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Hydrosilylation Reactions of Bis(dimethylsilyl)acetylenes: A Potential Route to Novel σ- and π-Conjugated Polymers

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Abstract. Chloroplatinic acid catalyzes hydrosilylation reactions between bis(dimethylsilyl)acetylenes and simple aromatic monoethynyl compounds, yielding styrenic derivatives. Reactions of the bis(dimethylsilyl)acetylenes with aromatic diethynyl compounds yield conjugated short chain oligomers.

Many organic polymers and small molecules containing acetylenic moieties exhibit electrical conductivity or are useful as carbon precursors.[2] Organometallic acetylenic polymers have also been prepared and intensively investigated. In particular, organosilicon polymers containing acetylene units in the main chain have been shown to be useful preceramic materials and/or electrical conductors.[3]

Reflecting our own interest in organic and organosilicon acetylenic systems,[4] we were intrigued by reports of dehydrocondensation reactions occurring between trialkylsilanes and substituted acetylenes (eq. 1):[5]

$$Et_3SiH + HC{\equiv}CR \xrightarrow[I_2]{H_2PtCl_6} Et_3SiC{\equiv}CR + H_2 \qquad (1)$$

In accordance with this report, we reacted bis(dimethylsilyl)acetylene **1**, with phenylacetylene in an attempt to synthesize compound **2**. However, we found that the reaction did not proceed as predicted; instead, the β-trans-hydrosilylation product **3**, was produced in 66% yield (eq. 2). The presence of compound **2** was not detected in any of our experiments. Pursuing this reaction further, we eventually found that I_2 inhibited the hydrosilylation reaction somewhat, and better results were obtained using chloroplatinic acid alone as the catalyst.[6]

What was further surprising to us was that no products resulting from Si-H addition across the bis-silylated triple bond were recovered. The relative unreactivity of this bond was confirmed in an experiment in which **1** alone was treated with chloroplatinic acid. Compound **1** was recovered unchanged. Additionally, we have found that under these conditions compound **1** reacts with only aromatic substituted acetylenes;

reaction with propargyl chloride produced a complex mixture of products. A brief summary of our results is presented in Table 1.

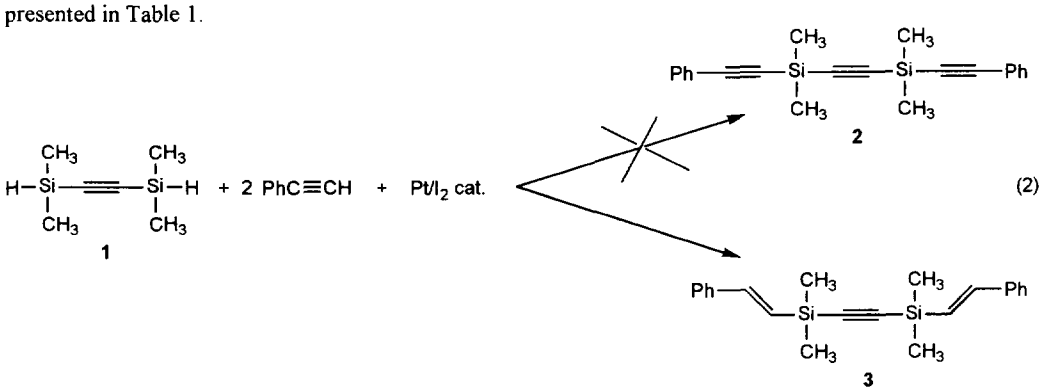
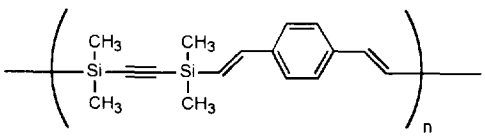


Table 1. Reactions of **1** with Various Monosubstituted Acetylenes

Acetylene	Yield (%)
phenylacetylene	66
1-bromo-3-ethynylbenzene	48[7]
1-bromo-4-ethynylbenzene	52[8]
propargyl chloride	complex mixture of products

In an attempt at utilizing this methodology to prepare polymers, compound **1** was reacted with 1,4-diethynylbenzene and 1,3-diethynylbenzene in separate experiments. In both cases, toluene was used as the solvent and the reaction mixtures were heated at 75°C for five hours. The yellow, powdery products **4**[9] (from 1,4-) and **5**[10] (from 1,3-) were isolated by precipitation into methanol in 56-57% yield. In both cases, ^{1}H and ^{13}C NMR spectroscopy indicated that hydrosilylation had occurred as observed previously with the monosubstituted acetylenes. The products were shown by ^{1}H NMR integration to be short chain oligomers consisting of 5-7 repeat units.



