butenoate. The preceding procedure was used with *p*-nitrobenzaldehyde instead of benzaldehyde, and the reaction temperature was maintained at −30 °C. The reaction mixture was quenched at −30 °C with methanolic hydrochloric acid to provide the mixture of hydroxy esters directly as an oil consisting of 76% of the methyl 2-pentenoate and 24% of the methyl 3-butenoate (65% threo, 35% erythro) as determined by NMR analysis. Upon standing, crystalline methyl 2-methyl-5-hydroxy-5-(4-nitrophenyl)-2-pentenoate separated. After two recrystallizations from toluene the melting point was 73–74 °C. ^{1}H NMR (acetone-d_6, D_2O, δ, *J* (Hz)): 1.74 (d, ^4J = 1.5, 3 H, CH_3), 2.68 (m, 2 H, CH_2-4), 3.40 (s, 1 H, OH), 3.68 (s, 3 H, OCH_3), 5.05 (t, *J* = 6, 1 H, CH-5), 6.86 (tq, ^3J = 7, ^4J = 1.5, 1 H, =CH-3), 7.72 (d, *J* = 8, 2 H, ArH), 8.24 (d, *J* = 8, 2 H, ArH). Anal. Calcd for $C_{13}H_{15}O_5N$: C, 58.86; H, 5.70, N, 5.28. Found: C, 58.88, H, 5.45; N, 5.07. The supernatant oil consisted of 45% γ adduct, 19% erythro α adduct, and 36% threo α adduct as determined from the ^{1}H NMR spectrum (in acetone-d_6, D_2O, δ, *J* (Hz)): *erythro*-methyl 2-methyl-2-(α-hydroxy-*p*-nitrobenzyl)-3-butenoate, 1.15 (s, 3 H, CH_3), 3.40 (s, 1 H, OH), 3.70 (s, 3 H, OCH_3), 4.95 (dd, ^3J = 18, ^2J = 1.5, 1 H, =CH-4), 5.18 (dd, ^3J = 11, ^2J = 1.5, 1 H, =CH-4), 5.25 (s, 1 H, ArCH), 6.37 (dd, *J* = 18, 11, 1 H, =CH-3), 7.61 (d, *J* = 8, 2 H, ArH), 8.19 (d, *J* = 8, 2 H, ArH); threo isomer, 1.16 (s, 3 H, CH_3), 3.40 (s, 1 H, OH), 3.74 (s, 3 H, OCH_3), 4.94 (dd, ^3J = 18, ^2J = 1, 1 H, =CH-4), 5.12 (dd, ^3J = 11, ^2J = 1, 1 H, =CH-4), 5.34 (s, 1 H, ArCH), 6.17 (dd, *J* = 18, 11, 1 H, =CH-3), 7.62 (d, *J* = 8, 2 H, ArH), 8.18 (d, *J* = 8, 2 H, ArH).

Reaction of 4 with Acetic Acid-*d*. To a solution of 0.1 mL (0.5 mmol) of 4 in 0.8 mL of THF-d_8 were added 30 μL of acetic acid-*d* and 50 μL of tetrabutylammonium acetate (0.1 M in THF-d_8). The ^{1}H NMR spectrum of the solution after 2 days showed 93% unchanged 4 and 7% methyl 2-deuterio-2-methyl-3-butenoate: 1.14 (t, J_d = 1, 1 H, $CDCH_3$), 3.50 (s, 3 H, OCH_3), 4.97 (dd, ^3J = 10, ^2J = 2, 1 H, =CH_2), 5.03 (dd, ^3J = 17, ^2J = 2, 1 H, =CH_2), 5.84 (ddt, *J* = 17, 10, J_d = 1, 1 H, =CH).

Reaction of 3 with Methanol-*d*. To a solution of 0.12 mL (0.5 mmol) of 3 in 0.8 mL of THF-d_8 was added 50 μL of tetrabutylammonium acetate (0.1 M in THF-d_8). The ^{1}H NMR spectrum of the solution showed 67% ethyl 3,5-hexadienoate-*2-d* (1.21 (t, *J* = 7, CH_3), 3.03–3.08 (m, 0.6 H, CHD), 4.08 (q, *J* = 7, 2 H, OCH_2), 4.99 (dd, ^3J = 10, ^2J = 2, 1 H, =CH_2), 5.11 (dd, ^3J = 17, ^2J = 2, 1 H, =CH_2), 5.77 (dtt, *J* = 15, 7, J_d = 1, 1 H, =CH-3), 6.14 (dd, *J* = 15, 10, 1 H, =CH-4), 6.32 (ddd, *J* = 17, 10, 10, 1 H, =CH-5)) and 33% ethyl sorbate-*2-d* (1.23 (t, *J* = 7, 3 H, CH_3), 1.82 (d, *J* = 5.5, 3 H, CH_3), 4.12 (q, *J* = 7, 2 H, OCH_2), 6.14 (dd, *J* = 16, 5.5, 1 H, =CH-5), 6.23 (dd, *J* = 16, 10, 1 H, CH-4), 7.21 (dd, *J* = 15, 10, 0.5 H, =CH-3 adjacent to =CH-2), 7.20 (dt, *J* = 10, J_d = 2, 0.5 H, =CH-3 adjacent to =CD-2)).

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Registry No. (*Z*)-**1**, 114996-00-8; (*E*)-**1**, 114996-01-9; (*Z*)-**2**, 114996-02-0; (*E*)-**2**, 114996-03-1; (*Z,E*)-**3**, 114996-05-3; (*E,E*)-**3**, 114996-06-4; **4**, 114996-04-2; **5**, 114996-14-4; **13**, 39149-91-2; **14**, 114996-13-3; TASF, 59218-87-0; ethyl 3-butenoate, 1617-18-1; methyl tiglate, 6622-76-0; ethyl 3,5-hexadienoate, 81838-64-4; sorbic acid chloride, 2614-88-2; benzaldehyde, 100-52-7; ethyl 5-hydroxy-5-phenylpent-2-enoate, 114996-07-5; ethyl 2-(hydroxyphenylmethyl)but-3-enoate, 89922-39-4; ethyl 5-hydroxy-2-methyl-5-phenylpent-2-enoate, 114996-08-6; ethyl 2-(hydroxyphenylmethyl)-2-methylbut-3-enoate, 114996-09-7; methyl 5-hydroxy-2-methyl-5-phenylpent-2-enoate, 92186-72-6; methyl 2-(hydroxyphenylmethyl)-2-methylbut-3-enoate, 92186-70-4; methyl 5-hydroxy-5-(4-nitrophenyl)-2-methylpent-2-enoate, 108733-47-7; methyl 2-(hydroxy(4-nitrophenyl)methyl)-2-methylbut-3-enoate, 114996-10-0; *p*-nitrobenzaldehyde, 555-16-8; ethyl 5-hydroxy-5-(4-nitrophenyl)pent-2-enoate, 114996-11-1; ethyl 2-(hydroxy(4-nitrophenyl)methyl)but-3-enoate, 114996-12-2; ethyl 3,5-hexadienoate-*2-d*, 114996-15-5; ethyl sorbate-*2-d*, 114996-16-6.

Palladium- and Nickel-Catalyzed Reaction of Trimethylsilyl Cyanide with Acetylenes. Addition of Trimethylsilyl Cyanide to the Carbon–Carbon Triple Bonds[1]

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The reaction of trimethylsilyl cyanide (1) with acetylenes in the presence of a transition-metal complex was investigated. The structures of starting acetylenes and catalysts and both amounts of solvent and 1 highly affected product distributions. The $PdCl_2$/pyridine catalyzed reaction of phenylacetylene and para-substituted phenylacetylenes with 1 resulted in the addition of 1 to the carbon–carbon triple bonds to give cyano-substituted vinylsilanes in good to high yields with high regio- and stereoselectivity. Ortho-substituted phenylacetylenes gave addition products less stereoselectively. Stereoselectivity affording *Z* adducts decreased in the order of para- > meta- > ortho-substituted phenylacetylenes. The $NiCl_2$/DIBAH-catalyzed reaction of arylacetylenes was less stereoselective regardless of substitution patterns of arylacetylenes used. When the nickel-catalyzed reaction of arylacetylenes was run without solvent using an excess amount of 1, 5-amino-1*H*-pyrrole-2-carbonitriles were obtained as a single product, instead of the above simple addition products. The reaction of terminal aliphatic acetylenes with 1 also gave addition products with moderate stereoselectivity. Internal acetylenes gave complex mixtures including addition products and/or pyrrole derivatives. Diarylacetylenes afforded 5-amino-1*H*-pyrrole-2-carbonitriles selectively in the presence of a palladium or nickel catalyst (without solvent and an excess amount of 1). Intramolecular cyclization of a 1,6-diyne was also studied.

In recent years, vinylsilanes have played an ever increasing role in synthetic organic chemistry.[2,3] For their potential utility, much attention has been focused on exploring synthetic methods of functionalized vinylsilanes.

Table I. The Addition of Me_3SiCN (1) to Phenylacetylene (2)[a]

entry	catalyst	additive	solvent	temp, °C	yield, %[b]	*Z*:*E*[c]
1	$PdCl_2$		toluene	40	10	100:0
2	$PdCl_2$		toluene	70	15	97:3
3	$PdCl_2$		toluene	reflux	67	94:6
4	$PdCl_2$		xylene	reflux	85 (77)	94:6
5	$PdCl_2$		CH_3CN	40	3	*d*
6	$PdCl_2$		CH_3CN	reflux	55	97:3
7	$PdCl_2$		PhCN	120	69	95:5
8	$PdCl_2$	pyridine	toluene	80	33	96:4
9	$PdCl_2$	pyridine	toluene	reflux	96 (90)	95:5
10	$PdCl_2$	pyridine	xylene	reflux	94 (75)	95:5
11	$PdCl_2$	Et_3N	xylene	reflux	82	96:4
12	$PdCl_2$	α,α'-bipyridyl	xylene	reflux	90 (80)	95:5
13[e]	$PdCl_2$	pyridine	toluene	reflux	33	*d*
14[f]	$PdCl_2$			reflux	(53)[g]	81:19
15	$Pd(OAc)_2$		toluene	reflux	32	96:4
16	$(PhCN)_2PdCl_2$		toluene	reflux	65	95:5
17	$(PhCN)_2PdCl_2$		xylene	reflux	80	95:5
18	$PdBr_2$	pyridine	toluene	reflux	66	95:5
19	$PdCl_2$	PPh_3	toluene	reflux	11	96:4
20	$Pd(PPh_3)_4$		toluene	reflux	13	96:4
21	$Pd(PPh_3)_4$		xylene	reflux	30	95:5
22	$NiCl_2$	DIBAH	toluene	reflux	41[h]	72:28
23[f]	$NiCl_2$	DIBAH		reflux	*i*	
24[f]	$NiCl_2$	Et_3Al		reflux	*j*	

[a] Reaction conditions: phenylacetylene (0.55 mL, 5 mmol), Me_3SiCN (1) (1.34 mL, 10 mmol), catalyst (0.2 mmol), additive (0.4 mmol), and solvent (10 mL) for 20 h unless otherwise noted. [b] GLC yields based on **2**. Isolated yields are in parentheses. [c] Determined by GLC. [d] Not determined. [e] Et_3SiCN was used in place of **1**. [f] 30 mmol of **1** was used. [g] 5-Amino-1*H*-pyrrole-2-carbonitrile **5** was isolated in 14% yield. [h] 10% of **5** was isolated. [i] 58% of **5** was isolated. See eq 3 in text. [j] 66% of **5** was isolated. See eq 3 in text.

