

Synthesis of Ethynyl-Substituted Precursors to Carbon-Nitrogen-Sulfur Extended Structures: Reactions of $C_3N_3F_3$ and C_2N_2S with Alkali-Metal (Trimethylsilyl)acetylides

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The reaction of 2,4,6-trifluoro-1,3,5-triazine with lithium 2-(trimethylsilyl)acetylide affords 2,4,6-tris(trimethylsilyl)ethynyl-1,3,5-triazine, a potential precursor to highly cross-linked carbon-nitrogen materials. The reaction of lithium and sodium 2-(trimethylsilyl)acetylide with 3,4-dichloro-1,2,5-thiadiazole results in ring opening and produces bis(2-(trimethylsilyl)ethynyl) sulfur and cyanogen as the major products. The anticipated 3,4-bis(2-(trimethylsilyl)ethynyl)-1,2,5-thiadiazole was obtained as only a minor product.

Introduction

Our research is directed toward the preparation of low-dimensional, hydrogen-free materials that are electrically conductive, stable in ambient atmosphere, and refractory. We intend to incorporate heteroatoms such as nitrogen and sulfur into a carbon skeletal framework. We anticipate that the presence of the heteroatoms will alter the conductivity and might introduce electrochemical catalytic activity.¹ Examples of such materials involve C_3N_3 or C_2N_2S units linked by ethynyl (acetylenic and diacetylenic) groups in two-dimensional, sheetlike anisotropic structures. We are interested in anisotropic and high aspect ratio (fiberlike) conductive solids because they have applications as conductive fillers in polymeric and ceramic matrix composites.

We envision that the target C-N and C-N-S materials can be produced from ethynyl-substituted heteroaromatics such as 1,3,5-triazine and 1,2,5-thiadiazole. Efforts to prepare trimethylsilyl-substituted ethynyltriazines and ethynylthiadiazoles led us to the synthesis of 2,4,6-tris[2-(trimethyl)silylethynyl]-1,3,5-triazine (1) and the characterization of reactions between 3,4-dichloro-1,2,5-thiadiazole (2) and acetylenic salts of lithium and sodium.

The most widely used synthetic route to poly(2-(trimethylsilyl)ethynyl)-substituted aromatics involves the reaction between an aromatic bromide or iodide and (trimethylsilyl)acetylene in the presence of palladium or copper catalysts. This method has been used extensively by Vollhardt and co-workers to replace multiple halogens on the same molecule² and by Neenan and Whitesides to prepare acetylenic precursors to carbon-based materials.³ The structures that we sought to prepare required triethynyl-substituted triazines and 3,4-diethynyl-1,2,5-thiadiazole as precursors.

Whereas the trifluoro- and trichloro-substituted triazines and the dichloro-substituted thiadiazole are commercially available, the corresponding bromo- and iodo-substituted derivatives are not. Therefore we could not readily employ Pd-catalyzed substitution for the production of our desired precursors. Since the electron-withdrawing nitrogen and sulfur atoms enhance the reactivity of the heteroaromatics toward nucleophilic substitution, we chose to explore the introduction of the ethynyl groups using lithium or sodium 2-(trimethylsilyl)acetylide.

Results and Discussion

We prepared 1 by the reaction of 2,4,6-trifluoro-1,3,5-triazine 3 with lithium 2-(trimethylsilyl)acetylide 4 in hexane at -78°C . Compound 1 is a colorless air-stable solid, extremely soluble in organic solvents and is fairly volatile above 100°C in vacuum. The ^{13}C NMR spectrum in deuteriochloroform shows four resonances corresponding to each of the alkynyl carbons, the ring carbons and the methyl carbons of the trimethylsilyl groups. The FT-IR spectrum shows the characteristic C-H stretches of the trimethylsilyl group at $2962\text{--}2900\text{ cm}^{-1}$, together with a weak acetylenic stretch at 2170 cm^{-1} . The strong absorptions of the aromatic ring appear at $1500\text{--}1400\text{ cm}^{-1}$. Mass spectroscopic analysis showed the molecular ion as the highest peak at $m/e = 369$, and a fragmentation pattern which is consistent with the trisubstituted ring structure (vide infra).

