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THE STEREOCHEMISTRY OF ORGANOMETALLIC COMPOUNDS

XXXVI *. REGIO- AND STEREO-CHEMICAL CONTROL IN THE NICKEL-CATALYSED HYDROCYANATION OF SILYLALKYNES

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Summary

The regioselectivity of hydrocyanation of silylalkynes can be controlled by varying the size of the groups attached to silicon leading, for example, to efficient preparations of *E*-3-trialkylsilyl-2-alkyl-2-alkenenitriles. High yields of the silylalkene nitriles can be obtained by using either acetone cyanohydrin or hydrogen cyanide as reagents.

Introduction

Recently we reported the preparation of α,β-unsaturated nitriles by nickel-catalysed hydrocyanation of alkynes [1]. However, although good yields of nitriles were obtained, the regioselectivity of addition was not high for many of the reactions. The results showed that the regioselectivity was very susceptible to steric effects. In this paper we describe the hydrocyanation of 1-silylalkynes in which the size of the groups substituted on silicon is varied. The use of a silyl group to control regioselectivity has other advantages in that the silylalkynes are easily prepared and the silyl substituent may be replaced by other functional groups at some stage after hydrogen cyanide addition.

Preparation of silylalkynes

All the silylalkynes used in this study were prepared by coupling the appropriate alkynyllithium and trialkylsilyl chloride together [2], the use of alkynyllithiums rather than the corresponding alkynyl-Grignard reagents giving much better yields [3–5].

$$R{-}C{\equiv}C{-}Li + Cl{-}SiR_3 \rightarrow R{-}C{\equiv}C{-}SiR_3$$

* For part XXV see ref. 13, also a summary of some of this work has been published [9].

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Hydrocyanation of silylalkynes

(i) Preparative aspects

Previous hydrocyanations of alkynes have been carried out by heating a solution of the alkyne in benzene with hydrogen cyanide, nickel tetrakistriphenylphosphite, and triphenylphosphite for 18 h at 120°C. The molar ratio of catalyst/ligand/substrate was 1/12/185. However it was found in this study that good yields of nitriles could only be obtained for trialkylsilylalkynes by increasing the catalyst/substrate ratio to 1/90 or to 1/45 (with concomitant increase in the amount of free ligand see Table 1). When the very large Ph_3Si group was present it was necessary to increase the ratio to 1/18 to obtain a good yield (reaction 7). Only when both alkyne substituents were large did the reaction fail ($R^1 = Me_3Si$, $R^2 = Me_3Si$, reaction 10, $R^1 = Bu^tMe_2Si$, $R^2 = Bu^t$, reaction 6).

The preparation and use of hydrogen cyanide can present several difficulties, therefore it is important to note that we have found that hydrogen cyanide can be replaced by acetone cyanohydrin in these reactions without loss of yield (reactions 16 and 17). When the alkyne was not too volatile it was possible to obtain good yields simply by heating a solution of the alkyne, catalyst, excess ligand and acetone cyanohydrin in toluene under reflux overnight.

