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Cyanation of Allylic Carbonates and Acetates Using Trimethylsilyl Cyanide Catalyzed by Palladium Complex

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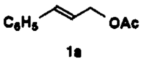
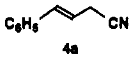
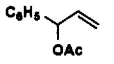
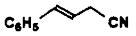
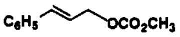
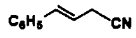
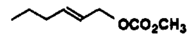
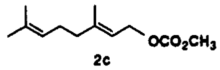
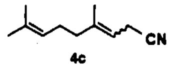
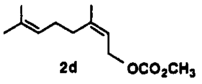
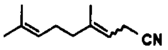
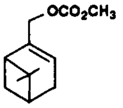
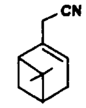
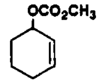
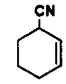
Summary: Allylic carbonates and acetates are cyanated with trimethylsilyl cyanide in the presence of a catalytic amount (5 mol % based on the allylic substrates) of $Pd(PPh_3)_4$ or $Pd(CO)(PPh_3)_3$ in THF under reflux to afford β,γ-unsaturated nitriles in high yields.

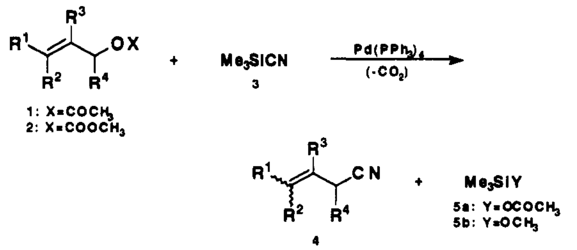
Palladium-catalyzed transformations of allylic acetates 1 and carbonates 2 have received much attention as methods of organic synthesis.[1] In the presence of palladium catalysts, these allylic substrates provide π-allyl palladium intermediates, which react with various nucleophiles such as stabilized anions and amines.[2] However, there is no precedent for cyanides as nucleophiles,[3] even though reaction would afford useful β,γ-unsaturated nitriles.[5,6] Recently, trimethylsilyl cyanide (Me_3SiCN:3) has been widely recognized as a potent cyanation reagent[8] and utilized in cyanations of aryl halide[9a] and alkyne[9b] catalyzed by palladium complex. We have recently developed novel reactions utilizing organosilylstannanes[10a] and disilanes[10b] as silicon reagents. During the course of these studies, we have found a new reaction with Me_3SiCN. In this paper, we disclose the first example of cyanation of allylic carbonates 2 and acetates 1 catalyzed by palladium complexes, where Me_3SiCN (3) is highly efficient as a cyanide source (eq 1).

The results are listed in Table I. When cinnamyl acetate (**1a**) was allowed to react with 2 equiv of Me_3SiCN, cinnamyl cyanide (**4a**) was formed regio- and stereoselectively in 98% yield (entry 1). Under the same reaction conditions, 1-phenyl-2-propenyl acetate (**1b**) also affords the same products (entry 2), suggesting π-allyl palladium intermediacy. The corresponding carbonate derivative, cinnamyl methyl carbonate (**2a**), also provides **4a** in 98% yield (entry 3). Nature of the catalyst precursor affects the reaction markedly. $Pd(PPh_3)_4$ and $Pd(CO)(PPh_3)_3$ show high catalytic activity. However, other representative catalyst precursors were not effective; yields of **4a** under the same reaction conditions as entry 3 are as follows: $Pd(OAc)_2$, 4%; $PdCl_2(PPh_3)_2$, trace; $Pd(DBA)_2$ (DBA =

Table I. Palladium Complex Catalyzed Cyanation of Allylic Carbonates and Acetates Using Trimethylsilyl Cyanide^{a}

entry	allylic compd	time/h	product	yield^{b}/%	*E*/*Z*
1^{c}	 **1a**	16	 **4a**	(98)	> 99
2	 **1b**	23	 **4a**	82	> 99
3	 **2a**	16	 **4a**	92 (98)	> 99
4	 **2b**	5	 **4b**	78	80/20
5	 **2c**	5	 **4c**	89	71/29
6	 **2d**	5	 **4c**	80	71/29
7^{c,d}	 **2e**	15	 **4d**	92	-
8	 **2f**	18	 **4e**	88	-

