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# Palladium-Catalyzed Cyanation of Propargylic Carbonates with Trimethylsilyl Cyanide

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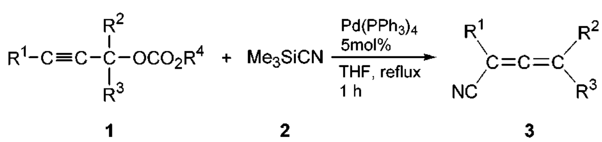
## ABSTRACT




**An equimolar mixture of propargylic carbonate (1) and trimethylsilyl cyanide (2) in THF under reflux affords cyanoallene (3) in the presence of a catalytic amount (5 mol %) of $Pd(PPh_3)_4$. In the reaction, the trimethylsilyl moiety of 2 effectively traps the leaving group of 1. The use of 2 in excess (6 equiv) provides dicyanated products (7 or 8) in high yields.**

The allylic substitution reaction of allylic esters catalyzed by a palladium complex is one of the most successful homogeneous transition metal catalysis reactions in organic synthesis.[1] The reaction proceeds via an $\eta^3$-allylpalladium species to afford a wide variety of products. On the other hand, much less attention has been paid to the corresponding reactions using propargylic esters as substrates.[2]

We recently reported the first example of a cyanation reaction of allylic carbonates using trimethylsilyl cyanide[3] as well as the first general silylation reaction of allylic acetates and trifluoroacetates using organodisilanes.[4] During the course of these studies, we found a new cyanation of propargylic carbonates using trimethylsilyl cyanide. There is no precedent for the palladium-catalyzed cyanation of propargylic esters, giving cyanoallenes[5] that are highly versatile starting materials in various organic transformations. Here we report a new preparation method for cyanoallenes via cyanation of propargylic carbonates catalyzed by a palladium complex.

Reaction of an equimolar mixture of propargylic carbonate (**1**) and trimethylsilyl cyanide (**2**) in THF under reflux affords cyanoallene (**3**) in the presence of a catalytic amount (5 mol

(1)

%) of $Pd(PPh_3)_4$ (eq 1, Table 1). As shown in entries 1 and 2, **1a** and **1a′** afforded **3a** in high isolated yields. Propargylic

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**Table 1.** Cyanation of Propargylic Carbonates (**1**) with 1 equiv of Trimethylsilyl Cyanide (**2**)[a]

| entry | Propargylic Carbonate | Product | Yield[b] /% |
|---|---|---|---|
| 1 | $n$-C$_6$H$_{13}$–C≡C–C(Me)(Me)–OCO$_2$Me **1a** | (n-C$_6$H$_{13}$)(NC)C=C=C(Me)(Me) **3a** | 91 |
| 2 | $n$-C$_6$H$_{13}$–C≡C–C(Me)(Me)–OCO$_2$Et **1a'** | **3a** | 88 |
| 3 | Me$_2$CHCH$_2$CH$_2$–C≡C–C(Me)(Me)–OCO$_2$Et **1b** | (Me$_2$CHCH$_2$CH$_2$)(NC)C=C=C(Me)(Me) **3b** | 86 |
| 4 | $n$-C$_4$H$_9$–C≡C–C(Et)(Me)–OCO$_2$Et **1c** | (n-C$_4$H$_9$)(NC)C=C=C(Et)(Me) **3c** | 86 |
| 5 | $n$-C$_6$H$_{13}$–C≡C–C(Et)(Me)–OCO$_2$Me **1d** | (n-C$_6$H$_{13}$)(NC)C=C=C(Et)(Me) **3d** | 91 |
| 6 | H–C≡C–C(CH$_2$CHMe$_2$)(Me)–OCO$_2$Et **1e** | (H)(NC)C=C=C(CH$_2$CHMe$_2$)(Me) **3e** | 57 |
| 7[c] | $n$-C$_6$H$_{13}$–C≡C–C(Me)(H)–OCO$_2$Et **1f** | (n-C$_6$H$_{13}$)(NC)C=C=C(Me)(H) **3f** | 49 |
| 8[c] | $n$-C$_6$H$_{13}$–C≡C–C(H)(H)–OCO$_2$Et **1g** | (n-C$_6$H$_{13}$)(NC)C=C=C(H)(H) **3g** | 35 |

[a] A mixture of propargylic carbonate (**1**, 1.00 mmol), Me$_3$SiCN (**2**, 1.00 mmol), Pd(PPh$_3$)$_4$ (0.050 mmol), and THF (4.0 mL) was stirred under reflux for 1 h. [b] Isolated yield. [c] For 20 h.

carbonates such as **1b**−**e** gave new cyanoallenes **3b**−**e**, respectively (entries 3−6). The reaction is rather sluggish with the substrate **1f** ($R^2 = H$) or **1g** ($R^2 = R^3 = H$) (entries 7 and 8). The products were easily isolated by Kugelrohr distillation (**3a**−**f**) or column chromatography on silica gel (**3g**). The new compounds are all fully characterized by means of NMR, MS, and elemental analyses; see the Supporting Information.

