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Disilane-Catalyzed and Thermally Induced Oligomerizations of Alkynes: A Comparison

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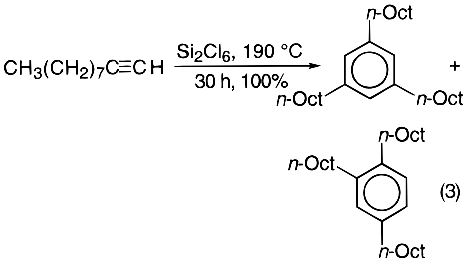
The alkynes RC≡CR (R = H, Et, Ph), RC≡CH (R = $Me(CH_2)_5$, $Me(CH_2)_7$, Ph, Me_3Si, EtO_2C), and RC≡CR′ (R = Ph, R′ = C_6F_5; R = Me, R′ = Ph) trimerize to corresponding benzene derivatives in 30−100% yields in the presence of Si_2Cl_6 as a procatalyst at 170−200 °C over 20−48 h. These reactions represent only the second example of nonmetal-catalyzed alkyne trimerizations. The unsymmetrical alkynes $Me_3SiC{\equiv}CH$, $EtO_2CC{\equiv}CH$, and $PhC{\equiv}CC_6F_5$ gave symmetrical 1,3,5-substituted benzenes, while the others led to isomeric mixtures. A 1:2 molar mixture of PhC≡CH and PhC≡CPh provided an isomeric mixture (45% yield) consisting mainly of 1,2,4,5-tetraphenylbenzene. While $Si_2(OMe)_6$ also catalyzed alkyne trimerizations (though not as efficiently as Si_2Cl_6), Si_2Me_6 did not, suggesting an electronegativity influence in the formation of the $Cl_3Si^\bullet$ radicals shown to be involved in these reactions. Somewhat unexpectedly, however, neither Si_2F_6 nor *sym*-$Si_2Me_2Cl_4$ catalyzed alkyne trimerizations. Experimental support for the radical pathway proposed for the alkyne trimerization observed herein is presented. In the absence of disilane procatalyst, PhC≡CH gave an isomeric mixture of dimers, *p*-$MeC_6H_4C{\equiv}CH$ afforded predominantly a single dimer, and 1-ethynyl-1-cyclohexene provided exclusively a single dimer, whereas RC≡CH (R = alkyl) and PhC≡CMe did not react upon heating under the same conditions.

Introduction

In a recent communication[1] we reported reactions 1−5 as illustrations of only the second example of alkyne cyclotrimerizations catalyzed by a nonmetallic species and disclosed for the first time examples of such transformations demonstrated to proceed by a free radical mechanism.

$$PhC{\equiv}CPh \xrightarrow[2\ d,\ 70\%]{Si_2Cl_6,\ 170\text{-}180\ °C} C_6Ph_6 \qquad (1)$$

$$EtC{\equiv}CEt \xrightarrow[2\ d,\ 45\%]{Si_2Cl_6,\ 200\ °C} C_6Et_6 \qquad (2)$$



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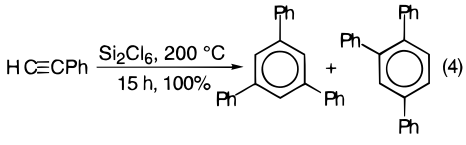
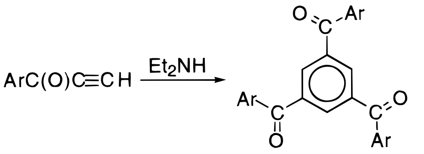


(4)

$$HC{\equiv}CH \xrightarrow[2\ d,\ 90\%]{Si_2Cl_6,\ 210\ °C} C_6H_6 \qquad (5)$$

To our knowledge the only other nonmetal-catalyzed reaction of a similar nature is that shown in reaction 6.[2−4]



(6)

Evidence has been put forth supporting a pathway for reaction 6 involving initial Michael addition of Et_2NH to the CH carbon of the alkyne to form an eneamine-one, followed by addition of two aryl ethynyl ketone molecules with subsequent regeneration of the catalyst upon trimer formation.[3] By contrast, we adduced evidence that reactions 1−5 transpire via an addition−elimination of $SiCl_3$ radicals as depicted in Scheme 1 for the trimerization of PhC≡CPh. Here Si_2Cl_6 acts as a procatalyst that generates catalytic $SiCl_3$ in an equilibrium dissociation at the temperatures employed for reactions 1−5. At 450 °C, reactions 1 and 5 had earlier been reported to give low yields of **1** and **2**, respectively, presumably via silylene ($SiCl_2$) intermediates generated in the thermal disproportionation of Si_2Cl_6.[5] On the other hand, Bertholet

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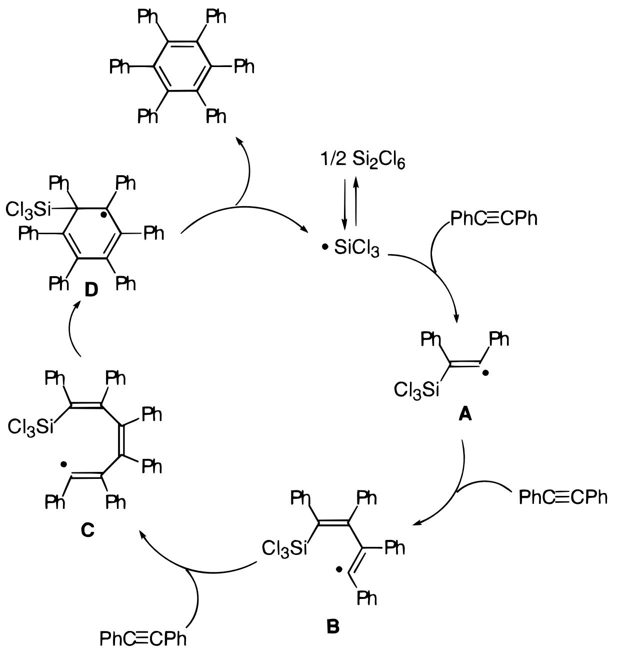
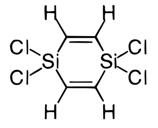
Scheme 1





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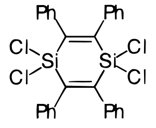

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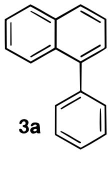

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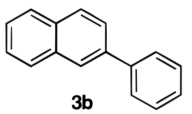

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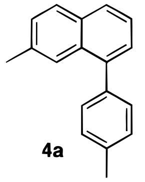

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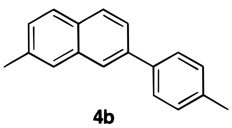

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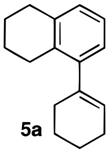

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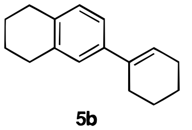

5b

observed in 1866 that acetylene thermally cyclotrimerizes to benzene in low yield at 400 °C.[6]

In the present report we extend the scope of our study of Si_2Cl_6 as an alkyne trimerization procatalyst to the alkynes $Me_3SiC{\equiv}CH$, $EtO_2CC{\equiv}CH$, $C_6F_5C{\equiv}CPh$, $PhC{\equiv}CMe$, $CH_3(CH_2)_5C{\equiv}CH$, and 1-ethynyl-1-cyclohexene. We also describe our results using $Si_2(OMe)_6$ and Si_2F_6 as procatalysts. A comparison is then made on the course of the thermal reaction of several conjugated terminal alkynes (wherein isomeric dimers such as **3**−**5** are formed) with trimerizations of these alkynes catalyzed by $SiCl_3$ radicals.