Hydrosilylation[4] of functionalized acetylenes would be one of the simplest, synthetic methods of functionalized vinylsilanes. Hydrometalation[5] and carbometalation[6] of silylacetylenes are also effective for producing functionalized vinylsilanes with defined stereo- and regiochemistry. Recently, silylmetalation of acetylenes has also been widely studied.[7] Although the addition of SiX species to acetylenes may be the other candidate for synthesis of functionalized vinylsilanes, very little has been reported in the literature so far. The palladium-catalyzed addition of disilanes (SiSi)[8] and the addition of silylstannane (SiSn)[9] to acetylenes has been reported recently. A limited example of the addition of silylamine (SiN) to acetylenes leading to amino-substituted vinylsilanes is also known.[10] These additions of SiX species to acetylenes generally proceed in a syn manner.

Trimethylsilyl cyanide (1) has been known as a versatile reagent to introduce a cyano group into organic molecules.[3] The addition of SiCN, however, seems to be limited to a carbon–oxygen or carbon–nitrogen double bond. Although the addition of SiCN or a carbon–carbon multiple bond has not been known, the reaction should provide a useful method for the synthesis of cyano-substituted vinylsilanes, which are amenable for further synthetic elaboration. In this paper, we describe the transition-metal-catalyzed addition of silyl cyanide to acetylenes, which shows the first example of the addition of SiCN to nonpolar carbon–carbon multiple bonds (eq 1).[11] The addition of SiCN to

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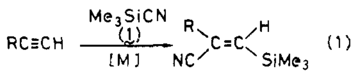
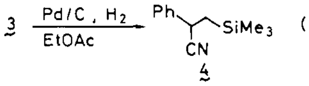


(1)

acetylenes is regioselective and the degree of stereoselectivity depends on the structure of substrate and catalyst used.

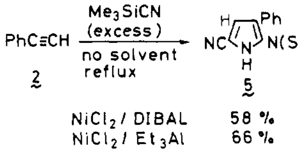
Results and Discussion

Reaction of Trimethylsilyl Cyanide with Phenylacetylene. Palladium-catalyzed addition of trimethylsilyl cyanide (1) to phenylacetylene (2) gave 2-phenyl-3-(trimethylsilyl)prop-2-enenitrile (3)[12] as the major product. This reaction provides a new synthetic method for the preparation of stereodefined functionalized vinylsilanes. A palladium catalyst is effective for the reaction to proceed, whereas Lewis acids such as $AlCl_3$, $SnCl_2$, $SnCl_4$, and $ZnCl_2$ are not effective for the addition of 1 to 2. The general procedure for the reaction is described in the Experimental Section, and the results are summarized in Table I. The regio- and stereochemistry of this novel addition reaction of 1 to 2 has been unequivocally established as follows. The regiochemistry was confirmed by the hydrogenation of 3 to give 2-phenyl-3-(trimethylsilyl)propanenitrile (4) (eq 2). The syn addition of 1 to 2 was confirmed by the coupling constant ($^3J_{CN-H}$ = 17 Hz) between the CN and the vinyl proton in ^{13}C NMR.[13] Thus, the addition of 1 to the carbon–carbon triple bond was highly regio- and stereoselective under varying reaction conditions. An increase in the reaction temperature resulted in an increase in the yield of 3 (entries 1–4 and 5–7 in Table I). Stereoselectivity depended on the reaction temperatures to some extent (entries 1–4). The reaction rate was accelerated by the addition of pyridine. Although the role of pyridine is not clear, pyridine may trap HCl and/or HCN which was generated in situ by moisture. Use of Et_3SiCN in place of 1 decreased the product yield (entry 13). The best result with respect to both a yield and stereoselection was obtained in run 9 in Table II. The reaction of 2 with an excess amount of 1 in the absence of solvent gave mainly the addition product 3, along with a low yield of an unexpected product, 5-[bis(trimethylsilyl)amino]-4-phenyl-1*H*-pyrrole-2-carbonitrile (5)[14] (entry 14).



(2)

With regard to catalysts, wide ranges of transition-metal complexes were examined for their catalytic activity. Although both $PdCl_2$/DIBAH (i-Bu_2AlH) and palladium carbon were not effective, other palladium complexes, such as $Pd(OAc)_2$, $PdCl_2$, $PdBr_2$, $(PhCN)_2PdCl_2$, and $Pd(PPh_3)_4$ showed catalytic activity. Phosphine ligand tends to retard the reaction (entries 19–21). Many other transition-metal complexes were also examined; however, they showed little or no catalytic activity: those complexes include $NiCl_2$, $Ni(PPh_3)_2(CO)_2$, $Ni[P(OPh)_3]_4$, $Ni(COD)_2$, H_2PtCl_6, $Cu(acac)_2$, Cp_2Co, $CpCo(CO)_2$, $Co_2(CO)_8$, $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$, $(PPh_3)_3RhCl$, $Rh_6(CO)_{16}$, $[RhCl(CO)_2]_2$, $W(CO)_6$. When the reaction of 1 with 2 was carried out by using Ni(0) catalyst, which was generated in situ from $NiCl_2$ with 2 equiv of DIBAH (i-Bu_2AlH), addition product 3 was obtained in 41% yield, accompanied by 5 in 10% yield (entry 22). When this reaction was carried out without solvent, using an excess amount of 1 in the presence of Ni(0) catalyst, 5 was isolated as the single product after column chromatography on silica gel (entries 23 and 24 in Table I and eq 3). An initial product of reaction 3 should be tris(trimethylsilyl) compound 7, which was desilylated through the isolation procedure to give 5. The compound 7 consists of one molecule of 2 and three molecules of 1. Reaction 3 offers a new and efficient procedure for construction of pyrrole rings from acetylenes.[15]



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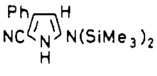

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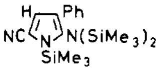

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Reaction of Trimethylsilyl Cyanide with Terminal Aromatic Acetylenes. The results obtained in the reaction of 1 with substituted phenylacetylenes are shown in Table II. The reaction conditions employed were the same as the ones used for run 9 in Table I. The reaction of 1 with arylacetylenes is also highly regio- and stereoselective. In all cases the silyl group was attached to the external olefin carbon atom. A wide variety of functional groups can be tolerated on the addition of 1 to arylacetylenes, including methoxy, fluoro, chloro, and even methylenedioxy. However, in the reaction of (p-bromophenyl)acetylene, along with the expected product 11, 12 was formed as a major product, where the bromine atom on the aromatic ring had been replaced by a cyano group (entry 5).[16] Attempted selective formation of 12 was not successful even in the reaction with an excess amount of 1 with prolonged heating. The addition of 1 to (p-nitrophenyl)acetylene did not take place, the starting material being recovered. The reaction of (p-acetylphenyl)acetylene gave a complex mixture. Stereoselectivity of the reaction of meta- and para-substituted phenylacetylenes was generally high (>92%) in favor of Z isomers, as shown in entries 1–7 in Table II. On the other hand, ortho-substituted phenylacetylenes reacted with 1 to yield a mixture of Z and E isomers, the ratio of which were ca. 8:2 (entries 8–10). The regio- and stereoselectivity are independent of the electronic nature of the substituents on the phenyl ring; however, the stereoselectivity of the products is influenced by the position of the substituent on phenyl ring. Thus, stereoselectivity in the addition of 1 to substituted phenylacetylenes decreased in the following order: para > meta > ortho substitution. A similar tendency was observed in the reaction with naphthylacetylenes (entries 7 and 10).

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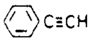
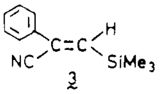
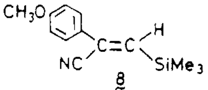
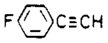
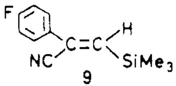
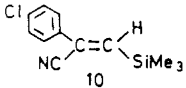
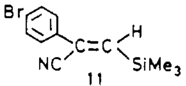
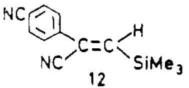
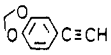
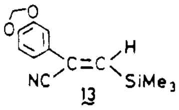
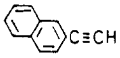
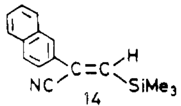
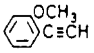
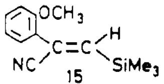
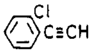
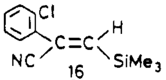
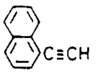
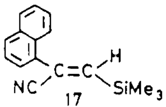
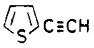
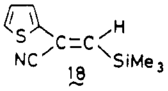
(16) Recently, we reported the Pd-catalyzed cyanation of aryl iodides with 1. See ref 1b.

Table II. Addition of Me_3SiCN (1) to Arylacetylenes

entry	arylacetylene	product	yield, %[b]	*Z*:*E*[c]
1		 **3**	96 (90)	95:5
2		 **8**	92 (90)	95:5
3		 **9**	52 (38)	*d*
4		 **10**	50 (47)	94:6
5		 **11**	17 (14)	*d*
		 **12**	26 (19)	*d*
6		 **13**	61 (56)	92:8
7		 **14**	77 (54)	93:7
8		 **15**	90 (85)	83:17
9		 **16**	26 (23)	81:29
10		 **17**	80 (68)	71:29
11		 **18**	39	*d*

[a] Reaction conditions: arylacetylene (5 mmol), Me_3SiCN (1) (1.34 mL, 10 mmol), $PdCl_2$ (32 mg, 0.2 mmol), pyridine (32 μL, 0.4 mmol), and toluene (10 mL) for 20 h. [b] GLC yields based on arylacetylene. Isolated yields are in parentheses. [c] Determined by GLC. [d] The ratio of *Z*:*E* could not be determined by GLC; however, *Z* selectivity is >95% from their ^1H NMR.

