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Disilane-Catalyzed Cyclotrimerization of Acetylenes

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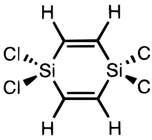
Eighty-two years after the discovery by Bertholet in 1866 that acetylene thermally trimerizes to benzene in low yield at temperatures in excess of 400 °C,[1] Reppe reported that this reaction is catalyzed near room temperature in solutions of nickel complexes.[2] Since then, alkyne trimerization has become one of the most intensely studied synthetically useful transformations, and many transition-metal systems including salts, oxides, organometallic derivatives, and zerovalent metals have been found to catalyze this reaction via a mechanism involving alkyne coordination to the metal.[3] In 1980 it was reported that the nonmetallic compound diethylamine catalyzes the cyclotrimerization of aryl ethynyl ketones to 1,3,5-triaroyl benzenes.[4] Evidence for an ionic mechanism was put forth in 1994 for this reaction in which Michael addition of diethylamine to the CH carbon of the triple bond to form an eneamineone was followed by addition of two aryl ethynyl ketone molecules with subsequent regeneration of diethylamine by elimination from the trimer.[5] Because this reaction depends on the formation of an enamineone resonance-stabilized by an aroyl carbonyl, this cyclotrimerization appears to be restricted to aroylethynes. We report here the second example of alkyne cyclotrimerizations catalyzed by a nonmetal compound and the first example of a catalyst that operates by a free-radical mechanism. The alkynes in the reactions reported herein include disubstituted as well as monosubstituted ethynes.

In 1971 it was reported that the gas-phase reaction of acetylene with hexachlorodisilane at 450 °C gave **1** in 30% yield, presumably via $SiCl_2$ diradicals produced by the disproportionation of Si_2Cl_6.[6] When we allowed diphenylacetylene to react with Si_2Cl_6 in a sealed tube at this temperature, only an insoluble black solid was formed. However, by lowering the temperature, hexaphenylbenzene was obtained in reasonable yield (eq 1).[7] That

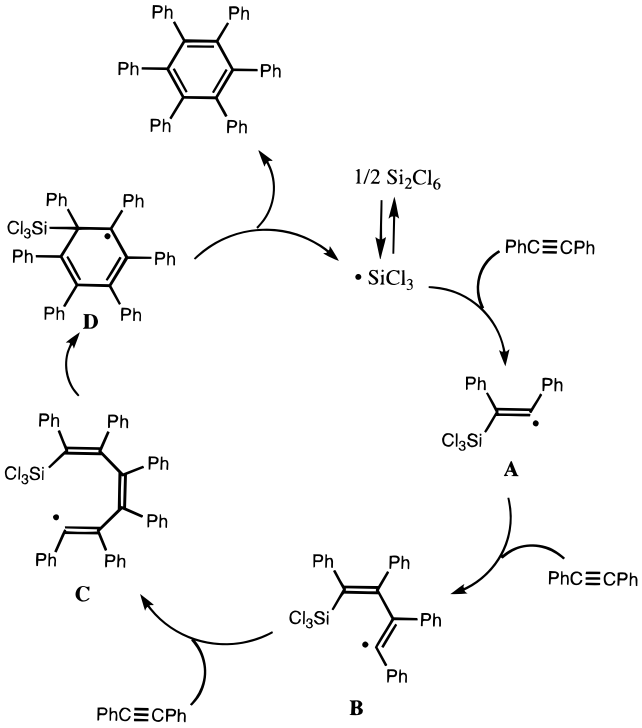
$$3\ PhC{\equiv}CPh \xrightarrow[\text{2 d, 60\%}]{Si_2Cl_6\ \text{(64 mol \%), 170-180 °C}} C_6Ph_6 \qquad (1)$$

Si_2Cl_6 acted as a procatalyst that undergoes no net change in our reaction was shown by the single ^{29}Si NMR peak at δ 12.52 ppm for Si_2Cl_6 in the reaction mixture, which was confirmed by recording this spectrum again after addition of authentic Si_2Cl_6. Further confirmation was secured by quantitatively converting the Si_2Cl_6 in the reaction mixture to $Si_2(NMe_2)_6$ with excess $HNMe_2$ followed by comparison of the ^1H NMR, ^{13}C NMR, and EI mass spectra with those of an authentic sample. Recycling the same sample of Si_2Cl_6 five times in separate reactions with diphenyl acetylene revealed no loss in C_6Ph_6 yield.