TABLE 1

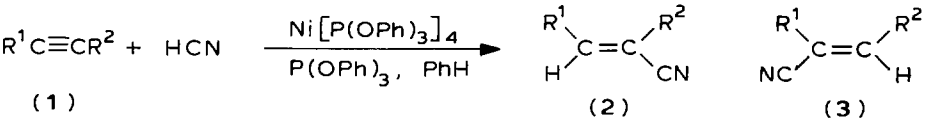
YIELDS AND REGIOSELECTIVITY FOR HYDROCYANATION OF SILYLALKYNES

Reaction number	Alkyne		Conditions [a]	Ratio catalyst/ alkyne	Ratio 2/3	Yield (%)
	R^1	R^2				
1	Bu^tMe_2Si	H	HCN	1/45	35/65	57
2	Bu^tMe_2Si	Me	HCN	1/45	98/2	88
3	Bu^tMe_2Si	Bu	HCN	1/45	97/3	85
4	Bu^tMe_2Si	Bu	HCN	1/90	97/3	40
5	Bu^tMe_2Si	Ph	HCN	1/45	90/10	73
6	Bu^tMe_2Si	Bu^t	HCN	1/45	–	–
7	Ph_3Si	Bu	HCN(72 h)	1/18	100/0	75
8	Ph_3Si	Bu	HCN	1/90	100/0	10
9	Ph_3Si	Bu	HCN(42 h)	1/90	100/0	30
10	Me_3Si	$SiMe_3$	HCN(72 h)	1/18	–	–
11	Me_3Si	H	HCN	1/185	25/75	24
12	Me_3Si	H	HCN	1/40	25/75	74
13	Me_3Si	H	2eq $Me_2C(OH)CN$ [b]	1/45	25/75	75
14	Me_3Si	Me	HCN	1/185	80/20	60
15	Me_3Si	Me	HCN	1/90	80/20	90
16	Me_3Si	Me	$Me_2C(OH)CN$	1/90	80/20	81
17	Me_3Si	Me	$Me_2C(OH)CN$	1/45	80/20	87
18	Me_3Si	Bu	HCN	1/90	72/28	94
19	Me_3Si	Bu	1eq $Me_2C(OH)CN$ [b]	1/45	72/28	75
20	Me_3Si	Bu	2eq $Me_2C(OH)CN$ [b]	1/45	72/28	90
21	Me_3Si	Ph	HCN	1/90	0/100	80
22	Me_3Si	Ph	2eq $Me_2C(OH)CN$ [b]	1/45	0/100	81

[a] Reactions for 18 h at 120°C in autoclave unless otherwise stated. [b] Reactions carried out by heating under reflux in toluene solution for 18 h.

(ii) Regiochemistry

It has been reported previously that whereas straight chain terminal alkynes e.g. hex-1-yne (**1**: $R^1 = Bu$, $R^2 = H$) give predominantly the branch chain nitriles **3** ($R^1 = Bu$, $R^2 = H$), reaction of 3,3-dimethylbut-1-yne (**1**: $R^1 = Bu^t$; $R^2 = H$) gave predominantly the linear nitrile (**2**: $R^1 = Bu^t$; $R^2 = H$). These results suggested that



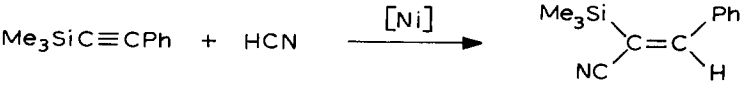
the electronic preference for the branch chain nitrile found in hex-1-yne could not compete with the steric effect of the t-butyl group in the reaction of 3,3-dimethylbut-1-yne. The hydrocyanation of alkynes containing the large t-butyldimethylsilyl group therefore investigated to see if this substituent could dominate the regioselectivity of reaction. In all cases (except the case of t-butyldimethylsilylethyne) the nitrile became attached to the carbon atom remote from the bulky silyl group (reactions 2, 3, 4 and 5). Even when a phenyl group was substituted on the alkyne (**1**: $R^1 = Bu^tMe_2Si$; $R^2 = Ph$) isomer **2** predominated.

Reactions of triphenylsilyl derivatives appeared to be even more selective and reaction occurred exclusively at the carbon atom remote from the triphenylsilyl group (reactions 7, 8 and 9).

Only for t-butyldimethylsilylethyne (**1**: $R^1 = Bu^tMe_2Si$; $R^2 = H$) did nitrile attachment to the carbon atom bound to silicon predominate. The ratio of terminal to branched nitriles **2**/**3** = 35/65 (reaction 1) suggested that the t-butyldimethylsilyl group was effectively smaller than a t-butyl group in this reaction. The preference for branch chain nitrile may be partially due to stabilization by silicon of the incipient carbon–nickel bond in the transition state favouring the branched product [1].