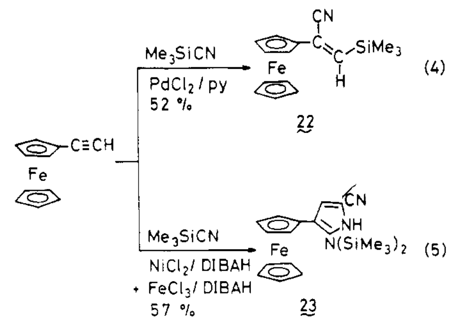
Table III. Nickel-Catalyzed Addition of Me_3SiCN (1) to Arylacetylenes[a]

entry	arylacetylene	product	yield, %[b]	*Z*:*E*[c]
1	$C_6H_5C{\equiv}CH$ (**2**)	**3**	41	71:29
2	$4\text{-}CH_3OC_6H_4C{\equiv}CH$	**8**	52	81:29
3	$2\text{-}CH_3OC_6H_4C{\equiv}CH$	**15**	59 (45)	80:20
4	$2\text{-}ClC_6H_4C{\equiv}CH$	**16**	49	78:22

[a] Reaction conditions: arylacetylene (5 mmol), Me_3SiCN (1) (1.34 mL, 10 mmol), $NiCl_2$ (26 mg, 0.2 mmol), 1 N DIBAH in hexane (0.4 mL, 0.4 mmol), and toluene (10 mL) for 20 h. [b] GLC yields based on arylacetylene. [c] Determined by GLC.

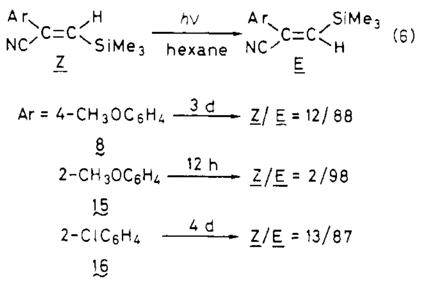
As shown in Table III, in nickel-catalyzed reaction of arylacetylenes, a mixture of *Z* and *E* isomers was obtained regardless of the substitution patterns in the starting arylacetylenes used. In each case, 5-aminopyrrole-2-carbonitrile (similar to **5**) was obtained as a byproduct in 10–15% yield. When Ni-catalyzed reactions were carried out under the reaction conditions used for reaction 3 (an excess amount of **1** and no solvent), 5-aminopyrrole-2-carbonitriles were obtained as a major product (Table IV).[1c] Aryl groups always resided at the C-4 position. The reaction of (2,4,6-trimethylphenyl)acetylene with **1** under the same reaction conditions did not occur.

The reaction of **1** with ferrocenylacetylene proceeded in a similar manner as that of arylacetylenes described above. Under the Pd-catalyzed reaction, an addition product **22**, which has a *Z* stereochemistry, was obtained (eq 4). For the Ni/Fe-catalyzed reaction, a pyrrole derivative **23** was produced (eq 5). In sharp contrast with arylacetylenes, reaction 5 did not proceed under Ni(0) catalyst alone. Combination of Ni(0) and Fe(0) catalysts is essential for



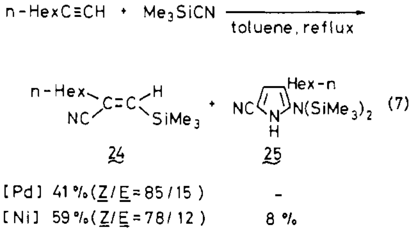
reaction 5 to proceed. Fe(0) alone is also not an effective catalyst.

The conversion of *Z* isomers to *E* isomers was carried out by photochemical procedure.[17] A slow isomerization occurred under UV irradiation of a *Z,E* mixture or a pure *Z* isomer (eq 6). Thus, irradiation of a pure **15Z** in hexane



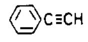
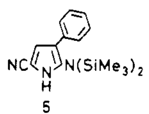
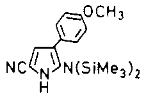
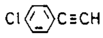
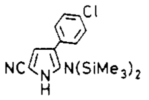
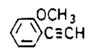
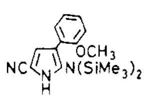
with a 300-W high-pressure Hg lamp in a Pyrex test tube at room temperature under nitrogen for 20 h gave **15E** almost quantitatively. The high yield of the product (>95%) indicated no dimerization or polymerization occurred during the irradiation. Similarly, **8Z** and **16Z** were isomerized to **8E** and **16E**, respectively. Isomerization of **16Z** to **16E** was very slow and the photochemical equilibrium was reached after 4 days. An attempt for isomerization of ferrocenyl derivative **22Z** to the **22E** was made in vain. It was confirmed that thermal isomerization of **8Z** to **8E** failed to proceed (180 °C without solvent for 30 h). By this photochemical procedure, the *E* isomer could be obtained selectively from a mixture of *Z* and *E* isomers.

Reaction of Terminal Aliphatic Acetylenes. The reaction of 1-octyne with **1** proceeded in a similar way to that of arylacetylenes (eq 7). In the $PdCl_2$/pyridine-

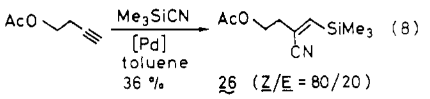


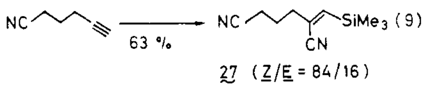
catalyzed reaction in refluxing toluene, 1-octyne reacted with **1** to give a stereoisomeric mixture of the adduct **24**, in which the CN moiety was attached at the internal position. In the $NiCl_2$/DIBAH-catalyzed reaction, the addition product **24** was obtained as the main product, together with a small amount of pyrrole derivative **25**. In contrast to the Ni-catalyzed reaction of **2** (eq 3), **25** was obtained in a low yield even when the reaction was run without solvent in an excess amount of **1**. This result may be due to the consumption of 1-octyne by oligomerization or polymerization under the reaction conditions employed.[18] To examine the compatibility of various functional groups, the palladium-catalyzed reaction of terminal aliphatic acetylenes containing a functional group with **1** has been examined. In particular, the effect of a functional group on regio- and stereoselectivity may be of interest. Some functional groups, i.e., acetoxy, siloxy, or cyano group, did not affect the reaction with respect to regio- and stereoselectivity (eq 8–10). The $PdCl_2$/pyridine-catalyzed

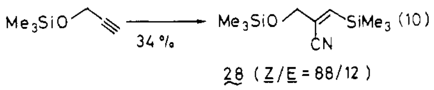
Table IV. Synthesis of 5-Amino-1*H*-pyrrole-2-carbonitriles[a]

entry	arylacetylene	product	yield, %[b]
1	 **2**	 **5**	58
2		 **19**	66
3		 **20**	52
4		 **21**	54

[a] Reaction conditions: arylacetylene (2.5 mmol), Me_3SiCN (**1**) (2.0 mL, 15 mmol), $NiCl_2$ (13 mg, 0.1 mmol), 1 N DIBAH in hexane (0.2 mL, 0.2 mmol), and 20 h. [b] Isolated yields based on arylacetylene.







reaction of propargyl compounds, e.g., propargyl acetate, bromide, and phenoxide, with **1** did not give addition products.[19] In contrast, propargyl silyl ether gave addition product **28** in 34% yield (eq 10).

The development of a transition-metal-catalyzed construction of a carbocyclic framework by use of enynes[20] and

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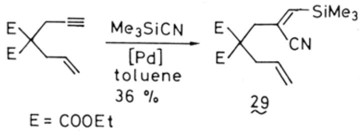
[17] Photocatalyzed isomerization of (*E*)- to (*Z*)-vinylsilanes has been reported. Seyferth, D.; Vaughan, L. G.; Suzuki, R. *J. Organomet. Chem.* **1964**, *1*, 437.

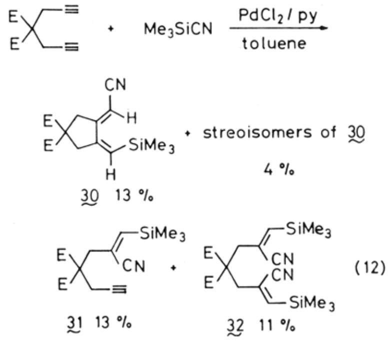
[18] For a review on nickel-catalyzed oligomerization of acetylenes and related reactions, see: Jolly, P. W. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 8, pp 649–670.

[19] Palladium-catalyzed reaction of propargyl esters and halides with a variety of nucleophiles leading to acetylenic and/or allenic compounds has been well-known. Jeffery-Joung, T.; Linstrumelle, G. *Tetrahedron Lett.* **1980**, *21*, 5019. Ruitenberg, K.; Kleijn, H.; Elsevier, C. J.; Meijer, J.; Vermeer, P. *Tetrahedron Lett.* **1981**, *22*, 1451. Elsevier, C. J.; Stehouwer, P. M.; Westmijze, H.; Vermeer, P. *J. Org. Chem.* **1983**, *48*, 1103. Tsuji, J.; Watanabe, H.; Minami, I.; Shimizu, I. *J. Am. Chem. Soc.* **1985**, *107*, 2196. Tabuchi, T.; Inanaga, J.; Yamaguchi, M. *Chem. Lett.* **1987**, 2275.

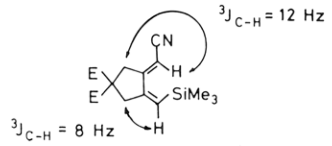
diynes[21] has continued to attract attention. With acetylenes having an olefinic function or an acetylenic one in the suitable position, construction of carbocyclic framework containing useful functional groups was expected to take place. The $PdCl_2$/pyridine-catalyzed reaction of a 1,6-enyne with **1** resulted in addition of **1** to the carbon–carbon triple bond to give **29** in 36% yield (eq 11). The carbon–carbon double bond remained intact under the reaction conditions and no cyclization product was observed. On the other hand, the reaction of a 1,6-diyne, diethyl dipropargylmalonate, with **1** gave a cyclization product, **30**, along with the usual addition products **31** and **32** (eq 12). The stereochemistry of the main product **30** was tentatively assigned on the basis of the coupling constant ($^3J_{C-H}$) in ^{13}C NMR.



(11)



(12)



Reaction of Trimethylsilyl Cyanide with Internal Acetylenes. The $PdCl_2$/pyridine-catalyzed reaction of internal acetylenes with **1** occurred slowly compared to that of terminal ones. In particular, acetylenes having two sterically bulky groups, e.g., bis(trimethylsilyl)acetylene, phenyl(trimethylsilyl)acetylene,[22] and phenyl-*tert*-butylacetylene, did not react with **1** in toluene, with starting materials being recovered. To verify the difference in reactivity between an internal carbon–carbon triple bond and a terminal one, the intramolecular competitive reaction of 1-phenylpenta-1,4-diyne was carried out. As expected, addition of **1** took place only at a terminal carbon–carbon triple bond to afford **33** in 47% yield (eq 13).

