A New Method for the Construction of the Pyrrole Ring by the Carbonylcobalt-Catalyzed Reaction of Trimethylsilyl Cyanide with Acetylenes. Its Scope and Limitations[1]

Naoto Chatani*,[2] and Terukiyo Hanafusa[3]

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan, and The Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka 567, Japan

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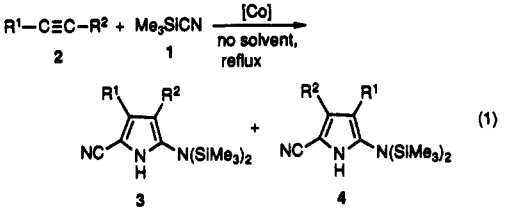
The carbonylcobalt-catalyzed reaction of acetylenes with trimethylsilyl cyanide (1) to give 5-amino-1*H*-pyrrole-2-carbonitriles is described. Reaction of the symmetric internal acetylenes, 4-octyne (**2a**) and 2,9-dimethyl-5-decyne (**2b**), with 1 in the presence of a cobalt complex gave **3a** and **3b**, respectively, in high yield. From unsymmetric acetylenes were obtained mixtures of regioisomeric pyrroles. The regioisomeric ratio depended on the substitution pattern of the acetylenes and on the kind of substituents possessed by the acetylenes. In the case of the internal unsymmetric acetylenes, **2c-2f**, isomers in which the bulkier of the two substituents appeared at the 4-position of the pyrrole ring were obtained as the main products. However, the reaction of internal acetylenes bearing an ester group (**2g** and **2h**) gave a reversed selectivity. In case of the terminal acetylenes, 1-octyne (**2k**), **2l**, and **2m**, isomers in which the alkyl group was located at the 3-position of the pyrrole ring were obtained highly selectively. A new cobalt complex (8), prepared by the reaction of $Co_2(CO)_8$ with excess 1, catalyzed the formation of pyrrole **3a** from **2a** and 1. The stoichiometric reaction of complex 8 with **2a** also gave **3a** in a good yield.

Trimethylsilyl cyanide (1) has attracted considerable attention as a versatile reagent for the introduction of cyano groups into organic molecules.[4] Although a wide variety of transformations involving the use of 1 are known, the substrates used have been limited to polar compounds like aldehydes,[5] ketones,[6] and epoxides.[7] There are no examples of the reaction of 1 with nonpolar substrates like olefins and acetylenes. We reported earlier[1d] that the palladium-catalyzed reaction of arylacetylenes with 1 resulted in the addition of 1 across the carbon–carbon triple bond to give cyano-substituted vinylsilanes in good yield with high regio- and stereoselectivity. This novel reaction was the first example of the addition of 1 to a carbon–carbon multiple bond and was made possible by the use of a transition metal. Heretofore, Lewis acids were widely used as catalysts in the reaction of polar compounds with 1.[8] In the course of a study of the transition-metal-catalyzed reaction of acetylenes with 1, we discovered a new synthesis of 5-amino-1*H*-pyrrole-2-carbonitriles[9] by the palladium- or nickel-catalyzed reaction of aryl- and diarylacetylenes with a stoichiometric excess of 1 in the absence of solvent.[10] Unfortunately, this synthesis lacked the generality, that would render it useful to synthetic organic chemists. Aliphatic acetylenes were not suitable substrates for the formation of 5-amino-1*H*-pyrrole-2-carbonitriles. We now describe the synthesis of 5-amino-1*H*-pyrrole-2-carbonitriles by the cobalt-catalyzed reaction of a variety of substituted acetylenes with 1.[11]



(1)

Results and Discussion

Treatment of 4-octyne (**2a**) with excess 1 without solvent in the presence of $CpCo(CO)_2$ at the boiling point of 1 (bath temperature 120–130 °C) for 20 h gave 5-[bis(trimethylsilyl)amino]-3,4-dipropyl-1*H*-pyrrole-2-carbonitrile (**3a**) in 93% yield (eq 1, $R^1 = R^2 = n$-Pr) (entry 1, Table

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(2) Department of Applied Chemistry.

(3) The Institute of Scientific and Industrial Research.

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(8) For papers on the transition-metal-catalyzed reactions of 1, see: (a) Yamasaki, Y.; Maekawa, T.; Ishihara, T.; Ando, T. *Chem. Lett.* **1985**, 1387. (b) Kusumoto, T.; Hiyama, T.; Ogata, K. *Tetrahedron Lett.* **1986**, *27*, 4197. (c) Imi, K.; Yanagihara, N.; Utimoto, K. *J. Org. Chem.* **1987**, *52*, 1013. (d) Mukaiyama, T.; Soga, T.; Takenoshita, H. *Chem. Lett.* **1989**, 997. (e) Mukaiyama, T.; Soga, T.; Takenoshita, H. *Chem. Lett.* **1989**, 1273. (f) Mukaiyama, T.; Takenoshita, H.; Yamada, M.; Soga, T. *Chem. Lett.* **1990**, 229. (g) Mukaiyama, T.; Takenoshita, H.; Yamada, M.; Soga, T. *Chem. Lett.* **1990**, 1259. (h) Okuda, F.; Watanabe, Y. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1201.

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(10) Chatani, N.; Hanafusa, T. *Tetrahedron Lett.* **1986**, *27*, 4201.

