

Tetraethynylmethane[†]

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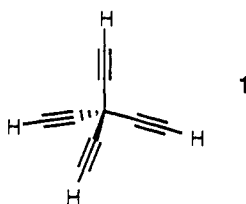
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Tetraethynylmethane (**1**) is the archetypal high carbon content monomer whose polymerization can, in principle, lead to a three-dimensional carbon network homologous to diamond.^{1,2} The search for new high carbon content materials has included numerous studies on the synthesis and polymerization of polyacetylenic monomer units featuring a planar topography (e.g., tetraethynylethylene;³ polyethynylated aromatics⁴). While these monomers, in fact, do afford highly cross-linked polymeric products, difficulties in characterization complicate attempts to assess the bonding arrangement in these materials. Thus, the relationship between monomer geometry and "dimensionality" of the polymer (three-dimensional network or two-dimensional sheet) remains obscure. However, an inherently nonplanar monomeric hub^{5,6} such as **1** could eliminate this ambiguity: oligomerization of tetraethynylmethane to furnish two-dimensional "graphitic" sheets would not be possible on energetic grounds. In this communication we report the synthesis of this intriguing and long sought after species¹ via a route which features (1) application of the Claisen rearrangement to furnish the sterically encumbered quaternary carbon in **1** and (2) development of an acetylene synthesis that proceeds in a very congested and demanding environment.



[†] Dedicated to Professor Philip C. Myhre on the occasion of his 60th birthday.
[‡] To whom correspondence concerning the X-ray crystal structure of **7** should be addressed.

(1) (a) Alberts, A. H.; Wynberg, H. *J. Chem. Soc., Chem. Commun.* **1988**, 748. (b) Diederich, F.; Rubin, Y. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1101. (c) Bunz, U.; Vollhardt, K. P. C.; Ho, J. S. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1648.

(2) Nondiamondoid three-dimensional carbon networks lie more in the realm of theoretical constructs than experimental ones at present. For leading references, see: Johnston, R. L.; Hoffmann, R. *J. Am. Chem. Soc.* **1989**, *111*, 810.

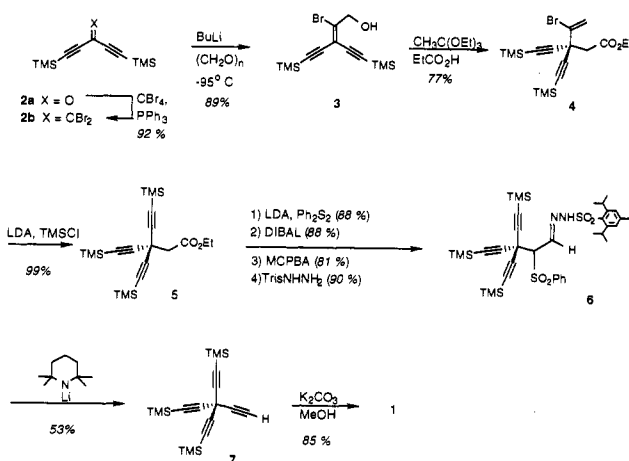
(3) Rubin, Y.; Knobler, C. B.; Diederich, F. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 698 and references cited therein.

(4) (a) Neenan, T. X.; Callstrom, M. R.; Scarmoutzos, L. M.; Stewart, K. R.; Whitesides, G. M.; Howes, V. R. *Macromolecules* **1988**, *21*, 3525. (b) Callstrom, M. R.; Neenan, T. X.; Whitesides, G. M. *Macromolecules* **1988**, *21*, 3528. (c) Neenan, T. X.; Whitesides, G. M. *J. Org. Chem.* **1988**, *53*, 2489.

(5) The strategy of constructing infinite three-dimensional frameworks by the condensation polymerization of tetrahedral hub molecules with appropriately functionalized spacer rods attached (e.g., CdL₄, CuL₄, C(C₆H₄CN)₄) has been explored in the elegant work of Robson; see: Abrahams, B. F.; Hoskins, B. F.; Robson, R. *J. Am. Chem. Soc.* **1991**, *113*, 3606 and references cited therein.

(6) The formal cyclooligomerization and polymerization of diethynylmethane-derived monomers has been studied extensively by Scott; de Meijere, A.; Jaekel, F.; Simon, A.; Borrmann, H.; Kohler, J.; Johnels, D.; Scott, L. T. *J. Am. Chem. Soc.* **1991**, *113*, 3955 and references cited therein.