A single-crystal X-ray structure⁴ determination of 1 was performed using crystals obtained by sublimation. The structure consists of individual molecules arranged in sheets parallel to the a - b plane. As shown in Figure 1, each molecule is planar with the exception of its methyl group carbons. The maximum deviation from the least squares plane through the $(\text{CN})_3$ central framework and

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(1) Callstrom, R. C.; Neenan, T. X.; McCreery, R. L.; Alsmeyer, D. C. *J. Am. Chem. Soc.* 1990, 112, 4954.

(2) Diercks, R.; Armstrong, J. C.; Boese, R.; Vollhardt, K. P. C. *Angew. Chem.* 1986, 98, 270; *Angew. Chem., Int. Ed. Engl.* 1986, 25, 268.

(3) Neenan, T. X.; Whitesides, G. M. *J. Org. Chem.* 1988, 53, 2489.

(4) Kouvetakis, J.; Dupon, R.; Merlino, S. *Acta Crystallogr., Sec. C*, submitted.

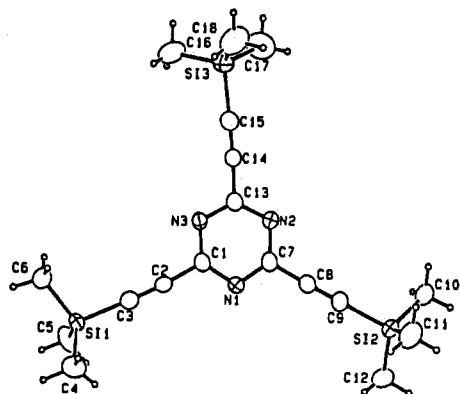


Figure 1. Structure of $(\text{CN})_3(\text{C}\equiv\text{CSiMe}_3)_3$.

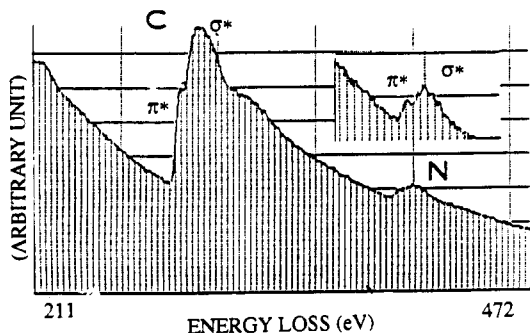
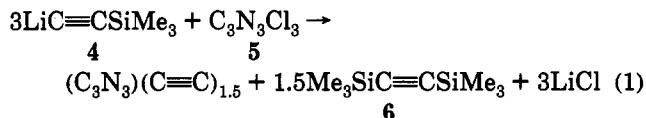


Figure 2. Electron energy loss spectrum of a C-N polymer. The core-edge excitations of both the carbon and the nitrogen show π -to- π^* electronic transitions.

the acetylenic branches including the silicon atoms is 0.1 Å. The molecule is, however, slightly distorted. The N1-C7-N2 angle is 125.5° , while the opposite C1-N3-C13 angle is 114.5° . This distortion from 120° presumably originates from packing effects in the solid state. The C≡C and the C-N bond lengths appear to be within normal range.

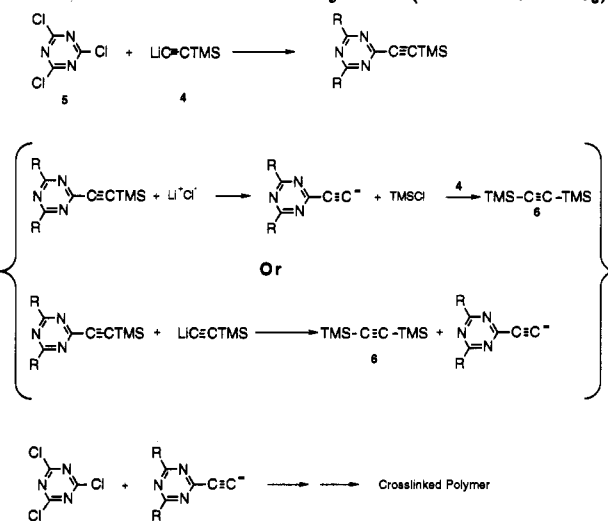
Our efforts to prepare 1 by reaction of 2,4,6-trichloro-1,3,5-triazine (5) with 4 resulted in black polymers which were characterized by elemental analysis, gel permeation chromatography (GPC), infrared spectroscopy and electron energy loss spectroscopy. GPC indicated a broad molecular weight distribution with some fragments having a M_w greater than 100 000. The infrared spectra showed acetylenic vibrations at 2150 cm^{-1} and ring type stretching modes at $1600\text{--}1450\text{ cm}^{-1}$. The electron energy loss spectra of both carbon and nitrogen showed π -to- π^* excitations indicating that both elements are sp or sp^2 hybridized (Figure 2). A mechanism of formation of these polymers is suggested in Scheme 1.