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Table I. Synthesis of 5-Amino-1*H*-pyrrole-2-carbonitriles by the Reaction of Me_3SiCN with Acetylenes[a]

entry	acetylene	R^1	R^2	catalyst	additive	yield,[b] %	product[c]
1	**2a**	Pr	Pr	$CpCo(CO)_2$		93	**3a**
2[d]	**2a**	Pr	Pr	$CpCo(CO)_2$		13	**3a**
3	**2b**	*i*-C_5H_{11}	*i*-C_5H_{11}	$CpCo(CO)_2$		92	**3b**
4	**2b**	*i*-C_5H_{11}	*i*-C_5H_{11}	$Co_2(CO)_8$		86	**3b**
5	**2c**	Bu	Me	$CpCo(CO)_2$		82	**3c:4c** = 39:61
6	**2c**	Bu	Me	$CpCo(CO)_2$	PPh_3	61	**3c:4c** = 37:63
7	**2c**	Bu	Me	$CpCo(CO)_2$	pyridine	43	**3c:4c** = 36:64
8	**2c**	Bu	Me	Cp_2Co		71	**3c:4c** = 36:64
9	**2c**	Bu	Me	$Co_2(CO)_8$		95	**3c:4c** = 36:64
10	**2c**	Bu	Me	$Co_2(CO)_8$	$AlCl_3$	26	**3c:4c** = 42:58
11	**2c**	Bu	Me	$Me_3SiCo(CO)_4$		85	**3c:4c** = 36:64
12	**2c**	Bu	Me	"$Co(Me_3SiCN)$"[e]		64	**3c:4c** = 32:68
13	**2d**	Ph	Me	$CpCo(CO)_2$		94	**3d:4d** = 14:86
14	**2d**	Ph	Me	$Co_2(CO)_8$		85	**3d:4d** = 11:89
15	**2e**	Ph	*n*-Pr	$CpCo(CO)_2$		76	**3e:4e** = 26:74
16	**2f**	Ph	*t*-Bu	$Co_2(CO)_8$		30	**3f:4f** = 93:7[f]
17	**2g**	$CH_3COO(CH_2)_2$	Me	$CpCo(CO)_2$		79	**3g:4g** = 70:30[g]
18	**2h**	$PhCOO(CH_2)_2$	Me	$Co_2(CO)_8$		93	**3h:4h** = 60:40[g]
19	**2i**	Ph	CH=CHBu	$CpCo(CO)_2$		53	**3i:4i** = 20:80[f,g]
20	**2j**	Ph	Ph	$CpCo(CO)_2$		30	**3j**
21	**2k**	*n*-Hex	H	$Co_2(CO)_8$		47	**3k:4k** = 73:27
22	**2l**	$CH_3COO(CH_2)_2$	H	$CpCo(CO)_2$		42	**3l:4l** = 90:10
23	**2m**	$NC(CH_2)_3$	H	$CpCo(CO)_2$		82	**3m:4m** = 95:5

[a] Reaction conditions: A mixture of acetylene (2.5 mmol), Me_3SiCN (15 mmol, 2.0 mL), catalyst (0.1 mmol), and additive (0.2 mmol) refluxed for 20 h, unless otherwise noted. [b] Isolated yields, based on acetylene. [c] Product ratios were determined by GC. [d] Toluene (5 mL) was used as the solvent. [e] "$Co(Me_3SiCN)$" was prepared by the reaction of $Co_2(CO)_8$ with Me_3SiCN (see text). [f] The regiochemistry is tentatively assigned. [g] Product ratios were determined by ^1H NMR.

I). Product **3a** may have been produced by the desilylation of **5**, the initial product, during column chromatography on silica gel. Compound **5** formally consists of one molecule of 4-octyne and three molecules of **1**. The use of toluene as a solvent led to a decreased yield (entry 2). 2,5-Dimethyl-5-decyne (**2b**) also reacted with **1**, to give pyrrole derivative **3b** in high yield (entries 3 and 4). The reaction of 2-heptyne (**2c**) with **1** in the presence of $CpCo(CO)_2$ gave a mixture of 5-[bis(trimethylsilyl)-amino]-4-butyl-3-methyl-1*H*-pyrrole-2-carbonitrile (**4c**) and its regioisomer **3c**, in 82% total yield (entry 5). 2-Heptyne was chosen as a representative substrate to determine reaction conditions under which a highly regioselective formation of 5-amino-1*H*-pyrrole-2-carbonitriles could be achieved. Comparable regioselectivity was observed with different catalysts (entries 5–12). Thus, the use of PPh_3, pyridine, or $AlCl_3$ resulted in a decreased yield but did not affect regioselectivity (entries 6, 7, and 10). Unfortunately, reaction conditions under which a high yield of either **3c** or **4c** could be obtained were not found. Although **3c** and **4c** could not be separated by either column chromatography or gel permeation chromatography, pure **4c** could be obtained by repeated recrystallization of the mixture of **3c** and **4c** from hexane. The structure of **4c** was confirmed by X-ray analysis. Other unsymmetric internal acetylenes (**2d–2i**) also gave mixtures of regioisomers. The assignment of regiochemistry of the products was made on the basis of their ^1H NMR spectra. When the ^1H NMR spectra of **3c** and **4c** were compared, **4c** was found to display a methyl group proton signal at lower (2.14 ppm) field and nonequivalent methylene proton signals at 2.19–2.24 ppm. Compound **3c** showed a methyl group proton signal at higher (1.80 ppm) field and an equivalent methylene proton signal at 2.50 ppm (Figure 1). Thus, the signal due to the methyl or methylene protons of the alkyl substituents at the C-3 position of the pyrrole ring

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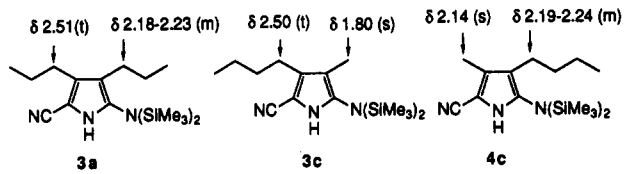


3a **3c** **4c**

Figure 1. Chemical shifts of selected protons of **3a**, **3c**, and **4c**.

appeared downfield from those of the alkyl substituent at the C-4 by ca. 0.3–0.4 ppm. These characteristic chemical shifts proved useful in assigning the regiochemistry of the other pyrroles prepared in this study.