Scheme I



The synthesis of tetraethynylmethane commences with the known dibromide **2b**,³ readily available in excellent yield from ketone **2a** (Scheme I). Selective lithiation of one of the two bromine atoms in **2b** afforded a putative⁷ alkenyllithium species which was stable to alkylidene carbene formation at -95°C but condensed smoothly with gaseous formaldehyde to provide allylic alcohol **3** in good yield. Our initial attempts to apply Claisen methodology for the introduction of the remaining two skeletal carbon atoms of tetraethynylmethane were frustrated by the extreme base lability of alcohol **3**. Thus, attempts to deprotonate the acetate formed from **3**, or to utilize the alkoxide anion derived from **3** in a conjugate addition reaction preliminary to the [3,3] shift, led to extensive decomposition. Eventually, the acid-mediated Johnson orthoester variant of the Claisen rearrangement proved serviceable, provided that an antioxidant was included in the reaction, yielding the key tetrasubstituted precursor **4**. The triethynylated ester **5**, available by a straightforward elimination/silylation sequence, is one of the few completely characterized⁸ triethynylated methane species which bear an additional carbon appendage. Conversion of the acetic acid residue in **5** to the fourth alkyne unit proved to be the most challenging aspect of this synthesis. Initial attempts employing a variety of precedented acetylene syntheses failed with the sterically encumbered substrate **5**. Eventual recourse to a modification of a procedure reported by Shibuya⁹ (sulfone rather than sulfide, [(2,4,6-triisopropylphenyl)sulfonyl]hydrazone rather than tosylhydrazone) provided the tetraethynylated species **7** in good yield from **6**. The target molecule tetraethynylmethane (**1**) could be isolated in excellent yield as a white, powdery solid following desilylation of **7**.

Unfortunately, solid tetraethynylmethane rapidly decomposed to a brown oil over the course of a few minutes at room temperature in either the presence or absence of oxygen. Spectroscopic analysis of the decomposition product(s) (¹H, ¹³C NMR, MS) revealed the presence of hydrated species (**1** + 2H₂O) and a preponderance of NMR signals normally associated with aliphatic moieties. A dilute sample of **1** frozen in C₆D₆ could be maintained at 0 °C for at least 3 weeks without any evidence of deterioration. In contrast, the trimethylsilylated tetraethynylmethane precursor **7** is much more robust: it can be handled under ambient conditions without event.

(7) For leading references on the lithiation of 1,1-dibromoalkenes, see: Harada, T.; Katsuhira, T.; Oku, A. *J. Org. Chem.* **1992**, *57*, 5805.

(8) Masson et al. (Masson, J.-C.; Le Quan, M.; Cadiot, P. *Bull. Soc. Chim. Fr.* **1968**, 1085) describe the preparation of tetrapropynylmethane via the condensation of propynylmagnesium bromide with carbon tetrabromide, in analogy with their synthesis of tetrapropynylsilicon. The physical evidence presented in support of this claim consists of a boiling point (36 °C/2.8 mm) and an IR absorption (2210 cm⁻¹). We have attempted to reproduce this result, but have been unable to identify any material whose spectral data (¹H NMR, IR, GC/MS) is consistent with that expected for tetrapropynylmethane.

(9) Kano, S.; Yokomatsu, T.; Shibuya, S. *J. Org. Chem.* **1978**, *43*, 4366.

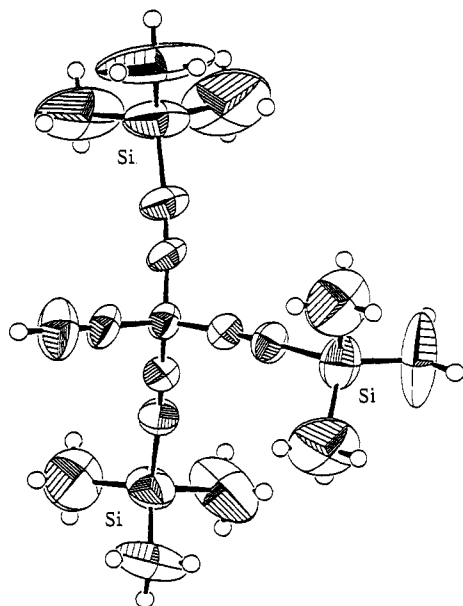


Figure 1. X-ray crystal structure of 7.

X-ray crystallographic analysis of the silyl-protected species 7 (Figure 1) both confirmed the spectroscopically based structural assignment and revealed some of the subtle geometric consequences which attend crowding four alkynyl units about a single carbon atom. Thus, the $C(sp^3)-C(sp)$ bonds (1.48, 1.50 Å) are lengthened by approximately 0.04 Å compared with "standard"

model systems,¹⁰ while the alkyne bonds themselves (1.14, 1.16 Å) are all contracted by a similar amount. In essence, it appears that the internal alkyne carbons have been "displaced" outward by ~ 0.04 Å away from the central sp^3 carbon, perhaps as a consequence of steric crowding. However, none of the alkyne units display a deviation from linearity of more than 4° .

In summary, we have prepared tetraethynylmethane (**1**) in 10 steps and in 16% overall yield from bis trimethylsilyl ketone **2a**. Tetraethynylmethane is quite labile under ambient conditions, perhaps as a result of geometrically "distorted" alkyne units, while the trimethylsilylated precursor **7** could be handled without event. Exploration of the oligomerization/polymerization chemistry of **1** and its analogs is underway, and results will be reported in due course.

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Supplementary Material Available: Experimental procedures, characterization data (1H NMR, ^{13}C NMR, IR, LRMS, HRMS or combustion analysis), and copies of 1H NMR and ^{13}C NMR spectra for **3**, **4**, **5**, **6**, **7**, and **1** and tables of positional parameters, interatomic distances and angles, anisotropic thermal parameters and a labeled diagram for the X-ray structural determination of **7** (30 pages). Ordering information is given on any current masthead page.

(10) Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; John Wiley and Sons: New York, 1972.