Regio- and Stereo-chemical Control in the Nickel-catalysed Addition of HCN to Alkynes. A Simple Synthesis of *(E)*-2-Alkyl-3-trialkylsilylalk-2-enenitriles

Gary D. Fallon, Neil J. Fitzmaurice, W. Roy Jackson, and Patrick Perlmutter*

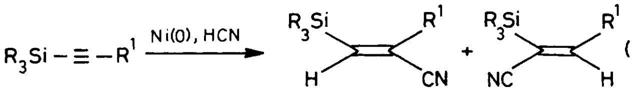
Chemistry Department, Monash University, Clayton, Victoria, Australia 3168

By varying the steric bulk of silicon substituents attached to alk-1-ynes it is possible to control, to a high degree, the regiochemical outcome of nickel(0)-catalysed hydrocyanations of alk-1-ynes: the crystal structure of one adduct is included which establishes that the *stereo*chemical outcome of the reaction is a result of addition of HCN to the alkyne to give an (*E*)-product; overall, these results constitute a simple method for the preparation of (*E*)-2-alkyl-3-trialkylsilylalk-2-enenitriles.

Recently it was demonstrated that hydrocyanation of simple alkynes could be readily achieved using nickel tetrakistriphenylphosphite catalysis.[1] This led to regioisomeric mixtures, however, and a solution to this problem has been developed and is reported here. From earlier work[1] it was evident that the steric bulk of a substituent influenced the regioselectivity of addition. With this in mind, a variety of silylated alkynes was prepared and examined in the hydrocyanation reaction, equation (1).

The reasons for using silicon-based substituents are threefold. Firstly, the starting materials are easily prepared;[2] secondly, the steric bulk of the substituent can be easily varied, and thirdly, the substituent should be easy to remove at some stage subsequent to HCN addition.

As can be seen from Tables 1 and 2, silylalkynes are good substrates for nickel-catalysed HCN addition, the reactions proceeding in good to excellent chemical yields.† From Table 1 it is apparent that in all cases except t-butyldimethylsilylacetylene the silicon substituent effectively directs the nitrile away from the silicon-bearing carbon. Thus, for alk-1-ynes, 2-alkyl-3-trialkylsilylalk-2-enenitriles are produced in high yield and purity.



(1) (2)

(1)

Table 1. Results from the hydrocyanation of 1-(t-butyldimethylsilyl)alk-1-ynes.[a,b]

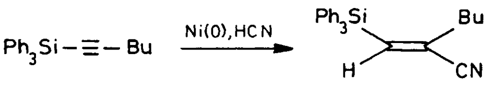
R^1	Yield[c] (%)	Ratio (**1**) : (**2**)[d]
H	57	35 : 65
Me	88	98 : 2
Bu	85	97 : 3
Ph	73	90 : 10

[a] See equation (1). [b] Reaction conditions are similar to those reported previously (ref. 1) except that the catalyst : substrate ratio was usually increased to 1 : 90 or 1 : 45. [c] Yield after distillation or recrystallisation. [d] Determined by g.c. as before (ref. 1).

Table 2. Results from the hydrocyanation of 1-trimethylsilylalk-1-ynes.[a,b]

R^1	Yield[c] (%)	Ratio (**1**) : (**2**)[d]
H	74	25 : 75
Me	90 (87)[e]	80 : 20
Bu	94 (90)[e]	72 : 28
Ph	80 (80)[e]	20 : 80

[a—d] See footnotes to Table 1. [e] Reaction carried out in toluene solution at reflux with acetone cyanohydrin in place of HCN.

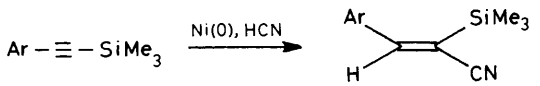


(3)

(2)

---

† All new compounds reported here gave satisfactory spectroscopic and elemental analyses.