$Me_3SiC\equiv CSiMe_3$ $PhC\equiv CSiMe_3$ $PhC\equiv CBu\text{-}t$

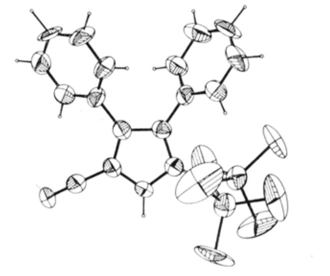
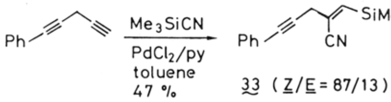
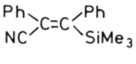


Figure 1. ORTEP drawing of **36**.



(13)

Diphenylacetylene reacted with **1** in the presence of $PdCl_2$ in refluxing toluene to give a complex mixture including the adduct **34**, 1,2-dicyano-1,2-diphenylethylene (**35**), and 5-[bis(trimethylsilyl)amino]-3,4-diphenyl-1*H*-pyrrole-2-carbonitrile (**36**). However, when the reaction was run with no solvent using an excess amount of **1**, **36** was obtained as the single product (eq 14).[1c] The structure of **36** was assigned on the basis of its spectral data and was confirmed by X-ray crystallographic analysis (Figure 1). The use of solvent (toluene, CH_3CN, DMF) resulted in a reduced yield. The reaction without solvent may be essential to produce a pyrrole derivative. Although $PdCl_2$/DIBAH was not effective, other palladium complexes, e.g., $PdBr_2$ (71%), $Pd(OAc)_2$ (79%), $(PPh_3)_2PdCl_2$ (48%), and $Pd(PPh_3)_4$ (62%), showed catalytic activity. Ni(0) catalysts, $NiCl_2$/DIBAH (89%) and $NiCl_2/Et_3Al$ (80%), were also found to be effective for reaction 14, but $NiCl_2$ alone had no catalytic activity.



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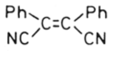

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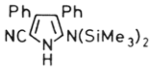

36

$$PhC\equiv CPh \xrightarrow[\text{PdCl}_2,\ \text{no solvent}]{\text{Me}_3\text{SiCN}} \mathbf{36}\ \ 88\% \qquad (14)$$

Summary

The addition of **1** to terminal acetylenes can be accomplished in the presence of a catalytic amount of a Pd or Ni complex. This reaction represents the first example for the addition of **1** to a carbon–carbon multiple bond. From a synthetic point of view, the present reaction provides a new, highly regio- and stereodefined synthetic method for the preparation of functionalized (cyano-substituted) vinylsilanes. Furthermore, an unprecedented conversion of acetylenes to 5-amino-1*H*-pyrrole-2-carbonitriles by the reaction of acetylenes with an excess amount of **1** without solvent was also found.

In contrast to the extensive studies on the Lewis acid mediated reaction of **1**, very few studies on the transition-metal-mediated reaction of **1** have been carried out.[23,24]

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Further studies of transition-metal-catalyzed reaction of 1 with the other type of substrates and the mechanism of the present reaction are in progress.

Experimental Section

General Methods. Boiling points and melting points are uncorrected. Infrared spectra were taken on a Hitachi 260-10 spectrometer; absorptions are reported in reciprocal centimeters. ^1H NMR were recorded on a Bruker-WM 360 and are reported in ppm from internal tetramethylsilane on a δ scale. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, c = complex, and br = broad), coupling constant (Hz), integration, and interpretation. ^{13}C NMR were recorded on a Bruker-WM 360 and are reported in ppm from tetramethylsilane on a δ scale. Mass spectra were recorded on a JMS-DX 300. Ultraviolet spectra were recorded on a Hitachi ESP-3T. Elemental analyses were performed on a Perkin-Elmer 240C or a Yanagimoto CHN-Corder MT-2. Analytical GLC was carried out on a Hitachi 663-50 equipped with a 3-m × 3-mm stainless column packed with 5% Silicone OV-1 on 60–80-mesh Chromosorb W and nitrogen as a carrier gas. Capillary GLC analyses were carried out on a Shimazu 9A equipped with Shimazu Hicap-CBP1 capillary column and helium as a carrier gas. Column chromatography was performed with 70–230-mesh Merck Kieselgel 60 using mixtures of hexane–EtOAc of varying composition as eluent. Preparative TLC was performed with Merck Kieselgel 60 F_{254}. Gel permeation LC was performed with Japan Analytical Ind. LC-08 using chloroform as eluent.

Materials. Phenylacetylene, 1-octyne, 4-octyne, and diphenylacetylene were commercially available. (Methoxy-, (fluoro-, (chloro-, (bromo-, and ((methylenedioxy)phenyl)acetylene and naphthylacetylene were prepared according to Corey's method.[25] (4-Nitrophenyl)acetylene,[26] (3,5-dimethylbenzyl)acetylene,[27] 1-phenylpenta-1,4-diyne,[28] and ferrocenylacetylene[29] were prepared by the methods reported in the literature. Thienylacetylene was prepared by an alternative method in the literature.[30] Enyne **29** and diyne **30** were prepared by propargylation of diethyl allylmalonate and diethyl malonate, respectively. $Pd(PPh_3)_4$,[31] $(PPh_3)_2PdCl_2$,[32] and $(PhCN)_2PdCl_2$[33] were prepared by the literature procedures. Me_3SiCN and toluene were distilled from CaH_2 and stored under nitrogen. Et_3SiCN was prepared by the treatment of Et_3SiBr with AgCN.[34]

General Procedure. In a typical procedure, to a solution containing phenylacetylene (0.55 mL, 5 mmol) and Me_3SiCN (1.34 mL, 10 mmol) in toluene (10 mL) were added $PdCl_2$ (36 mg, 0.2 mmol) and pyridine (32 μL, 0.4 mmol). The mixture was refluxed with stirring for 20 h under nitrogen. Monitoring of the reaction by GLC showed that the reaction was complete within 10 h. Analysis of the reaction mixture by GLC showed the formation of 2-phenyl-3-(trimethylsilyl)prop-2-enenitrile (3) in 93% yield (*Z*/*E* = 94/6). The solution was evaporated in vacuo, and the residue was chromatographed on silica gel (hexane/EtOAc, 9/1) followed by bulb-to-bulb distillation, bp 130–140 °C (25 mmHg), to give pure 3 in 90% yield.

2-Phenyl-3-(trimethylsilyl)-(*Z*)-prop-2-enenitrile (3Z): bp 95–96 °C (0.9 mmHg); ^1H NMR ($CDCl_3$) δ 0.35 (s, 9 H, $SiCH_3$), 7.10 (s, 1 H, =CH), 7.37–7.41 (m, 2 H, Ph), 7.61–7.63 (m, 3 H, Ph); ^{13}C NMR ($CDCl_3$) δ –1.40 ($SiCH_3$), 117.9 (CN, $^3J_{CN-H}$ = 17 Hz), 125.7, 127.9, 128.9, 129.6, 135.1 (Ph, =C), 147.6 (=CH); IR (neat) 3060, 2960, 2890, 2220 (CN), 1560 (C=C), 1490, 1450, 1250, 975, 860, 840, 755, 685 cm^{-1}; mass spectrum, *m*/*e* 201 (M^+). Anal. Calcd for $C_{12}H_{15}NSi$: C, 71.59; H, 7.51; N, 6.96. Found: C, 71.84; H, 7.27; N, 6.99.

Hydrogenation of 3Z to 4. 2-Phenyl-3-(trimethylsilyl)-propanenitrile (4). In a 50-mL stainless steel autoclave were placed **3Z** (0.20 g, 1 mmol), Pd/C (40 mg), and EtOAc (5 mL). The autoclave was charged with H_2 (5 atm) and then stirred at 25 °C for 15 h. After the reaction, the catalyst was filtered, and the solvent was evaporated in vacuo to give 4 (0.194 g, 97% yield). Pure 4 was obtained by bulb-to-bulb distillation (0.161 g, 80% yield): ^1H NMR ($CDCl_3$) δ 0.03 (s, 9 H, $SiCH_3$), 1.21 (dd, *J* = 6.9, 14.8 Hz, 1 H, CH_2), 1.37 (dd, *J* = 9.1, 14.8 Hz, 1 H, CH_2), 3.80 (dd, *J* = 6.9, 9.1 Hz, 1 H, CH), 7.29–7.37 (m, 5 H, Ph); IR (neat) 3075, 3040, 2960, 2900, 2240 (CN), 1600 (Ph), 1500, 1455, 1420, 1255, 920, 860, 755, 695 cm^{-1}; mass spectrum, *m*/*e* 203 (M^+).

2-Phenyl-3-(trimethylsilyl)-(*E*)-prop-2-enenitrile (3E). In a 20-mL reaction flask was placed $NiCl_2$ (26 mg, 0.2 mmol), and then 1 N DIBAH (i-Bu_2AlH) in hexane (0.4 mL, 0.4 mmol) was added. After the addition, the color of the catalyst turned to black. Then, phenylacetylene (0.55 mL, 5 mmol) and Me_3SiCN (1.34 mL, 10 mmol) were added to the reaction flask, and the mixture was heated to reflux under nitrogen for 20 h. The solvent was evaporated in vacuo, and the residue was chromatographed (silica gel; hexane/EtOAc, 9/1) to give 0.510 g of a yellow oil. Preparative TLC (hexane/EtOAc, 9/1) gave 0.188 g of a *Z*,*E* mixture of 3 (*Z*/*E* = 80/20) in an early fraction (R_f 0.53–0.59) and 0.251 g of an enriched 5 in a later one (R_f 0.36–0.53). Gel permeation of the early fraction gave a pure **3E** (purity >98%): ^1H NMR ($CDCl_3$) δ 0.02 (s, 9 H, $SiCH_3$), 6.88 (s, 1 H, =CH), 7.37–7.39 (c, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ –0.56 ($SiCH_3$), 119.4 (CN, $^3J_{CN-H}$ = 11 Hz), 125.7, 128.4, 128.6, 129.5, 135.6 (Ph, =C), 152.2 (=CH). The *E* configuration of this compound was confirmed by the coupling constant ($^3J_{CN-H}$ = 11 Hz).[13]

2-(4-Methoxyphenyl)-3-(trimethylsilyl)-(*Z*)-prop-2-enenitrile (8Z). This compound was prepared from (4-methoxyphenyl)acetylene (0.65 mL, 5 mmol) and Me_3SiCN (1.34 mL, 10 mmol) according to the general procedure. Bulb-to-bulb distillation (100–110 °C (0.25 mmHg)) gave 1.039 g of a crude product (90% yield), which on preparative TLC (hexane/EtOAc, 9/1; R_f 0.41–0.62) afforded 0.726 g of **8Z**: ^1H NMR ($CDCl_3$) δ 0.32 (s, 9 H, $SiCH_3$), 3.83 (s, 3 H, OCH_3), 6.91 (d, *J* = 8.5 Hz, 2 H, Ar), 6.92 (s, 1 H, =CH), 7.55 (d, *J* = 8.5 Hz, 2 H, Ar); ^{13}C NMR ($CDCl_3$) δ –1.30 ($SiCH_3$), 55.5 (OCH_3), 107.2 (CN, $^3J_{CN-H}$ = 18 Hz), 114.3, 118.3, 127.1, 128.0 (Ar, =C), 114.4 (=CH), 161.1 (ArO); IR (neat) 2970, 2910, 2840, 2220 (CN), 1605, 1585, 1515, 1285, 1250, 1185, 1035, 975, 860, 840 cm^{-1}; UV (hexane) λ 288 (ϵ 9400), 304 (7600) nm; mass spectrum, *m*/*e* 231 (M^+). Anal. Calcd for $C_{13}H_{17}NOSi$: C, 67.49; H, 7.41; N, 6.05. Found: C, 67.77; H, 7.27; N, 6.07.