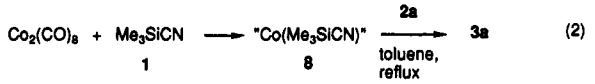
In most cases, unsymmetric acetylenes gave mixtures of regioisomeric pyrroles. The isomers in which the bulkier substituent resided at the C-4 position were the main products. As was the case for **3c** and **4c**, repeated recrystallization of the mixtures of isomers gave pure **4d**, **4e**, and **4f**. Curiously, acetylenes bearing an ester substituent gave a reversed regioselectivity. Thus, **3g** and **3h** were the main products from **2g** and **2h**, respectively (entries 17 and 18). Pyrrole **3h** was obtained in pure form by repeated recrystallization. Its regiochemistry was assigned from its ^1H NMR spectral data, with the criteria outline above. Although diphenylacetylene (**2j**) reacted with **1** in the presence of palladium or nickel catalyst to give pyrrole derivative **3j** in a high yield, as reported previously,[10] a low yield of **3j** was obtained from the cobalt-catalyzed reaction (entry 20).

A remarkably different product regiochemistry was observed in the reaction of terminal acetylenes with **1**. The reaction of 1-octyne (**2k**) with **1** in the presence of $Co_2(CO)_8$ gave **3k** together with **4k**, in 47% total yield (**3k:4k** = 73:27) (entry 21). The assignment of regiochemistry was based on the ^1H NMR spectra. Thus, **3k** displayed a vinyl proton signal at higher field than did **4k**. The presence of an electron-withdrawing substituent on one of the acetylenic carbon atoms improved the regioselectivity (entries 22 and 23). Because the major isomers **3k**, **3l**, and **3m** were very sensitive to moisture, they could not be isolated in pure form. Phenylacetylene (**2o**) gave a black syrup that contained only a trace amount of the expected pyrroles.

Although the mechanism for the formation of the pyrrole ring is not clear, it is nevertheless worthwhile to describe some experimental results that suggest the existence of possible reaction intermediates. To begin, it is well-known that (acetylene)cobalt complexes can be readily obtained by the reaction of acetylenes with $Co_2(CO)_8$ and that those acetylene complexes are significant intermediates in both cobalt-catalyzed and stoichiometric reactions of acetylenes.[12] Thus, complexes **6** and **7** were prepared by

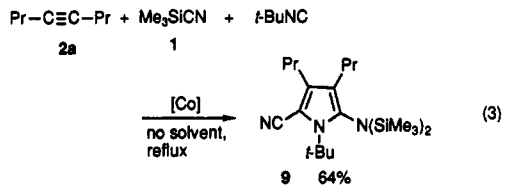
6 **7**

treatment of $Co_2(CO)_8$ with **2a** and **2j**, respectively, by a conventional method.[13] However, treatment of **6** or **7** with **1** did not give **3a** or **3j**, respectively. This result suggested that (acetylene)cobalt complexes like **6** and **7** were not important catalysts in the formation of the pyrroles. However, treatment of $Co_2(CO)_8$ with **1** at the boiling point of **1** gave a white complex **8**, which was accompanied by a violent evolution of carbon monoxide.[14] The complex **8** was extremely sensitive to air and moisture. The reaction of **8** with **2a** in refluxing toluene gave **3a** in 64% yield (eq 2). The complex also catalyzed the reaction of **2c** with



(2)

1, to give a mixture of **3c** and **4c** (entry 11, Table I). Although the structure of **8** is not known, it is believed that **8** is a precursor of the active catalytic species in the reactions described here. The $CpCo(CO)_2$-catalyzed reaction of **2a** with **1** in the presence of *t*-BuNC gave 5-[bis(trimethylsilyl)amino]-*N*-*tert*-butyl-3,4-dipropyl-1*H*-pyrrole-2-carbonitrile (**9**) (eq 3), which formally consists of one molecule of **2a**, two molecules of **1**, and one molecule of *t*-BuNC. This result demonstrated that at least one molecule of **1** could act as the equivalent of Me_3SiNC in the reaction shown in eq 1.[15,16]



(3)

9 64%

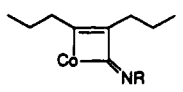
(12) For a detailed description of (acetylene)cobalt complexes, see: Kemmitt, R. D. W.; Russell, D. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, 1982, Vol. 5.

(13) For a review on (acetylene)cobalt complexes, see: Dickson, R. S.; Fraser, P. J. *Adv. Organomet. Chem.* **1974**, *12*, 323.

(14) Because of its extreme sensitivity to air and moisture, complex **8**, could not be isolated and was not fully characterized. Some transition metal–Me_3SiCN complexes are known. See: Seyferth, D.; Kahlen, N. *J. Am. Chem. Soc.* **1960**, *82*, 1080. Jones, R. A.; Seeberger, M. H. *J. Chem. Soc., Dalton Trans* **1983**, 181. Pombeiro, A. J. L.; Hughes, D. L.; Pickett, C. J.; Richards, R. L. *J. Chem. Soc., Chem. Commun.* **1986**, 246.

(15) Spectroscopic studies suggest that trimethylsilyl cyanide exists mainly as the cyanide, with the equilibrium $Me_3SiCN \rightleftarrows Me_3SiNC$ lying well to the left. See: Seckar, J. A.; Thayer, J. S. *Inorg. Chem.* **1976**, *15*, 501, and references cited therein. See also: Arnold, D. E. J.; Cradock, S.; Ebsworth, E. A. V.; Murdoch, J. D.; Rankin, D. W. H.; Skea, D. C. J.; Harris, R. K.; Kimber, B. J. *J. Chem. Soc., Dalton Trans.* **1981**, 1349.

(16) Although the reaction mechanism is not clear, we hypothesize that the reaction proceeds via the iminocobaltacyclobutene complex **10**. The related *tert*-butyl complex **10** (R = *t*-Bu) is known. See: Wakatsuki, Y.; Miya, S.; Yamazaki, H.; Ikuta, S. *J. Chem. Soc., Dalton Trans* **1986**, 1201.