Experimental Section

General Methods. All reactions were carried out under anhydrous conditions using conventional vacuum lines and Schlenk ware. Diethyl ether, pentane, and tetrahydrofuran (THF) were distilled from sodium/benzophenone, and $CHCl_3$ was distilled from CaH_2 under nitrogen. Hexachlorodisilane, hexamethyldisilane, 1,2-dimethyltetrachlorodisilane, diphenylacetylene, 1-decyne, 1-octyne, phenylacetylene, 3-hexyne, 3-butyn-2-one, ethyl propiolate, ethyl-2-butynoate, iodopentafluorobenzene, benzene, trimethylsilylacetylene, 4-ethynyltoluene, pyridine-2-bromide, pyridine-3-bromide, and 1-ethynyl-1-cyclohexene were purchased from Aldrich Chemical Co., and hexamethoxydisilane was purchased from Gelest Inc. All were used as received without further purification. Si_2F_6 was synthesized from SbF_3 and Si_2Cl_6 according to a literature method.[7] Phenyl pentafluorophenylacetylene was synthesized from iodopentafluorobenzene and copper phenylacetylenide[8] and was purified by sublimation. ^1H and ^{13}C NMR spectra were recorded on a Varian VXR-300 instrument and mass spectra were obtained on a Finnigan 4000 (70 eV EI or CI). GC−MS experiments were carried out using a Finnigan Magnum ion trap detector (Finnigan MAT, San Jose, CA) configured in the electron impact ionization mode with automatic gain control. A DB5-MS separation column (30 m, 0.25 mm i.d., 0.25 μm film thickness) was used, and the injector and transfer line temperature was fixed at 250 °C. Elemental analyses were performed on a Perkin-Elmer series II CHNS/O analyzer by the Instrumental Services unit in our department. Melting points were measured with a Thomas-Hoover capillary apparatus and were uncorrected.

Catalytic Synthesis of Benzene. After Si_2Cl_6 (0.27 g, 1.0 mmol) was placed in a steel pressure reactor, it was cooled by liquid N_2, and gaseous acetylene (0.26 g, 10 mmol) was introduced. Adventitious acetone was first eliminated from the acetylene with a dry ice trap. The reactor was closed and heated to 210 °C in an oil bath for 48 h. The reactor was then cooled to room temperature, vented, and opened, yielding 0.50 g of a liquid whose ^1H and ^{13}C NMR spectra indicated that C_6H_6 was the only hydrocarbon present (ca. 90% conversion). After hydrolyzing the Si_2Cl_6 with H_2O at 4 °C, 0.20 g (2.6 mmol, 77% yield) of C_6H_6 was isolated upon separation from the aqueous phase. ^1H NMR ($CDCl_3$, δ 7.12) and ^{13}C NMR ($CDCl_3$, δ 128.0) data compared favorably with literature values.[12]

Catalytic Synthesis of Hexaphenylbenzene. The synthesis and characterization of this compound was described in our preliminary communication.[1]

Catalytic Synthesis of Hexaethylbenzene. In a thick-walled quartz tube, 3-hexyne (0.50 g, 6.1 mmol) was introduced, followed by 0.80 g (3.0 mmol) of Si_2Cl_6. The tube was argon flushed for a few minutes, and then it was cooled in liquid nitrogen and flame sealed under vacuum. The tube was placed inside a steel pressure reactor, which was heated to 200 °C with an oil bath. The pressure was approximately 2 atm during the 48 h reaction. The reactor was then allowed to cool to room temperature, and the tube was opened under nitrogen. The reaction product was analyzed as a mixture of hexaethylbenzene and starting materials. The conversion of 3-hexyne to product in this reaction was determined to be 51%

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by ^1H NMR spectroscopic integration. After dectantation of the Si_2Cl_6 and starting materials from the colorless crystals that formed, hexaethylbenzene was obtained in 45% yield after washing with $CHCl_3$ and drying under vacuum. ^1H NMR ($CDCl_3$): δ 2.65 (q, CH_2, 12H), 1.20 (t, CH_3, 18H). ^{13}C NMR ($CDCl_3$): δ 137.8, 22.1, 15.7. HRMS(EI): calcd for $C_{18}H_{30}$, 246.23475; found, 246.23480. These data compare favorably with literature values.[9]

Catalytic Synthesis of Isomeric Trihexylbenzenes. 1-Octyne (2.20 g, 20.0 mmol) was added to a thick-walled quartz tube, followed by 1.40 g (5.0 mmol) of Si_2Cl_6. The tube was flushed with nitrogen, and then it was cooled in liquid nitrogen and flame sealed under vacuum. The tube was heated at 180 °C in an oil bath for 30 h. After cooling the tube to room temperature, a brown oily material was obtained, which was analyzed by GC−MS as a mixture of two isomeric trimers in a ca. 1:1 ratio. The conversion of starting material was 100%. Filtration through silica gel gave 2.00 g of a mixture of the two isomers in 90% yield. No attempt was made to separate the two isomers. Bp: ∼140 °C/0.03 mm. ^1H NMR of mixture ($CDCl_3$): δ 6.80−7.05 (m, 3H), 0.87−2.56 (m, 39H). ^{13}C NMR of the mixture ($CDCl_3$): δ 142.7, 140.3, 140.2, 137.7, 129.2, 128.9, 125.8, 125.7, 36.0, 31.8, 31.6, 31.3, 28.5, 22.6, 22.5, 18.4, 14.1, 14.0. HRMS (EI): calcd for $C_{24}H_{42}$, 330.328651; found, 330.3290040. The ^1H NMR spectrum of this isomeric mixture compared favorably with that found in the literature.[9] No ^{13}C NMR data were found in the literature for these isomeric compounds.

