Palladium-Catalyzed Coupling Reactions of 1-(Tributylstannyl)-1-octen-3-ol

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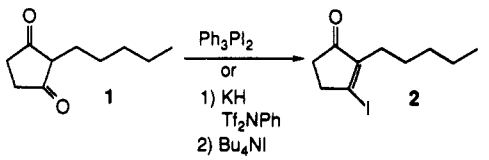
Summary: Coriolic acid and B- and C-type prostaglandins were synthesized in good yields with use of palladium-catalyzed coupling reactions. These syntheses demonstrate that the palladium-catalyzed coupling reaction will tolerate a number of unprotected functional groups, including carboxylic acids.

The palladium-catalyzed coupling of organotin reagents and a variety of organic electrophiles enjoys a number of distinct advantages, the most important of which are that the reaction takes place under mild, neutral conditions and tolerates a wide variety of unprotected functional groups on either coupling partner.[2] The value of the coupling reaction will be shown in this paper by the syntheses of several natural products containing a variety of functional groups.[3] These natural products include B- and C-type prostaglandins and coriolic acid.

Results and Discussion

The first class of compounds studied was a model system. Diketone 1[4] was transformed into vinyl iodide **2** with use of diiodotriphenylphosphorane[5] in 90% yield (eq 1).



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A better synthesis of **2** was achieved though the generation of an unstable vinyl triflate[6] followed by quenching with tetrabutylammonium iodide. The synthesis of the vinyl iodide with a vinyl triflate intermediate represents a new method of generating vinyl iodides. The palladium-catalyzed coupling of **2** with (*E*)-1-(tributylstannyl)-1-octen-3-ol (**3**)[7] afforded **4** in 71% yield (eq 2).

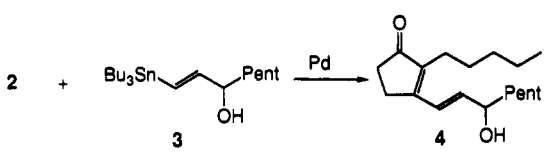

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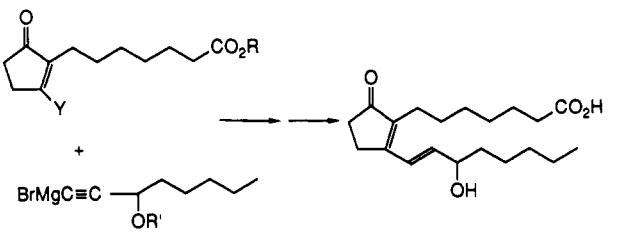
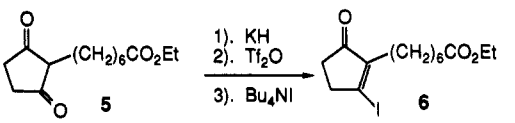
Table I. Syntheses of PGB_1 with Use of Grignard Reagents



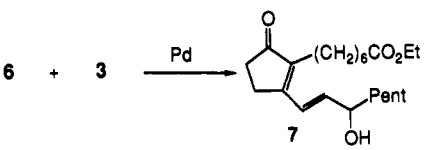
entry no.	Y	R	R′	overall yield, %	ref
1	H	Et	Bu^t	14	10a
2	H	H	THP	9.3	10b
3	OMe	Bu^t	THP	6.3	10c
4	OEt	H	THP	20	10d,e
5	OMe	Et	THP	12.9	8
6	OMe	H	THP	not given	10f

The next system studied was the B-type prostaglandin (PGB_1). Unlike the case for the model system, the reaction of 1 equiv or more of diiodotriphenylphosphorane with diketone **5**[8] failed to afford any of the desired vinyl iodide **6** (eq 3). Formation of an unstable vinyl triflate from **5**



(3)

followed by reaction with tetrabutylammonium iodide produced **6** in 76% yield. The palladium-catalyzed coupling of **6** with **3** gave the ethyl ester of PGB_1 (**7**)[9] in 73% yield (eq 4). The overall yield for the conversion of **5** to



(4)

7 was 55%. Comparisons of this synthetic route to previous syntheses not utilizing palladium catalysis (Table I) shows that using the palladium-catalyzed coupling of vinyltins and vinyl iodides results in yields of prostaglandin B_1 that are between 2.5 and 9 times larger than the yields for reactions with Grignard reagents.[8,10]

The 8-methyl C-type prostaglandin (8-methyl-PGC_1)[11] was the third class of compounds studied. Diketone **8**[11] was converted into the somewhat stable vinyl triflate **9** in 60% yield (eq 5). The palladium-catalyzed coupling of **9** with nonracemic (*S*)-**3**[7,12] gave 8-methyl-PGC_1 (**10**) in 60% yield (eq 6).

