Carbon Network Building Blocks: Triethynyl Methanol and Derivatives

Albert H. Alberts* and Hans Wynberg

Department of Organic Chemistry, University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands

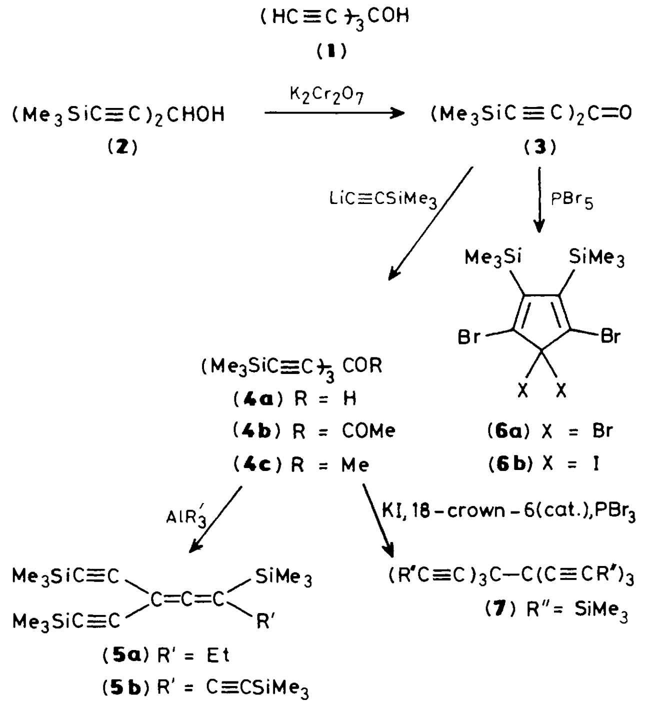
Triethynyl methanol, a key intermediate in the synthesis of carbon nets, and some derivatives have been synthesized by oxidation of the corresponding secondary alcohol and reaction with lithio(trimethylsilyl)acetylene.

In view of the theoretical description of fascinating three-dimensional carbon nets[1] and the current interest in new polyacetylenic materials,[2] the synthesis of monomers from which to build these polymeric networks is now a major challenge. We report a practical synthetic route to triethynyl methanol (**1**), a key compound in a strategy to realize carbon nets.[3]

The secondary alcohol (**2**) was prepared according to the literature procedure.[4] Oxidation of the compound with potassium dichromate–sulphuric acid in acetone below 10 °C afforded, after three extractions with ether and two with pentane, the corresponding ketone (**3**) in excellent yield (95%) (Scheme 1). Addition of lithio(trimethylsilyl)acetylene to (**3**) in hexane at room temperature gave rise to the protected triethynyl methanol (**4a**) (90% yield), obtained as a white air-stable solid after chromatography on silica gel (10% ether–pentane). The product was contaminated with 5—10% of the corresponding bis-trimethylsilylated tertiary alcohol. The structure of this impurity was confirmed by comparison (^{1}H n.m.r. and i.r. data and g.l.c. retention times) with an authentic sample prepared by reacting the lithio(trimethylsilyl)acetylide with ethyl propiolate (5% of a white solid). Distillation of (**4a**) *in vacuo* (120—122°/0.05 mm) did not remove the impurity. An analytically pure sample was obtained after repeated precipitation from pentane at -70 °C (m.p. 50—52 °C). Running the addition reaction to (**3**) in tetrahydrofuran (THF) caused the content of the contaminant to become as high as 30% and in that case the crude product did not solidify. Procedures involving diethyl carbonate[3] gave even more unsatisfactory results [10—15% yield of (**4a**) in THF at 45 °C]. Heating crude (**4a**) with acetic anhydride at 120 °C for 5—10 min gave the acetate (**4b**) in 70% yield, analytically pure after two re-crystallizations from methanol at -25 °C (m.p. 112—113 °C). Deprotection of (**4a**) or (**4b**) with dilute NaOH–CH$_2$Cl$_2$ at room temperature gave the desired triethynyl methanol (**1**) in 90% yield as a colourless oil, purified by molecular distillation at 60 °C/1 atm. (^{1}H n.m.r.: δ 2.8; i.r.: 3300, 2100 cm^{-1}).