(3)

Unequivocal evidence for the stereochemistry of addition came from the reaction of 1-triphenylsilylhex-1-yne with HCN, equation (2). The *X*-ray single crystal structure‡ of nitrile (**3**), given below, shows that HCN adds to the alkyne to give an (*E*)-product.† This is in line with results of similar additions of HCN to alkenes.[3]

The trimethylsilyl group was also examined in the hydrocyanation reaction (Table 2) and was found to give mixtures of (**1**) and (**2**) in all cases. 1-Trimethylsilyl-2-phenylethyne gave mainly isomer (**2**) which was readily purified by chromatography. This discovery should provide direct access to substituted cinnamonitriles, equation (3).

We have also found that rather than carrying out the reaction in a sealed autoclave (in order to retain the volatile HCN), simply heating the reactants in toluene with acetone cyanohydrin in place of HCN gave excellent results (Table 2). Only when both alkyne substituents are bulky, for example, R^1 = $SiMe_3$ is the conversion into the nitrile very poor (<5%) using either method.

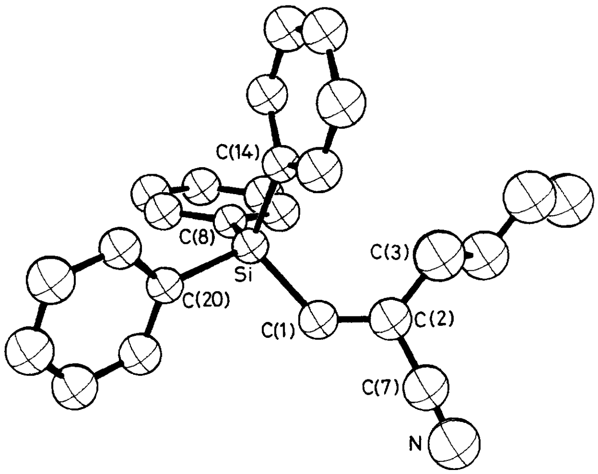


Figure 1. ORTEP diagram of (**3**) viewed perpendicular to the plane through Si, C(1), C(2), C(3), and C(7): the largest deviation from this plane is C(2) at 0.011(7) Å. Thermal ellipsoids are drawn at 50% probability level.

In conclusion, we have demonstrated that nickel(0) catalysed addition of HCN to silylalkynes proceeds in high chemical yields. Variation of the steric bulk of the silyl substituent has led to a simple method for preparing, for the first time, (*E*)-2-alkyl-3-trialkylsilylalk-2-enenitriles of high regio- and stereo-chemical purity.[4]

We thank Johnson-Matthey for a loan of metals and the Australian Research Grants Scheme for financial support.

Received, 7th August 1984; Com. 1156

References

1 W. R. Jackson and C. G. Lovel, *J. Chem. Soc., Chem. Commun.*, 1982, 1231; *Aust. J. Chem.*, 1983, **36**, 1975.
2 Whilst this work was in progress a method similar to that used by us, for the preparation of 1-trialkylsilylalk-1-ynes, appeared: S. Rajagopalan and G. Zweifel, *Synthesis*, 1984, 111.
3 W. R. Jackson and C. G. Lovel, *Aust. J. Chem.*, 1982, **35**, 2053.
4 For a recent method for the preparation of (*Z*)-2-silylalkenenitriles, see Y. Sano and Y. Minomi, *J. Chem. Soc., Chem. Commun.*, 1982, 56 and I. Matsuda, H. Okada, and Y. Haimi, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 528.

---

‡ *Crystal data:* diffraction data (Cu-K_α) for (**3**) were collected with a Philips PW1100 automated four-circle diffractometer on a crystal of size 0.25 × 0.25 × 0.25 mm the structure solved by direct methods using the SHELX system; space group $P1$, a = 9.373(5), b = 14.691(8), c = 9.706(5) Å, α = 90.07(2), β = 126.09(3), γ = 90.89(2)°; D_c = 1.13, D_m = 1.17(3) g cm^{-3} for M_z = 367.60 and Z = 2, $F(000)$ = 398, μ = 9.2 cm^{-1}. Refinement was by full-matrix techniques with isotropic thermal parameters for Si, C, and N; hydrogen atoms not included. R_F = 10.9% for 2704 reflections with $I > 3\sigma(I)$ and $6° < 2\theta < 120°$. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.