As the catalyst precursor, Pd(PPh$_3$)$_4$ showed high catalytic activity as shown in Table 1. Other palladium complexes such as PdCl$_2$, PdCl$_2$(PhCN)$_2$, PdCl$_2$(PPh$_3$)$_2$, and Pd(DBA)$_2$ (DBA = dibenzylideneacetone) showed no catalytic activity. As for the solvent, THF gave the best results. Toluene and dioxane can be used, but DMF and acetonitrile totally suppressed the catalytic activity.

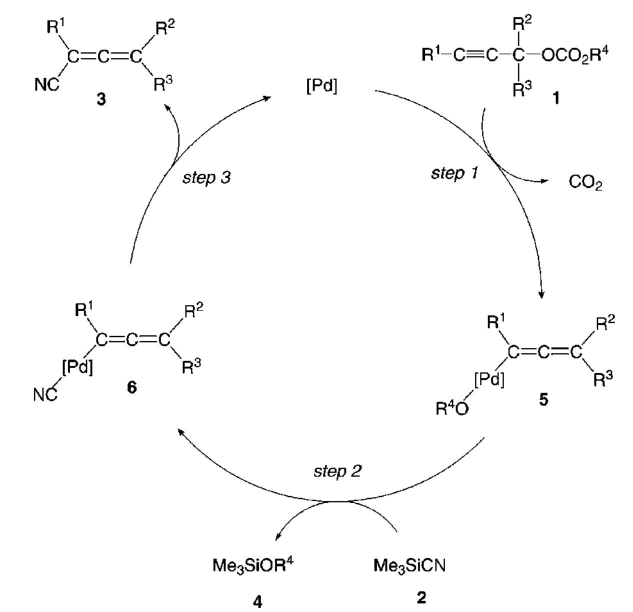
The fate of the trimethylsilyl moiety of **2** was determined by $^{29}$Si NMR measurement of the resulting reaction mixture. After the reaction shown in entry 1, a small amount of C$_6$D$_6$ as an NMR-lock was added to the filtered reaction mixture. The $^{29}$Si resonance of Me$_3$SiOMe (**4a**) appeared at 17.64 ppm (lit.: 17.75 ppm)[6a] and a very small resonance of **2** appeared at −12.31 ppm (lit.: −12.12 ppm)[6b] (eq 2). This observation

$$\mathbf{1a} + \underset{^{29}\mathrm{Si}:\,-12.31\ \mathrm{ppm}}{\mathbf{2}} \xrightarrow[-\,CO_2]{Pd(PPh_3)_4} \mathbf{3a} + \underset{^{29}\mathrm{Si}:\,17.64\ \mathrm{ppm}}{\underset{\mathbf{4a}}{Me_3SiOMe}} \qquad (2)$$

clearly indicates that the trimethylsilyl moiety of **2** effectively traps the leaving group (-OMe) from **1** after the decarboxylation.

The most plausible catalytic cycle for the present cyanation is illustrated in Scheme 1. The catalytic cycle is initiated by

**Scheme 1**




the oxidative addition of propargylic carbonate (**1**) to the Pd(0) catalyst center to afford an allenylpalladium species[7] (step 1). Then, transmetalation of **5** with trimethylsilyl cyanide (**2**) affords the corresponding (allenyl)(cyano)-palladium species (**6**) with concomitant formation of **4** (step 2); formation of **4** has been confirmed by $^{29}$Si NMR analysis of **4a** (eq 2). Similar transmetalation of **2** with an $\eta^3$-allylpalladium complex has been confirmed by a stoichiometric reaction between **2** and the palladium complex.[3a] Finally, reductive elimination of **6** provides cyanoallenes (**3**) as the product, regenerating the active catalyst species (step 3).