^{a} A mixture of allylic acetate 1 or carbonate 2 (1.50 mmol), Me_3SiCN (3.0 mmol), $Pd(PPh_3)_4$ (0.075 mmol), and THF (6.0 mL) was stirred under reflux. ^{b} Isolated yields. Numbers in parentheses show GLC yields determined by the internal standard method. ^{c} Catalyst precursor: $Pd(CO)(PPh_3)_3$. ^{d} In toluene (6.0 mL) under reflux.



(1)

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[1] (a) Tsuji, J. *Organic Synthesis with Palladium Compounds*; Springer-Verlag: New York, 1980. (b) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapter 19.

[2] Trost, B. M. *Acc. Chem. Res.* **1980**, *13*, 385.

[3] Reaction of π-allyl palladium complexes with cyanide ion afforded cyano-bridged π-allyl complexes.[4a] Cyano addition reaction (hydrocyanation) with π-allyl palladium complexes gave saturated nitriles.[4b]

[4] (a) Shaw, B. L.; Shaw, G. *J. Chem. Soc. A* **1971**, 3533. (b) Alexander, C. W.; Jackson, W. R. *J. Chem. Soc., Perkin Trans. 2* **1972**, 1601.

[5] (a) Murakami, M.; Kato, T.; Mukaiyama, T. *Chem. Lett.* **1987**, 1167. (b) Hayashi, Y.; Mukaiyama, T. *Chem. Lett.* **1987**, 1811. (c) Araki, S.; Minami, K.; Butsugan, Y. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 629.

[6] Palladium-catalyzed reaction of α-acetoxy-β,γ-unsaturated nitriles with nucleophiles[7a] and palladium-catalyzed decarboxylation–allylation of allylic esters of α-substituted cyanoacetic acids[7b] afforded β,γ-unsaturated nitriles as products.

[7] (a) Tsuji, J.; Ueno, H.; Kobayashi, Y.; Okumoto, H. *Tetrahedron Lett.* **1981**, *22*, 2573. (b) Tsuji, J.; Yamada, T.; Minami, I.; Yuhara, M.; Nisar, M.; Shimizu, I. *J. Org. Chem.* **1987**, *52*, 2988.

[8] (a) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: Berlin, 1983; pp 6-20. (b) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworths: London, 1981.

[9] (a) Chatani, N.; Hanafusa, T. *J. Org. Chem.* **1986**, *51*, 4714. (b) Chatani, N.; Takeyasu, T.; Horiuchi, N.; Hanafusa, T. *J. Org. Chem.* **1988**, *53*, 3539.

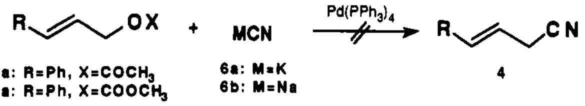
[10] (a) Tsuji, Y.; Obora, Y. *J. Am. Chem. Soc.* **1991**, *113*, 9368. (b) Tsuji, Y.; Lago, R. M.; Tomohiro, S.; Tsuneishi, H. *Organometallics* **1992**, *11*, 2353.

0022-3263/93/1958-0016$04.00/0

dibenzylideneacetone), 5%; $PdCl_2(PhCN)_2$, 5%; $Pt(PPh_3)_4$, 0%; $Ru_3(CO)_{12}$,[11a,b] 4%; $Mo(CO)_6$,[11c] 3%.