The highly exothermic reaction outlined in Scheme 1 first produced (trimethylsilyl)ethynyl-substituted triazine intermediates which subsequently undergo loss of the protecting trimethylsilyl groups to yield conjugated polymers. We anticipated that complete elimination of the TMS groups would result in a highly cross-linked carbon nitrogen network of composition $(\text{C}_3\text{N}_3)(\text{C}\equiv\text{C})_{1.5}$ or " C_2N " (eq 1). Elemental analysis and a lower than expected yield



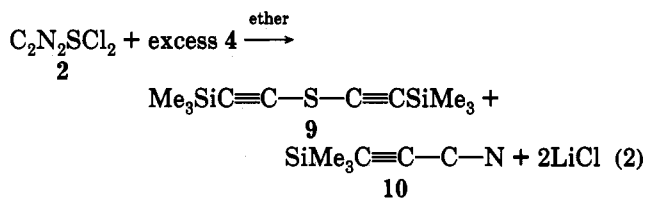
of 6, however, indicate that the TMS groups are not completely eliminated from the polymer.

Scheme 1. Reaction of 2,4,6-Trichlorotriazine with Excess Lithium 2-(Trimethylsilyl)acetylide to Produce Cross-Linked Polymers ($\text{R} = \text{C}\equiv\text{CSiMe}_3$)



We anticipate that oxidative coupling polymerization of the tris-alkyne $(\text{C}_3\text{N}_3)(\text{C}\equiv\text{CH})_3$ (7) would lead to a C-N open network of composition $(\text{C}_3\text{N}_3)(\text{C}\equiv\text{C})_3$ or " C_3N ". On the basis of literature precedents,^{5,6} carbonate-catalyzed protodesilylation of 1 in methanol was envisaged to provide 7. However, in a preliminary experiment, the major product (59%) from such treatment of 1 was the new tris-acetal 8, presumably (Scheme 2) a result of the base-catalyzed addition of methanol to the electrophilic alkyne units of 7.⁷ Experiments using fluoride-mediated desilylation are in progress.

The reaction of 3,4-dichloro-1,2,5-thiadiazole 2 with 4 did not yield the expected ethynyl-substituted thiadiazoles. Instead, bis(2-(trimethylsilyl)ethynyl) sulfur⁸ (9) and 3-(trimethylsilyl)propynynitrile (10) were obtained in substantial yields (eq 2).



The reaction products can be explained by nucleophilic attack of 4 on the sulfur atom of the thiadiazole heterocycle (Scheme 3). This substitution, which presumably involves the d orbitals of the sulfur atom of the thiadiazole ring, is followed by release of cyanogen gas which reacts with lithium 2-(trimethylsilyl)acetylide to give acetylenic cyanide 10. A wide variation in the reaction conditions (lower temperatures and use of more benign solvents, e.g., hexane vs tetrahydrofuran) did not change the course of the reaction. This ring-opening reaction appears to be a thermodynamically favored process for both enthalpic and entropic reasons.