Stabilization by silicon of this type may be responsible for the preference for branch-chain nitrile from the hydrocyanation of trimethylsilylethyne (**1**: $R^1 = Me_3Si$; $R^2 = H$) (reactions 11 and 12). The ratio of **2** to **3** was 25/75 for this compound demonstrating that the steric effect for the trimethylsilyl group was significantly less than for the t-Bu^tMe_2Si-group. Reactions of trimethylsilylalk-1-ynes (**1**: $R = Me_3Si$; $R^2 =$ Me or Bu) (reactions 14 to 20) not surprisingly gave regiomixtures in which the minor isomer **2** was present in significant amounts, 20–30%.

The relatively small size of the trimethylsilyl group may be synthetically useful in that hydrocyanation of 1-trimethylsilyl-2-phenylethyne led to regiospecific formation of the (*Z*)-α-trimethylsilylcinnamonitrile (reaction 21).

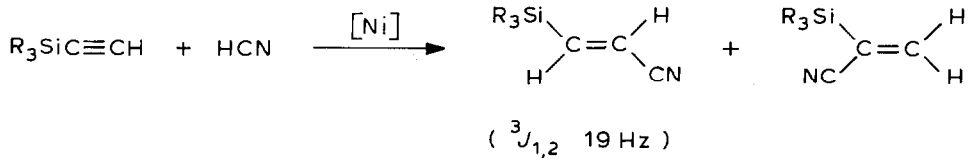


This reaction could well provide a general synthesis of such derivatives containing a wide range of aryl groups *.

* *Note added in proof.* It has recently been found that although this reaction is regioselective it is not regiospecific and significant amounts of the minor isomer (**2**; $R^1 = Me_3Si$, $R^2 = Ph$) (20 to 30%) may be formed. The isomers are easily separated by chromatography and sometimes by selective crystallisation.

(iii) Stereochemistry

The stereochemistry of hydrocyanation of both alkenes and alkynes [1] has been shown to be almost exclusively *syn*. Not surprisingly, therefore, the minor products from hydrocyanations of both trimethyl- and t-butyldimethyl-silylethynes were shown to have the *E*-stereochemistry from their ^{1}H NMR spectrum.



However, although ^{1}H NMR coupling constants have been used to assign the stereochemistry of the products of hydrocyanation of terminal alkynes, no assignment had been made for the products from disubstituted alkynes. Although addition to such alkynes has also been assumed to be *syn*, at least in one case, the hydrocyanation of dimethyl acetylenedicarboxylate, the stereochemistry of the product is suspected to be that of *anti*-addition [8]. Thus, when a crystalline product was obtained from the hydrocyanation of 1-triphenylsilylhex-1-yne, it was considered important to establish the structure by an X-ray single crystal structure determination [9]. The *syn*-stereochemistry of addition was unambiguously established and presumably applies to hydrocyanation of most disubstituted alkynes. Exceptions may occur when electron-withdrawing groups e.g. CO_2Me are substituted on the alkyne possibly leading to a significant change in the mechanism of reaction.

Conclusions

Hydrocyanation of t-butyldimethylsilylalkynes leads almost exclusively to (*E*)-2-alkyl-3-t-butyldimethylsilyl-2-alkenenitriles. In contrast reaction of 1-trimethylsilyl-2-phenylethyne gives a predominance of (*Z*)-2-trimethylsilyl-3-phenylprop-2-enenitrile. The utility of these compounds as intermediates in organic synthesis is being explored.

Experimental

Silylalkyne synthesis

A solution of the appropriate alkyne (14 mmol) in THF (50 ml) was cooled to −78°C. To this was added dropwise a solution of n-butyllithium (13 mmol) in hexane. After stirring for 2 h at −78°C a solution of trialkylsilyl chloride (12 mmol) in THF (10 ml) was added. The reaction mixture was then allowed to warm to room temperature and stirring was continued for 0.5–3 days. Treatment with a saturated ammonium chloride solution followed by extraction with ether gave the product which was purified either by distillation or recrystallization.