Catalytic Synthesis of Isomeric Trioctylbenzenes. 1-Decyne (1.00 g, 7.30 mmol) was added to a 25 mL Schlenk flask which had been flushed with argon. Si_2Cl_6 (0.20 g, 0.74 mmol) was introduced to the flask, and upon mixing, the colorless starting materials became yellow immediately. The flask was cooled in liquid nitrogen and evacuated. The flask was then heated at 190 °C in an oil bath for 30 h. After cooling to ambient temperature, a brown oily material was obtained, which was found by ^1H NMR spectroscopy to be a mixture of 1,3,5-trioctylbenzene and 1,2,4-trioctylbenzene. Conversion of 1-decyne to these products was found to be quantitative, and the two products were found to form in a ca. 1:1 ratio according to GC−MS. Si_2Cl_6 was separated by washing the reaction mixture with an aqueous solution saturated with NaOH. No attempt was made to separate the two isomers. Bp: 239−240 °C (2 Torr). ^1H NMR ($CDCl_3$): δ 7.06(s), 7.05(s), 6.95(s), 6.92(s), 6.81(s), 2.57 (t, CH_2, 6H), 1.57 (br, CH_2, 6H), 1.29 (br, CH_2, 30H), 0.89 (t, CH_3, 9H). ^{13}C NMR ($CDCl_3$): δ 142.7, 140.3, 140.2, 137.3, 129.2, 129.0, 125.8, 125.7, 36.0, 35.6, 32.8, 32.4, 31.9, 31.6, 31.5, 29.9, 29.5, 29.3, 18.4. HRMS(EI): calcd for $C_{30}H_{54}$, 414.52255; found, 515.42247. The ^1H NMR and MS spectra compared favorably with literature values.[9] To our knowledge, no ^{13}C NMR data were reported for the two isomeric compounds.

Catalytic Synthesis of Isomeric Triphenylbenzenes. To a 25 mL flask equipped with a magnetic stirrer and a reflux condenser was introduced phenylacetylene (0.75 g, 7.2 mmol). The flask was flushed with argon, and then 0.32 g (1.2 mmol) of hexachlorodisilane was added. After stirring the reaction mixture for a few minutes, the flask was stoppered with a septum. The flask was heated to 200 °C in an oil bath and held at that temperature for 15 h. A liquid (probably hexachlorodisilane, bp 144−146 °C) was seen to reflux during reaction. After cooling the reaction mixture to room temperature, a thick brown material was obtained, which was dissolved in 10 mL of benzene. A yellow precipitate (0.70 g, 93% yield) formed upon adding 10 mL of pentane to the benzene solution. The precipitate was analyzed by GC−MS as a ca. 1:1 mixture of two isomers. The conversion of the starting materials was quantitative since no phenylacetylene starting material was detected by ^1H and ^{13}C NMR spectroscopies. No attempt was made to separate the isomers. ^1H NMR ($CDCl_3$): δ 7.78 (s, central C_6H_3), 7.63−7.71 (m, 13H), 7.35−7.55 (m, 21H), 7.14−7.21 (m, 15H). ^{13}C NMR ($CDCl_3$): δ 142.3, 141.5, 141.1, 141.1, 141.0, 140.6, 140.3, 139.5, 131.1, 129.9, 129.9, 129.8, 129.4, 128.8, 128.8, 127.9, 127.9, 127.5, 127.4, 127.3, 127.1, 127.0, 126.6, 126.5, 126.1, 125.2. HRMS(EI): calcd for $C_{24}H_{18}$, 306.14085; found, 306.14060. The NMR data compare favorably with literature values for 1,3,5-triphenylbenzene and 1,2,4-triphenylbenzene.[10,13]

Catalytic Synthesis of 1,3,5-Tris(trimethylsilyl)benzene. In a thick-walled quartz tube, trimethylsilylacetylene (0.30 g, 3.0 mmol) was introduced, followed by hexachlorodisilane (0.31 g, 1.6 mmol). The tube was cooled in liquid nitrogen and flame sealed under vacuum. The tube was placed inside a pressure reactor, which was gradually heated to 190 °C in an oil bath. After 20 h at that temperature, the reactor was allowed to cool to room temperature. The tube was opened in a hood, and the brown liquid was analyzed by ^1H, ^{13}C NMR, and MS spectroscopies as a mixture of the title product and starting materials. The conversion of starting materials was determined by ^1H NMR spectroscopy to be ca. 50%. A small quantity of colorless crystals formed in ca. 30% yield after allowing the reaction mixture to remain in a refrigerator for 1 day. ^1H NMR ($CDCl_3$): δ 7.67 (s, phenyl, 3H), 0.27 (s, CH_3, 27H). ^{13}C NMR ($CDCl_3$): δ 138.8, 138.2, −1.12. MS (EI): The ^1H and ^{13}C NMR data compare favorably with literature values.[11] MS (EI): *m/z* (ion, relative intensity) 294.1 (M^+, 5.60), 279.1 ($M^+ - CH_3$, 32.07). HRMS (EI): calcd for $C_{15}H_{30}Si_3$, 294.16554; found, 294.16559.

Catalytic Synthesis of Tetraphenylbenzenes. A mixture of diphenylacetylene and phenylacetylene in a 2:1 molar ratio [0.520 g (2.92 mmol) of diphenylacetylene and 0.151 g (1.48 mmol) of phenylacetylene] was placed in a thick-walled quartz tube, and then 0.50 g (1.8 mmol) of hexachlorodisilane was injected. The tube was cooled in liquid nitrogen, flame sealed under vacuum, and heated to 185 °C for 20 h in an oil bath. Crystals were seen to form during the reaction. After cooling to room temperature, the tube was opened in a hood. A ^1H NMR spectrum of the mixture revealed 100% conversion of starting material. After the reaction mixture was shaken with 10 mL of chloroform, crystals floating on the surface isolated by filtration were shown to be hexaphenylbenzene by ^1H and ^{13}C NMR spectroscopies.[1] The yellow chloroform filtrate was cooled to 4 °C in a refrigerator, after which ca. 15 mL of pentane was added to the solution, giving a yellow precipitate. The precipitate was filtered, washed with 3 × 1 mL of pentane, and dried under vacuum to give 0.30 g of 1,2,4,5-tetraphenylbenzene (as deduced from the one singlet for the central aromatic ring in the ^1H NMR spectrum) in 45% yield. ^1H NMR ($CDCl_3$): δ 7.52 (s, central ring, 2H); 7.22 (s, phenyl, 20H). ^{13}C NMR ($CDCl_3$): δ 140.9, 139.6, 133.0, 129.9, 127.9, 126.6. MS (EI): *m/z* (ion, relative intensity) 382.1 (M^+, 21.46), 305.3 ($M^+ - C_6H_5$, 1.51). HRMS (EI): calcd for $C_{30}H_{22}$, 382.17215; found, 382.17148. No NMR data were found for 1,2,4,5-tetraphenylbenzene in the literature.