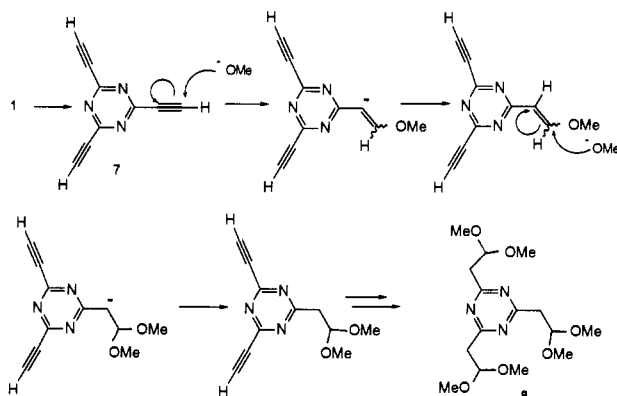
(5) Austin, W. B.; Bilow, N.; Kelleghan, W. J.; Lau, K. S. Y. *J. Org. Chem.* 1981, 46, 2280.

(6) Tilley, J. Y.; Zawoiski, S. *J. Org. Chem.* 1988, 53, 386.

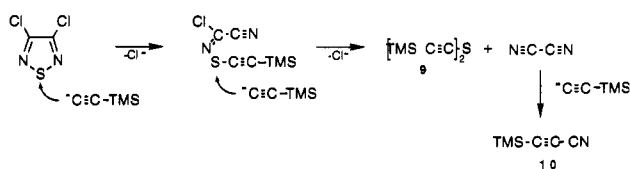
(7) Dickstein, J. I.; Miller, S. I. In *The Chemistry of the Carbon-Carbon Triple Bond*; Patai, S., Ed.; Wiley: Chichester, 1978; Part 2, p. 813.

(8) Brandsma, L. *Preparative Acetylenic Chemistry*, 2nd ed.; Elsevier: Amsterdam, 1989. Pages 155 and 229 for $\text{R}\text{C}\equiv\text{C}-\text{CN}$ ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_4\text{H}_9, \text{C}_6\text{H}_{13}$, and 1-cyclohexynyl) and page 139 for $\text{S}(\text{C}\equiv\text{CSiMe}_3)_2$.

Scheme 2. Possible Mechanism for the Base-Catalyzed Addition of Methanol to the Acetylenic Units of 7



Scheme 3. Reaction of 3,4-Dichlorothiadiazole with Excess Lithium 2-(Trimethylsilyl)acetylide



A low-melting highly polar solid, however, appeared as minor byproduct when the reaction was carried out at -91°C in hexane. Although it was never produced in sufficient quantities to characterize properly, the minor component exhibited a mass spectrum and a ^{13}C NMR spectrum, consistent with a 2-(trimethylsilyl)ethynyl-substituted nitrile sulfide ($\text{SiMe}_3\text{-C}\equiv\text{C-C}\equiv\text{N}^+\text{-S}^-$). It is worth noting that the corresponding nitrile oxides, the oxygen analogs, have been well described.⁹

While the reaction of 2 with $\text{LiC}\equiv\text{CSiMe}_3$ (4) did not yield the expected product, it may offer a convenient route to precursors to novel ceramics. For example, adducts of 3-(trimethylsilyl)propynyl nitrile (10) with boron halides, upon heating, may result in boron-carbon-nitride-semiconductor materials. Alternately, desilylation of 9 may result in carbon-sulfur linear polymers (similar to carbyne) that may exhibit unique properties.

Reactions between 2 and $\text{NaC}\equiv\text{CSiMe}_3$ produced the expected 3,4-bis(2-(trimethylsilyl)ethynyl)-1,2,5-thiadiazole (11) in addition to 9 and 10 only when it was performed at low temperatures in inert solvents. Low yields of 11 were detected by GC/MS analysis of reactions conducted at -78°C in hexane.

Conclusions

We have synthesized 1 by the reaction of trifluorotriazine 2 with $\text{LiC}\equiv\text{CSiMe}_3$ and determined its crystal structure. We have also found that reactions of 3,4-dichloro-1,2,5-thiadiazole with trimethylsilyl ethynyl salts of lithium and sodium yield $\text{S}(\text{C}\equiv\text{CSiMe}_3)_2$, $\text{SiMe}_3\text{C}\equiv\text{C-CN}$, and $(\text{C}_2\text{N}_2\text{S})(\text{C}\equiv\text{CSiMe}_3)_2$ which are potentially useful for synthesis of covalent ceramic or conductive materials.