2-(4-Fluorophenyl)-3-(trimethylsilyl)-(*Z*)-prop-2-enenitrile (9Z). This compound was prepared from (4-fluorophenyl)acetylene (0.60 g, 5 mmol) and Me_3SiCN (1.34 mL, 10 mmol) according to the general procedure. Bulb-to-bulb distillation (130–140 °C (15 mmHg)) gave 0.413 g of a crude product (38% yield), which on preparative TLC (hexane/EtOAc, 9/1; R_f 0.50–0.63) afforded 0.303 g of pure 9: ^1H NMR ($CDCl_3$) δ 0.34 (s, 9 H, $SiCH_3$), 7.01 (s, 1 H, =CH), 7.09 (t, *J* = 8.6 Hz, 2 H, Ar), 7.60 (dd, *J* = 5.1, 8.6 Hz, 2 H, Ar); ^{13}C NMR ($CDCl_3$) δ –1.42 ($SiCH_3$), 117.8 (CN), 115.9, 126.8, 127.6, 131.4 (Ar, =C), 147.4 (=CH), 162.2 (ArF); mass spectrum, *m*/*e* 219 (M^+ for ^{19}F). Anal. Calcd for $C_{12}H_{14}FNSi$: C, 65.71; H, 6.43; N, 6.39. Found: C, 65.15; H, 6.08; N, 6.78.

2-(4-Chlorophenyl)-3-(trimethylsilyl)-(*Z*)-prop-2-enenitrile (10Z). This compound was prepared from (4-chlorophenyl)acetylene (0.68 g, 5 mmol) and Me_3SiCN (1.34 mL, 10 mmol) according to the general procedure. After the reaction, the solid precipitated in toluene (10 mg, 0.6% yield, yellow needles, mp >280 °C) and was collected by filteration. The solid was not soluble in common organic solvents. Although the solid could not be fully characterized, it contained two molecules of acetylene and two molecules of cyano, judging from spectral data and elemental analyses. IR (Nujol) 2220 (CN), 1590 cm^{-1}; mass spectrum, *m*/*e* 324 (for ^{35}Cl). The solvent was evaporated, and then bulb-to-bulb distillation (120–130 °C (0.35 mmHg)) gave 0.551 g of crude 10 (47% yield). Preparative TLC (hexane/EtOAc, 9/1; R_f 0.59–0.68) afforded 0.406 g of pure 10: mp 42–43 °C; ^1H NMR ($CDCl_3$) δ 0.34 (s, 9 H, $SiCH_3$), 7.07 (s, 1 H, =CH), 7.37

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(d, *J* = 8.7 Hz, 2 H, Ar), 7.55 (d, *J* = 8.7 Hz, 2 H, Ar); IR ($CDCl_3$) 2960, 2900, 2220 (CN), 1595, 1585, 1555, 1490, 1400, 1395, 1250, 1095, 1010, 970, 855, 840, 700 cm^{-1}; mass spectrum, *m/e* 235 (M^+ for ^{35}Cl). Anal. Calcd for $C_{12}H_{14}ClNSi$: C, 61.13; H, 5.98; N, 5.94; Cl, 15.04. Found: C, 61.30; H, 6.07; N, 5.85; Cl, 15.33.

2-(4-Bromophenyl)-3-(trimethylsilyl)-(*Z*)-prop-2-enenitrile (11Z) and 2-(4-Cyanophenyl)-3-(trimethylsilyl)-(*Z*)-prop-2-enenitrile (12Z). These compounds were prepared from (4-bromophenyl)acetylene (0.91 g, 5 mmol) and Me_3SiCN (1.34 mL, 10 mmol) according to the general procedure. After the reaction, the solvent was evaporated in vacuo. Bulb-to-bulb distillation (140–150 °C (2 mmHg)) of the residue afforded 0.435 g of a mixture of **11** and **12**. Preparative TLC (hexane/EtOAc, 9/1) of the distillate gave 0.196 g of **11Z** (yield 14%) in an early fraction (R_f 0.54–0.64) and 0.156 g of **12Z** (yield 19%) in a later one (R_f 0.29–0.48). **11Z**: mp 45–46 °C; ^1H NMR ($CDCl_3$) δ 0.34 (s, 9 H, $SiCH_3$), 7.09 (s, 1 H, =CH), 7.47 (d, *J* = 8.8 Hz, 2 H, Ar), 7.54 (d, *J* = 8.8 Hz, 2 H, Ar); ^{13}C NMR ($CDCl_3$) δ −1.45 ($SiCH_3$), 117.5 (CN), 127.2, 132.1 (Ar), 124.0, 134.1 (Ar, =C), 148.4 (=CH), 157.2 (ArBr); IR (neat) 2960, 2900, 2220 (CN), 1590, 1585, 1555, 1490, 1395, 1255, 1075, 1005, 905, 860, 840, 820, 715 cm^{-1}; mass spectrum, *m/e* 281 (M^+ for ^{81}Br). Anal. Calcd for $C_{12}H_{14}BrNSi$: C, 51.43; H, 5.04; N, 5.00. Found: C, 51.21; H, 4.93; N, 4.97. **12Z**: mp 96–97 °C; ^1H NMR ($CDCl_3$) δ 0.36 (s, 9 H, $SiCH_3$), 7.25 (s, 1 H, =CH), 7.71 (s, 4 H, Ph); IR ($CDCl_3$) 2960, 2900, 2230 (CN), 1605, 1575, 1555, 1500, 1405, 1305, 1250, 975, 910, 845, 730 cm^{-1}; mass spectrum, *m/e* 226 (M^+). Anal. Calcd for $C_{13}H_{14}N_2Si$: C, 68.98; H, 6.23; N, 12.38. Found: C, 68.44; H, 6.02; N, 12.42.

2-(3,4-Benzodioxolyl)-3-(trimethylsilyl)-(*Z*)-prop-2-enenitrile (13Z). This compound was prepared from (3,4-(methylenedioxy)phenyl)acetylene (0.73 g, 5 mmol) and Me_3SiCN (1.34 mL, 10 mmol) according to the general procedure. Bulb-to-bulb distillation (130–140 °C (0.3 mmHg)) gave 0.689 g of crude **13** (56% yield). Preparative TLC (hexane/EtOAc, 9/1; R_f 0.38–0.64) of the distillate afforded 0.553 g of pure **13** (*Z*/*E* = 91/9): mp 66–67 °C; ^1H NMR ($CDCl_3$) δ 0.32 (s, 9 H, $SiCH_3$), 6.00 (s, 2 H, OCH_2O), 6.77–6.86 (m, 1 H, Ar), 6.89 (s, 1 H, =CH), 7.07 (d, *J* = 1.8 Hz, 1 H, Ar), 7.16 (dd, *J* = 8.2, 1.8 Hz, 1 H, Ar); IR ($CDCl_3$) 2970, 2900, 2220 (CN), 1610, 1560, 1510, 1490, 1450, 1355, 1250, 1040, 910, 855, 730 cm^{-1}; mass spectrum, *m/e* 245 (M^+). Anal. Calcd for $C_{13}H_{15}NO_2Si$: C, 63.64; H, 6.16; N, 5.71. Found: C, 63.74; H, 6.04; N, 6.00.

2-(3-Naphthyl)-3-(trimethylsilyl)-(*Z*)-prop-2-enenitrile (14Z). This compound was prepared from 3-naphthylacetylene (0.76 g, 5 mmol) and Me_3SiCN (1.34 mL, 10 mmol) according to the general procedure. Purification was carried out by column chromatography (silica gel; hexane/EtOAc, 8/2) and gel permeation LC to give pure **14**: mp 75–76 °C (hexane); ^1H NMR ($CDCl_3$) δ 0.38 (s, 9 H, $SiCH_3$), 7.23 (s, 1 H, =CH), 7.51–7.53 (m, 2 H, Ar), 7.69 (dt, *J* = 1.9, 8.7 Hz, 1 H, Ar) 7.82–7.90 (m, 3 H, Ar), 8.11 (d, *J* = 1.9 Hz, 1 H, Ar); ^{13}C NMR ($CDCl_3$) δ −1.33 ($SiCH_3$), 118.0 (CN), 122.0, 126.2, 126.9, 127.2, 127.7, 127.9, 128.7, 132.3, 133.2, 133.7 (Ar), 147.5 (=CH); IR (Nujol) 2230 (CN), 1600, 1555, 1280, 1250, 1130, 990, 940, 890, 880, 850, 810, 770, 750, 700 cm^{-1}; mass spectrum, *m/e* 251 (M^+). Anal. Calcd for $C_{16}H_{17}NSi$: C, 76.44; H, 6.82; N, 5.57. Found: C, 76.15; H, 6.65; N, 5.45.

2-(2-Methoxyphenyl)-3-(trimethylsilyl)-(*Z*)-prop-2-enenitrile (15Z). This compound was prepared from (2-methoxyphenyl)acetylene (0.65 mL, 5 mmol) and Me_3SiCN (1.34 mL, 10 mmol) according to the general procedure. After the reaction, the solvent was evaporated, and bulb-to-bulb distillation (90–100 °C (0.15 mmHg)) of the residue afforded 0.988 g of **15** (85% yield, *Z*/*E* = 84/16). Gel permeation LC of the distillate gave pure **15Z** and an enriched **15E**. A pure sample of **15E** was obtained by the photoisomeric procedure. **15Z**: ^1H NMR ($CDCl_3$) δ 0.33 (s, 9 H, $SiCH_3$), 3.89 (s, 3 H, OCH_3), 6.90–9.96 (m, 2 H, Ar), 6.93 (s, 1 H, =CH), 7.30–7.33 (m, 2 H, Ar); ^{13}C NMR ($CDCl_3$) δ −1.38 ($SiCH_3$), 55.71 (CH_3O), 118.2 (CN, $^3J_{CN\text{-}H}$ = 17 Hz), 111.6, 120.9, 129.5, 130.6 (Ar), 125.6, 126.3 (Ar, =C), 152.6 (=CH), 156.7 (PhO); IR (neat) 2970, 2910, 2840, 2225 (CN), 1605, 1590, 1495, 1470, 1255, 1125, 1030, 865, 845, 760 cm^{-1}; UV (hexane) λ 265 (ϵ 14 100), 300 (6700) nm; mass spectrum, *m/e* 231 (M^+). Anal. Calcd for $C_{13}H_{17}NOSi$: C, 67.49; H, 7.41; N, 6.05. Found: C, 67.76; H, 7.20; N, 6.09.