Catalytic Synthesis of Triethyl 1,3,5-Benzenetricarboxylate. In a thick-walled quartz tube, ethynyl propiolate (0.10 g, 1.0 mmol) was introduced under nitrogen and then Si_2Cl_6 (0.14 g, 0.50 mmol) was added. The tube was cooled in liquid nitrogen and flame sealed under vacuum. The tube was placed inside a steel pressure reactor, which was then heated to 170 °C for 20 h. The reaction product was a thick oily material consisting of a mixture of triethyl 1,3,5-benzenetricarboxylate and starting materials, as determined by ^1H and ^{13}C NMR spectroscopies. Distillation under reduced pressure gave 40 mg of product (40% yield). ^1H NMR ($CDCl_3$): δ 8.81 (s, C_6H_3, 3H), 4.36 (q, CH_2, 6H), 1.39 (t, CH_3, 9H). ^{13}C NMR ($CDCl_3$): δ 165.1, 134.4, 131.5, 61.6, 14.2. ^1H and ^{13}C NMR data for the 1,3,5-isomer are in agreement with those obtained from an authentic sample obtained from Aldrich Chemical Co.

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Catalytic Synthesis of 1,3,5-Triphenyl-2,4,6-tripentafluorophenylbenzene. Crystalline pentafluorophenylacetylene[8] (0.16 g, 0.60 mmol) was placed inside a thick-walled quartz tube preflushed with nitrogen. Hexachlorodisilane (0.20 g, 0.74 mmol) was then added, and the tube was cooled in liquid nitrogen and flame sealed under vacuum. During heating of the tube to 200 °C in an oil bath for 2 days, the reaction solution was observed to change from light yellow to black, concomitant with the formation of a light yellow precipitate. The tube was opened in a hood, and the reaction mixture was shaken with 5 mL of $CHCl_3$. The solid precipitate was separated by filtration and was dried under vacuum to give 0.12 g of the product (75% yield), which was identified as 1,3,5-triphenyl-2,4,6-tripentafluorophenylbenzene. Mp >300 °C. ^{1}H NMR ($CDCl_3$): δ 6.94−7.10 (m, 15H). ^{13}C NMR ($CDCl_3$): δ 129.2, 128.9, 128.3, 128.2, 128.0, 127.9, 127.7, 127.5, 127.4, 127.3. MS (EI): *m/z* (ion, relative intensity) 804.2 (M^+, 8.28), 637.0 ($M^+ - C_6F_5$, 0.70). MS (CI/NH_3, positive ion): *m/z* (ion, relative intensity) 804.2 (M^+, 1.51). MS (CI/NH_3), negative ion): *m/z* (ion, relative intensity) 804.4 (M, 61.86). Its mass spectrum compared favorably with literature values.[8] No ^{1}H, ^{13}C, or ^{19}F NMR spectral data were found in the literature.

Synthesis of $Si_2(NMe_2)_xCl_{6-x}$ (x = 2−6). Syntheses of $Si_2(NMe_2)_5Cl$ and $Si_2(NMe_2)_6$ have been reported elsewhere.[14] Hexachlorodisilane (2.69 g, 10.0 mmol) was added to a 250 mL flask equipped with a magnetic stirrer under nitrogen, followed by the addition of 100 mL of Et_2O. The flask was stoppered by a septum, and the solution was cooled to −178 °C by liquid nitrogen. The flask was weighed, and gaseous dimethylamine was then introduced from a cylinder into the flask, which was cooled by liquid nitrogen. A white precipitate was observed to form immediately. The weight of the flask was recorded frequently to make sure the required amount of $HNMe_2$ has been added (1.80 g for $Si_2(NMe_2)_2Cl_4$, 2.70 g for $Si_2(NMe_2)_3Cl_3$, 3.60 g for $Si_2(NMe_2)_4Cl_2$). After the introduction of $HNMe_2$, the flask was allowed to warm slowly to ambient temperature, and the reaction mixture was stirred well for another 20 h. The precipitate was filtered from the reaction mixture, and the solid material ($HNMe_2 \cdot HCl$) was washed with 3 × 30 mL of Et_2O. The filtrate was evaporated under vacuum. The products $Si_2(NMe_2)_2Cl_4$ and $Si_2(NMe_2)_3Cl_3$ were purified by distillation under vacuum, while $Si_2(NMe_2)_4Cl_2$ was obtained as a solid whose ^{13}C and ^{1}H NMR spectroscopy indicated that its purity was suitable for subsequent reactions. Product yields: $Si_2(NMe_2)_2Cl_4$ 45%, $Si_2(NMe_2)_3Cl_3$ 70%, $Si_2(NMe_2)_4Cl_2$ 85%. Characterizations of $Si_2(NMe_2)_2Cl_4$: ^{1}H NMR (C_6D_6): δ 2.31 (s, 6H); ^{13}C NMR (C_6D_6) δ 36.66; MS (CI/NH_3, positive ion): *m/z* (ion, relative intensity), 304.4 ($[M + NH_4]^+$, 9.27); bp 158−160 °C. Anal. Calcd for $C_4H_{12}Cl_4N_2Si_2$: C 16.78%; H 4.19%, N 9.79%, Cl 49.65%, Si 19.58%. Found: C 16.11%, H 4.40%, N 9.69%, Si 19.50%. The symmetric isomer was assumed here for product $Si_2(NMe_2)_2Cl_4$. $Si_2(NMe_2)_3Cl_3$ ^{1}H NMR (C_6D_6): δ 2.40 (s, 6H), 2.56 (s, 12H). ^{13}C NMR (C_6D_3): δ 36.83, 36.78. MS (EI): *m/z* (ion, relative intensity) 295.0 (M^+, 1.30). Bp: 220−222 °C. Anal. Calcd for $C_6H_{18}Cl_3N_3Si_2$: C 24.45%, H 6.11%, N 14.26%. Found: C 23.47%, H 6.41%, N 14.07%. ^{1}H $Si_2(NMe_2)_4Cl_2$ NMR (C_6D_6): δ 2.46 (s, 24H). ^{13}C NMR (C_6D_6): δ 37.02. MS (EI): *m/z* (ion, relative intensity) 302.1 (M^+, 0.71). Anal. Calcd for $C_8H_{24}Cl_2N_4Si_2$: C 23.76%, H 7.92%, N 18.48%. Found: C 22.80%, H 8.31%, N 18,27%. Mp: 70−72 °C. ^{1}H and ^{13}C NMR data of $Si_2(NMe_2)_4Cl_2$ compare favorably with literature values.[15]