10

R = $SiMe_3$, *t*-Bu

Table II. Transition-Metal-Catalyzed Reaction of Trimethylsilyl Cyanide with Acetylenes

$R_1C{\equiv}CR_2$		product yield as a function of catalyst[a]		
R^1	R^2	Pd	Ni	Co
Ph	H	×	○	×
Ph	Me	△	△	○
Ph	Ph	○	○	△
Hex	H	×	×	○
Pr	Pr	×	×	○

[a] Key: ○, 50–100%; △, 30–50%; ×, 0–30%.

In summary, the reactions described here provide a new method for the synthesis of multifunctional pyrroles, which should prove to be useful intermediates for the preparation of compounds of pharmaceutical or industrial interest.[17] As was reported earlier,[10] Pd and Ni complexes have been used as catalysts only for the reaction of mono- and diaryl-substituted acetylenes with **1** to give pyrrole derivatives. Hiyama found independently that Pd complexes catalyzed the formation of pyrroles by the reaction of silylacetylenes with **1**.[9c] Now it has been demonstrated that cobalt complexes are also useful catalysts for the construction of pyrrole rings from alkyl-substituted acetylenes. As shown in Table II, any type of 5-aminopyrrole-2-carbonitriles can be obtained in high yield from any type of acetylene by an appropriate selection of catalyst. The full characterization of the complex **8**, which seems to be a precursor of the active catalyst species in these reactions, is in progress.

Experimental Section

General Procedures. Melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. ^1H NMR spectra were recorded with Bruker WM-360 and JEOL GSX-270 instruments and are reported downfield (δ, ppm) from internal tetramethylsilane. ^{13}C NMR spectra were recorded with a JEOL GXS-270 instrument and are reported (δ, ppm) downfield from chloroform. Infrared spectra were recorded with a Hitachi 260-10 spectrometer. The positions of the absorptions are reported in reciprocal centimeters (cm^{-1}). Mass spectra were recorded at 70 eV with a JMS-DX 300m instrument. Elemental analyses were performed with Perkin-Elmer 240C or Yanagimoto CHN-Corder MT-2 analyzers by the ISIR Material Analysis Center of Osaka University. Analytical GC was performed with Shimazu 9A and 14A gas chromatographs equipped with Shimazu Hicap-CBP1 capillary columns, with helium as the carrier gas. Column chromatography was performed with 70–230-mesh Merck Kieselgel 60, with 9:1 mixtures of hexane/EtOAc as the eluant, unless indicated otherwise.

Materials. Most of the acetylenes (**2a, 2b, 2c, 2d, 2e, 2j, 2k, 2m, 2o**) were commercially available. The acetylenic esters **2g, 2h**, and **2l** were prepared by esterification of the corresponding acetylenic alcohols, which were obtained commercially. Acetylenes **2f** and **2i** were prepared by a literature method.[18] Me_3SiCN was obtained from Tokyo Kasei Co. and was distilled from CaH_2 before use. $Co_2(CO)_8$ was purchased from Strem and was used after recrystallization from hexane. $CpCo(CO)_2$ was purchased from Tokyo Kasei and was used without further purification.

General Procedure for the Carbonylcobalt-Catalyzed Reaction of Acetylenes with Trimethylsilyl Cyanide (1). In a 10-mL reaction flask were placed acetylene (2.5 mmol), Me_3SiCN

(17) For papers on 2-aminopyrroles, see: Wamhoff, H.; Wehling, B. *Synthesis* **1976**, 51. Johnson, R. W.; Mattson, R. J.; Sowell, J. W. *J. Heterocyc. Chem.* **1977**, *14*, 383. Mattson, R. J.; Sowell, J. W. *Synthesis* **1979**, 217. Laks, J. N. S.; Ross, J. R.; Bayomi, S. M.; Sowell, J. W. *Synthesis* **1985**, 291. Pichler, H.; Folkers, G.; Roth, H. J.; Eger, K. *Liebigs Ann. Chem.* **1986**, 1485. Eger, K.; Pfahl, J. G.; Folkers, G.; Roth, H. J. *J. Heterocycl. Chem.* **1987**, *24*, 425. Toja, E.; DePaoli, A.; Tuan, G.; Kettenring, J. *Synthesis* **1987**, 272. See also ref 9.

(18) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467.

(15 mmol, 2.0 mL), cobalt complex (0.1 mmol), and, if necessary, additive (PPh_3, pyridine, or $AlCl_3$; 0.2 mmol) in that order. The mixture was heated to reflux, with stirring, under N_2. After 20 h, the flask was cooled to room temperature and unreacted 1 was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel to yield the pure pyrroles. The 5-amino-1*H*-pyrrole-2-carbonitriles **3j** and **4o** have been described.[1d] The physical properties of new compounds are recorded below.

5-[Bis(trimethylsilyl)amino]-3,4-dipropyl-1*H*-pyrrole-2-carbonitrile (3a) (entry 1, Table I) was from 4-octyne (**2a**) (2.5 mmol, 0.38 mL). Purification by column chromatography gave pure **3a** (0.78 g, 93%) as a pale yellow solid. An analytical sample was obtained by recrystallization (hexane): white solid; mp 119–120 °C (hexane); ^1H NMR ($CDCl_3$) δ 0.08 (s, 18 H, $SiCH_3$), 0.92 (t, J = 7.5 Hz, 3 H, CH_3), 0.96 (t, J = 7.5 Hz, 3 H, CH_3), 1.42–1.52 (m, 2 H, CH_2), 1.60 (sextet, J = 7.5 Hz, 2 H, CH_2), 2.18–2.23 (m, 2 H, CH_2C=), 2.51 (t, J = 7.5 Hz, 2 H, CH_2C=), 7.80 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 1.62, 13.70, 14.64, 23.38, 23.44, 26.68, 27.91, 92.42, 115.78, 116.97, 136.00, 137.43; IR (Nujol) 3230 (NH), 2210 (CN), 1570 (C=C); MS, m/z 335 (M^+). Anal. Calcd for $C_{17}H_{33}N_3Si_2$: C, 60.84; H, 9.91; N, 12.52. Found: C, 61.07; H, 9.68; N, 12.57.