2-(2-Methoxyphenyl)-3-(trimethylsilyl)-(*E*)-prop-2-enenitrile (15E): ^1H NMR ($CDCl_3$) δ 0.08 (s, 9 H, $SiCH_3$), 3.95 (s, 3 H, CH_3O), 6.97–7.04 (m, 2 H, Ph), 6.99 (s, 1 H, =CH), 7.21 (dd, *J* = 1.7, 7.5 Hz, 1 H, Ph), 7.43 (td, *J* = 7.9, 1.7 Hz, 1 H, Ph); ^{13}C NMR ($CDCl_3$) δ −1.02 ($SiCH_3$), 55.63 (CH_3O), 119.1 (CN, $^3J_{CN\text{-}H}$ = 12 Hz), 111.1, 120.3, 130.7 (Ar), 124.6, 125.9 (Ar, =C), 153.5 (=CH), 157.0 (ArO); IR (neat) 2960, 2900, 2840, 2210 (CN), 1605, 1585, 1495, 1470, 1440, 1280, 1250, 1115, 1050, 1025, 1115, 1050, 1025, 1000, 865, 845, 755 cm^{-1}; UV (hexane) 260 (5400) nm; mass spectrum, *m/e* 231 (M^+). Anal. Calcd for $C_{13}H_{17}NOSi$: C, 67.49; H, 7.41; N, 6.05. Found: C, 67.26; H, 7.06; N, 5.96.

2-(2-Chlorophenyl)-3-(trimethylsilyl)-(*Z*)-prop-2-enenitrile (16Z). This compound was prepared from (2-chlorophenyl)acetylene (0.68 g, 5 mmol) and Me_3SiCN (1.34 mL, 10 mmol) according to the general procedure. After the reaction, the solvent was evaporated, and bulb-to-bulb distillation (80–90 °C (0.15 mmHg)) of the residue afforded 0.362 g of **16** (*Z*/*E* = 76/24). Gel permeation LC of the distillate gave 0.269 g of pure **16** (23% yield, *Z*/*E* = 75/25) as a colorless oil. The spectral data were obtained from the mixture: ^1H NMR ($CDCl_3$) δ 0.35 (s, *Z* isomer) and −0.08 (s, *E* isomer) [total 9 H, $SiCH_3$], 6.86 (s, *Z* isomer) and 7.40 (s, *E* isomer) [total 1 H, =CH], 7.26–7.53 (m, 4 H, Ar); IR (neat) 3070, 2960, 2900, 2220 (CN), 1595, 1570, 1465, 1435, 1300, 1250, 1125, 1060, 1035, 965, 855, 840, 750 cm^{-1}; mass spectrum, *m/e* 235 (M^+ for ^{35}Cl). Anal. Calcd for $C_{12}H_{14}NSiCl$: C, 61.13; H, 5.98; N, 5.94; Cl, 15.04. Found: C, 61.05; H, 5.81; N, 5.91; Cl, 15.11.

2-(2-Naphthyl)-3-(trimethylsilyl)prop-2-enenitrile (17). This compound was prepared from 2-naphthylacetylene (0.72 mL, 5 mmol) and Me_3SiCN (1.34 mL, 10 mmol) according to the general procedure. After the reaction, the solvent was evaporated in vacuo, and bulb-to-bulb distillation (120–130 °C (0.2 mmHg)) afforded 0.857 of **17** (68% yield, *Z*/*E* = 77/23). Preparative TLC (hexane/EtOAc = 9/1) of the distillate followed by gel permeation LC gave a **17Z** enriched fraction (*Z*/*E* = 91/9) and a **17E** enriched one (*Z*/*E* = 11/89). The spectral data were obtained from the mixture: ^1H NMR ($CDCl_3$) δ 0.40 (s, *Z* isomers) and −0.22 (s, *E* isomer) [total 9 H, $SiCH_3$], 6.90 (s, *Z* isomer) and 7.20 (s, *E* isomer), 7.45 (m, 2 H), 7.52–7.59 (m, 2 H), 7.85–7.89 (m, 2 H), and 8.07 (dd, *J* = 8.3, 0.9 Hz, 1 H) [Ar of *Z* isomer], 7.35 (dd, *J* = 7.0, 1.1 Hz, 1 H), 7.44–7.48 (m, 1 H), 7.53–7.58 (m, 2 H), 7.87–7.91 (m, 2 H), and 7.96 (dd, *J* = 8.9, 0.8 Hz, 1 H) [Ar of *E* isomer]; IR (neat) 3070, 2960, 2910, 2220 (CN), 1615 (C=C), 1585, 1575, 1510, 1395, 1255, 965, 865, 840, 805, 795, 780, 750, 695 cm^{-1}; mass spectrum, *m/e* 251 (M^+).

2-(2-Thienyl)-3-(trimethylsilyl)-(*Z*)-prop-2-enenitrile (18Z). This compound was prepared from 2-thienylacetylene (0.54 g, 4.8 mmol) and Me_3SiCN (1.34 mL, 10 mmol) according to the general procedure. Purification was carried out by bulb-to-bulb distillation (80–90 °C (0.4 mmHg)) followed by gel permeation LC to give pure **18**: ^1H NMR ($CDCl_3$) δ 0.32 (s, 9 H, $SiCH_3$), 6.80 (s, 1 H, =CH), 7.02 (ndd, *J* = 5.0, 3.7 Hz, 1 H, Ar), 7.26–7.29 (m, 2 H, Ar); IR (neat) 3110, 3075, 2960, 2900, 2220 (CN), 1560, 1510, 1425, 1305, 1250, 1220, 1050, 920, 840, 765, 695 cm^{-1}.

5-[Bis(trimethylsilyl)amino]-4-phenyl-1*H*-pyrrole-2-carbonitrile (5). In a 10-mL reaction flask was placed $NiCl_2$ (13 mg, 0.1 mmol), and then 1 N DIBAH in hexane (0.2 mL, 0.2 mmol) was added. After the color of the catalyst turned to black, Me_3SiCN (2.0 mL, 15 mmol) and phenylacetylene (0.28 mL, 2.5 mmol) were added to the reaction flask. The mixture was stirred under reflux for 20 h. The product was isolated by column chromatography (silica gel; hexane/EtOAc, 9/1) to give crude **5**. Purification of the crude product was carried out by column chromatography (silica gel; C_6H_6/EtOAc, 7/3) to afford 0.477 g of pure **5** (58% yield): mp 129–130 °C (hexane); ^1H NMR ($CDCl_3$) δ 0.08 (s, 18 H, $SiCH_3$), 6.98 (d, *J* = 3.0 Hz, 1 H, pyrrole), 7.21 (t, *J* = 7.3 Hz, 1 H, para proton of Ph), 7.34 (t, *J* = 7.3 Hz, 2 H, meta proton of Ph), 7.55 (d, *J* = 7.3 Hz, 2 H, ortho proton of Ph), 8.71 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 1.64 ($siCH_3$), 94.8 (CN), 115.1, 118.2, 119.9 (pyrrole ring), 126.2, 127.0, 128.3, 134.4 (Ph), 138.2 (N–C–N); IR (Nujol) 3320 (NH), 2220 (CN) cm^{-1}; mass spectrum, *m/e* 327 (M^+). Anal. Calcd for $C_{17}H_{25}N_3Si_2$: C, 62.33; H, 7.69; N, 12.83. Found: C, 61.96; H, 7.58; N, 12.61.

5-[Bis(trimethylsilyl)amino]-4-(4-chlorophenyl)-1*H*-pyrrole-2-carbonitrile (20). This compound was prepared from (4-chlorophenyl)acetylene (0.34 g, 2.5 mmol) and Me_3SiCN (2.0 mL, 15 mmol) according to the same procedure as for **5**: mp 162–163 °C (hexane); ^1H NMR ($CDCl_3$) δ 0.09 (s, 18 H, $SiCH_3$), 6.95 (d, *J* = 2.8 Hz, 1 H, pyrrole), 7.31 (d, *J* = 8.6 Hz, 2 H, Ar), 7.50 (d, *J* = 8.6 Hz, 2 H, Ar), 8.70 (br s, 1 H, NH); IR (Nujol) 3290 (NH), 2210 (CN) cm^{-1}; mass spectrum, *m/e* 361 (M^+ for ^{35}Cl). Anal. Calcd for $C_{17}H_{24}N_3Si_2Cl$: C, 56.40; H, 6.68; N, 11.61; Cl, 9.79. Found: C, 56.47; H, 6.46; N, 11.74; Cl, 9.65.

5-[Bis(trimethylsilyl)amino]-4-(2-methoxyphenyl)-1*H*-pyrrole-2-carbonitrile (21). This compound was prepared from (2-methoxyphenyl)acetylene (0.33 mL, 2.5 mmol) and Me_3SiCN (2.0 mL, 15 mmol) according to the same procedure for **5**: mp 200–201 °C (hexane); ^{1}H NMR ($CDCl_3$) δ 0.02 (s, 18 H, $SiCH_3$), 3.79 (s, 3 H, OCH_3), 6.93 (t, *J* = 7.8 Hz, 2 H, Ar), 6.98 (d, *J* = 3.0 Hz, 1 H, pyrrole), 7.24 (d, *J* = 7.8 Hz, 1 H, Ar), 7.33 (d, *J* = 7.8 Hz, 1 H, Ar), 8.16 (br s, 1 H, NH); IR (Nujol) 3310 (NH), 2210 (CN) cm^{-1}; mass spectrum, *m/e* 357 (M^+). Anal. Calcd for $C_{18}H_{27}N_3OSi_2$: C, 60.46; H, 7.61; N, 11.75. Found: C, 60.20; H, 7.37; N, 11.63.

2-Ferrocenyl-3-(trimethylsilyl)-(*Z*)-prop-2-enenitrile (22). This compound was prepared from ferrocenylacetylene (0.210 g, 1 mmol) and Me_3SiCN (0.27 mL, 2 mmol) according to the general procedure. Column chromatography (silica gel; hexane/EtOAc, 9/1) of the reaction mixture gave 0.176 g of red brown needles (56% yield), which were recrystallized from hexane to give orange needles: mp 96 °C (hexane); ^{1}H NMR ($CDCl_3$) δ 0.29 (s, 9 H, $SiCH_3$), 4.20 (s, 5 H, Cp), 4.35 (t, *J* = 1.9 Hz, 2 H, Cp), 4.55 (t, *J* = 1.9 Hz, 2 H, Cp), 6.60 (s, 1 H, =CH); ^{13}C NMR ($CDCl_3$) δ −1.10, 66.81, 70.13, 71.37, 82.29 (Cp), 118.0 (CN, $^3J_{CN\text{-}H}$ = 18 Hz), 127.6 (=C), 141.9 (=CH); IR (Nujol) 2210 (CN), 1560 (C=C) cm^{-1}; UV (hexane) λ 251 (ϵ 11 800), 286 (11 500), 376 (1400) nm; mass spectrum, *m/e* 309 (M^+). Anal. Calcd for $C_{16}H_{19}NFeSi$: C, 62.14; H, 6.19; N, 4.53. Found: C, 62.27; H, 6.21; N, 4.51.