Catalytic Reactions of Diphenylacetylene with $Si_2(NMe_2)_xCl_{6-x}$ (x = 2−6). The sealed tube reactions were carried out under the same conditions as that of Si_2Cl_6 with diphenylacetylene. For the $Si_2(NMe_2)_2Cl_4$/PhC≡CPh reaction, the dominant product is hexaphenylbenzene (20% conversion), with less than a 2% conversion to isomeric 2,3,5,6-tetraphenyl-1,4-bis(dimethylamino)-1,4-dichloro-1,4-disilacyclohexadienes,[16] as determined by ^{1}H NMR spectroscopy. For the $Si_2(NMe_2)_3Cl_3$/PhC≡CPh system, although the main product is again hexaphenylbenzene (10% conversion), the conversion to the isomeric 1,4-disilacyclohexadienes increased to ca. 5%. For the $Si_2(NMe_2)_4Cl_2$/PhC≡CPh system, the hexaphenylbenzene conversion decreased to 5% and the conversion to isomeric 1,4-disilacyclohexadienes rose to 20%. However, in the $Si_2(NMe_2)_5Cl$/PhC≡CPh and $Si_2(NMe_2)_6$/PhC≡CPh systems, the exclusive product is 2,3,5,6-tetraphenyl-1,1,4,4-tetrakis(dimethylamino)-1,4-disilacyclohexadiene,[16] in about 45% and 20% conversions, respectively.

UV Irradiation of a 1-Octyne/Si_2Cl_6 Mixture. A quartz tube (10 mm diameter) was charged with 1-octyne (2.20 g, 20.0 mmol), followed by 0.25 equiv of hexachlorodisilane (1.40 g, 5.00 mmol). The mixture was cooled in liquid nitrogen, and the tube was flame sealed under vacuum. The reaction mixture was allowed to warm to room temperature and was irradiated continuously by a 450 W Hanovia Hg medium-pressure lamp. During the reaction, the quartz tube was water cooled. The reaction mixture was found to have turned yellow after the 20 h radiation time. The solution in the tube was analyzed by ^{1}H and ^{13}C NMR spectroscopies to be a mixture of starting materials, with barely detectable amounts of the isomeric trimers 1,2,4- and 1,3,5-trihexylbenzene. When the reaction time was prolonged to 48 h, starting materials, together with ca. 6% of these isomeric trimerization products (in 1:1 ratio), were observed by ^{1}H NMR spectroscopy. Removal of the volatiles under vacuum afforded 0.11 g (5%) of trimerization products. No attempts were made to isolate the isomers. ^{1}H NMR of the isomers ($CDCl_3$): δ 7.03−6.79 (m, 3H), 2.54−0.85 (m, 39H). ^{13}C ($CDCl_3$): δ 142.69, 140.32, 140.14, 137.67, 129.20, 128.92, 125.80, 125.67, 35.97, 35.60, 32.77, 32.33, 31.75, 31.58, 31.38, 29.52, 29.14, 22.64, 22.62, 14.11. HRMS (EI): calcd for $C_{24}H_{42}$, 330.328651; found, 330.3290042. The ^{1}H, ^{13}C NMR and mass spectra compared favorably with the values obtained from the previous Si_2Cl_6/1-octyne catalytic reaction.

Analogous reactions using $SiCl_4$ or $HSiCl_3$ as catalysts did not afford detectable amounts of trimerization product or any other product. Similarly, irradiating 1-octyne in the absence of Si_2Cl_6 failed to provide detectable quantities of any product.

Reaction of Hexachlorodisilane with 2,2-Diphenyl-1-picrylhydrazyl. 2,2-Diphenyl-1-picrylhydrazyl is a well-known free radical source.[17] Hexachlordisilane (0.30 g, 11.0 mmol) and 2,2-diphenyl-1-picrylhydrazyl (0.40 g, 10.0 mmol) were added to two NMR tubes under nitrogen. The tubes were cooled in liquid nitrogen and flamed sealed under vacuum. One of the tubes was heated to 190 °C for 20 h in an oil bath, while the other was kept at ambient temperature. During the reaction of the heated tube, the color of the reaction mixture changed from violet to brown. ESR spectroscopy on both samples revealed that the brown sample was almost ESR silent, with a signal 100 times weaker than that of the unheated sample.

Thermal Formation of 1- and 2-Phenylnaphthalenes, 3a and 3b. Into a 25 mL flask equipped with a reflux condenser, magnetic stirrer, and a nitrogen atmosphere was placed phenylacetylene (2.50 g, 24.5 mmol). The flask was heated to 170 °C for 30 h in an oil bath, giving a brown viscous material. The product was quite soluble in chloroform, and it was analyzed by GC−MS as a mixture of dimeric isomers (53.6% in a ∼10:1 ratio) and trimeric isomers (46.3% 1,3,5-triphenylbenzene and 1,2,4-triphenylbenzene in a ∼1:1 ratio).

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The conversion of this reaction by ^{1}H NMR spectroscopy was approximately 95% based on the starting material. Separation of the products by preparative TLC (hexane as eluent) gave 0.50 g (20%) of a mixture of **3a** and a trace of **3b**, whose presence was indicated by GC−MS. ^{1}H NMR (CDCl$_3$): δ 7.85−7.93 (m, 2H); 7.40−7.55 (m, 6H). ^{13}C NMR: δ 140.7, 140.2, 133.8, 131.6, 130.1, 128.2, 127.6, 127.2, 126.9, 126.0, 125.7, 125.4. HRMS (EI): calcd for $C_{16}H_{12}$, 204.09390; found, 204.09303. The ^{1}H and ^{13}C NMR data of **3a** compared favorably to literature values.[12]

Thermal Formation of 7-Methyl-1-*p*-tolylnaphthalene, 4a. In a 10 mL flask equipped with a magnetic stirrer, 4-ethynyltoluene (2.0 g, 17 mmol) was introduced under nitrogen. The flask was heated in an oil bath to 180 °C for 24 h. A thick brown material was obtained, which was found by GC−MS to consist of a dimer (∼85%), along with ∼5% of an isomeric dimer and a 10% mixture of isomeric trimers (1,3,5- and 1,2,4-tritoluylbenzene) in a ∼5:1 ratio. A sample of the major dimer **4a** was purified for NMR spectroscopy by preparative TLC (hexanes eluent). ^{1}H NMR (CDCl$_3$): δ 7.24−7.80 (m, 10H), 2.45 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (CDCl$_3$): δ 139.5, 138.0, 136.8, 135.6, 132.0, 131.8, 129.9, 128.9, 128.1, 127.9, 127.2, 127.0, 124.9, 124.5, 21.9, 21.3. The GC mass spectrum of the reaction mixture indicated the presence of the aromatic dimers (molecular weight 232), and an HRMS of the mixture confirmed this conclusion. HRMS: calcd for $C_{18}H_{16}$ 232.12520; found, 232.12519. The minor dimer is presumed to be **4b** (by analogy with the known structure of **3b**[12]). No ^{1}H or ^{13}C NMR data were found in the literature for isomers **4a** and **4b**.