1-(Trimethylsilyl)hex-1-yne

B.p. 65°C (oven)/22 mmHg. (Lit. [11] b.p. 67°C/5 mmHg). Yield 30%. ν_{max} (film) 1980s (C≡C) cm^{-1}. ^{1}H NMR δ (60 MHz) 0.1, s, 9H, $Si(CH_3)_3$; 0.8–1.6, m, 7H, $CH_3(CH_2)_2$; 2.2, m, 2H, CH_2–C=. Mass spectrum: *m/e* 154 (M^+, 2), 139 (100), 73 (30).

1-(Trimethylsilyl)-2-phenylethyne

B.p. 60°C/0.5 mmHg. (Lit. [12] b.p. 155°C) Yield 33%. ν_{max} (film) 2150s (C≡C) cm^{-1}. ^1H NMR δ (60 MHz) 0.4, s, 9, $Si(CH_3)_3$; 7.45, m, 5H, Ph. Mass spectrum: *m/e* 174 (M^+, 20), 159 (100).

(t-Butyldimethylsilyl)ethyne

B.p. 110°C. Yield 86%. ν_{max} (film) 3300w, 2050s (C≡C) cm^{-1}. (Found: C, 68.3; H, 11.5. $C_{18}H_{16}Si$ calcd.: C, 68.5; H, 11.5%). ^1H NMR δ (60 MHz) 0.2, s, 6H, $Si(CH_3)_2$; 1.0, s, 9H, $Si(^tBu)$; 2.5, s, 1H, H(2). Mass spectrum: *m/e* 140 (M^+, 5), 125 (7), 83 (100).

1-(t-Butyldimethylsilyl)prop-1-yne

B.p. 144°C. Yield 65%. ν_{max} (film) 2200s (C≡C) cm^{-1}. (Found: C, 69.8; H, 11.7. $C_9H_{18}Si$ calcd.: C, 70.0; H, 11.8%). ^1H NMR: δ (60 MHz) 0.1, s, 6H, $Si(CH_3)_2$; 0.9, s, 9H, $Si(^tBu)$; 1.9, s, 3H, CH_3. Mass spectrum: *m/e* 154 (M^+, 2), 97 (100).

1-(t-Butyldimethylsilyl)hex-1-yne

B.p. 92°C/15 mmHg. Yield 71%. ν_{max} (film) 2200s (C≡C) cm^{-1}. (Found: C, 73.1; H, 12.1. $C_{12}H_{24}Si$ calcd.: C, 73.4; H, 12.3%). ^1H NMR δ (60 MHz) 0.1, s, 6H, $Si(CH_3)_2$; 0.9, s, 9H, $Si(^tBu)$; 1.2–1.6, m, 7H, $CH_3(CH_2)_2$; 2.2, m, 2H, CH_2–C≡. Mass spectrum: *m/e* 196 (M^+, 1), 181 (1), 139 (100).

1-(t-Butyldimethylsilyl)-2-phenylethyne

B.p. 72°C/0.15 mmHg. Yield 60%. ν_{max} (film) 2150s (C≡C) cm^{-1}. (Found: M^+ 216.133. $C_{14}H_{20}Si$ calcd.: M^+ 216.133). ^1H NMR δ (60 MHz) 0.3, s, 6H, $Si(CH_3)_2$; 1.2, s, 9H, $Si(^tBu)$; 7.4, m, 5H, Ph. Mass spectrum: *m/e* 216 (M^+, 5), 201 (1), 159 (100).

1-(t-Butyldimethylsilyl)-3,3-dimethylbut-1-yne

B.p. 69°C/23 mmHg. Yield 67%. ν_{max} (film) 2200m, 2180s (C≡C) cm^{-1}. (Found: C, 73.7; H, 12.5. $C_{12}H_{24}Si$ calcd.: C, 73.4; H, 12.3%). ^1H NMR δ (60 MHz) 0.1, s, 6H, $Si(CH_3)_2$; 0.9, s, 9H, $Si(^tBu)$; 1.3, s, 9H, ^tBu. Mass spectrum: *m/e* 196 (M^+,1), 139 (100), 97 (20).

