Palladium-Catalyzed Three-Component Coupling of 1,1-Dibromoalkenes, Vinylzinc Chloride, and Soft Nucleophiles: One-Pot Synthesis of 1,3-Disubstituted Allenes

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ABSTRACT: The three-component coupling reaction of 1,1-dibromoalkenes 1, vinylzinc chloride 2, and carbon soft nucleophiles 3 was realized in the presence of the catalytic palladium/Xantphos species, and 1,3-disubstituted allenic products 5 were obtained in yields of up to 77%. The successive two palladium-catalyzed processes, namely the cross-coupling reaction and the allylic substitution, assembled 5 from the easily accessible starting compounds.

INTRODUCTION

Allenes have emerged as unique building blocks in synthetic organic chemistry, and their convenient synthetic methods have been highly desirable. Construction of allenic C=C=C frameworks by multicomponent coupling reactions of easily accessible compounds is an attractive procedure for preparing allenic compounds.

In 2000, we developed a palladium-catalyzed reaction for preparing various functionalized allenes 5 starting with 1-hydrocarbyl-2-bromo-1,3-dienes 4 and appropriate soft nucleophiles 3 (Scheme 1). By the use of a chiral palladium catalyst, the reaction could provide scalemic axially chiral allenes 5 in up to 94% ee. The reaction proceeds via (allylidene-π-allyl)palladium intermediate B, that is somewhat similar to the widely accepted intermediates in the Tsuji–Trost reaction. An analogous (allylidene-π-allyl)palladium species can be generated by the addition of an allenylmethyl ester to a zero-valent palladium species and its reaction with a soft nucleophile gives a comparable allenic product as well. Bromodiene substrates 4 were prepared by the regioselective cross-coupling reaction between 1,1-dibromoalkenes 1 and vinylzinc chloride 2 in the presence of catalytic Pd(PPh₃)₄.²

RESULTS AND DISCUSSION

In the previous reports, the two different palladium precatalysts were employed in the respective reaction steps in Scheme 1. While Pd(PPh₃)₄ (1.5 mol %) was chosen as a suitable precatalyst in the regioselective cross-coupling reaction of 1 with 2, the reaction between 3 and 4 was catalyzed by a palladium species (2.0 mol %) generated in situ from [PdCl(π-]

Scheme 1. Reported “Stepwise” Process of Preparing 1,3-Disubstituted Allenes Using Two Different Palladium Precatalysts

Scheme 2. Palladium-Catalyzed Three-Component Coupling of Preparing 1,3-Disubstituted Allenes

After the extensive optimization of the reaction conditions, indeed, the three-component coupling reactions have been realized. Here, we report details of our efforts toward this goal.
allyl)Cl]_2 and 2,2′-bis(diphenylphosphino)-1,1′-biphenyl (dpbp). Under the reported conditions, the two palladium species were not interconvertible. That is, the cross-coupling reaction between 1a and 2 was much slower and much less regioselective in the presence of the Pd/dpbp species (1.5 mol %) instead of Pd(PPh_3)_4. The reaction showed ca. 20% conversion and the formation of triene 6a was dominant under the otherwise identical conditions. Alternatively, the use of Pd(PPh_3)_4 (2.0 mol %) in the reaction between 3m and 4a provided the desired allenic product 5am in less than a 1% yield (Scheme 3).

Scheme 3. Specificity of Palladium Precatalysts in Converting 1a to 5am via 4a

![Scheme 3](image)

