Oligoacetylenic sulfides

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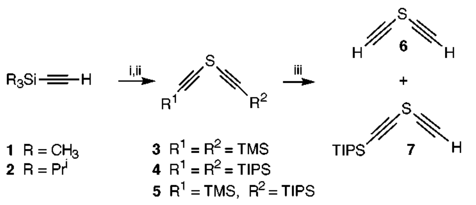
Linear acetylenic and diacetylenic sulfides consisting of up to eight triple-bond units with alternating sulfur atoms and acetylene units were synthesized.

The synthesis of conjugated or homoconjugated cyclic or linear oligoacetylene systems is a rapidly developing research frontier and has attracted considerable attention from both fundamental and applied viewpoints.[1] These all-carbon or carbon-rich acetylene-based scaffolds are expected to exhibit a variety of unusual structural, electronic, electrical and optical properties.[2–4] Linear rigid oligoacetylenic molecular rods of defined length in nanometer-sized structures could also serve as molecular wires in molecular electronic application.[5–7]

For the conjugated oligoacetylenic systems, a representative example is a compound with six conjugated diacetylene units synthesized by Diederich's group through end-capping polymerization.[8] Molecular wires end-capped with redox-active metal groups have also been reported.[9,10] The longest molecule of this group has up to ten conjugated acetylene units. Novel heterocycles comprising alternating phosphorus atoms and acetylene units reported by Scott's group are also known.[11] Dendrimers with acetylenic units[12] and alkynyl sulfides[13] have also been prepared. However, to the best of our knowledge, there is no report on linear oligoacetylenic compounds containing heteroatom bridging between all or some of the acetylene units. Based on our experience in the preparation and uses of acetylenic sulfoxides and related compounds in organic synthesis,[14] a systematic approach to the syntheses of oligomeric acetylenic sulfides with up to eight acetylene units is reported here.

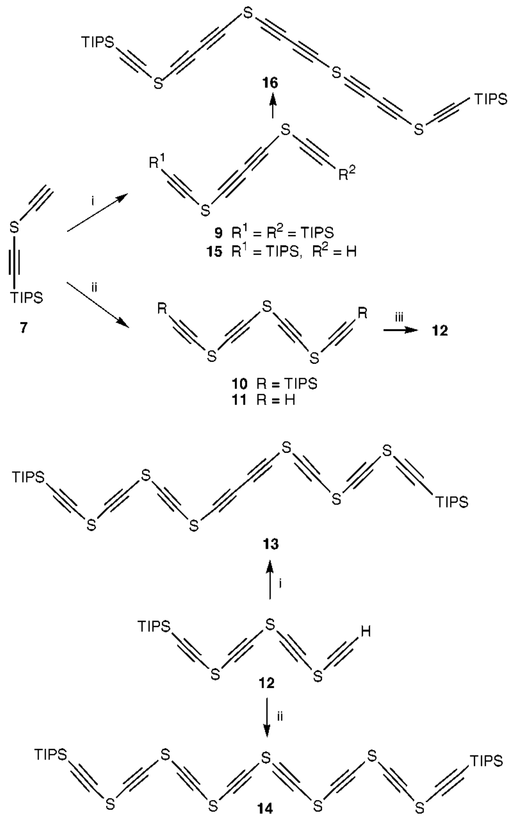
Two key reactions, namely sulfurization and oxidative coupling *via* Hay and Glaser-type related methods,[15] were used in building up the oligomeric acetylenic sulfides. Chain length is doubled in each cycle of the reaction.

The crucial starting material, a mono-protected bis-acetylene sulfide **7**, was first prepared. When an equal molar ratio of trimethylsilylacetylene **1** and triisopropylsilylacetylene **2** was treated with 1 equiv. of BuLi followed by 0.5 equiv. of SCl_2 at −78 °C, a mixture of silylated bis-acetylene sulfides (**3**–**5**) were formed (Scheme 1). The reaction mixture was placed under mild desilylation conditions (K_2CO_3/MeOH). The TMS group was hydrolyzed while the TIPS group remained intact. The volatile bis-acetylene sulfide **6** resulting from the hydrolysis of **3** was lost during work up and solvent evaporation. The remaining mono- and di-TIPS bis-acetylene sulfides **7** and **4** could be easily separated by column chromatography, with the mono-silylated compound **7** being the more polar component. The overall isolated yield of the desirable mono-protected compound **7** was 40%. The recovered di-TIPS acetylene sulfide **4** could also serve as the precursor of **7** through careful monodesilylation with KF in MeOH under close monitoring with TLC.



Scheme 1 *Reagents and conditions*: i, BuLi; ii, SCl_2, −78 °C; iii, K_2CO_3, MeOH.

Oxidative coupling and sulfurization reactions were then used in the chain elongation of the acetylenic sulfide. Several sets of oxidative coupling conditions for acetylene compounds were studied. Eventually, we found that the original Hay conditions[16] using CuCl and TMEDA afforded satisfactory results. For sulfurization, freshly distilled SCl_2 was used. Alternatively, a stable solid sulfurization agent, bis(benzenesulfonyl) sulfide **8**,[17] used extensively by Scott could also be used. As shown in Scheme 2, oxidative coupling of **7** afforded diacetylene compound **9** in 94% yield. Sulfurization of **7** with SCl_2 afforded sulfide **10** in 72% yield. Mono-deprotection of **10** to **12** was achieved by a carefully controlled desilylation procedure using KF in THF–H_2O in the presence of a catalytic amount of Bu_4NBr. The reaction was monitored closely *via* TLC and was stopped when **11** started to appear. Mono-deprotected **12** could be isolated in 35% yield after column chromatography with the recovery of about 16% of the starting material. If the desilylation reaction was allowed to run for a longer time at room temperature, the unprotected terminal acetylene compound **11** could also be isolated. The unprotected

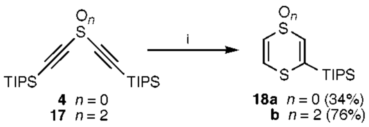


Scheme 2 *Reagents and conditions*: i, CuCl, TMEDA, air, $CHCl_3$; ii, BuLi or LIHMDS, then SCl_2 or **8** ($PhSO_2SSO_2Ph$); iii, KF, THF–H_2O, Bu_4NBr (cat.).