1-(Triphenylsilyl)hex-1-yne

M.p. 45-46.5°C. Yield 74%. ν_{max} (Nujol) 2200s (C≡C) cm^{-1}. (Found: C, 84.7; H, 7.3. $C_{24}H_{24}Si$ calcd.: C, 84.7; H, 7.1%). ^1H NMR δ (90 MHz) 0.9, m, 3H, CH_3; 1.5, m, 4H $(CH_2)_2$; 2.4, m, 2H, CH_2–C=; 7.5, m, 15H, $SiPh_3$. Mass spectrum: *m/e* 390 (M^+,30), 298 (35), 284 (68), 283 (60), 263 (100), 220 (40), 207 (50), 183 (40), 105 (70).

Hydrocyanation reactions

General procedures for the methods used are described below. The yields and isomeric ratios for the methods used are reported for each compound in Table 1.

Method A. Into a stainless steel Hoke-type autoclave and under a nitrogen atmosphere were placed benzene (25 ml), tetrakis(triphenylphosphite)nickel(0) (0.24 g, 0.2 mmol), triphenylphosphite, silylalkyne, and hydrogen cyanide in a ratio of either 1/12/90/78 or 1/12/45/39. The vessel was heated at 120°C for 18 h. On cooling most of the catalyst was removed by filtration after precipitation with

pentane (15 ml). Removal of the solvents, followed by distillation yielded the cyano-α,β-unsaturated silanes.

Method B. Identical in all respects to Method A, except that HCN was replaced by acetone cyanohydrin.

Method C. Into a pre-dried round bottom flask (100 ml) and under a nitrogen atmosphere were placed toluene (50 ml), tetrakis(triphenylphosphite)nickel(0) (0.24 g, 0.2 mmol), triphenylphosphite, silylalkyne, and acetone cyanohydrin in a ratio of 1/12/45/90. The reaction mixture was heated at reflux, under a positive pressure of nitrogen for 18 h. On cooling the reaction mixture was worked up in a manner similar to that described in Method A.

*(E)-3-Trimethylsilylprop-2-enenitrile (**2**: $R^1 = SiMe_3$, $R^2 = H$) and 2-trimethylsilylprop-2-enenitrile (**3**: $R^1 = SiMe_3$, $R^2 = H$)*

B.p. 55°C/21 mmHg. ν_{max} (film) 2225s (C≡N), 1600w (C=C) cm^{-1}. M^+ 125.066. $C_6H_{11}NSi$ calcd.: M^+ 125.066). ^1H NMR δ (90 MHz) **2**: 0.15, s, 9H, $Si(CH_3)_3$; 5.7, d, $^3J_{trans}$ 19 Hz, 1H, H(2); 7.1, d, $^3J_{trans}$ 19 Hz, 1H, H(3); **3**: 0.2, s, 9H, $Si(CH_3)_3$; 6.1, d, $^2J_{gem}$ 2.5 Hz, 1H, (*Z*)H; 6.6, d, $^2J_{gem}$ 2.5 Hz, 1H, (*E*)H. Mass spectrum: *m/e* 125 (M^+, 15), 110 (40), 84 (40), 73 (100).