1

Scheme 1



While the formation of **1** from acetylene and Si_2Cl_6 at 450 °C was attributed to $SiCl_2$ diradical formation,[6] it is reasonable to suppose that, under our milder conditions, $SiCl_3$ radicals induce the trimerization of $PhC{\equiv}CPh$ by an addition−elimination pathway depicted in Scheme 1. The presence of radicals in eq 1 was substantiated by the lack of detectable product when hydroquinone or 9,10-dihydroanthracene was added to the reaction

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[1] Bertholet, M. C. R. *Held. Seances Acad. Sci.* **1866**, 905.

[2] Reppe, W.; Schlichting, O.; Klager, K.; Toepel, T. *Liebigs Ann. Chem.* **1948**, *560*, 1.

[3] See, for example: (a) Takahashi, T.; Xi, Z.; Yamazaki, A.; Liu, Y.; Nakajima, K.; Kotora, M. *J. Am. Chem. Soc.* **1998**, *120*, 1672. (b) Yokota, T.; Sakurai, Y.; Sakaguchi, S.; Ishii, Y. *Tetrahedron Lett.* **1997**, *38*, 3923. (c) Marx, H. W.; Moulines, F.; Wagner, T.; Astruc, D. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1701. (d) Bose, R.; Matzger, A. J.; Mohler, D. L.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1478. (e) Bianchini, C.; Caulton, K. G.; Chardon, C.; Doublet, M. L.; Eisenstein, O.; Jackson, S. A.; Johnson, T. J.; Meli, A.; Peruzzini, M.; Streib, W. E.; Vacca, A.; Vizza, F. *Organometallics* **1994**, *13*, 2010. (f) Vollhardt, K. P. C. *Pure Appl. Chem.* **1993**, *65*, 153. (g) Baidossi, W.; Goren, N.; Blum, J. *J. Mol. Catal.* **1993**, *85*, 153. (h) Smith, D. P.; Strickler, J. R.; Gray, S. D.; Bruck, M. A.; Holmes, R. S.; Wigley, D. E. *Organometallics*, **1992**, *11*, 1275. (i) Bianchini, C.; Caulton, K.; Chardon, C.; Eisenstein, O.; Folting, K.; Johnson, T. J.; Meli, A.; Peruzzini, M.; Rauscher, D. J.; Streib, W. E.; Vizza, F. *J. Am. Chem. Soc.* **1991**, *113*, 5127. (j) DuToit, C. J.; Du Plessis, J. A. K.; Lackmann, G. *J. Mol. Catal.* **1989**, *53*, 67. (k) Borrini, A.; Dweisi, P.; Ingrosso, G.; Luckermi, A.; Serra, G. *J. Mol. Catal.* **1985**, *30*, 181. (l) Tysoe, W. T.; Nyberg, G. L.; Lambert, R. M. *J. Chem. Soc., Chem. Commun.* **1983**, *11*, 623.

[4] Balasubramanian, K.; Selvaraj, P.; Venkataramani, S. *Synthesis* **1980**, 29.

[5] (a) Matsuda, K.; Inoue, K.; Koga, N.; Nakamura, N.; Iwamura, H. *Mol. Cryst. Liq. Cryst.* **1994**, *253*, 33. (b) Matsuda, K.; Nakamura, N.; Iwamura, H. *Chem. Lett.* **1994**, 1765.

[6] Chernyshev, E. A.; Komalenkova, N. G.; Bashkuova, S. A. *Zh. Obshch. Khim.* **1971**, *41*, 1175.