5-[Bis(trimethylsilyl)amino]-3,4-bis(3-methylbutyl)-1*H*-pyrrole-2-carbonitrile (3b) (entry 3, Table I) was prepared from 2,9-dimethyl-5-decyne (**2b**) (2.5 mmol, 0.54 mL). Purification by column chromatography gave pure **3b** (0.90 g, 92%) as a pale yellow solid. An analytical sample was obtained by recrystallization (hexane): white solid; mp 76–78 °C (hexane); ^1H NMR ($CDCl_3$) δ 0.09 (s, 18 H, $SiCH_3$), 0.94 (d, J = 6.6 Hz, 12 H, CH_3), 1.30–1.37 (m, 2 H, CH_2), 1.42–1.48 (m, 2 H, CH_2), 1.60 (c, 2 H, CH), 2.21–2.25 (m, 2 H, CH_2C=), 2.52 (t, J = 7.2 Hz, 2 H, CH_2C=), 7.71 (br s, 1 H, NH); IR (Nujol) 3250 (NH), 2210 (CN), 1570 (C=C); exact mass for $C_{21}H_{41}N_3Si_2$ (M^+), calcd 391.2837, found 391.2831.

5-[Bis(trimethylsilyl)amino]-3-butyl-4-methyl-1*H*-pyrrole-2-carbonitrile (3c) and 5-[bis(trimethylsilyl)amino]-4-butyl-3-methyl-1*H*-pyrrole-2-carbonitrile (4c) (entry 5, Table I) were prepared from 2-heptyne (**2c**) (2.5 mmol, 0.33 mL). Purification by column chromatography gave a mixture of **3c** and **4c** (0.66 g, 82%; **3c**:**4c** = 39:61) as a pale yellow solid. Two recrystallizations (hexane) of the mixture produced pure **4c** as a white solid: mp 137–138 °C (hexane); ^1H NMR ($CDCl_3$) δ 0.08 (s, 18 H, $SiCH_3$), 0.94 (t, J = 7.6 Hz, 3 H, CH_3), 1.34–1.45 (c, 4 H, CH_2), 2.14 (s, 3 H, CH_3C=), 2.19–2.24 (m, 2 H, CH_2C=), 7.87 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 1.66, 11.16, 13.89, 23.22, 24.16, 31.99, 92.70, 115.62, 117.39, 131.35, 137.31; IR (Nujol) 3310 (NH), 2200 (CN), 1570 (C=C); MS, m/z 321 (M^+). Anal. Calcd for $C_{16}H_{31}N_3Si_2$: C, 59.75; H, 9.72; N, 13.07. Found: C, 59.86; H, 9.51; N, 13.08. Crystallographic data for **4c**: formula $C_{16}H_{31}N_3Si_2$; crystal system, triclinic; space group, $P\bar{1}$; cell dimensions, a = 8.710 (1) Å, b = 14.709 (2) Å, c = 8.620 (2) Å, α = 81.95 (1)°, β = 106.91 (1)°, γ = 98.48 (1)°, Z = 2, d_{calcd} = 1.028 g/cm^3. The spectra of the minor product (**3c**) were derived from the spectra of a mixture of **3c** and **4c**: ^1H NMR ($CDCl_3$) δ 0.07 (s, 18 H, $SiCH_3$), 0.91 (t, J = 7.6 Hz, 3 H, CH_3), 1.34 (sextet, J = 7.6 Hz, 2 H, CH_2), 1.51 (quintet, J = 7.6 Hz, 2 H, CH_2), 1.80 (s, 3 H, CH_3C=), 2.50 (t, J = 7.6 Hz, 2 H, CH_2C=), 7.83 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 1.53, 8.99, 13.95, 22.18, 25.55, 32.14, 91.94, 111.93, 115.81, 136.24, 137.68.

5-[Bis(trimethylsilyl)amino]-4-methyl-3-phenyl-1*H*-pyrrole-2-carbonitrile (3d) and 5-[bis(trimethylsilyl)amino]-3-methyl-4-phenyl-1*H*-pyrrole-2-carbonitrile (4d) (entry 14, Table I) were prepared from 1-phenyl-1-propyne (**2d**) (2.5 mmol, 0.32 mL). Purification by column chromatography gave a mixture of **3d** and **4d** (0.72 g, 85%; **3d**:**4d** = 11:89) as a pale yellow solid. Two recrystallizations (hexane) of the mixture produced pure **4d** as a white solid: mp 159–160 °C (hexane); ^1H NMR ($CDCl_3$) δ −0.01 (s, 18 H, $SiCH_3$), 2.17 (s, 3 H, CH_3C=), 7.24–7.50 (m, 5 H, Ph), 8.04 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 1.53, 11.54, 93.21, 115.55, 118.42, 126.34, 128.05, 129.79, 130.88, 134.24, 138.65; IR (Nujol) 3250 (NH), 2210 (CN), 1605, 1575, 1560 (C=C); MS, m/z 341 (M^+). Anal. Calcd for $C_{18}H_{27}N_3Si_2$: C, 63.29; H, 7.97; N, 12.30. Found: C, 63.09; H, 8.04; N, 12.25. The ^1H NMR spectrum of **3d** was derived from the spectrum of the mixture: ^1H NMR ($CDCl_3$) δ 0.13 (s, 18 H, $SiCH_3$), 1.95 (s, 3 H, CH_3C=), 7.24–7.50 (m, 5 H, Ph), 8.24 (br s, 1 H, NH).