Thermal Formation of 5-Cyclohex-1-enyl-1,2,3,4-tetrahydronaphthalene, 5a. Into a 10 mL flask equipped with a magnetic stirrer and a reflux condenser was introduced 1-ethynyl-1-cyclohexene (3.00 g, 28.3 mmol) under nitrogen. The flask was heated to 170 °C in an oil bath. After 15 h, a viscous brown material was obtained, which by GC−MS analyzed exclusively as a dimer (MW 212) judging from the absence of a singlet ^{1}H NMR peak in the reaction mixture expected for the hydrogen at the C(5) position of **5b**. Such a singlet was observed for the analogous minor product **3b** in the **3a**/**3b** reaction mixture. The conversion of this reaction was found to be quantitative by ^{1}H NMR spectroscopy. Compound **5a** was isolated by preparative TLC (hexanes eluent) in 80% yield. ^{1}H NMR (CDCl$_3$): δ 6.98−7.24 (m, 3H), 5.50 (s, 1H), 1.66−2.79 (m, 16H). ^{13}C NMR (CDCl$_3$): δ 144.8, 138.8, 137.0, 134.4, 127.5, 125.6, 125.2, 125.0, 30.2, 29.9, 27.0, 25.4, 24.4, 23.1, 23.1, 22.2. HRMS: calcd for $C_{16}H_{20}$, 212.15650; found, 212.15662. Anal. Calcd for $C_{16}H_{20}$: C 90.51%, H 9.49%. Found: C, 88.66%; H, 9.63%. No ^{1}H or ^{13}C NMR data were found in the literature for this compound.

In a comparison experiment, Si_2Cl_6 (0.20 g, 0.72 mmol) was used as a procatalyst under identical reaction conditions. In addition to the formation of dimer **5a** in 80% conversion (with a trace of **5b**), two isomeric trimers were found to form in 20% conversion in a ∼1:1 ratio as indicated by GC−MS. The presence of compound **5a** and the trimers was confirmed by ^{1}H and ^{13}C NMR spectroscopies.[13] The concentration of **5b**, however, was too low for ^{1}H NMR detection.

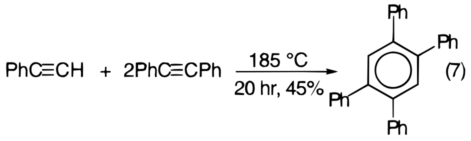
Heating 1-Phenyl-1-propyne with and without Si_2Cl_6. Equal amounts of 1-phenyl-1-propyne (0.15 g, 0.86 mmol) were added to four thick-wall quartz tubes, and to each of two of them was added (0.20 g, 0.74 mmol) Si_2Cl_6. The tubes were flame sealed under vacuum and were placed inside a pressure reactor, which was heated to 180 °C for 40 h in an oil bath. The two tubes containing the Si_2Cl_6 were found to contain the trimerized product 1,3,5-trimethyl-2,4,6-triphenylbenzene in 80% conversion, as judged by ^{1}H NMR spectroscopy. Colorless crystals that formed after standing at room temperature were used to obtained NMR spectra. ^{1}H NMR (CDCl$_3$): δ 7.2−7.6 (m, 15H), 1.8 (s, 9H). ^{13}C NMR (CDCl$_3$): δ 142.0, 131.5, 130.2, 129.7, 128.3, 127.2, 19.3. These data are in good agreement with literature values.[18] The tubes containing no Si_2Cl_6 were found by ^{1}H and ^{13}C NMR spectroscopies to contain only starting materials.

Thermal Reactions of Nonconjugated Alkynes. The nonconjugated alkynes 1-decyne and 1-octyne were heated at 190−200 °C for 48 h under nitrogen. Only starting materials were detected by GC−MS and by ^{1}H and ^{13}C NMR spectroscopies.

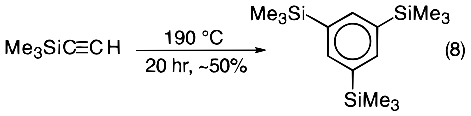
Results and Discussion

Our original intent was to synthesize **2**. Although the first low-yield preparation of this compound took place in the gas phase at ca. 450 °C,[5b] we attempted to carry out the same reaction in a sealed tube. Because that attempt produced an intractable black char, we repeated the reaction at 170−180 °C and observed the production of C_6Ph_6 (reaction 1). It was of interest, therefore, to explore the scope of this novel catalytic alkyne trimerization.

Si_2Cl_6-Catalyzed Alkyne Trimerization. Like diphenylacetylene, diethyl acetylene was easily converted to colorless crystalline hexaethyl benzene in the presence of Si_2Cl_6 (reaction 2). Terminal alkynes such as phenylacetylene, 1-octyne, and 1-decyne are similarly catalytically cyclotrimerized. Reactions carried out at atmospheric pressure at 170 °C for these alkynes were efficient, leading to 100% conversion of 1-octyne to isomeric trihexylbenzenes, while conversions of 1-decyne to trioctylbenzenes and of phenylacetylene to triphenylbenzenes were quantitative with only 10−15 mol % catalyst. In all three reactions, a ca. 1:1 mixture of only two isomers (the 1,3,5- and the 1,2,4-substituted benzenes) was formed, while the third isomeric possibility (the most sterically crowded 1,2,3-substituted product) was not detected. The isomers in all cases displayed two individual peaks in the GC−MS, and they were further characterized as mixtures by ^{1}H NMR, ^{13}C NMR, and high-resolution mass spectroscopies. That steric effects prevail in these reactions is also supported by the ca. 1:1 ratios of the 1,3,5- and 1,2,4-substituted products, since statistically this ratio is expected to be 1:3. By employing a mixture of phenylacetylene and diphenylacetylene in a 1:2 ratio, an isomeric tetraphenylbenzene mixture (consisting mainly of the 1,2,4,5-tetraphenylbenzene isomer) was found to form catalytically in good yield (reaction 7).