*(E)-2-Methyl-3-trimethylsilylprop-2-enenitrile (**2**: $R^1 = SiMe_3$, $R^2 = Me$) and (Z)-2-trimethylsilylbut-2-enenitrile (**3**: $R^1 = SiMe_3$, $R^2 = Me$)*

B.p. 75°C/17 mmHg. ν_{max} (film) 2225s (C≡N), 1600s (C=C) cm^{-1}. (Found: C, 60.3; H, 9.3; N, 10.0. $C_7H_{13}NSi$ calcd.: C, 60.4; H, 9.4; N, 10.1%). ^1H NMR δ (90 MHz) **2**: 0.2, s, 9H, $Si(CH_3)_3$; 2.0, d, ^4J 1.0 Hz, 3H, CH_3; 6.5, q, ^4J 1.0 Hz, 1H, H(3); **3**: 0.3, s, 9H, $Si(CH_3)_3$; 1.9, d, 3H, CH_3; 7.2, q, ^3J 7 Hz, 1H, H(3). Mass spectrum: *m/e* 139 (M^+, 40), 124 (100), 97 (35), 84 (70), 75 (50).

*2-Cyano-1-trimethylsilylhex-1-yne (**2**: $R^1 = SiMe_3$, $R^2 = Bu$) and Z-2-trimethylsilylhept-2-enenitrile (**3**: $R^1 = SiMe_3$, $R^2 = Bu$)*

B.p. 108°C/15 mmHg. ν_{max} (film) 2225s (C≡N), 1600s (C=C) cm^{-1}). (Found: C, 66.5; H, 10.6; N, 7.4. $C_{10}H_{19}NSi$ calcd.: C, 66.2; H, 10.6; N, 7.7%). ^1H NMR δ (90 MHz) 1.0–1.7, m, 7H, $CH_3(CH_2)_2$; 2.3, m, 2H, CH_2C=; **2**: 0.2, s, 9H, $Si(CH_3)_3$; 6.5, s, 1H, H(1); **3**: 0.3, s, 9H, $Si(CH_3)_3$; 7.1, t, ^3J 7.0 Hz, 1H, H(3). Mass spectrum: *m/e* 181 (M^+, 2), 180 (2), 166 (60), 139 (50), 80 (40), 73 (100).

*(Z)-3-Phenyl-2-trimethylsilylprop-2-enenitrile (**3**: $R^1 = SiMe_3$, $R^2 = Ph$)*

M.p. 76–77°C, b.p. 115°C (oven)/0.5 mmHg. ν_{max} (Nujol) 2220s (C≡N), 1600m (C=C) cm^{-1}. (Found: C, 71.6; H, 7.5; N, 7.0. $C_{12}H_{15}NSi$ calcd.: C, 71.3; H, 7.3; N, 7.0%). ^1H NMR δ (90 MHz) 0.2, s, 9H, $Si(CH_3)_3$; 7.3, m, 5H, Ph; 8.1, s, 1H, H(3). Mass spectrum: *m/e* 201 (M^+, 50), 186 (100), 170 (30), 159 (10), 84 (40), 73 (100).

*(E)-3-t-Butyldimethylsilylprop-2-enenitrile (**2**: $R^1 = {}^tBuMe_2Si$, $R^2 = H$) and 2-t-butyldimethylsilylprop-2-enenitrile (**3**: $R^1 = {}^tBuMe_2Si$, $R^2 = H$)*

B.p. 65°C (oven)/15 mmHg. ν_{max} (film) 2260s (C≡N), 1600s (C=C) cm^{-1}. (Found: C, 64.3; H, 10.6; N, 8.6. $C_9H_{17}NSi$ calcd.: C, 64.6; H, 10.2; N, 8.4%). ^1H NMR δ (90 MHz); **2**: 0.10, s, 6H, $Si(CH_3)_2$; 0.9, s, 9H, $Si({}^tBu)$; 5.7, d, $^3J_{trans}$ 19 Hz, 1H, H(2); 7.1, d, $^3J_{trans}$ 19 Hz, 1H, H(3); **3**: 0.2, s, 6H, $Si(CH_3)_2$; 0.95, s, 9H, $Si({}^tBu)$; 6.2, d, $^2J_{gem}$ 2 Hz, 1H, (*E*)H; 6.7, d, $^2J_{gem}$ 2 Hz, 1H, (*Z*)H. Mass spectrum: *m/e* 181 (M^+, 1), 167 (10), 152 (10), 112 (60), 111 (95), 110 (80), 84 (100).