At the outset, a possibility of the three-component coupling was investigated for the reaction between 1a, a vinyl nucleophile (2, 2′, or 2″), and 3m. The results of the screening are summarized in Table 1. A treatment of 1a with 2 (1.5 equiv) and 3m (1.5 equiv) in the presence of a palladium species generated from [Pd(η-allyl)Cl]_2 and dpbp (2.5 mol %) at 60 °C in THF for 24 h gave a mixture of 1a, 4a, 6a, and 5am in 44:2:51:3 molar ratio (determined by 1H NMR; entry 1). The use of vinyltin reagent 2 instead of 2 led to complete consumption of 1a, however, a considerable amount of uncharacterized species was formed together with 4a and 6a. Allene 5am was not detected in the reaction mixture (entry 2). The reaction with vinylmagnesium chloride 2 instead was very messy and the formation of 5am was not observed (entry 3). From the results in entries 1−3, zinc reagent 2 was chosen as a vinyl nucleophile. Preformed Pd(PPh_3)_4 was slightly more effective than the Pd/dpbp species giving a mixture of 4a, 6a, and 5am in 28:60:12 molar ratio. Although 1a was completely consumed, the main product was triene 6a, and the formation of allene 5am was still minimal (entry 4). The Pd/dppf precatalyst gave 4a as a major product, with a small amount of 5am (entry 5). The yield of 5am was improved to 31% by the use of DPEphos as an ancillary ligand, and the formation of 6a was somewhat suppressed (entry 6). Reducing the amount of 2 (1.0 equiv) or lowering the reaction temperature (40 °C) did not improve the 6a/5am ratios, while the reactions were slower (entries 7 and 8). Running the reaction at 80 °C in 1,4-dioxane dramatically improved the yield of 5am to 62% (entry 9). The use of a palladium species generated from [Pd(η-allyl)Cl]_2 and Xantphos further improved the selectivity of the reaction and 5am was isolated in a 77% yield (entry 10). The combination of Pd(dba)_2 and Xantphos was equally effective for the reaction to give 5am in a 74% isolated yield (entry 11).

Due to air-stability and easier handling of Pd(dba)_2, the conditions of entry 11 in Table 1 were chosen as the optimized conditions, and the reactions with various dibromoolefins 1 and nucleophiles 3 were conducted in the same way. The results of the three-component coupling are summarized in

Table 1. Optimization of Reaction Conditions for Three-Component Coupling between 1a, 2, and 3m

| entry | Pd precursor | ligand | vinyl-[M] | x | T (°C) | solvent | 1a/4a/6a/5am (%) |
|-------|--------------|--------|-----------|---|--------|---------|------------------|
| 1     | [Pd(η-allyl)Cl]_2 | dpbp   | 2          | 1.5 | 60     | THF     | 44/2/51/3        |
| 2     | [Pd(η-allyl)Cl]_2 | dpbp   | 2          | 1.5 | 60     | THF     | 0/48/52/0^d     |
| 3     | [Pd(η-allyl)Cl]_2 | dpbp   | 2          | 1.5 | 60     | THF     | messy            |
| 4"    | Pd(PPh_3)_4    | dpbp   | 2          | 1.5 | 60     | THF     | 0/28/60/12      |
| 5     | [Pd(η-allyl)Cl]_2 | dpbp   | 2          | 1.5 | 60     | THF     | 1/60/31/8       |
| 6     | [Pd(η-allyl)Cl]_2 | DPEphos| 2          | 1.5 | 60     | THF     | 0/51/16/33      |
| 7     | [Pd(η-allyl)Cl]_2 | DPEphos| 2          | 1.0 | 60     | THF     | 0/72/9/19       |
| 8     | [Pd(η-allyl)Cl]_2 | DPEphos| 2          | 1.5 | 40     | THF     | 0/82/7/11       |
| 9     | [Pd(η-allyl)Cl]_2 | DPEphos| 2          | 1.5 | 80     | 1,4-dioxane| 0/34/66     |
| 10    | [Pd(η-allyl)Cl]_2 | Xantphos| 2          | 1.5 | 80     | 1,4-dioxane| 0/0/10/90    |
| 11    | Pd(dba)_2      | Xantphos| 2          | 1.5 | 80     | 1,4-dioxane| 0/0/12/88    |