5-[Bis(trimethylsilyl)amino]-3-phenyl-4-propyl-1*H*-pyrrole-2-carbonitrile (3e) and 5-[bis(trimethylsilyl)amino]-4-phenyl-3-propyl-1*H*-pyrrole-2-carbonitrile (4e) (entry 15, Table I) were prepared from 1-phenyl-1-pentyne (**2e**) (2.5 mmol, 0.40 mL). Purification by column chromatography gave a mixture of **3e** and **4e** (0.70 g, 76%; **3e**:**4e** = 26:74) as a pale yellow solid. Two recrystallizations (hexane) of the mixture gave pure **4e** as a colorless solid: mp 155–156 °C (hexane); ^1H NMR ($CDCl_3$) δ 0.02 (s, 18 H, $SiCH_3$), 0.80 (t, J = 7.3 Hz, 3 H, CH_3), 1.44 (q, J = 7.3 Hz, 2 H, CH_2), 2.57 (t, J = 7.3 Hz, 2 H, CH_2C=), 7.23–7.39 (m, 5 H, Ph), 8.39 (br s, 1 H, NH); IR (Nujol) 3320 (NH), 2200 (CN), 1610, 1575, 1560 (C=C); MS, m/z 369 (M^+). Anal. Calcd for $C_{20}H_{31}N_3Si_2$: C, 64.98; H, 8.45; N, 11.37. Found: C, 64.97; H, 8.33; N, 11.35. The ^1H NMR spectrum of **3e** were derived from the spectrum of the mixture: ^1H NMR ($CDCl_3$) δ 0.16 (s, 18 H, $SiCH_3$), 0.80 (t, J = 7.3 Hz, 3 H, CH_3), 1.20–1.26 (m, 2 H, CH_2), 2.38–2.42 (m, 2 H, CH_2C=), 7.30–7.50 (m, 5 H, Ph), 8.50 (br s, 1 H, NH).

5-[Bis(trimethylsilyl)amino]-4-(1,1-dimethylethyl)-3-phenyl-1*H*-pyrrole-2-carbonitrile (3f) and 5-[bis(trimethylsilyl)amino]-3-(1,1-dimethylethyl)-4-phenyl-1*H*-pyrrole-2-carbonitrile (4f) (entry 16, Table I) were prepared from 1-phenyl-3,3-dimethyl-1-butyne (**2f**) (2.5 mmol, 0.45 mL). Purification by column chromatography gave a mixture of **3f** and **4f** (0.29 g, 30%; **3f**:**4f** = 93:7) as a pale yellow solid. Recrystallization (hexane) gave pure **3f** as a white solid: mp 230 °C (hexane); ^1H NMR ($CDCl_3$) δ 0.17 (s, 18 H, $SiCH_3$), 1.15 (s, 9 H, CH_3), 7.28–7.44 (m, 5 H, Ph), 7.90 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 1.92, 32.25, 32.73, 95.23, 114.83, 123.57, 127.50, 127.64, 130.97, 135.90, 136.21, 137.45; IR (Nujol) 3400 (NH), 2210 (CN), 1600, 1550 (C=C); MS, m/z 383 (M^+). Anal. Calcd for $C_{21}H_{33}N_3Si_2$: C, 65.73; H, 8.68; N, 10.95. Found: C, 65.90; H, 9.01; N, 10.94.

5-[Bis(trimethylsilyl)amino]-3-[2-(acetyloxy)ethyl]-4-methyl-1*H*-pyrrole-2-carbonitrile (3g) and 5-[bis(trimethylsilyl)amino]-4-[2-(acetyloxy)ethyl]-3-methyl-1*H*-pyrrole-2-carbonitrile (4g) (entry 17, Table I) were prepared from penta-3-yn-1-yl acetate (**2g**) (2.5 mmol, 0.31 mL). Purification by column chromatography gave a mixture of **3g** and **4g** (0.70 g, 79%; **3g**:**4g** = 69:31) as a pale yellow oil. The spectra are of the mixture. **3g** + **4g**: bp 160–170 °C (0.5 Torr); ^1H NMR ($CDCl_3$) δ [0.07 (s, **3g**), 010 (s, **4g**), 18 H, $SiCH_3$], [1.84 (s, **3g**), 2.18 (s, **4g**), 3 H, CH_3C=], [2.05 (s, **3g**), 2.07 (s, **4g**), 3 H, CH_3CO)], [2.61 (t, J = 7.7 Hz, **4g**), 2.85 (t, J = 6.9 Hz, **3g**), 2 H, CH_2C=], [4.11 (t, J = 7.7 Hz, **4g**), 4.18 (t, J = 6.9 Hz, **3g**), 2 H, CH_2O], 8.59 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 1.49, 1.56, 8.91, 11.08, 20.85, 20.95, 23.67, 25.34, 63.40, 63.58, 92.80, 93.20, 112.17, 112.51, 115.15, 115.25, 130.74, 131.31, 137.94, 138.49, 170.99, 171.02; IR (neat) 3280 (NH), 2220 (CN), 1745, 1725 (CO), 1575 (C=C); MS, m/z 351 (M^+); exact mass for $C_{16}H_{29}N_3O_2Si_2$ (M^+), calcd 351.1799, found 351.1802.