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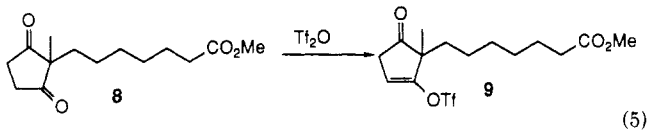

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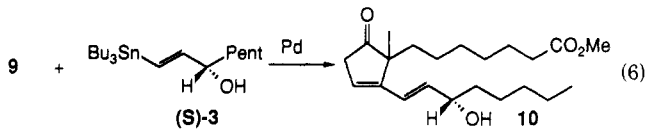

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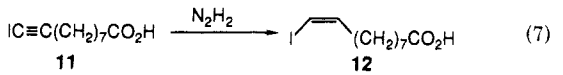
Coriolic acid[13] was the final system studied. Acetylenic iodide **11**[14] was reduced with diimide[15] to give vinyl iodide **12** in 66% yield (eq 7). The palladium-catalyzed coupling



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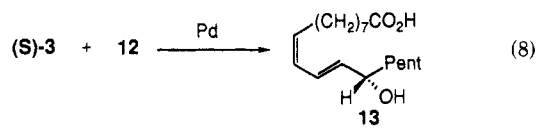
of **12** with (*S*)-**3** produced coriolic acid (**13**)[13,16] in 76% yield (eq 8). This is remarkable in that not only does coupling



(8)

take place in the presence of a free carboxylic acid but also good yields are obtained under mild reaction conditions. Whereas a recent report,[17] which used a palladium-catalyzed coupling of the methyl ester of **12** and the *tert*-butyldimethylsilyl ether of **3**, required 4 days at 60 °C to obtain a 60% yield of the protected coriolic acid, our coupling reaction with the unprotected reagents went in 8 h at 25 °C.

In this paper, the palladium-catalyzed coupling of organotin reagents and organic electrophiles was shown to tolerate functional groups, including ketones, esters, alcohols, and carboxylic acids. The synthesis of the ethyl ester of PGB_1 illustrates that transition-metal catalysis can significantly increase the yields of organic reactions.

Experimental Section

General Comments. Starting materials were obtained from either Aldrich Chemical Co., Alfa Products, or Sigma Chemical Co. Palladium(II) chloride was obtained from Johnson-Matthey Inc. through the metal loan program. Tetrahydrofuran (THF) and ether were distilled under nitrogen from sodium–benzophenone prior to use. Methylene chloride (CH_2Cl_2), pentane, dimethylformamide, and 1,2-dimethoxyethane were distilled from calcium hydride. Reactions were run under either a nitrogen or argon atmosphere. All melting points and boiling points are uncorrected. Melting points were determined with a Mel-Temp capillary melting point apparatus. The ^1H NMR spectra were recorded on a Varian T-60 (60 MHz), a IBM WP-270 (270 MHz), or a Bruker AC-300 (300 MHz) spectrometer with tetramethylsilane as an internal standard. The ^{13}C NMR spectra were recorded on either the Bruker AC-300 (75.5 MHz) or the IBM WP-270 (68 MHz) spectrometer with deuteriochloroform as the internal standard. Infrared spectra were obtained on either a Beckman Acculab or a Beckman 4240 spectrophotometer. Ultraviolet spectra were recorded on a Perkin-Elmer Techtron 635. Optical rotations were taken on a Rudolph Research Autopal III polarimeter. Elemental analyses were performed by Atlantic Microlab. 2-Pentyl-1,3-cyclopentanedione (**1**),[4] (*E*)-1-(tributylstannyl)-1-octen-3-ol (**3**),[7] (*S*)-(*E*)-1-(tributylstannyl)-1-octen-3-ol ((*S*)-**3**),[7,12] 2-(carbethoxyhex-6-yl)-1,3-cyclopentanedione (**5**),[8] 2-(carbomethoxyhex-6-yl)-2-methyl-1,3-cyclopentanedione (**8**),[11] bis(acetonitrile)palladium(II) chloride,[18] tetrakis(triphenylphosphine)palladium(0),[19] benzylchlorobis(triphenylphosphine)palladium(II),[20] and 10-iodo-9-decynoic acid (**11**)[14] were synthesized by literature procedures.