"The reaction was carried out with 1a (0.50 mmol), 2, and 3m (0.75 mmol) in the presence of a palladium catalyst (2.5 mol %) generated in situ from a palladium precursor and a bisphosphine ligand. ^d Determined by the 1H NMR measurement of the crude reaction mixture. ^f Isolated yield by silica gel chromatography. ^Uncharacterized species were detected together with 4a and 6a. ^Preformed tetrakis(triphenylphosphine)palladium(0) was used.
Bis(sulphonyl)methane-derived nucleophiles, or 1i, could be used in the present protocol to afford allenic products (entry 9). The major products in the reactions of 1a were the corresponding bromodienes 5aq and 5ar, which are from ethylmalonate and phenylmalonate, reacted in a 62% yield (entry 7), 1h (with a sec-alkyl, cyclohexyl, group) provided allene 5hm in a 14% yield (entry 8) and the reaction of 1i with a bulky tert-butyl substituent, gave allene 5gm in a 62% yield (entry 7). The major products in the reactions of 1h or 1i were the corresponding bromodienes 5 and trienes 6. The present protocol could be applicable to the other carbon soft nucleophiles as well. Sodium salts 3n and 3o, which are from ethylmalonate and phenylmalonate, reacted with 1a in the same way to give the allenic products in 68 and 69% yields, respectively (entries 10 and 11). The reaction of 3p, that is an anionic derivative from parent malonate, was sluggish and the yield of 5ap was 33% (entry 12). Bis(sulphonyl)methane-derived nucleophiles, 3q and 3r, could be used in the present protocol affording the allenic products in 49 and 61% yields, respectively (entries 13 and 14). Allenes 5ap, 5aq, and 5ar possess acidic hydrogen in them, and thus, they are capable of functioning as carbon soft nucleophiles, which may lead to the formation of bis-allenes 7 by the second three-component coupling with 1 and 2. However, bis-allenes 7 were not detected in the $^1$H NMR spectra nor isolated in all of the cases (entries 12–14). The reaction with nitrogen-nucleophile 3s was messy and the desired allenic product was not obtained, although 1a was completely consumed (entry 15). It should be mentioned that the reaction between preformed 4a and 3s catalyzed by Pd/dpbp gave the allenic product in an 89% yield.4c

Plausible reaction pathways in the present three-component coupling reaction are outlined in Scheme 4. Whereas 1a did not react with 3m in the absence of 2 under the optimized conditions, the initial formation of bromodiene 4 from 1 and 2 is almost certain. Indeed, a reaction of 1a with 2 (1.0 equiv to 1a) without 3m under the same conditions afforded 4a, together with unreacted 1a and 6a (1a/4a/6a = 14:77:9 molar ratio determined by the $^1$H NMR measurement). The oxidative addition of 4 to the Pd(0) species forms C, which is in equilibrium with B with the dissociation of the bromide ligand from the palladium center.4d Intermediate C reacts with...
2 to give triene 6, the major side-product of the present protocol, via D by the standard cross-coupling process. On the other hand, (alkylidene-α-allyl)palladium intermediate B reacts with 3, just like the Tsuji−Trost reaction, to give allene S. Due to the wide bite-angle of Xantphos, the palladium center in C is rather congested. Whereas the alkylidene-α-allyl ligand in B is much more compact than the combination of the σ-butyadienyl/bromo ligands in C, the congestion at the palladium atom is somewhat diminished in B. As a consequence, Xantphos in B/C might drive the equilibrium toward B, leading to a higher yield of allene S.

**CONCLUSIONS**

We have established the three-component coupling reaction of 1,1-dibromoalkenes 1, vinylzinc chloride 2, and carbon soft nucleophiles 3 leading to various 1,3-disubstituted allenes S in yields of up to 77%. The reaction is effectively catalyzed by the palladium/Xantphos species, and the successive two palladium-catalyzed processes, namely the cross-coupling reaction and the allylic substitution like the Tsuji−Trost reaction, assembled the allenic products in good yields from the easily accessible starting compounds.