Other alkyne functionalities apparently survive our catalytic cyclotrimerization process. Reaction 8 proceeds regioselectively, producing only the symmetrical isomer



(as indicated by GC−MS and by ^{1}H and ^{13}C NMR

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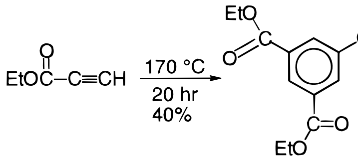
[18] Dietl, H.; Reinheimer, H.; Moffat, J.; Maitlis, P. M. *J. Am. Chem. Soc.* **1970**, *92*, 2276.

spectroscopies) probably because of the steric hindrance caused by the crowded trimethylsilyl groups. The cyclotrimerizations of ethyl propiolate giving triethyl 1,3,5-benzenetricarboxylate and phenylpentafluorophenylacetylene giving 1,3,5-phenyl-2,4,6-tripentafluorophenylbenzene were also successful (reactions 9 and 10, respectively). The regioselectivity of reaction 10 is perhaps somewhat surprising in view of the similarity in size of the substituents relative to those in $Me(CH_2)_5C{\equiv}CH$, $Me(CH_2)_7C{\equiv}CH$, and $PhC{\equiv}CH$, for example, which lead to isomeric mixtures of substituted benzenes. The regioselectivity of reaction 10 may be associated with minimization of Coulombic repulsions of the fluorines by alternating C_6F_5 with C_6H_5 substituents. On the other hand, trimerization was not observed for p-$ClC_6F_4C{\equiv}CPh$ or propargyl chloride. Although a reaction did occur with propargyl bromide (as indicated from aromatic signals detected by ^1H and ^{13}C NMR spectroscopies), the reaction was complicated by the formation of numerous side products that we were unable to separate. As with other metallic and organometallic catalysts,[19] bis(trimethylsilyl)acetylene and bis(phenylsilyl)acetylene also failed to cyclotrimerize in the presence of Si_2Cl_6. The formation of unidentified oligomers in these cases may be associated with the steric hindrance of the silyl groups and/or steric strain in the cyclotrimerized products.[20]



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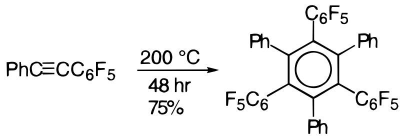

(10)

In attempts to synthesize triazines from nitriles, reactions of benzonitrile, pentafluorobenzonitrile, and acetonitrile with hexachlorodisilane were carried out under conditions similar to those described above. No desired products were detected in the complex reaction mixtures that resulted. Although the strength of the CN triple bond (204 kcal/mol) is quite comparable with that of the $C{\equiv}C$ bond (200 kcal/mol),[21] the greater polarity of the CN bond apparently does not favor a radical pathway under our conditions.

Other Disilanes. Hexamethyldisilane was also employed as a potential procatalyst, but no catalytic effect was detected for the aforementioned substrates. Hexamethyoxydisilane was also evaluated as a procatalyst with diphenyl acetylene and with 1-octyne as substrates. Under the conditions used for the same reactions involving Si_2Cl_6, $Si_2(OMe)_6$ led to lower yields of corresponding trimerized products (30% for diphenylacetylene and 40% for 1-decyne). While it is tempting to speculate that a higher electronegativity of the silicon substituents favors homolysis of the Si–Si bond to form silyl radicals, we were somewhat surprised to observe that Si_2F_6 did not catalyze the trimerization of 1-decyne and phenylacetylene under identical conditions in a pressure reactor (170–200 °C, 2 days, molar ratio of acetylene/catalyst = 100:20). For reasons that are not entirely clear, *sym*-$Si_2Me_2Cl_4$ also did not catalyze alkyne cyclotrimerization.

Further Investigation of the Reaction Pathway. Several experiments have been carried out to test the $SiCl_3$ radical pathway for these trimerizations for which we presented evidence earlier.[1] To evaluate the series $Si_2(NMe_2)_xCl_{6-x}$ ($x = 0$, 2–6) as catalysts, Si_2Cl_6 was reacted with the corresponding stoichiometric amount of $HNMe_2$. Here $Si_2(NMe_2)Cl_5$ ($x = 1$) is missing because it could not be obtained in pure form by this method. When the series was reacted with diphenylacetylene under the same reaction condition, interesting reaction product distribution patterns were observed. For $x = 0$, only the cyclotrimerization product hexaphenylbenzene was obtained. For the disilane in which $x = 2$, however, the yield of hexaphenylbenzene dropped dramatically to about 20% compared with the 70% yield observed with Si_2Cl_6. In addition to the dominant trimerization product, a minor product 2,3,5,6-tetraphenyl-1,4-dichloro-1,4-bis(dimethylamino)-1,4-disilacyclohexadiene was also detected (ca. 2% conversion) by ^1H NMR. An increased ratio of the same 1,4-disilacyclohexadiene was observed in the reaction of $Si_2(NMe_2)_3Cl_3$ ($x = 3$) with diphenylacetylene (hexaphenylbenzene 10%, 1,4-disilacyclohexadiene 5%). In the reaction of $Si_2(NMe_2)_4Cl_2$ ($x = 4$) with diphenylacetylene, however, the trimerization product became the minor product (5%), while the formation of the 1,4-disilacyclohexadiene is dominant (20%). Not surprisingly, reactions of $Si_2(NMe_2)_5Cl$ and $Si_2(NMe_2)_6$ with diphenylacetylene gave only 1,1,4,4-tetrakis(dimethylamino)-2,3,5,6-tetraphenyl-1,4-disilacyclohexadiene in 45% and 20% yield, respectively. No cyclotrimerization product was detected in these two cases. We rationalize these observations on the basis of a process involving competition reactions as follows. When only electron-withdrawing Cl groups are present, the homolytic cleavage of the Si–Si bond is favored at a temperature around 200 °C. This result is consistent with the formation of hexaphenylbenzene as the sole product in the Si_2Cl_6 case. The introduction of electron-inducting NMe_2 groups is expected to inhibit the thermal generation of silyl radicals owing to the greater electron density on the Si atoms and therefore stronger Si–Si bonds. As more NMe_2 groups are added on to the dislane, thermal generation of the silylenes $Si(NMe_2)Cl$ and/or $Si(NMe_2)_2$ via disproportionation becomes increasingly favored probably because of the weakness of Si–N bonds compared with Si–Cl bonds.

Additional evidence for the $SiCl_3$ radical-induced cyclotrimerization of alkynes was obtained from the results of theoretical calculations of electron density on Si for a series of silyl radicals possessing different substituents.[22] It was reported that the electron densities on Si of three silyl radicals pertinent to the present discussion are $SiMe_3$ (81.0%), $SiCl_3$ (57.3%), and quite surprisingly 84.4% in the case of SiF_3. If silyl radical-

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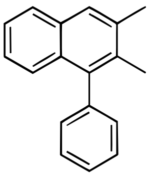
induced alkyne cyclotrimerization proceeds by electrophilic attack of the radical on the electron-rich alkynyl carbons, then this calculation predicts that $SiCl_3$ radicals are more reactive than $SiMe_3$ radicals. The calculations are also consistent with the inertness of Si_2F_6 as a procatalyst for alkyne cyclotrimerization despite the greater electronegativity of fluorine compared with chlorine.