3-Iodo-2-pentyl-2-cyclopenten-1-one (2). The oil was removed from 0.2521 g (0.08824 g of KH, 2.200 mmol) of 35% potassium hydride (KH) with use of dry, distilled pentane. A slurry of the KH, 0.3365 g (2.000 mmol) of **1**, and 30 mL of dry, distilled THF was stirred at room temperature for 1 h. The slurry was cooled to −78 °C, and 0.7860 g (2.200 mmol) of *N*-phenyltriflamide in 10 mL of THF was added. After 1 h, the solution was warmed to 0 °C and 1.1 g (3.0 mmol) of tetrabutylammonium iodide (Bu_4NI) was added. The slurry was heated to 50 °C for 8 h. Ether was added, and the solids were removed by filtration through silica gel. The solvent was removed under reduced pressure. Column chromatography (20% ethyl acetate (EtOAc)/hexane on silica gel) afforded 0.5556 g (99.90%, 1.998 mmol) of **2** as a yellow oil: ^1H NMR ($CDCl_3$) δ 3.00 (m, 2 H), 2.51 (m, 2 H), 2.25 (t, J = 7 Hz, 2 H), 1.35 (m, 6 H), 0.89 (t, J = 7 Hz, 3 H); ^{13}C NMR ($CDCl_3$) 202.3, 151.4, 135.6, 39.2, 36.7, 31.6, 27.4, 26.9, 22.4, 14.0; IR (film) 2950, 2910, 2860, 2840, 1700, 1610 cm^{-1}. Anal. Calcd for $C_{10}H_{15}IO$: C, 43.18; H, 5.44. Found: C, 43.25; H, 5.45.

2-Pentyl-3-(3-hydroxy-1-octen-1-yl)-2-cyclopenten-1-one (4). A solution of 0.277 g (1.00 mmol) of **2**, 0.46 g (1.1 mmol) of **3**, 0.025 g (0.03 mmol) of benzylchlorobis(triphenylphosphine)-palladium(II), and 10 mL of dry THF was heated in a 55 °C oil bath for 72 h. The solvent was removed under reduced pressure. The resulting oil was stirred in ether/half-saturated, aqueous potassium fluoride solution overnight. The ether layer was dried with $MgSO_4$, and the solvent was removed under reduced pressure. Column chromatography (30% EtOAc/hexane on silica gel) gave 0.200 g (71.2 mmol, 71.2% yield) of **4** as a yellow oil: ^1H NMR ($CDCl_3$) δ 6.85 (d, J = 15 Hz, 1 H), 6.25 (dd, J = 6, 15 Hz, 1 H), 4.40 (bs, 2 H), 2.40 (m, 6 H), 1.35 (m, 14 H), 0.95 (m, 6 H); IR (film) 3420, 2950, 2920, 2850, 1685, 1635, 1595 cm^{-1}; UV λ_{EtOH} 278 nm (2.79×10^4); HRMS calcd for $C_{15}H_{29}O_2$ (M − 1) 277.2168, found 277.2176.