While only monocyanated products (**3**) were obtained with the use of 1 equiv of **2** (vide supra), the use of **2** in excess (6 equiv) provided dicyanated products (**7**) in high yields

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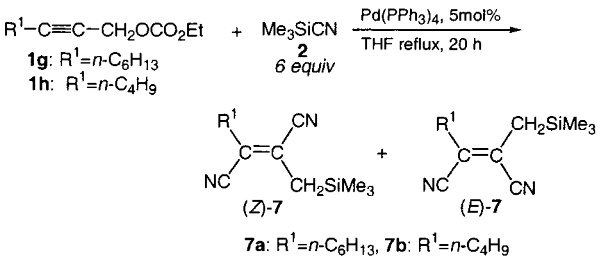


(3)

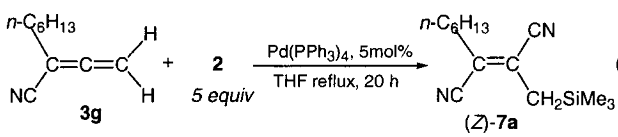
(eq 3 and Table 2). With **1g** and **1h** ($R^2 = R^3 = H$) as the substituents, **7a** and **7b** were obtained, respectively, in high

**Table 2.** Dicyanation of **1g** and **1h** with **2**[a]

| entry | $R^1$ | catalyst | yield of **7**[b] | $(Z)/(E)$[b] |
|---|---|---|---|---|
| 9 | $n$-$C_6H_{13}$ | $Pd(PPh_3)_4$ | 83 (80)[c] | 100/0 |
| 10 | $n$-$C_4H_9$ | $Pd(PPh_3)_4$ | 82 (78)[c] | 100/0 |
| 11 | $n$-$C_6H_{13}$ | $PdCl_2$ | 88 | 70/30 |
| 12 | $n$-$C_6H_{13}$ | $PdCl_2(PhCN)_2$ | 76 | 71/29 |
| 13 | $n$-$C_6H_{13}$ | $PdCl_2(PPh_3)_2$ | 56 | 66/34 |

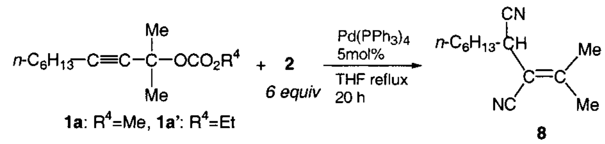
[a] A mixture of propargylic carbonate (1.0 mmol), $Me_3SiCN$ (6.0 mmol), catalyst (0.050 mmol), and THF (4.0 mL) was stirred under reflux for 20 h. [b] Determined by GC. [c] Isolated yield.

yields (entries 9 and 10).[8] The use of $Pd(PPh_3)_4$ as the catalyst afforded the ($Z$)-isomer stereoselectively (entries 9 and 10), while a mixture of the stereoisomers was obtained with the use of $PdCl_2$, $PdCl_2(PhCN)_2$, and $PdCl_2(PPh_3)_2$[9] as catalysts (entries 11−13). For formation of the dicyanated products (**7**), the cyanoallenes (**3**) must be the intermediate. Indeed, ($Z$)-**7a** was obtained in 93% yield from **3g** in the presence of $Pd(PPh_3)_4$ as catalyst under the standard catalytic conditions (eq 4), while **7a** was not obtained at all without the



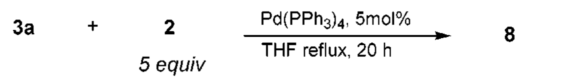
(4)

palladium catalyst. The palladium-catalyzed addition of **2** to simple allenes has been reported.[10] On the other hand, the reaction of **1a** and **1a′** ($R^3 = R^4 = Me$) with an excess of **2** (6 equiv) is rather anomalous, affording **8** as the product which is isolated in 77% yield from **1a** and fully characterized (eq 5).[11] The mechanism for the formation of **8** remains



(5)

unclear, although **8** was produced in 89% yield by reaction of **3a** with 5 equiv of **2** in the presence of $Pd(PPh_3)_4$ (eq 6).



(6)

In conclusion, trimethylsilyl cyanide (**2**) is a potent cyanation reagent for propargylic carbonates (**1**) in the presence of $Pd(PPh_3)_4$ as catalyst. One equivalent of **2** affords cyanoallenes (**3**), while further reaction of the cyanoallenes to **7** or **8** occurs in the presence of excess **2**.

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**Supporting Information Available:** Detailed experimental procedures and characterization data for the products. This material is available free of charge via Internet at http://pubs.acs.org.

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(8) **7a** was not detected at all with 1 equiv of **2** in entry 8 of Table 1.

(9) These palladium complexes were not active as catalysts for the monocyanation using 1 equiv of **2** (eq 1). Evidently, the presence of excess **2** animated the complexes as the catalysts.

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(11) The product **8** was formed in the catalytic reaction and did not change during the isolation process. In the reaction, toluene can be used as solvent. It is noteworthy that no deuterium incorporation into **8** happened even when the reaction was carried out in toluene-$d_8$ as the solvent.