Further support for the $SiCl_3$ radical pathway was obtained from UV irradiation of disilane/alkyne mixtures. UV light is well-known for its ability to generate radical species.[23] When a mixture of Si_2Cl_6 and 1-octyne (1:4 molar ratio) was sealed in a water-cooled quartz tube and irradiated for 20 h by UV light, a ~1% conversion to the cyclotrimerization products 1,3,5- and 1,2,4-trihexylbenzene in a 1:1 ratio (by GC−MS) was detected by ^{1}H, ^{13}C NMR, and HRMS spectroscopies. When the reaction time was prolonged to 48 h, a conversion of 6% (with an isolated yield of 5%) was realized. However, reactions under the same conditions in the absence of Si_2Cl_6 or in the presence of $HSiCl_3$ (a known $SiCl_3$ radical source[24]) or $SiCl_4$ afforded no detectable cyclotrimerization products, according to ^{1}H NMR, ^{13}C NMR, and GC−MS spectroscopies. When X-ray radiation was utilized (on a Rigaku rotating anode unit using a Mo source, $\lambda = 0.71069$ Å), no cyclotrimerization products were detected even with prolonged radiation times and the observation of a color change to brown.

In another experiment, a mixture of the stable radical source 2,2-diphenyl-1-picrylhydrazyl and Si_2Cl_6 (molar ratio 1:1:1) was introduced to an NMR tube, followed by flame sealing the tube under vacuum. Upon heating the tube to 190 °C for 20 h, the initial violet color of the stable free radical was changed to brown. Moreover, the intensity of the ESR signal of the reaction mixture was about 100 times weaker, compared with the signal intensity of the unreacted mixture of Si_2Cl_6 and 2,2-diphenyl-1-picrylhydrazyl in the same molar ratio. While these results are consistent with quenching of $SiCl_3$ radicals, they could be the result of other side reactions. NMR spectroscopic analysis could not be performed owing to the insolubility of the reaction product.

Although it was hoped that $Hg(SiCl_3)_2$ would be a source of $SiCl_3$ radicals upon heating, we were unable to detect any cyclotrimerization product in a sealed tube reaction of $Hg(SiCl_3)_2$ with 1-decyne (in 1:5 molar ratio) at 150 °C for 30 h. Indeed, a search of the literature revealed no example of $Hg(SiCl_3)_2$ serving as a radical source.

Thermal Dimerization of Alkynes. To our knowledge only three reports have appeared that describe the thermal dimerization of alkynes. One of these investigations dealt with high-pressure reactions of 30−60% phenylacetylene in MeOH or EtOH, which at 220 °C gave the aromatic dimers **3a** and **3b**, three unspecified trimers, and 75% of polymers.[25] The high-temperature (700−1100 °C) behavior of phenylacetylene was the subject of a second investigation,[26] in which many products (in addition to dimers and trimers) were produced, in concentrations that are functions of the temperature. In the third study, the formation of the aromatic product **6** from the cyclodimerization of 1-phenyl-1-propyne by γ-irradiation in the presence of Ph_2CO was described.[27]



6

When we heated phenylacetylene to 170 °C for 15 h in the absence of solvent and catalyst, a 95% conversion of starting material was observed, with the concomitant formation of 53.6% dimers **3a** and **3b** in a 10:1 ratio and 46.3% trimers (1,3,5-triphenylbenzene and 1,2,4-triphenylbenzene) in a 1:1 ratio. By analogy, 4-ethynyltoluene and 1-ethynyl-1-cyclohexene were expected to undergo analogous reactions under similar conditions to give 7-methyl-*p*-tolylnaphthalene **4a** and 5-cyclohex-1-enyl-1,2,3,4-tetrahydronaphthalene **5a** as the major products, respectively, and corresponding cyclotrimerization products in comparable but smaller conversion. With 4-ethynyltoluene, however, we obtained a very viscous reaction mixture after 15 h at 170 °C, which analyzed by GC−MS as 90% dimers **4a** and **4b** in a 17:1 ratio and only 10% trimers (1,3,5-tri-*p*-tolylbenzene and 1,2,4-tri-*p*-tolylbenzene) in a ~5:1 ratio. Interestingly, under the same reaction conditions, 1-ethynyl-1-cyclohexene quantitatively gave only dimer **5a**, with no indication of the presence of the trimers or oligomers by GC−MS and ^{1}H and ^{13}C NMR spectroscopies.

A radical pathway for high-temperature (700−1100 °C) phenyacetylene dimerization has been proposed, wherein adsorption of a free hydrogen atom from the reaction vessel is the initial step.[26] Whether this mechanism applies to our thermolyses at ~200 °C is open to question. Nonetheless, our observation of the formation of **3a**, **4a**, **5a**, and small amounts of **3b** and **4b** (owing to steric crowding) is consistent with this mechanism. Surprisingly, the presence of Si_2Cl_6 under the conditions used to thermolyze 1-ethynylcyclohexene had a relatively minor effect on the formation of dimer **5a** and resulted in only 20% trimer production.

The existence of conjugated multiple bonds is apparently important to the resonance stabilization of thermally produced radicals, and so it is not surprising that 1-decyne and 1-octyne, which contain no conjugated multiple bonds, afforded no detectable evidence of reaction even after 40 h at 200 °C. However, when Si_2Cl_6 was present in the above systems, the cyclotrimerization product 1,2,4/1,3,5-trioctylbenzenes and 1,2,4/

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1,3,5-trihexylbenzenes were formed in good yields, as described earlier.

Interestingly, neither 2- nor 3-ethynyl pyridine dimerize thermally at 200 °C. Only unidentified oligomeric species were detected. When 2- and 3-ethynyl pyridine are heated to 180 °C in the presence of Si_2Cl_6, no trimerization product(s) is obtained and only oligomeric species were detected.

The terminal hydrogen of alkynes is apparently essential to thermally induced radical generation and structure rearrangements through hydrogen migration.[27] Thus 1-phenyl-1-propyne heated at 190 °C for 40 h gave no detectable dimerization product according to GC−MS and ^1H and ^{13}C NMR spectroscopies.

Although compounds **3a**, **3b**, **4a**, and **5a** have been synthesized by means other than those described here, they have not been reported as products of thermal dimerization. Thus **3a** and **3b** have been made by dehydrogenating the corresponding cyclohexenylnaphthalenes.[28] Compound **4a** was synthesized by oxidizing 6-methyl-4-*p*-tolyl-1,2-dihydronaphthalene in the presence of selenium at 280 °C,[29] while **5a** was obtained from 5-(2-hydroxycyclohexyl)tetralin using $ZnCl_2$ as a catalyst.[30] Heretofore, products **4a**, **4b**, or **5a** have not been reported to form through thermal dimerization.

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