(E)-2-Methyl-3-t-butyldimethylsilylprop-2-enenitrile (2: $R^1 = {}^tBuMe_2Si$, $R^2 = Me$)

B.p. 102°C/16 mmHg. ν_{max} (film) 2250s (C≡N), 1600s (C=C) cm^{-1}. (Found: C, 65.9; H, 10.7; N, 7.3. $C_{10}H_{19}NSi$ calcd.: C, 66.2; H, 10.6; N, 7.7%). ^1H NMR δ (90 MHz) **2**: 0.15, s, 6H, $Si(CH_3)_2$; 0.9, s, 9H, $Si({}^tBu)$; 2.0, d, ^4J 1.5 Hz, 3H, Me; 6.6, q, ^3J 1.5 Hz, 1H, H(3). Mass spectrum: *m/e* 181 (M^+, 4), 166 (5), 124 (100), 97 (20), 84 (40).

(E)-2-Cyano-1-t-butyldimethylsilylhex-1-ene (2: $R^1 = {}^tBuMe_2Si$, $R^2 = Bu$)

B.p. 62°C/0.3 mmHg. ν_{max} (film) 2250s (C≡), 1590s (C=C) cm^{-1}. (Found: C, 70.0; H, 11.5; N, 6.2. $C_{13}H_{25}NSi$ calcd.: C, 69.9; H, 11.3; N, 6.3%). ^1H NMR δ (90 MHz) **2**: 0.15, s, 6H, $Si(CH_3)_2$; 0.9, s, 9H, $Si({}^tBu)$; 1.2–1.7, m, 7H, $CH_3(CH_2)_2$; 2.2–2.9, m, CH_2–C=; 6.5, s, 1H, H(1). Mass spectrum: *m/e* 223 (M^+, 2), 208 (3), 166 (100), 84 (35), 73 (40).

(E)-3-t-Butyldimethylsilyl-2-phenylprop-2-enenitrile (2: $R^1 = {}^tBuMe_2Si$, $R^2 = Ph$) and (Z)-2-t-butyldimethylsilyl-3-phenylprop-2-enenitrile (3: $R^1 = {}^tBuMe_2Si$, $R^2 = Ph$)

B.p. 114°C/0.5 mmHg. ν_{max} (film) 2260s (C≡N), 1610s, (C=C) cm^{-1}. (Found: C, 74.3; H, 8.8; N, 5.9. $C_{15}H_{21}NSi$ calcd.: C, 74.0; H, 8.7; N, 5.8%). ^1H NMR δ (90 MHz) **2**: −0.15, s, 6H, $Si(CH_3)_2$; 0.9, s, 9H, $Si({}^tBu)$; 6.9, s, 1H, H(3); 7.4, s, 5H, Ph; **3**: 0.0, s, 6H, $Si(CH_3)_2$; 1.0, s, 9H, $Si({}^tBu)$; 7.3, s, 5H, Ph; 8.2, s, 1H, H(3). Mass spectrum: *m/e* 243 (M^+, 5), 228 (20), 186 (10), 84 (55).

(E)-2-Cyano-1-triphenylsilylhex-1-ene 2: $R^1 = Ph_3Si$, $R^2 = Bu$)

M.p. 82.5–83.5°C. ν_{max} (Nujol) 2240s (C≡N), 1600s (C=C) cm^{-1}. (Found: C, 81.8; H, 7.1; N, 3.9. $C_{25}H_{25}N$ calcd.: C, 81.8; H, 6.9; N, 3.8%). ^1H NMR δ (90 MHz) 0.7–1.5, m, 7H, $CH_3(CH_2)_2$; 2.0, m, 2H, CH_2–C=; 7.0, s, 1H, H(1); 7.3–7.6, m, 15H, $Si(Ph)_3$. Mass spectrum: *m/e* 367 (M^+, 70), 324 (100), 181 (90).

Acknowledgement

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