**EXPERIMENTAL SECTION**

**General Information.** All anaerobic and/or moisture-sensitive manipulations were carried out with standard Schlenk techniques under prepurified nitrogen or with glove box techniques under prepurified argon. 1H NMR (at 400 MHz) and 13C NMR (at 101 MHz) chemical shifts are reported in ppm downfield of internal tetramethylsilane. Tetrahydrofuran and 1,4-dioxane were distilled from benzophenone-ketyl under nitrogen prior to use. Pd[(PPh3)2]0 [Pd(α-allyl)Cl]212 Pd(dba)212 dpbb,7 DPEphos9 and 1,3-benzodithiole-1,1,3,3-tetraoxide (BDT)13 were prepared as reported. All other chemicals were obtained from commercial sources and used without additional purification.

1,1-Dibromo-1-alkenes (1a–i). These compounds were prepared from the commercially available aldehydes by the reported methods14 and were characterized by comparison of their NMR spectra with those reported previously (1a, 1b, 1c, 1d, 1e, 1f, 1g, 1h, 1i).

**Palladium-Catalyzed Three-Component Coupling Reaction of 1,2, and 3.** The reaction conditions and the results are summarized in Table 2. A general procedure is given below. To a mixture of 1 (0.45–0.50 mmol), 3-H (1.5 equiv to 1), NaH (1.6 equiv to 1), Pd(dba)2 (2.5 mol %), and Xantphos and the successive two palladium-catalyzed processes, namely the cross-coupling reaction and the allylic substitution like the Tsuji−Trost reaction, assembled the allenic products in good yields from the easily accessible starting compounds. **Dimethyl 2-[4-(4-Methoxyphenyl)buta-2,3-dienyl]-propane-1,3-dioate (5bm).** Pale-yellow oil. Yield: 109 mg (0.32 mmol; 71%) starting with 1e (131 mg; 0.50 mmol). This is a known compound and was characterized by a comparison of its NMR spectra with those reported previously.

**Dimethyl 2-Methyl-2-[4-(4-Trifluoromethylenyl)buta-2,3-dienyl]propane-1,3-dioate (5cm).** Pale-yellow oil. Yield: 73 mg (0.23 mmol; 51%) starting with 1d (137 mg; 0.45 mmol). 1H NMR (CDCl3): δ 1.46 (s, 3H), 2.25 (s, 3H), 2.30 (s, 6H), 2.66 (dt, J = 7.6 and 2.4 Hz, 2H), 3.66 (s, 3H), 3.70 (s, 3H), 5.18 (td, J = 7.6 and 6.8 Hz, 1H), 6.20 (dt, J = 6.8 and 2.4 Hz, 1H), 6.84 (s, 2H). 13C{1H} NMR (CDCl3): δ 19.9, 20.9, 21.1, 35.6, 52.47, 52.48, 53.9, 85.9, 89.8, 128.4, 128.9, 136.19, 136.24, 172.1, 172.2, 207.7. ESI-HRMS calculated for C19H24O4Na (M + Na): 365.0977; found: 365.0970.

**Dimethyl 2-Methyl-2-[4-(2,4,6-trimethylphenyl)buta-2,3-dienyl]propane-1,3-dioate (5dm).** Pale-yellow oil. Yield: 103 mg (0.32 mmol; 63%) starting with 1f (156 mg; 0.50 mmol). 1H NMR (CDCl3): δ 1.53 (s, 3H), 2.76–2.78 (m, 2H), 3.67 (s, 3H), 3.71 (s, 3H), 5.51 (td, J = 7.3 and 6.4 Hz, 1H), 6.84 (dt, J = 6.4 and 2.4 Hz, 1H), 7.42–7.54 (m, 4H), 7.73 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 8.2 Hz, 1H), 8.17 (d, J = 8.0 Hz, 1H). 13C{1H} NMR (CDCl3): δ 20.0, 35.6, 52.57, 52.59, 53.8, 88.3, 91.0, 123.4, 125.4, 125.6, 126.7, 126.0, 127.5, 130.9, 130.17, 133.8, 172.1, 172.2, 207.7. ESI-HRMS calculated for C19H24O4Na (M + Na): 339.1572; found: 339.1565.