Experimental Section

General Procedure. Operations were carried out either in an inert atmosphere dry box (Vacuum Atmospheres Model HE

493 MO 20-40) under a nitrogen bypass or by using standard Schlenk and high-vacuum-line techniques. Melting points were determined using a Thomas Hoover melting point apparatus. Infrared spectra of the solids and liquids were obtained as KBr pellets, as thin films on NaCl plates, or as mulls (fluorolube oil and Nujol) on a DIGILAB FPS 60A FTIR spectrometer. Infrared spectra of gases were obtained using a 10-cm path length glass cell with KBr windows. NMR spectra for ^1H were recorded at 300 MHz and for ^{13}C were recorded at 75 MHz on a Varian XL-300 NMR spectrometer. Mass spectra were obtained by GC/MS on a HP 5995 spectrometer. Elemental analyses were performed at Galbraith Laboratories at Knoxville, TN or at Atlantic Microlabs, Norcross, GA. (Trimethylsilyl)acetylene, 3,4-dichloro-1,2,5-thiadiazole (2), sodium amide, and 1,3,5-trichloro-2,4,6-triazine, purchased from Aldrich Chemical Co., and 1,3,5-trifluoro-2,4,6-triazine, purchased from Pfaltz and Bauer Co., were used without further purification. Diethyl ether and tetrahydrofuran were distilled from purple sodium benzophenone ketyl solutions.

Synthesis of 2,4,6-Tris(trimethylsilyl)ethynyl-1,3,5-triazine. Lithium 2-(trimethylsilyl)acetylide (4) was prepared by slowly treating an ether solution of trimethylsilyl acetylene with 1.6 M *n*-butyllithium in hexane at -78°C and was isolated as a colorless solid by removal of the solvent in vacuo. To a suspension of 4 (7.3 g, 70 mmol) in dry, degassed hexane was added a solution of 2,4,6-trifluoro-1,3,5-triazine (3, 2.5 g, 18.5 mmol) in hexane at -78°C . The mixture was stirred under nitrogen for 24 h at -78°C and at ambient temperature for another 24 h. The reaction mixture was then poured into 100 mL of water. The resulting organic layer and three hexane extracts were dried with MgSO_4 . The drying agent was separated by filtration and the solvent was removed in vacuo. The resulting light brown residue (70% yield) was purified by sublimation to yield a colorless crystalline solid (55% yield). The material melts without apparent decomposition at 160°C .

IR (KBr): 2962 w, 2900 sh, 1625 m, 1490 sh, 1490 vst, 1415 sh, 1320 st, 1245 st, 995 st, 845 vst, 760 w, 702 w, 660 w, 603 sh, 495 sh, 430 sh. MS: M^+ 369, ($\text{M} - \text{CH}_3^+$) 354; $[(\text{SiMe}_3\text{C}\equiv\text{C-CN})_2 - \text{CH}_3^+]$, 231; $[(\text{SiMe}_3\text{C}\equiv\text{C-CN}) - \text{CH}_3^+]$ 108; $(\text{SiMe}_3\text{C}\equiv\text{CSiMe}_3)^+$ 170; SiMe_3^+ 73. ^{13}C NMR (CDCl_3): δ 0.91 (CH_3), 99.89 and 102.10 (acetylenic carbons), 159.56 (ring carbons). Elemental analysis found (%): C 57.66; H, 8.01; N, 10.20; Si, 20.29. Calculated (%): C, 58.50; H, 7.30; N, 11.30; Si, 22.8.

Reactions of 3,4-Dichloro-1,2,5-thiadiazole with Lithium 2-(Trimethylsilyl)acetylide. Lithium (trimethylsilyl)acetylide (4) was prepared by slowly treating an ether solution of (trimethylsilyl)acetylene (6.25 g, 64.5 mmol) with 40 mL of 1.6 M *n*-butyllithium in hexane at -78°C . The solution was allowed to warm to 0°C , stirred for 2 h, and then treated with a hexane solution of 3,4-dichloro-1,2,5-thiadiazole (5.0 g, 32.2 mmol). After stirring for an additional 5 h, the solution was allowed to warm to room temperature and the various components were separated by trap-to-trap distillation through a series of three traps maintained at 0, -45 , and -196°C . The colorless liquids collected in the first trap and second trap were identified by GC/MS as 9 and 10, respectively. The third trap contained hexane and ether. The dark brown liquid that remained in the reaction vessel was primarily 9 and was separated from a black residue by low-pressure distillation. The identity of 9 (60% overall yield) and 10 was verified by ^{13}C NMR in deuterated chloroform, GC/MS, and by infrared spectroscopy. Reactions at lower temperatures (-45 , -78°C) in hexane produced nearly identical results. 9: ^{13}C NMR (CDCl_3) δ 103.77, 85.72, 0.48; IR 2108 cm^{-1} acetylenic absorption; GC/MS M^+ = 226. 10: ^{13}C NMR (CDCl_3) δ 114.71, 94.96, 75.88, -1.29 ; IR 2250 , 2130 cm^{-1} ; GC/MS M^+ = 123.

