz), 3.80 (dd, 1H, $J = 12.0$, 4.0 Hz), 4.53 (m, 1H), 4.64 (d, 2H, $J = 6.4$ Hz), 5.17 (dd, 1H, $J = 7.3$, 7.3 Hz), 6.17 (dd, 1H, $J = 15.8$, 7.8 Hz), 6.71 (d, 1H, $J = 15.8$ Hz), 7.36 (m, 10H), IR (neat) 3050, 3025, 1805 cm^{-1}. MS (EI): m/e (relative intensity) = 219, 131, 115, 91 (100).

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