Aliphatic allylic carbonates **2b–d** also readily gave the corresponding β,γ-unsaturated nitriles regioselectively in high yields, but with modest stereoselectivity (entries 4–6). Geranyl methyl carbonate (**2c**) provided a mixture of *E*/*Z* isomers in the same ratio as neryl methyl carbonate (**2d**) (entries 5 and 6).[12] Compared with the allylic carbonates **2**, the corresponding allylic acetates **1** such as (*E*)-2-hexenyl, geranyl, and neryl acetates afforded lower conversions (10–50%), though selectivities were high. Hence, allylic carbonates **2** are more suitable substrates for the present reaction. Alicyclic allylic carbonates also afford the corresponding nitriles in high yields (entries 7, 8). Under the standard conditions (reflux in THF), almost no **2e** was consumed. However, the cyanation readily proceeds at higher reaction temperature: reflux in toluene (entry 7) or at 110 °C in diglyme.

KCN (**6a**) was employed in THF medium as the cyanide source in the palladium-catalyzed cyanation of iodobenzene.[14] We compared the reactivity of KCN as well as NaCN (**6b**) with Me_3SiCN. Under the same reaction conditions as entry 1, **1a** did not react at all with KCN or NaCN. On the other hand, **2a** was consumed completely in the reaction with KCN. However, the reaction was not clean and afforded cinnamyl methyl ether in 40% yield by palladium-catalyzed decarboxylation.[7b] The consumption of **2a** was low (<20%) in the reaction with NaCN. In either case, no **4** is obtained with KCN or NaCN as the cyanide source (eq 2).



(2)

The fate of the trimethylsilyl moiety of Me_3SiCN in the reaction was clarified by ^{29}Si-NMR in THF locked with C_6D_6. After the reaction with allylic acetates **1**, 1 equiv of trimethylsilyl acetate (**5a**) (22.06 ppm; lit.[15a] 22.0 ppm) was found in the reaction mixture, along with excess Me_3SiCN (−12.30 ppm; lit.[15b] −12.12 ppm) which remained almost intact. In the reaction with allylic carbonates **2**, formation of methoxytrimethylsilane (**5b**) (17.66 ppm; lit.[15c] 17.75 ppm) was confirmed similarly. The strong oxophilicity of the trimethylsilyl functionality may favor the reaction by effective trapping of the oxygen-containing leaving group, i.e., $-OCOCH_3$ and $-OCH_3$.

A typical procedure is as follows: A 20-mL flask was charged with $Pd(PPh_3)_4$ (0.075 mmol; 5 mol %), THF (6.0 mL), cinnamyl methyl carbonate (**2a**; 1.5 mmol), and Me_3SiCN (**3**; 3.0 mmol) under an argon flow. The reaction was carried out under reflux for 16 h. The mixture was then passed through a short Florisil column (8-mm i.d. × 70 mm) to give a clear yellow solution. GLC analysis (OV-17 or PEG-HT) with naphthalene as an internal standard showed cinnamyl cyanide (**4a**) was formed in 98% yield. The product was isolated by Kugelrohr distillation in 92% yield (198 mg).

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Supplementary Material Available: ^1H- and ^{13}C-NMR, IR, and MS spectral data for the products (2 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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[11] (a) Tsuji, Y.; Mukai, T.; Kondo, T.; Watanabe, Y. *J. Organomet. Chem.* **1989**, *369*, C51. (b) Kondo, T.; Mukai, T.; Watanabe, Y. *J. Org. Chem.* **1991**, *56*, 487. (c) Trost, B. M.; Lautens, M. *J. Am. Chem. Soc.* **1982**, *104*, 5543.

[12] The *E*/*Z* ratio does not depend on the conversion of **2**. Therefore, isomerization between *E*/*Z* isomers during the course of the reaction is unlikely. The ratio might be governed by the relative stability of syn and anti π-allyl palladium intermediates.[13]

[13] Maitlis, P. M.; Espinet, P.; Russell, M. J. H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 6, pp 385–454.

[14] Sekiya, A.; Ishikawa, N. *Chem. Lett.* **1975**, 277.

[15] (a) Bassingdale, A. R.; Posnan, T. B. *J. Organomet. Chem.* **1975**, *175*, 273. (b) Marsmann, H. C. *Chem. Ztg.* **1972**, *96*, 286. (c) Van den Berghe, E. V.; Van der Kelen, G. P. *J. Organomet. Chem.* **1973**, *59*, 175.