Palladium-catalysed Addition of Trimethylsilyl Cyanide to Arylacetylenes

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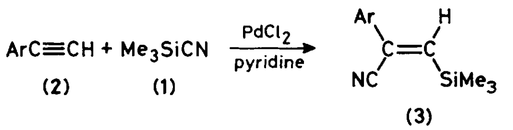
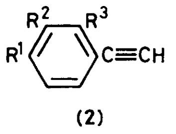
The reaction of arylacetylenes with trimethylsilyl cyanide (**1**) in the presence of a palladium complex resulted in addition of (**1**) across the carbon–carbon triple bond with high regio- and stereo-selectivity to give β-cyano-β-arylalkenylsilanes.

In recent years, organosilicon reagents have found many applications in organic synthesis. Although the addition of trimethylsilyl cyanide, Me_3SiCN, (**1**) to carbon–oxygen and carbon–nitrogen double bonds is well known,[1] no example of the addition of (**1**) to a carbon–carbon multiple bond has been reported,[2] to the best of our knowledge. We now report that the addition of (**1**) to arylacetylenes can be accomplished by the use of a palladium catalyst. The reaction gives β-cyano-β-arylalkenylsilanes in good yields with high regio- and stereo-selectivity, equation (1).

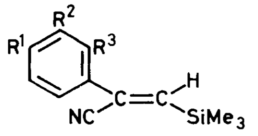
In a typical procedure, 5 mmol of phenylacetylene (**2a**) was treated with 10 mmol (1.3 ml) of (**1**) and a catalytic amount (0.2 mmol, 36 mg) of palladium chloride and pyridine (0.4 mmol, 32 μl) in refluxing toluene (10 ml) for 20 h under nitrogen. Analysis of the reaction mixture by g.l.c. showed it to contain 2-phenyl-3-trimethylsilyl-(*Z*)-prop-2-enenitrile (**3a**) in 93% yield. Distillation gave pure (**3a**), [b.p. 95—96 °C (0.9 mmHg)]; i.r. (neat) 2200 (CN), 1560 (C=C) cm^{-1}; ^1H n.m.r. ($CDCl_3$) δ 0.35 (s, 9H, SiMe), 7.10 (s, 1H, =CH), 7.37—7.41 (m, 2H, Ph), and 7.61—7.63 (m, 3H, Ph); ^{13}C n.m.r. ($CDCl_3$)



(1)



(2)



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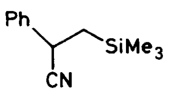

(4)

a; $R^1 = R^2 = R^3 = H$
b; $R^1 = OMe, R^2 = R^3 = H$
c; $R^1, R^2 = -OCH_2O-, R^3 = H$
d; $R^1 = F, R^2 = R^3 = H$
e; $R^1 = Cl, R^2 = R^3 = H$
f; $R^1 = Br, R^2 = R^3 = H$
g; $R^1 = CN, R^2 = R^3 = H$
h; $R^1 = R^2 = H, R^3 = OMe$

δ −1.40 (SiMe), 117.92 (CN), 125.67, 127.94, 128.89, 129.57, 135.10 (Ph, =C-), and 147.56 (=CH); *m/z* 201 (M^+, 100%).† The regio- and stereo-chemistry of this novel addition reaction of (**1**) to arylacetylenes was unequivocally established as follows. The *cis* addition of (**1**) to the carbon–carbon triple bond was confirmed by the coupling constant (*J* 17 Hz) between the CN carbon and the vinyl proton in the ^{13}C n.m.r. spectrum. The regiochemistry was confirmed by hydrogenation (Pd–C in EtOAc, 97%) of (**3a**) to give (2-cyano-2-phenylethyl)trimethylsilane (**4**), identified by spectroscopic methods.

The results obtained for some substituted phenylacetylenes are listed in Table 1. The reaction was compatible with functional groups such as methylenedioxy, methoxy, fluoro, and chloro groups and gave (*Z*)-β-cyano-β-arylalkenylsilanes (**3a**)—(**3e**)‡ and (**3h**) selectively. However in the reaction of *p*-bromophenylacetylene (**2f**), the expected product (**3f**) was formed, along with (**3g**), where the bromine on the aromatic ring had been replaced by a cyano group.

Table 1. Palladium-catalysed reaction of arylacetylenes with trimethylsilyl cyanide (**1**).

ArC≡CH	Product	Yield/%[a]
(**2a**)	(**3a**)	93 (90)
(**2b**)	(**3b**)	88 (85)
(**2c**)	(**3c**)	56 (55)
(**2d**)	(**3d**)	52 (38)
(**2e**)	(**3e**)	43 (40)
(**2f**)	(**3f**)	17 (14)[b]
	(**3g**)	26 (14)[b]
(**2h**)	(**3h**)	78

[a] G.l.c. yields based on the acetylene. Isolated yields (by distillation) are in parentheses. [b] Isolated by preparative t.l.c.

The present reaction provides a new route to synthetically useful regio- and stereo-defined polyfunctional compounds.[3] Moreover, it represents the first example of transition metal-catalysed addition of trimethylsilyl cyanide (**1**) to a carbon–carbon multiple bond.

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References

1 E. Colvin, 'Silicon in Organic Synthesis,' Butterworths, London, 1981; W. P. Weber, 'Silicon Reagents for Organic Synthesis,' Springer-Verlag, Berlin, 1983.
2 The reaction of (**1**) with enones is known to give 1,4-addition: K. Utimoto, Y. Wakabayashi, T. Horiie, M. Inoue, Y. Shishiyama, M. Obayashi, and H. Nozaki, *Tetrahedron*, 1983, **39**, 976.
3 For a recent method for the preparation of regio- and stereo-isomers of (**3a**), see: G. D. Fallon, N. J. Fitzmaurice, W. R. Jackson, and P. Perlmutter, *J. Chem. Soc., Chem. Commun.*, 1985, 4, and references cited therein.

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† We gratefully acknowledge Dr. I. Matsuda, Nagoya University, for a gift of 3-phenyl-2-trimethylsilyl-(*E*)-prop-2-enenitrile: I. Matsuda, H. Okada, and Y. Izumi, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 528.

‡ Satisfactory spectral data and elemental analyses were obtained for all new compounds. Characteristic spectra data include: i.r. (neat or $CDCl_3$) 2215—2220 (CN) cm^{-1}; ^1H n.m.r. ($CDCl_3$) δ 0.32—0.36 (s, SiMe) and 6.90—7.26 (s, =CH); ^{13}C n.m.r. ($CDCl_3$) δ −1.3—−1.5 (SiMe) and 117.2—118.1 (CN); *m/z*, M^+.