**Dimethyl 2-Methyl-2-[4-(1-Naphthyl)buta-2,3-dienyl]propane-1,3-dioate (5em).** Pale-yellow oil. Yield: 103 mg (0.32 mmol; 63%) starting with 1e (156 mg; 0.50 mmol). 1H NMR (CDCl3): δ 1.53 (s, 3H), 2.76–2.78 (m, 2H), 3.67 (s, 3H), 3.71 (s, 3H), 5.51 (td, J = 7.3 and 6.4 Hz, 1H), 6.84 (dt, J = 6.4 and 2.4 Hz, 1H), 7.42–7.54 (m, 4H), 7.73 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 8.2 Hz, 1H), 8.17 (d, J = 8.0 Hz, 1H). 13C{1H} NMR (CDCl3): δ 20.0, 35.6, 52.57, 52.59, 53.8, 88.3, 91.0, 123.4, 125.4, 125.6, 126.7, 126.0, 127.5, 130.9, 130.17, 133.8, 172.1, 172.2, 207.7. ESI-HRMS calculated for C19H24O4Na (M + Na): 339.1572; found: 339.1565.

**Dimethyl 2-(4-Ferrocenylbuta-2,3-dienyl)propane-1,3-dioate (5fm).** Red-orange oil. Yield: 101 mg (0.26 mmol; 53%) starting with 1f (185 mg; 0.50 mmol). 1H NMR (CDCl3): δ 1.51 (s, 3H), 2.58–2.70 (m, 2H), 3.72 (s, 3H), 3.74 (s, 3H), 4.11 (s, 3H), 4.15–4.17 (m, 2H), 4.20–4.24 (m, 2H), 5.15 (td, J = 7.3 and 6.4 Hz, 1H), 5.84 (dt, J = 6.4 and 2.4 Hz, 1H). 13C{1H} NMR (CDCl3): δ 19.9, 35.8, 52.57, 52.62, 53.8, 67.0, 67.1, 68.35, 68.36, 69.2, 80.3, 87.8, 90.8, 172.1, 172.2, 205.8. ESI-HRMS calculated for C21H26FeO4Na (M + Na): 405.0765; found: 407.0765.

**Dimethyl 2-(5,5-Dimethyl-2,3-hexadienyl)-2-methylpropane-1,3-dioate (5gm).** Colorless oil. Yield: 79 mg (0.31 mmol; 62%) starting with 1g (121 mg; 0.50 mmol). This is a known compound and was characterized by a comparison of its NMR spectra with those reported previously.

**Dimethyl 2-(4-Cyclohexyl-2,3-butenylidene)-2-methylpropane-1,3-dioate (5hm).** Colorless oil. Yield: 20 mg
Pale-yellow solid. Yield: 104 mg (0.245 mmol; 49%) starting with propane-1,3-dioate (5ar).

1Phenyl-5,5-bis(phenylsulfonyl)penta-1,2-diene (Saq). Pale-yellow solid. Yield: 107 mg (0.34 mmol; 69%) starting with 1a (131 mg; 0.50 mmol). 1H NMR (CDCl3): δ 1.21 (t, J = 7.2 Hz, 3H), 2.05 (q, J = 7.2 Hz, 2H), 4.57 (t, J = 7.2 Hz, 2H), 7.17–7.20 (m, 1H), 7.25–7.31 (m, 4H), 7.32–7.35 (m, 2H), 7.63 (m, 2H), 7.89 (m, 2H), 8.5, 14.1, 14.2, 25.3, 31.8, 58.0, 61.30, 61.32, 89.3, 94.6, 126.9, 127.0, 128.6, 134.3, 171.175, 171.179, 206.8. ESI-HRMS calculated for C19H24O4: 317.1753; found: 317.1758.

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ASSOCIATED CONTENT
Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b03444.

1H NMR spectra, 13C NMR spectra, and 19F NMR spectrum of allenic products 5 (PDF)
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