Ethyl Ester of PGB_1 (7). A solution of 0.1272 g (0.4988 mmol) of **5**, 3 mL of dry dimethoxyethane, and 0.0603 g (35%, 0.525 mmol) of potassium hydride (the oil was removed with dry pentane) was cooled to −78 °C. With stirring, 0.090 mL (0.15 g, 0.54 mmol) of triflic anhydride was added to the solution. After 30 min at −78 °C, the solution was warmed to room temperature. The solvent was removed under reduced pressure. A slurry was made by the addition of 2 mL of CH_2Cl_2 and 18 mL of pentane. The slurry was filtered, and the solvent was removed under reduced pressure. A solution on the resulting oil, 5 mL of dry THF, and 0.277 g (0.750 mmol) of Bu_4NI was stirred at room temperature for 6 h. The solvent was removed under reduced pressure. Column chromatography (20% EtOAc/hexane on silica gel) yielded 0.1378 g (0.3788 mmol, 75.94%) of a yellow oil (**6**): ^1H NMR ($CDCl_3$) δ 4.1 (q, J = 7 Hz, 2 H), 2.9 (m, 2 H), 2.3 (m, 6 H), 1.3 (m, 11 H); IR (film) 2920, 2850, 1730 cm^{-1}. A solution of 0.0854 g (0.235 mmol) of **6**, 0.1174 g (0.2815 mmol) of **3**, 17.6 mg (0.0235 mmol) of benzylchlorobis(triphenylphosphine)palladium(II), and 2.4 mL of dry, distilled THF was heated at 60 °C for 36 h. The solution was filtered, and the solvent was removed under reduced pressure. The resulting oil was partitioned between ether and half-saturated aqueous potassium fluoride solution. The

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ether layer was dried with $MgSO_4$, and the solvent was removed under reduced pressure. The resulting oil was partitioned between hexane and acetonitrile. The solvent was removed from the acetonitrile layer under reduced pressure. Column chromatography (30% EtOAc/hexane on silica gel) yielded 62.4 mg (0.172 mmol, 73.2% yield) of **7** as a yellow oil: ^1H NMR ($CDCl_3$) δ 6.85 (d, J = 16 Hz, 1 H), 6.25 (dd, J = 5, 16 Hz, 1 H), 4.40 (m, 1 H), 4.15 (q, J = 6.5 Hz, 2 H), 2.7 (m, 2 H), 2.35 (m, 5 H), 1.3 (m, 13 H); IR (film) 3430, 2920, 2845, 1730, 1685, 1635, 1590 cm^{-1}; UV λ_{EtOH} 278 nm (2.85×10^4).

Methyl 7-(5-Triflato-1-methyl-2-oxo-4-cyclopenten-1-yl)-heptanoate (9). To a stirred solution of 0.226 g (1.10 mmol) of 2,6-di-*tert*-butyl-4-methylpyridine, 0.255 g (1.00 mmol) of **8**, and 10 mL of dry, distilled CH_2Cl_2 was rapidly added 0.18 mL (0.30 g, 1.10 mmol) of triflic anhydride at room temperature. The reaction mixture was then heated at reflux for 24 h. Pentane was added, and the mixture was filtered. The solvent was removed under reduced pressure. Column chromatography (30% EtOAc/hexane on silica gel) afforded 0.230 g (0.596 mmol, 59.6%) of **9** as a yellow oil: ^1H NMR ($CDCl_3$) δ 6.10 (t, J = 2 Hz, 1 H), 3.70 (s, 3 H), 3.10 (d, J = 2 Hz, 2 H), 2.4 (m, 2 H), 1.7 (m, 10 H), 1.30 (s, 3 H); HRMS calcd for $C_{15}H_{22}F_3O_6S$ (M + 1) 387.1090, found 387.1099.

Methyl Ester of 8-Methylprostaglandin C_1 (10). A slurry of 0.185 g (0.479 mmol) of **9**, 0.220 g (0.528 mmol) of (*S*)-**3**, 55 mg (0.048 mmol) of tetrakis(triphenylphosphine)palladium(0), 60 mg (1.4 mmol) of lithium chloride, and 5 mL of dry, distilled THF was heated at 60 °C for 48 h. The solids were removed by filtration. The filtrate's solvent was removed under reduced pressure. The resulting oil was partitioned between hexane and acetonitrile. The solvent was removed under reduced pressure from the acetonitrile extracts. Column chromatography (30% EtOAc/hexane on silica gel) afforded 0.104 g (0.286 mmol, 59.7% yield) of **10** as a yellow oil: ^1H NMR ($CDCl_3$) δ 6.10 (m, 3 H), 4.20 (m, 1 H), 3.60 (s, 3 H), 2.90 (m, 2 H), 2.30 (t, J = 7 Hz, 4 H), 1.4 (m, 23 H); HRMS calcd for $C_{22}H_{34}O_4$ (M - 2) 362.2457, found 362.2448.