[7] In a thick-walled quartz tube was placed diphenylacetylene (0.50 g, 2.8 mmol) followed by 0.50 g (1.8 mmol) of hexachlorodisilane which was added under nitrogen by a syringe. The tube was cooled in liquid nitrogen and was flame sealed under vacuum. The tube was heated to 170−180 °C in an oil bath for 2 days, during which time the color of the solution changed to brown after 1 h and then to black after 1 day. Single crystals were observed to form at the bottom of the tube. After allowing the tube to cool to room temperature, it was opened and the solid product was washed with 3 × 0.5 mL of $CHCl_3$ and dried under vacuum to give 0.3 g (60% yield) of crystalline product which was identified as hexaphenylbenzene: mp 455−457 °C. ^1H NMR (300 MHz, C_6D_6): δ 6.69−7.15 (m, C_6H_5, 30H). ^{13}C NMR (75 MHz, C_5D_6): δ 140.60, 140.28, 131.41, 126.55, 125.16. MS (EI, 70 eV): *m/z* (ion, rel intensity) 534.2 (M^+, 22.53), 457.2 ($M^+ - C_6H_5$, 0.80). Anal. Calcd for $C_{42}H_{30}$: C, 94.38; H, 5.62. Found: C, 93.25; H, 5.73. The NMR data are identical to those reported: *The Aldrich library of ^{13}C and ^1H FT NMR Spectra*. 1st ed.; Aldrich Chemical Co.: Milwaukee, WI, 1993.

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mixture as radical traps. Acid-catalyzed cyclo-trimerization of diphenylacetylene by HCl formed by hydrolysis of Si_2Cl_6 in the presence of adventitious water was ruled out by failure of the reaction with HCl (in Et_2O) or with $SiCl_4$ that had been partially hydrolyzed by exposure to moist air. That silicon tetrachloride by itself is ineffective as a catalyst in our reactions is reasonable in view of its exceedingly high first dissociation energy (ca. 111 kcal/mol[8]). Because the dissociation energy of $SiCl_3$ (that is generated from Si_2Cl_6) to $SiCl_2$ is only ca. 66 kcal/mol,[8] $SiCl_2$ as a reactive intermediate cannot be ruled out *a priori*. However, the products obtained under our experimental conditions, when compared with the more drastic conditions resulting in the formation of **1**,[6] favor the relatively simple pathway involving $SiCl_3$ radicals depicted in Scheme 1. Although attempts to trap one or more of the intermediates **A**−**D** in Scheme 1 with hydrogen donors such as 9,10-dihydroanthracene or 9,10-dihydrophenanthrene failed, we were able to detect $HSiCl_3$ and the corresponding aromatized hydrogen donor dehydrogenated product by ^{1}H NMR spectroscopy. This result further substantiates the formation of $SiCl_3$ radicals via Si−Si bond cleavage. Trichlorosilane and anthracene were also detected when a mixture consisting only of Si_2Cl_6 and 9,10-dihydroanthracene was heated to 190 °C for 80 h. As noted earlier, the presence of 9,10-dihydroanthracene in Scheme 1 inhibited hexaphenylbenzene formation (reaction 1). However, when 1-decyne was employed in the presence of this hydrogen donor or 9,10-dihydrophenanthrene, quantitative trimerization was detected as well as the formation of $HSiCl_3$ and aromatization of the hydrogen donor. This result is consistent with the idea that alkyl ethynes are more competitive for $SiCl_3$ radicals (even at low concentrations) than diphenyl acetylene.

Equation 1 has been extended to other alkyne substrates, among which are those shown in eqs 2−5. Apparently terminal alkynes undergo cyclo-trimerization in high conversion more easily than nonterminal examples for steric reasons. At 20 mol % Si_2Cl_6, eq 2 gave a 30% conversion after 2 days, and for reasons that are not clear, this conversion was not appreciably increased after 6 days. Equation 3 gives an 80% conversion to products even at 5 mol % Si_2Cl_6 after 30 h. To rule out catalysis by the walls of the steel pressure vessel in eq 5, the reaction was run in the absence of Si_2Cl_6, whereupon only starting material was recovered. Interestingly, in the absence of Si_2Cl_6, phenyl acetylene was found to give mainly dimerized products (α and *β*-phenyl naphthalene) along with an isomeric mixture of trimers under the conditions of eq 4, whereas 3-hexyne and 1-decyne were thermally stable in the absence of Si_2Cl_6.[9]

$$\mathrm{EtC{\equiv}CEt} \xrightarrow[\text{2 d, 45\%}]{\mathrm{Si_2Cl_6}\text{ (49 mol \%), 200 °C}} \mathrm{C_6Et_6} \tag{2}$$