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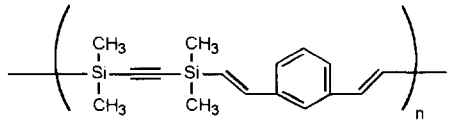

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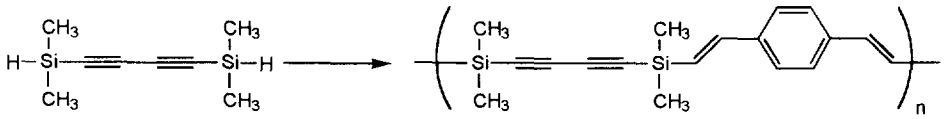
These polymers do not melt but are soluble in common organic solvents. These materials could possess interesting electrical properties since each repeating unit consists of alternating phenylene-vinylene and bis-silylated acetylene units. It is well known that poly(phenylene-vinylene)s are excellent organic electrical conductors, and poly(silylene-acetylenes) are also known to possess electrical conductivity through σ- and π-conjugation.[3]

Preliminary experiments show that bis(dimethylsilyl)diacetylene **6**, also reacts with 1,4-diethynylbenzene to form conjugated polymers (eq. 3):



(3)

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Complete investigations on the synthesis and properties of these novel conjugated polymers are currently underway in our laboratories.

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[6] Procedure: A 25-mL, round-bottomed flask was equipped with a stir bar and capped with a septum. Compound **1** (0.5 g, 3.5 mmol), phenylacetylene (0.77 mL, 7.0 mmol), and hexane (5 mL) were added to the flask to make a clear solution. Several drops of CPA solution were added with stirring. A moderate exotherm was observed. After one hour of stirring, a white precipitate had formed. After a total of 5 hours stirring at room temperature, all volatiles were evaporated from the reaction mixture. The pale yellow solid residue was recrystallized from chloroform/methanol, yielding compound **3** as white needles (0.56 g, 46%, mp 131°C). Yields from this reaction were as high as 66%. ^{1}H NMR (ppm) 0.36 (s, 12H, -CH_3), 6.44 (d, 2H, vinyl, J = 19 Hz), 7.09 (d, 2H, vinyl, J = 19 Hz), 7.32-7.48 (mult, 10H, aromatic); ^{13}C NMR (ppm) -1.12 (SiCH_3), 113.2 (*C*≡*C*), 125.2, 126.6, 128.3, 128.5, 137.9, 145.7.

[7] ^{1}H NMR (ppm) 0.40 (s, 12H, -CH_3), 6.48 (d, 2H, vinyl), J = 19 Hz), 7.02 (d, 2H, vinyl, J = 19 Hz), 7.23-7.63 (mult, 8H, aromatic); ^{13}C NMR (ppm) -1.23 (-Si*C*), 113.1 (*C*≡*C*), complex set of peaks between 122 and 144 ppm.

[8] ^{1}H NMR (ppm) 0.36 (s, 12H, -SiCH_3), 6.43 (d, 2H, vinyl, J = 19 Hz), 7.00 (d, 2H, vinyl, J = 19 Hz), 7.29-7.47 (dd, 8H, aromatic); ^{13}C NMR (ppm) -1.21 (-Si*C*), 113.2 (*C*≡*C*), 122.2, 126.2, 128.1, 131.6, 136.8, 144.3.

[9] ^{1}H NMR (ppm) 0.35 (s, 12H, -SiCH_3), 6.44 (d, 2H, vinyl, J = 19 Hz), 7.05 (d, 2H, vinyl, J = 19 Hz), 7.42-7.44 (broad, 4H, aromatic); traces of ethynyl protons appear as a resonance at 3.15 ppm; traces of α-addition product are also present as evidenced by peaks at 5.8 and 6.0 ppm; ^{13}C NMR (ppm) -1.10, 78.0, 83.6, 113.0, 125.5, 126.5, 126.9, 132.3, 137.9, 145.2.

[10] ^{1}H NMR (ppm) 0.35 (s, 12H, -SiCH_3), 6.45 (d, 2H, vinyl, J = 19 Hz), 7.05 (d, 2H, vinyl, J = 19 Hz), 7.26-7.55 (mult, 4H, aromatic); traces of ethynyl protons appear as a resonance at ~3.0 ppm; traces of α-addition product are also present as evidenced by peaks at 5.8 and 6.0 ppm; ^{13}C NMR (ppm) -1.10, 77.3, 84.0, 113.2, complex set of peaks between 125 and 145 ppm.

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