5-[Bis(trimethylsilyl)amino]-4-ferrocenyl-1*H*-pyrrole-2-carbonitrile (23). In a 10-mL flask were placed $NiCl_2$ (13 mg, 0.1 mmol) and $FeCl_3$ (5 mg, 0.03 mmol), and then 1 N DIBAH in hexane (0.2 mL, 0.2 mmol) was added. After the color of the catalyst turned to black, Me_3SiCN (0.81 mL, 6 mmol) and ferrocenylacetylene (0.21 g, 1 mmol) were added to the flask. The mixture was stirred under reflux for 20 h. The product was isolated by column chromatography (silica gel; hexane/EtOAc, 9/1) to give 0.248 g of crude **23** (57% yield). Recrystallization from hexane gave pure **23**: mp 170 °C dec; ^{1}H NMR ($CDCl_3$) δ 0.09 (s, 18 H, $SiCH_3$), 4.05 (s, 5 H, Cp), 4.17 (t, *J* = 1.8 Hz, 2 H, Cp), 4.43 (t, *J* = 1.8 Hz, 2 H, Cp), 6.90 (s, 1 H, =CH), 7.98 (br s, 1 H, NH); IR (Nujol) 3310 (NH), 2200 (CN), 1580 (C=C) cm^{-1}; UV (dioxane) λ 268 (ϵ 16 400) nm; mass spectrum, *m/e* 435 (M^+). Anal. Calcd for $C_{21}H_{29}N_3FeSi_2$: C, 57.92; H, 6.71; N, 9.65. Found: C, 57.78; H, 6.87; N, 9.64.

2-[(Trimethylsilyl)methylene]octanenitrile (24). This compound was prepared from 1-octyne (0.74 mL, 2.5 mmol) and Me_3SiCN (0.67 mL, 5 mmol) according to the same procedure for **3E**. Purification was carried out by column chromatography (silica gel, C_6H_6), giving 0.257 g of pure **24** (54% yield, *Z*/*E* = 78/22): bp 140–150 °C (28 mmHg) (bulb-to-bulb distillation); ^{1}H NMR ($CDCl_3$) δ 0.23 (s, 9 H, $SiCH_3$), 0.89 (t, *J* = 6.6 Hz, 3 H, CH_3), 1.28–1.34 (m, 6 H, CH_2), 1.53–1.57 (m, 2 H, CH_2), 2.28 (dt, *J* = 7.5, 1.3 Hz, 2 H, CH_2C=), 6.36 (t, *J* = 1.3 Hz, =CH of *Z* isomer) and 6.51 (s, =CH of *E* isomer) [total 1 H]; ^{13}C NMR ($CDCl_3$) δ −1.40 ($SiCH_3$), 14.01 (CH_2), 22.50, 27.74, 28.31, 31.45 (CH_2), 39.04 (*C*H_2C=), 118.9 (CN of *Z* isomer, $^3J_{CN\text{-}H}$ = 16 Hz), 129.1 (=C), 148.8 (=CH); IR (neat) 2960, 2940, 2855, 2220 (CN), 1590 (C=C), 1470, 1255, 1095, 1020, 860, 845, 765, 750, 695 cm^{-1}; mass spectrum, *m/e* 209 (M^+). Anal. Calcd for $C_{12}H_{14}NSi$: C, 68.83; H, 11.07; N, 6.69. Found: C, 68.95; H, 10.88; N, 6.75.

2-[(Trimethylsilyl)methylene]-5-acetoxybutanenitrile (26). This compound was prepared from 3-butynyl acetate (0.29 g, 2.5 mmol) and Me_3SiCN (0.67 mL, 5 mmol) according to the general procedure. Purification was carried out by bulb-to-bulb distillation (150–160 °C (30 mmHg)) followed by gel permeation LC to give a mixture of **26Z** and **26E** as a colorless oil (0.124 g, 23% yield). The spectral data were obtained from the mixture: ^{1}H NMR ($CDCl_3$) δ 0.25 (s, *Z* isomer) and 0.21 (s, *E* isomer) [total 9 H], 2.07 (s, *Z* isomer) and 2.06 (s, *E* isomer) [total 3 H, CH_3CO], 2.62 (dt, *J* = 6.3, 1.2 Hz, *Z* isomer) and 2.63 (m, *E* isomer) [total 1 H, CH_2C=], 4.25 (t, *J* = 6.3 Hz, *Z* isomer) and 4.28 (t, *J* = 6.3 Hz, *E* isomer) [total 2 H, CH_2O], 6.49 (t, *J* = 1.2 Hz, *Z* isomer) and 6.72 (s, *E* isomer) [total 1 H, =CH]; ^{13}C NMR ($CDCl_3$) δ −1.54 (*Z* isomer) and −0.61 (*E* isomer) [$SiCH_3$], 20.7 (CH_3), 37.9 (*Z* isomer) and 33.2 (*E* isomer) [*C*H_2C=], 61.6 (*Z* isomer) and 61.8 (*E* isomer) [CH_2], 118.3 (*Z* isomer) and 119.0 (*E* isomer) [CN], 124.4 (*Z* isomer) and 124.9 (*E* isomer) [C], 152.4 (*Z* isomer) and 152.7 (*E* isomer) [=CH], 170.7 (CO); IR (neat) 2960, 2900, 2220 (CN), 1740 (CO), 1590 (C=C), 1395, 1375, 1230, 1040, 860, 840, 765, 750, 695; mass spectrum, *m/e* 196 (M^+ − Me).

2-[(Trimethylsilyl)methylene]hexane-1,6-dinitrile (27). This compound was prepared from 5-hexynenitrile (0.23 mL, 2.5 mmol) and Me_3SiCN (0.67 mL, 5 mmol) according to the general procedure. Purification was carried out by bulb-to-bulb distillation (170–180 °C (28 mmHg)) followed by gel permeation LC to give a *E*/*Z* isomeric mixture of **27** (0.165 g, 34% yield). The spectral data were obtained from this mixture: ^{1}H NMR ($CDCl_3$) δ 0.25 (s, *Z* isomer) and 0.23 (s, *E* isomer) [total 9 H, $SiCH_3$], 1.95 (quintet, *J* = 7.0 Hz, 2 H, CH_2), 2.39 (t, *J* = 7.0 Hz, 2 H, CH_2CN), 2.48 (dt, *J* = 1.1, 7.0 Hz, 2 H, CH_2C=), 6.52 (d, *J* = 1.1 Hz, *Z* isomer) and 6.66 (t, *J* = 0.8 Hz, *E* isomer) [total 1 H, =CH]; IR (neat) 2950, 2880, 2240 (CN), 2205 (CN), 1585 (C=C), 1450, 1420, 1310, 1250, 1110, 835, 760, 745, 690 cm^{-1}; mass spectrum, *m/e* 192 (M^+). Anal. Calcd for $C_{10}H_{16}N_2Si$: C, 62.45; H, 8.38; N, 14.56. Found: C, 62.45; H, 8.38; N, 14.56.

2-[((Trimethylsilyl)oxy)methyl]-3-(trimethylsilyl)prop-2-enenitrile (28). This compound was prepared from propargyl trimethylsilyl ether (0.38 mL, 2.5 mmol) and Me_3SiCN (0.67 mL, 5 mmol) according to the general procedure. Purification was carried out by bulb-to-bulb distillation (140–150 °C (30 mmHg)) followed by gel permeation LC to give a mixture of **28Z** and **28E** as a colorless oil. The spectral data were obtained from the mixture: ^{1}H NMR ($CDCl_3$) δ 0.16 (s, 9 H, $SiCH_3$), 0.25 (s, 9 H, $OSiCH_3$), 4.20 (d, *J* = 1.9 Hz, 2 H, CH_2), 6.70 (t, *J* = 1.9 Hz, 1 H, =CH); IR (neat) 2975, 2910, 2230 (CN), 1600 (C=C), 1460, 1415, 1375, 1260, 1140, 1090, 1065, 845, 750 cm^{-1}; mass spectrum, *m/e* 227 (M^+).

2-[(Trimethylsilyl)methylene]-4,4-bis(ethoxycarbonyl)-hept-6-enenitrile (29). This compound was prepared from ethyl allylpropargylmalonate (0.60 g, 2.5 mmol) and Me_3SiCN (0.67 mL, 5 mmol) according to the general procedure. Purification was carried out by bulb-to-bulb distillation (200–210 °C (22 mmHg)) followed by preparative TLC (hexane/EtOAc, 80/20; R_f 0.53–0.67) to give 0.312 g of **29** (19% yield). A sample for characterization was obtained by gel permeation LC: ^{1}H NMR ($CDCl_3$) δ 0.23 (s, 9 H, $SiCH_3$), 1.27 (t, *J* = 7.0 Hz, 6 H, CH_3), 2.72 (d, *J* = 7.4 Hz, 2 H, CH_2), 2.89 (s, 2 H, CH_2), 4.17–4.25 (m, 4 H, OCH_2), 5.14 (d, *J* = 3.2 Hz, 1 H, =CH_2), 5. 16 (d, *J* = 12.0 Hz, 1 H, =CH_2), 5.58–5.70 (m, 1 H, =CH), 6.50 (s, 1 H, =C*H*Si) [the minor absorption at δ 6.67 (s) may indicate the presence of the *E* isomer]; IR (neat) 3080, 2970, 2960, 2900, 2220 (CN), 1735 (CO), 1640, 1580, 1445, 1370, 1285, 1255, 1210, 1190, 860, 845 cm^{-1}; mass spectrum, *m/e* 337 (M^+). Anal. Calcd for $C_{17}H_{27}NO_4Si$: C, 60.50; H, 8.06; N, 4.15. Found: C, 60.33; H, 8.02; N, 4.26.