$$\mathrm{CH_3(CH_2)_7C{\equiv}CH} \xrightarrow[\text{30 h, 100\%}]{\mathrm{Si_2Cl_6}\text{ (10 mol \%), 190 °C}} \text{1,3,5 and 1,2,4-}\mathrm{C_6H_3}(n\text{-Oct})_3 \ (\sim 1{:}1 \text{ ratio}) \tag{3}$$

$$\mathrm{PhC{\equiv}CH} \xrightarrow[\text{15 h, 100\%}]{\mathrm{Si_2Cl_6}\text{ (17 mol \%), 200 °C}} \text{1,3,5 and 1,2,4-}\mathrm{C_6H_3Ph_3} \ (\sim 1{:}1 \text{ ratio}) \tag{4}$$

$$\mathrm{HC{\equiv}CH} \xrightarrow[\text{vessel, 2 d, 90\%}]{\mathrm{Si_2Cl_6}\text{, 210 °C, pressure}} \mathrm{C_6H_6} \tag{5}$$

We found that $Si_2(OMe)_6$ also catalyzes alkyne cyclotrimerization, although conversions are substantially lower than with Si_2Cl_6 under the same conditions (e.g., 40% and 30% conversion in eqs 3 and 4, respectively). On the other hand, no reactions were detected using Si_2Me_6 as a potential procatalyst, even when present in high molar ratios and in reactions lasting up to 150 h. We suggest that the decreasing catalytic activity in the order $Si_2Cl_6 > Si_2(OMe)_6 > Si_2Me_6$ is attributable to an accompanying decrease in the electron-withdrawing power of the silicon substituents. Such an electronic effect can be expected to strengthen the Si−Si bond, thus diminishing thermal production of silyl radicals. In all three of the above disilanes, the substituent−silicon bonds[8,10] are considerably stronger than the Si−Si linkage.[10] Interestingly, the reaction of $Si_2(NMe_2)_6$ with alkynes follows a stoichiometric course leading to 1,1,4,4-tetrakis(dimethylamino)-1,4-disilacyclohexadienes.[9]

In Scheme 1, cleavage of an Si−substituent bond in intermediate **A** by an $SiCl_3$ radical to give $SiCl_4$ and $SiCl_2$ is apparently less favored than sequential attack of **A** by two additional PhC≡CPh molecules. When intermediate **C** is formed, the drive to a stable aromatic product causes an $SiCl_3$ radical to be extruded from this intermediate. Further substantiation for Si−Si bond cleavage in the action of Si_2Cl_6 and $Si_2(OMe)_6$ in these reactions was sought by heating a mixture of these compounds in hopes of forming the crossover product $Cl_3SiSi(OMe)_3$. Only a complicated mixture of $Si_2Cl_{6-x}(OMe)_x$ products could be detected by ^{1}H NMR spectroscopy, however.

Others have reported that Me_3SiCl and Pd/C (10% palladium on carbon) is a catalyst for cyclo-trimerizing alkynes to the corresponding benzene derivatives.[11] It was found in this system that both trimethylchlorosilane and palladium were necessary for the reaction to occur. Although the authors suggest that the seemingly heterogeneous process might in fact be a homogeneous one (possibly through the formation of a soluble catalytic palladium species), they were not able to detect or isolate an intermediate. To determine if silyl radicals produced under these conditions could be catalyzing the cyclo-trimerization, we repeated the reaction with Si_2Cl_6 and 1-octyne at 140 °C using a mixture of Si_2Cl_6 and 10% palladium on carbon, and also an $Si_2Cl_6/PdCl_2$ mixture. Surprisingly, the conversions to trimers were only 7.00% for $Pd/C/Si_2Cl_6$ system and 11.0% for $PdCl_2/Si_2Cl_6$ system; much lower than Si_2Cl_6 by itself under the same conditions (70% conversion). At the higher temperature these palladium catalysts apparently act as radical traps, perhaps by an oxidative addition process—a possibility we are currently examining.

Experiments are underway to evaluate the scope and limitations of the alkynes and group 14 procatalysts congeneric with disilanes that can be employed in these novel reactions.

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(8) Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246.

(9) Yang, J.; Verkade, J. To be published.

(10) Moeller, T. *Inorganic Chemistry*; John Wiley & Sons: New York, 1982.

(11) Jhingan, A. K.; Maier, W. F. *J. Org. Chem.* **1987**, *52*, 1161.