5-[Bis(trimethylsilyl)amino]-3-[2-(benzoyloxy)ethyl]-4-methyl-1*H*-pyrrole-2-carbonitrile (3h) and 5-[bis(trimethylsilyl)amino]-4-[2-(benzoyloxy)ethyl]-3-methyl-1*H*-pyrrole-2-carbonitrile (4h) (entry 18, Table I) were prepared from pent-3-yn-1-yl benzoate (**2h**) (2.5 mmol, 0.52 mL). Purification by column chromatography gave a mixture of **3h** and **4h** (0.96 g, 93%) as a pale yellow solid. Two recrystallizations (hexane) of the mixture gave pure **3h** as a colorless solid: mp 122–124 °C (hexane); ^1H NMR ($CDCl_3$) δ 0.12 (s, 18 H, $SiCH_3$), 1.87 (s, 3 H, CH_3C=), 3.30 (t, J = 6.8 Hz, 2 H, CH_2C=), 4.47 (t, J = 6.8 Hz, 2 H, CH_2O), 7.39–7.45 (m, 1 H, Ph), 7.51–7.56 (m, 1 H, Ph), 8.02–8.08 (m, 1 H, Ph), 8.60 (br, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 1.47, 8.97, 25.45, 63.92, 92.78, 112.56, 115.22, 128.19, 129.58, 130.01, 130.75, 132.80, 138.03, 166.43; IR (neat) 3300 (NH), 2200 (CN), 1720 (CO), 1600 (Ph), 1570 (C=C), MS, m/z 413 (M^+). Anal. Calcd for $C_{21}H_{31}N_3O_2Si_2$: C, 60.97; H, 7.55; N, 10.16. Found: C, 61.08; H, 7.59; N, 10.11. The spectra of **4h** were derived from those of mixture: ^1H NMR ($CDCl_3$) δ 0.06 (s, 9 H, $SiCH_3$), 0.07 (s, 9 H, $SiCH_3$), 2.23 (s, 3 H, CH_3C=), 2.72–2.79 (m, 2 H, CH_2C=), 4.32–4.39 (m, 2 H, CH_2O); ^{13}C NMR ($CDCl_3$) δ 1.58, 11.13, 23.80, 63.75, 93.12, 111.98, 115.32, 128.28, 129.52, 130.14, 131.43, 132.88, 138.56, 166.43; IR (Nujol) 1690 (CO).

5-[Bis(trimethylsilyl)amino]-3-phenyl-4-(1-hexenyl)-1*H*-pyrrole-2-carbonitrile (3i) and 5-[bis(trimethylsilyl)-

amino]-4-phenyl-3-(1-hexenyl)-1*H*-pyrrole-2-carbonitrile (4i) (entry 19, Table I) were prepared from 1-phenyloct-3-en-1-yne (**2i**) (2.5 mmol, 0.46 g). Purification by column chromatography gave a mixture of **3i** and **4i** (0.54 g, 53%) as a pale yellow solid. The spectra are of the mixture. **3i + 4i**: ^{1}H NMR ($CDCl_3$) δ [0.06 (s, **3i**), 0.12 (s, **4i**), 18 H, $SiCH_3$], 0.97 (t, J = 6.8 Hz, 3 H, CH_3), 1.3-1.5 (c, 4 H, CH_2), 2.3-2.5 (c, 2 H, CH_2C=), [6.98 (d, J = 16.4 Hz, **4i**), 6.95 (d, J = 16.5 Hz, **3i**), 1 H, CH=], [7.17 (d, J = 16.4 Hz, **4i**), 7.20 (d, J = 16.4 Hz, **3i**), 1 H, CH=], [8.21 (br s, **4i**), 8.54 (br s, **3i**), 1 H, NH]; IR (Nujol) 3240 (NH), 2200 (CN), 1590, 1570 (C=C); MS, m/z 409 (M^+); exact mass for $C_{23}H_{35}N_3Si_2$ (M^+), calcd 409.2370, found 409.2370.

5-[Bis(trimethylsilyl)amino]-3-hexyl-1*H*-pyrrole-2-carbonitrile (3k) and 5-[bis(trimethylsilyl)amino]-4-hexyl-1*H*-pyrrole-2-carbonitrile (4k) (entry 21, Table I) were prepared from 1-octyne (**2k**) (2.5 mmol, 0.37 mL). Purification by column chromatography gave a mixture of **3k** and **4k** (0.39 g, 47%; **3k:4k** = 73:27) as a pale yellow oil. The spectra are of the mixture. **3k + 4k**: ^{1}H NMR ($CDCl_3$) δ [0.07 (s, **4k**), 0.08 (s, **3k**), 18 H, $SiCH_3$], 0.84-0.89 (m, 3 H, CH_3), 1.26-1.64 (m, 8 H, CH_2), [2.18-2.25 (m, **4k**), 2.51 (t, J = 7.5 Hz, **3k**), CH_2], [5.44 (d, J = 3.0 Hz, **3k**), 6.62 (d, J = 2.8 Hz, **4k**), 1 H, CH=], [7.89 (br s, **3k**), 8.10 (br s, **4k**), 1 H, NH]; ^{13}C NMR ($CDCl_3$) δ 13.99, 14.02, 22.53, 22.57, 25.13, 26.76, 28.58, 29.46, 30.06, 30.27, 31.51, 92.91, 93.47, 105.44, 115.38, 115.77, 118.61, 119.92, 137.46, 138.03, 140.49; IR (neat) 3280 (NH), 2200 (CN), 1590, 1570 (C=C); MS, m/z 335 (M^+); exact mass for $C_{17}H_{33}N_3Si_2$ (M^+), calcd 335.2214, found 335.2226.

5-[Bis(trimethylsilyl)amino]-3-[2-(acetyloxy)ethyl]-1*H*-pyrrole-2-carbonitrile (3l) and 5-[bis(trimethylsilyl)amino]-4-[2-(acetyloxy)ethyl]-1*H*-pyrrole-2-carbonitrile (4l) (entry 22, Table I) were prepared from 3-butyn-1-yl acetate (**2l**) (2.5 mmol, 0.29 g). Purification by column chromatography gave a mixture of **3l** and **4l** (0.35 g, 42%; **3l:4l** = 90:10) as a pale yellow oil. The spectra are of the mixture. **3l + 4l**: ^{1}H NMR ($CDCl_3$) δ [(0.08, s, **3l**), 0.10 (s, **4l**), 18 H, $SiCH_3$], [(2.05, s, **3l**), (2.07, s, **4l**), 3 H, CH_3CO], [(2.61, t, J = 7.2 Hz, **4l**), (2.86, t, J = 6.9 Hz, **3l**), 2 H, CH_2C=], [(4.21, t, J = 7.2 Hz, **4l**), (4.23, t, J = 6.9 Hz, **3l**), 2 H, CH_2O], [(5.50, d, J = 2.4 Hz, **3l**), (6.68 (d, J = 2.8 Hz, **4l**), 1 H, CH=], 8.47 (br s, 1 H, NH); IR (neat) 3270 (NH), 2200 (CN), 1745 (CO), 1725 (CO), 1570 (C=C); MS, m/z 337 (M^+); exact mass for $C_{15}H_{27}N_3O_2Si_2$ (M^+), calcd 337.1642, found 337.1631.