Reactions of 3,4-Dichloro-1,2,5-thiadiazole with Sodium 2-(Trimethylsilyl)acetylide. Sodium (trimethylsilyl)acetylide was prepared by slowly adding (trimethylsilyl)acetylene to a slurry of sodium amide in ether at -45°C . Ammonia was liberated, and insoluble sodium (trimethylsilyl)acetylide precipitated from solution. When gas evolution ceased, the mixture was stirred for 10 h at room temperature, and the solvent was removed in vacuo. The resulting colorless solid was characterized by infrared spectroscopy and by hydrolysis experiments. Hydrolysis of a sample of the crude sodium ((trimethylsilyl)acetylide) produced (trimethylsilyl)acetylene in 90% yield. Reactions of 3,4-dichloro-

(9) Just, G.; Dahl, K. *Can. J. Chem.* 1970, 48, 966.

1,2,5-thiadiazole with sodium (trimethylsilyl)acetylide at 0 °C in ether, or hexane, yielded 9 and 10 as major products. Reaction at -78 °C in hexane also produced 9 and 10 and in addition afforded a small quantity of 3,4-(trimethylsilyl)ethynyl-1,2,5-thiadiazole (11). Compound 11 was not isolated but was characterized by GC/MS (highest peak observed at $m/e = 278$).

Protodesilylation of 1 To Produce 2,4,6-Tris(2,2-dimethoxyethyl)-1,3,5-triazine. Nitrogen was bubbled through a solution of 1 (289 mg, 0.78 mmol) in MeOH (20 mL) for 5 min before anhydrous K_2CO_3 (85.8 mg, 0.621 mol) was added. Within a few seconds, the clear colorless solution became cloudy, and within minutes a deep color appeared. After 1.5 h, TLC (SiO_2 , EtOAc/ CH_2Cl_2 1:1) indicated the consumption of 1 and the presence of one major product. The deep purple mixture was diluted with EtOAc (20 mL) and was poured into 10% aqueous NaH_2PO_4 (50 mL). The aqueous phase was extracted further with EtOAc (2 × 20 mL). The first two EtOAc phases, which contained most

of the product by TLC, were combined and washed with 10% aqueous NaH_2PO_4 (50 mL), brine, dried ($MgSO_4$), and filtered. The third EtOAc extract was used to back-extract the aqueous phase and rinse the drying agent. Combined clear dark brown filtrates were concentrated by rotary evaporation just to dryness. The residue was passed through SiO_2 (1 × 10 cm), eluting with EtOAc/ CH_2Cl_2 (1:4). Amber product containing fractions were concentrated by rotary evaporation to dryness. The residue was taken up in pentane, and the small amount of brown flocculent precipitate which resulted was removed by filtration. Concentration of the filtrate and storage of the residue under 0.1 mmHg for 1 h left 8 as a pale brown oil (159.9 mg, 59%). IR (neat, NaCl plates) 2990 m, 2941 s, 2837, 1544 s, 1391 m, 1228, 1193 s, 1124 s, 1070 s, 1025, 976 m. 1H NMR ($CDCl_3$) δ 3.14 (d, $J = 6.1$ Hz, 6H), 3.33 (s, 18H), 5.05 ppm (t, $J = 6.1$ Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 42.39, 52.95, 102.70, 175.33 ppm. Anal. Calcd for $C_{15}H_{27}N_3O_6$: C, 52.16; H, 7.88; N, 12.17. Found: C, 52.53; H, 7.67; N, 12.11.