Table 1 Spectral data of acetylenic sulfides

Compound	δ_C sp^3 (Pr^i)	δ_C sp	δ_H	ν_{max}/cm^{-1}	$\lambda_{max}{}^a$/nm (ε/dm^3 mol^{-1} cm^{-1})
4	11.23, 18.49	87.75, 100.49	1.05(s)	2098	231 (20600)
7	11.23, 18.49	67.82, 84.22,^{b} 86.18, 101.29	1.06(s), 2.97(s)	3303, 2103	
9	11.23, 18.51	68.50, 82.09, 84.48, 102.84	1.11(s)	2104	
10	11.22, 18.51	81.56, 83.06, 85.97, 101.37	1.07(s)	2102	231 (41500)
11		66.38, 81.94, 82.16, 84.66^b	2.99(s)	3289, 2098	
12	11.20, 18.51	66.51, 81.21, 81.65, 82.53, 83.58, 84.58^b, 85.77, 101.47	1.07(s), 2.99(s)	3297, 2103	
13	11.23, 18.53	67.45, 79.87, 80.66, 81.69,83.85, 83.92, 85.68, 101.65	1.12(s)	2101	260 (97400)
14	11.22, 18.53	80.85, 81.26, 81.74, 82.01,82.55, 83.67, 85.72, 101.58	1.07(s)	2100	237 (63900)

^{a} In cyclohexane. ^{b} C≡*C*H.



Scheme 3 *Reagents and conditions*: i, Na_2S, Al_2O_1, DMF–MeOH.

and mono-protected acetylenic sulfides **11** and **12** are very unstable, especially when concentrated.

Freshly prepared **12** was subjected to the coupling and sulfurization cycles to extend the chain to eight acetylene units. Coupling afforded diacetylene compound **13** in 55% yield. For the sulfurization process, we found that BuLi reacted with the triple bonds of **12** to give complicated products. Therefore, LIHMDS was used instead and **14** was prepared in 25% yield using **8** as the sulfurization agent. Monodesilylation of **9** to **15** could also be achieved under carefully controlled conditions. However, the coupling product **16**, which could be detected by FAB MS, was extremely unstable and could not be isolated in pure form.

All these new acetylenic sulfides were characterized by NMR, IR and MS. Some of the spectral data are summarized in Table 1. The typical IR frequency of the triple bond is around 2100 cm^{-1}, and the terminal acetylene C–H signal appears around 3300 cm^{-1}. UV spectra of oligoacetylene sulfides **4**, **10**, **13** and **14** were also recorded. There is no observable bathochromic shift (λ_{max} = 231–237 nm) for compounds **4**, **10** and **14** as the chain length increased. This indicated that the degree of conjugation between the acetylene units is weak. Compound **13**, being a diacetylene compound, showed a slight bathochromic shift (λ_{max} = 260 nm) relative to compounds **4**, **10**, **14** and had a large molar absorptivity.

We also explored the chemistry of double conjugate addition of nucleophiles to the terminal positions of the bis-acetylene sulfides and the corresponding sulfones.[18] Reactions with Na_2S impregnated on neutral alumina[19] took place readily in DMF–MeOH mixture at 0 °C and room temperature respectively for **4** and **17** (Scheme 3). However, to our surprise the mono-desilylated compounds **18a**,**b** were the only isolated products. The structure of cyclic sulfone **18b** was confirmed by X-ray analysis (Fig. 1).†

In summary, the first syntheses of a series of oligoacetylenic sulfides with alternating sulfur atoms and acetylene or diacetylene units were accomplished using the monoprotected bis-acetylene sulfide **7** as the starting material. Studies on the synthesis of some cyclic and metal end-capped analogs[20] are in progress.

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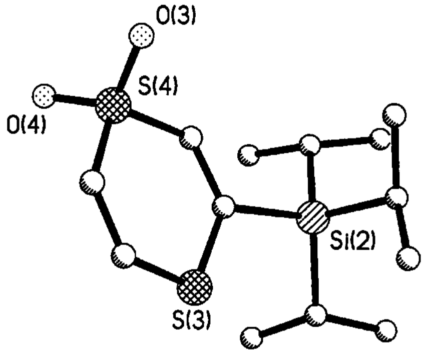

Fig. 1 X-Ray structure of **18b**.

Notes and references

† *Crystal data* for **18b**: $C_{13}H_{24}O_2S_2Si$, M = 304.53, triclinic, $P\bar{1}$ (no. 2), a = 7.9504(5), b = 15.857(1), c = 16.001(1) Å, α = 118.632(1), β = 98.449(1), γ = 97.355(1)°, V = 1705.0(2) Å^3, Z = 4, T = 293 K, μ(Mo-Kα) = 3.76 cm^{-1}, 10061 reflections measured, 7271 unique, R(int) = 0.0128, final R_1 = 0.039, wR_2 = 0.1061 (based on F^2) for 7271 [$I > 2\sigma(I)$] observed reflections. CCDC 182/1493. See http://www.rsc.org/suppdata/cc/a9/a908220d/ for crystallographic data in .cif format.

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