5-[Bis(trimethylsilyl)amino]-3-(3-cyanopropyl)-1*H*-pyrrole-2-carbonitrile (3m) and 5-[bis(trimethylsilyl)amino]-4-(3-cyanopropyl)-1*H*-pyrrole-2-carbonitrile (4m) (entry 23, Table I) were prepared from 5-hexynenitrile (**2m**) (2.5 mmol, 0.23 mL). Purification by column chromatography gave a mixture of **3m** and **4m** (0.65 g, 82%; **3m:4m** = 95:5) as a pale yellow oil. The spectra of the major isomer (**3m**) were derived from the spectra of the mixture: ^{1}H NMR ($CDCl_3$) δ 0.09 (s, 18 H, $SiCH_3$), 1.97 (quint, J = 7.1 Hz, 2 H, CH_2), 2.33 (t, J = 7.1 Hz, 2 H, CH_2), 2.69 (t, J = 7.1 Hz, 2 H, CH_2), 5.48 (m, 1 H, CH), 8.55 (br, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 1.27, 16.17, 25.54, 26.03, 93.09, 105.42, 114.67, 119.30, 134.36, 141.02; IR (neat) 3270 (NH), 2245, 2205 (CN), 1565 (C=C); MS, m/z 318 (M^+); exact mass for $C_{15}H_{26}N_4Si_2$ (M^+), calcd 318.1696, found 318.1711.

5-[Bis(trimethylsilyl)amino]-*N*-*tert*-butyl-3,4-dipropyl-1*H*-pyrrole-2-carbonitrile (9). In a 10-mL reaction flask were placed 4-octyne (**2a**) (2.5 mmol, 0.38 mL), Me_3SiCN (12.5 mmol, 1.7 mL), *t*-BuNC (5 mmol, 0.58 mL), and $CpCo(CO)_2$ (0.1 mmol, 13 μL). The mixture was heated to reflux, with stirring, under N_2. After 20 h, the flask was cooled to room temperature and unreacted **1** and *t*-BuNC were evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc) to afford 5-[bis(trimethylsilyl)amino]-*N*-*tert*-butyl-3,4-dipropyl-1*H*-pyrrole-2-carbonitrile (**9**) (0.62 g, 64%) as a pale yellow solid. An analytical sample was obtained by recrystallization (hexane): mp 135-136 °C (hexane); ^{1}H NMR ($CDCl_3$) δ 0.13 (s, 18 H, $SiCH_3$), 0.92 (t, J = 7.4 Hz, 3 H, CH_3), 0.97 (t, J = 7.4 Hz, 3 H, CH_3), 1.39-1.50 (m, 2 H, CH_2), 1.59 (sextet, J = 7.4 Hz, 2 H, CH_2), 1.77 (s, 9 H, *t*-Bu), 2.18-2.23 (m, 2 H, CH_2), 2.52 (t, J = 7.4 Hz, 2 H, CH_2); IR (Nujol) 2190 (CN), 1540 (C=C); MS, m/z 391. Anal. Calcd for $C_{21}H_{41}N_3Si$: C, 64.39; H, 10.55; N, 10.73. Found: C, 64.57; H, 10.31; N, 10.65.

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Supplementary Material Available: ^{1}H and ^{13}C NMR spectra of pure **3a** and **4c** and of mixtures of **3g + 4g**, **3i + 4i**, **3k + 4k**, **3l + 4l**, and **3m + 4m** (15 pages). Ordering information is given on any current masthead page.

Photosensitized [2+2] Cycloreversion Reactions of Arylated Cage Compounds in Nonpolar Solvents. Highly Efficient Adiabatic Exciplex Isomerization

Eietsu Hasegawa,*[,1] Keiji Okada,[2] Hiroshi Ikeda, Yoshiro Yamashita,[3] and Toshio Mukai[4]

Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980, Japan

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Photosensitized [2+2] cycloreversion reactions of arylated cage compounds **1** to dienes **2** using several cyanoaromatics as sensitizers are reported. In acetonitrile, **1a** isomerized to **2a** via an efficient cation-radical chain process. In contrast, the isomerization of **1a** to **2a** proceeded via an exciplex in benzene. Interestingly, the exciplex emission maximum observed in the fluorescence quenching by **1a** was the same as that by **2a**. Such a coincidence was also observed in a series of arylated cage compounds **1a-d** and dienes **2a-d** in various solvents. These observations together with the results obtained from reaction and exciplex emission quenching experiments clearly demonstrated the occurrence of adiabatic exciplex isomerization of **1** to **2**. Efficiencies (A_e) of the adiabatic process obtained by comparing the intensities of the observed exciplex emissions with those of diene exciplex emissions were quite high and became almost quantitative in some cases. A_e values were found to increase as (1) the oxidation potentials ($E_{1/2}^{ox}$) of cage compounds **1a-d** decreased, (2) the reduction potentials ($E_{1/2}^{red}$) of sensitizers increased, and (3) the solvent polarity (E_T) increased.

In the last two decades, an enormous amount of data on the photochemical behaviors of electron donor and electron acceptor pairs has been accumulated.[5] Irradiations of electron donor-acceptor systems produce sol-

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