3-(Cyanomethylene)-4-[(trimethylsilyl)methylene]cyclopentane-1,1-dicarboxylic Acid Diethyl Ester (30): mp 37–38 °C; ^{1}H NMR ($CDCl_3$) δ 0.18 (s, 9 H, $SiCH_3$), 1.26 (t, *J* = 7.1 Hz, 6 H, CH_3), 3.10 (d, *J* = 2.4 Hz, 2 H, CH_2C=), 3.31 (d, *J* = 2.4 Hz, 2 H, CH_2C=), 4.22 (q, *J* = 7.1 Hz, 4 H, CH_2O), 5.54 (t, *J* = 2.4 Hz, 1 H, =CH), 6.28 (t, *J* = 2.4 Hz, 1 H, =CH); ^{13}C NMR ($CDCl_3$) δ −0.94 ($SiCH_3$), 14.01 (CH_3), 40.12, 40.52 (CH_2), 57.40 (C), 62.09 (CH_2O), 88.94 (CN), 117.5, 128.0, 149.6, 161.6 (=C), 170.3 (C=O); IR (neat) 2980, 2960, 2210 (CN), 1730 (C=O), 1625, 1585, 1465, 1445, 1415, 1390, 1365, 1295, 1280, 1250, 1190, 1155, 1095, 1070, 1050, 1010, 855 cm^{-1}; mass spectrum, *m/e* 335 (M^+). Anal. Calcd for $C_{17}H_{25}NO_4Si$: C, 60.86; H, 7.51; N, 4.18. Found: C, 60.57; H, 7.23; N, 4.38.

2-[(Trimethylsilyl)methylene]-4,4-bis(ethoxycarbonyl)-6-hexynecarbonitrile (31): ^{1}H NMR ($CDCl_3$) δ 0.24 (s, 9 H, $SiCH_3$), 1.28 (t, *J* = 7.1 Hz, 6 H, CH_3), 2.08 (t, *J* = 2.8 Hz, ≡CH), 2.83 (t, *J* = 2.8 Hz, 2 H, CH_2C≡), 3.08 (s, 2 H, CH_2C=), 4.24 (m, 4 H, OCH_2), 6.64 (s, 1 H, =CH); IR (neat) 3275, 2980, 2960, 2900, 2210 (CN), 1730 (C=O), 1580 (C=C), 1465, 1450, 1435, 1365, 1280, 1250, 1200, 1095, 1070, 1045, 1010, 865, 845, 695 cm^{-1}; mass spectrum, *m/e* 335 (M^+).

2,6-Bis[(trimethylsilyl)methylene]-4,4-bis(ethoxycarbonyl)hexanedinitrile (32). This compound was prepared from ethyl dipropargylmalonate (0.60 g, 2.5 mmol) and Me_3SiCN (0.67 mL, 5 mmol) according to the general procedure. After the solvent was evaporated, column chromatography (silica gel;

hexane/EtOAc, 85/15) of the residue gave 0.531 g of the product mixture. Preparative TLC (hexane/EtOAc, 85/15; R_f 0.57–0.66) afforded 0.122 g of pure **32**: mp 68–70 °C (hexane); ^{1}H NMR ($CDCl_3$) δ 0.24 (s, 18 H, $SiCH_3$), 1.29 (t, J = 7.1 Hz, 6 H, CH_3), 2.99 (s, 4 H, CH_2), 4.25 (q, J = 7.1 Hz, 4 H, OCH_2), 6.63 (s, 2 H, =CH); ^{13}C NMR ($CDCl_3$) δ −1.62 ($SiCH_3$), 13.9 (CH_3), 40.7 (CH_2), 62.2 (OCH_2), 118.4 (CN, $^3J_{CN-H}$ = 17 Hz), 122.4 (=C), 157.1 (=CH), 168.8 (CO); IR (neat) 2980, 2970, 2910, 2225 (CN), 1730 (CO), 1585, 1450, 1370, 1280, 1255, 1205, 1190, 1120, 1065, 1045, 1015, 850, 770, 755, 695 cm^{-1}; mass spectrum, m/e 434 (M^+). Anal. Calcd for $C_{21}H_{34}N_2O_4Si_2$: C, 58.03; H, 7.88; N, 6.44. Found: C, 58.53; H, 8.00; N, 6.47.

5-Phenyl-2-[(trimethylsilyl)methylene]-4-hexynenitrile (33). This compound was prepared from 1-phenyl-1,4-pentadiyne (0.35 g, 2.5 mmol) and Me_3SiCN (0.67 mL, 5 mmol) according to the general procedure. After the solvent was removed in vacuo, bulb-to-bulb distillation (110–120 °C (0.4 mmHg)) gave a 0.463 g of a crude product. The distillate was purified by gel permeation LC to give 0.249 g of pure **33**. The spectral data were obtained on this mixture: ^{1}H NMR ($CDCl_3$) δ 0.27 (s, Z isomer) and 0.25 (s, E isomer) [total 9 H, $SiCH_3$], 3.46 (d, J = 1.7 Hz, Z isomer) and 3.40 (d, J = 0.5 Hz, E isomer) [total 2 H, CH_2], 6.86 (t, J = 1.7 Hz, Z isomer) and 6.69 (d, J = 0.5 Hz, E isomer) [total 1 H, =CH], 7.30–7.33 (m, 3 H, Ph), 7.43–7.46 (m, 2 H, Ph); IR (neat) 3080, 3060, 3040, 2960, 2910, 2220 (CN), 2200 (CN), 1595, 1575, 1490, 1445, 1415, 1320, 1255, 1070, 1430, 850, 760, 690 cm^{-1}; mass spectrum, m/e 239 (M^+).

2,3-Diphenyl-3-(trimethylsilyl)prop-2-enenitrile (34): mp 102–103 °C (hexane); ^{1}H NMR ($CDCl_3$) δ 0.31 (s, 9 H, $SiCH_3$), 6.81 (d, J = 7.0 Hz, 2 H, Ph), 7.10–7.22 (m, 8 H, Ph); ^{13}C NMR ($CDCl_3$) δ −0.93 ($SiCH_3$), 119.6 (CN), 123.3, 126.6, 126.9, 128.0, 128.2, 128.3, 129.2, 135.1, 140.8 (Ph, =CCN), 165.0 (=CSi); IR ($CDCl_3$) 3150, 3060, 3030, 2960, 2900, 2210 (CN), 1595, 1490, 1445, 1265, 1255, 1025, 850, 695, 645 cm^{-1}; mass spectrum, m/e 277 (M^+). Anal. Calcd for $C_{18}H_{19}NSi$: C, 77.93; H, 6.90; N, 5.05. Found: C, 78.12; H, 6.89; N, 4.87.

5-[Bis(trimethylsilyl)amino]-3,4-diphenyl-1*H*-pyrrole-2-carbonitrile (36). In a 10-mL flask were placed diphenylacetylene (0.45 g, 2.5 mmol), Me_3SiCN (2.0 mL, 15 mmol), and $PdCl_2$ (18 mg, 0.1 mmol). The mixture was refluxed with stirring for 20 h under nitrogen. The excess Me_3SiCN was evaporated in vacuo. Column chromatography (silica gel; hexane/EtOAc, 85/15) of the residue afforded 0.887 g of a pale yellow solid (88% yield), which was essentially pure. A sample for the spectral data was obtained by recrystallization of the solid from hexane: mp 186–187 °C (hexane); ^{1}H NMR ($CDCl_3$) δ 0.01 (s, 18 H, $SiCH_3$), 7.09–7.27 (m, 10 H, Ph), 8.80 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 1.59 ($SiCH_3$), 92.7 (CN), 139.5 (NCN); IR (Nujol) 3330 (NH), 2200 (CN) cm^{-1}; mass spectrum, m/e 403 (M^+). Anal. Calcd for $C_{23}H_{29}N_3Si_2$: C, 68.43; H, 7.24; N, 10.41. Found: C, 68.66; H, 7.10; N, 10.42.

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Lower Nitrogen Oxide Species as Catalysts in a Convenient Procedure for the Iodination of Aromatic Compounds

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A simple method for the iodination of aromatic compounds, using I^- as the iodine source and O_2 and catalytic amounts of $NO^+BF_4^-$ as the oxidant, is presented. The reactions are performed at 25 °C in CF_3COOH/CH_2Cl_2 or CF_3COOH/CH_3COOH mixtures and compounds with as different reactivities as the halobenzenes and 1-methoxynaphthalene can be iodinated in very good yields. A set of relative rates, isotope effects, and isomer distributions in accordance with the electrophilic action of an "I^+" species are presented. The formation of "I^+" is discussed in terms of possible outer-sphere and inner-sphere electron-transfer steps. Aromatic bromination and to a lesser extent chlorination can be performed by using similar methods.

Introduction

Although aryl iodides have been successfully used in organic synthesis for more than a century, e.g., in the syntheses of Ullman[1a] and Heck,[1b] more extensive progress has been retarded due to the lack of simple and reliable methods of their preparation.[2] Aromatic compounds can generally be iodinated by iodine[3] only in the presence of a Lewis acid,[5] a hydrogen iodide trap,[6] or, most commonly, an oxidizing agent[7-11] (Scheme I).

Scheme I. Various Mechanisms of Electrophilic Aromatic Iodination

$$\begin{array}{llr}
\text{activation:} & I_2 + L \longrightarrow \text{“}I^+\text{”} + LI^- & (1)\\
 & I_2 + Ag^+ \longrightarrow \text{“}I^+\text{”} + AgI & (2)\\
 & 0.5I_2 + \text{ox} \longrightarrow \text{“}I^+\text{”} + \text{red}^- & (3)\\
\text{oxidation of } I^-\text{:} & I^- + \text{ox} \longrightarrow 0.5I_2 + \text{red}^- & (4)\\
\text{iodination:} & \text{“}I^+\text{”} + \text{ArH} \longrightarrow \text{Ar(H)}I^+ \xrightarrow[-H^+]{\text{slow}} \text{ArI} & (5)\\
\text{overall reaction:} & I_2 + \text{ArH} \longrightarrow \text{ArI} + \text{HI} & (6)\\
 & \text{ox} + 0.5I_2 + \text{ArH} \longrightarrow \text{ArI} + H^+ + \text{red}^- & (7)
\end{array}$$

A variety of oxidants have been used to bring about the transformation of eq 3. HNO_3/H_2SO_4, as used in the

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[1] (a) Fanta, P. E. *Synthesis* 1974, 9. (b) Heck, R. F. *Org. React. (N.Y.)* 1982, *27*, 345.

[2] Merkushev, E. V. *Russ. Chem. Rev. (Engl. Transl.)* 1984, *53*, 583.

[3] Other reagents for direct iodination include ICl and *N*-iodo amides. Indirect methods for aromatic iodination include initial thallation,[4a] mercuration,[4b] and diazotation. For an extensive summary, see ref 2.

[4] (a) McKillop, A.; Hunt, J. D.; Zelesko, M. J.; Fowler, J. S.; Taylor, E. C.; McGillivray, G.; Kienzle, F. *J. Am. Chem. Soc.* 1971, *93*, 4841. Braun, S. L.; Dürmeyer, E.; Jacob, K.; Vogt, W. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* 1983, *38B*, 696. (b) Barluenga, J.; Campos, P. J.; Gonzales, J. M.; Asensio, G. *J. Chem. Soc., Perkin Trans. 1* 1984, 2623.

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