Attempts to quaternize the central carbon atom in (**4**) gave surprising results. On addition of triethyl aluminium in hexane at room temperature, analogous to reactions of triaryl systems,[6] (**4b**) was rapidly converted into a mixture of products, from which the allenic material (**5a**) could be isolated in 20% yield as a colourless oil after centrifugal t.l.c. (silica gel, pentane) (i.r.: 1910, 2200 cm^{-1}). Reaction of (**4b**), inspired by the successful quaternization of protected propargylic acetates,[7] again gave rise to the formation of mixtures in which the tetraethynyl component showed up as the allene (**5b**). Tetraethynyl methane, a precursor of the first synthetic three-dimensional carbon network isomeric with diamond and graphite, remained elusive.

Treatment of (**4a**) with PBr$_3$ in diethyl ether at 0 °C gave rise to a complex mixture of compounds. The colour of the solution indicated the presence of cyclopentadienic



Scheme 1

material(s). From the reaction of (**3**) with PBr_5 in hexane, we were able to characterize the tetrabromide (**6a**) in 35% yield (60% with excess PBr_5) as a green–yellow solid (m.p. 46—47 °C). Stirring (**6a**) with powdered KI in acetone to effect a Finkelstein-type dimerization,[4] gave the corresponding di-iodide (**6b**) (m.p. 112—113 °C). By carrying out the Finkelstein dimerization of (**4a**) at room temperature in $CHCl_2$ using KI and a catalytic amount of 18-crown-6, adding to this mixture one equivalent of PBr_3 to generate the tertiary halide *in situ*, we were able to demonstrate the formation of the hexaethynyl ethane derivative (**7**) in 5% yield after repeated preparative t.l.c. (silica gel, pentane). Formation of (**7**) under these extremely mild conditions as well as the high yields obtained in the sequence (**2**) → (**3**) → (**4**) indicates that steric hindrance is unimportant in these systems.

Finally, in an experiment to prepare analytically pure (**4a**) from (**4b**) (methanol–HCl, room temp.), we obtained the methyl ether (**4c**) in 60% yield [purified by sublimation *in vacuo* (m.p. 49—52 °C)]. Using ethanol as solvent and trifluoroacetic acid as a catalyst (reflux, 30 min), the corresponding ethyl ether was produced in 90% yield as a crystalline solid (m.p. 102—103 °C) after sublimation.

The efficient synthesis of the triethynyl methanol (**1**) and the isolation of the protected monomers (**5a**) and (**5b**) completes the first stage of the realization of complex acetylenic networks and the preparation of epitaxial diamondoid material *via* synthetic organic pathways.

Received, 18th January 1988; Com. 8/00144H

References

1 R. Hoffmann, M. Kertesz, and T. Balaban, *J. Am. Chem. Soc.*, 1987, **109**, 6742, and references cited therein; I. V. Stankevich, M. V. Nikerov, and D. A. Bochvar, *Russ. Chem. Rev.*, 1984, **53**, 640.

2 A. G. McDiarmid, *Synth. Met.*, 1987, **21**, 79.

3 The t-butyl, methyl, and phenyl-substituted triethynyl methanols were reported earlier: C. K. Tseng, K. G. Migliorese, and S. I. Miller, *Tetrahedron*, 1974, **30**, 377.

4 H. Hauptmann, *Tetrahedron Lett.*, 1974, 3587.

5 H. Hauptmann, *Tetrahedron*, 1976, 1293, reported the preparation of ketone (**3**) in 80% yield *via* catalytic oxidation.

6 D. W. Harney, A. Meisters, and T. Mole, *Aust. J. Chem.*, 1974, **27**, 1639.

7 R. D. Nicholas, *Acc. Chem. Res.*, 1987, **20**, 207.