Coriolic Acid (13). A 40% aqueous KOH solution (11 mL) was cooled in an acetone/ice bath, and 3.48 g (30.0 mmol) of azodicarbonamide was added with stirring. After 1 h, the solid (dipotassium azodicarboxylate) was isolated by filtration and washed with cold methanol. Acetic acid (6 mL) was added dropwise to a slurry of the dipotassium azodicarboxylate, 0.2945 g (1.001 mmol) of **11**, and 16 mL of distilled methanol. The reaction solution was stirred for 6 h and then was partitioned between water and ether. The organic layer was dried with $MgSO_4$, and the solvent was removed under reduced pressure. Column chromatography (30% EtOAc/hexane on silica gel) afforded 0.1952 g (65.85%, 0.6592 mmol) of **12** as a yellow oil: ^1H NMR ($CDCl_3$) δ 6.15 (m, 2 H), 2.4 (m, 4 H), 1.4 (m, 10 H). A solution of 75.2 mg (0.254 mmol) of **12**, 0.1165 g (0.279 mmol) of (*S*)-**3**, 2.6 mg (0.0095 mmol) of bis(acetonitrile)palladium(II) chloride, and 2.5 mL of dry, distilled dimethylformamide was stirred at room temperature for 8 h. The reaction solution was partitioned between ether and water. The ether layer was dried with $MgSO_4$. The solvent was removed under reduced pressure. The resulting oil was partitioned between acetonitrile and hexane. The solvent was removed from the acetonitrile layer under reduced pressure. Column chromatography (10% methanol/CH_2Cl_2 on silica gel) afforded 56.7 mg (0.192 mmol, 75.6% yield) of a yellow oil (**13**): ^1H NMR ($CDCl_3$) δ 6.50 (dd, J = 11, 15 Hz; 1 H), 6.1 (bs, 1 H), 5.97 (dd, J = 11, 11 Hz; 1 H), 5.65 (dd, J = 7, 15 Hz; 1 H), 5.43 (dt, J = 7, 11 Hz; 1 H), 4.2 (m, 1 H), 2.45 (t, J = 7 Hz, 2 H), 1.8 (m, 20 H), 1.0 (t, J = 6 Hz, 3 H); $[\alpha]_D$ = +7.6° (c = 1.13, $CHCl_3$) (lit.[13b] $[\alpha]_D$ = +7.8° (c = 1.15, $CHCl_3$)).

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Alkynylation of Organometallic Systems. A New, Simple Method for the Introduction of Terminal Acetylides: Formation of Rhodium(III) and Iridium(III) σ-Acetylide Complexes†

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Summary: Reaction of *trans*-$(Ph_3P)_2Ir(CO)(Cl)$ and *trans*-$(Ph_3P)_2Rh(CO)(Cl)$ with $RC{\equiv}CI^+Ph\cdot{}^-OSO_2CF_3$ in toluene at room temperature gives the corresponding iridium(III) and rodium(III) σ-acetylide complexes in 89-96% isolated yields.

Transition-metal σ-acetylide or σ-alkynyl complexes, $RC{\equiv}CML_n$, are of current interest and are the subject of considerable research activity for a variety of reasons.[1,2] First, the parent acetylide, $HC{\equiv}C$, is isoelectronic with both CO and CN. Second, alkynes are unique among carbon ligands in the variety and modes of multisite interactions possible with transition metals. Third, their susceptibility to both electrophilic[3] and nucleophilic[4] attack allows for further transformations and ready functionalization.[5] Fourth, they are of some interest in organic and organometallic synthesis.[6] Fifth, they have implications in catalysis[7] and the preparation of novel, new materials.[8]

† Dedicated to the memory of John K. Stille.

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