



Synthesis of oligoenynes and oligomeric conjugated diacetylenes

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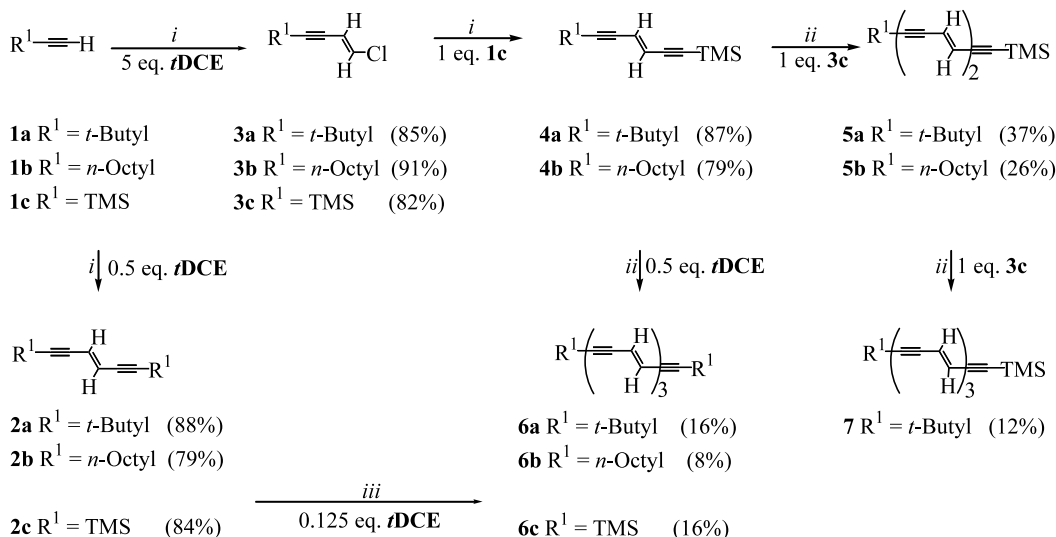
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Abstract—Novel oligoenynes and oligomeric conjugated diacetylenes have been synthesized via a new Pd/Cu-catalyzed reaction scheme. This Sonogashira-style preparation of oligoenynes has complementary properties to previously published procedures via ionic intermediates. © 2003 Elsevier Science Ltd. All rights reserved.

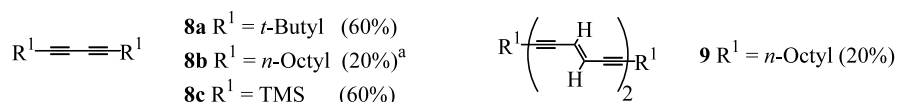
The tremendous growth in interest in the chemistry and physics of conjugated polymers has led to an increased demand for well-defined oligomers thereof for the detailed study of the evolution of optoelectronic properties in relation to, e.g. the length, planarity and stacking features of the conjugated systems. Such studies are extensive for e.g. the fields of oligothiophenes,¹ oligoarylenevinylenes,² and oligotriacetylenes.³ There are, however, only a few accounts in the literature in which oligodiacetylenes (ODAs) have been synthesized and characterized.^{4,5} This is remarkable, given the widespread interest in polydiacetylenes [PDAs; backbone

structure $-(C\equiv C-CR=CR)_n-$]; >2000 published papers since 1990.⁶ Furthermore, spectroscopic characterizations of these ODAs have largely been limited to NMR, IR, and UV–vis measurements, especially for ODAs and PDAs in solution. For instance, data on *both* the absorption and emission spectrum in solution are, to the best of our knowledge, only reported for the trimeric ODA, (3*E*)-Me₃C-(C≡C-CH=CH)₃-C≡C-CMe₃.⁷ As part of our ongoing investigation into PDAs,^{8–10} we were thus interested in synthesizing and characterizing a number of ODAs, with a special focus on their absorption and emission spectra in solution,



Scheme 1. Reagents and conditions: (i) 5 mol% Pd(PPh₃)₄, 10 mol% CuI, 2 equiv. piperidine in dry THF, rt; (ii) cat. NaH/1 equiv. MeOH, then (i) with either *t*DCE or **3c**; (iii) cat. NaH/0.25 equiv. MeOH, then (i) with *t*DCE.

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Scheme 2. Diacetylenes formed during ODA syntheses. ^aUnisolated yield as determined by GC–MS.

fluorescence anisotropy and direction of transition dipole moments, as well as possible electronic effects of end groups.¹¹

Wudl and Bitler^{4,12,13} were the first to report on the synthesis of stereospecific all-*trans* ODAs up to the pentamer bearing *t*-butyl end groups. Subsequently, Giesa and Schulz⁵ reported the syntheses of similar ODAs with *t*-butyl end groups up to the heptamer. Lindsell et al.¹⁴ have also prepared short *cis*- and *trans*-ODAs bearing phenyl and trimethylsilyl (TMS) groups. In all these instances, however, reactions involved ionic intermediates and low temperatures (–78°C). Since we wished to prepare ODAs bearing an *n*-alkyl chain,¹⁵ it was decided to avoid making use of small, hard nucleophiles like methyl and *n*-butyl anions, due to the potential competition of α -H-abstraction from the alkyl side-chain during formation of alkynyl and alkenynyl metal halide intermediates.

In this context, the Sonogashira^{16,17} reaction offers milder reaction conditions for syntheses of ODAs. Hence, Pd/Cu-catalyzed coupling (Scheme 1) of terminal acetylenes **1a**, **1b** and **1c** with *trans*-1,2-dichloroethene (*t*DCE) in a 1:0.5 ratio afforded ODAs **2a**, **2b** and **2c**, respectively, with **2a** being obtained in better yields than via an ionic route.^{4,5} Reaction of terminal acetylenes **1a**, **1b** and **1c** with a large excess of *t*DCE affords the synthons **3a**, **3b** and **3c**, respectively, also in better yield than was obtained for ionic coupling reactions with *trans*-1,2-diiodoethene.^{4,5} A further improvement for the synthesis of compounds **3a**, **3b** and **3c** is that in contrast to the *trans*-1,2-diiodoethene or *trans*-1-chloro-2-iodoethene required for the ionic coupling, our approach makes use of commercially available *t*DCE.

Compounds **3a** and **3b** were reacted with trimethylsilylacetylene **1c** to afford **4a** and **4b**, respectively, with again better yields being obtained for the former than via an ionic approach.^{4,5} Removal of the TMS groups in **4a**, **4b** and **2c** via NaH/MeOH, and subsequent Pd/Cu-catalyzed coupling with *t*DCE in turn affords **6a**, **6b** and **6c**, respectively. Similar deprotection of **4a** and **4b** and subsequent reaction with **3c** gave **5a** and **5b**, respectively. Further reaction of desilylated **5a** with **3c** afforded trimer **7**.

All coupling reactions were carried out under anhydrous conditions and N₂ atmosphere (Glaser reaction conditions). These conditions also provide access to even more extensively conjugated enyne-like oligomers, which arise from self-coupling of terminal alkynes and deprotected oligoenynes under our reaction conditions (Scheme 2).

A Pd/Cu-catalyzed coupling of terminal acetylenes **1a**, **1b** and **1c** resulted in symmetrical diacetylenes **8a**, **8b** and

8c, respectively, while desilylated **4b** leads to formation of **9** under the same reaction conditions. The latter diacetylene was unstable in both the solid state and in solution, and readily polymerized under the influence of visible light.

Vollhardt and Winn¹⁸ have reported on the formation of similar by-products in the reactions of *t*DCE with small terminal acetylenes. Siemsen et al.¹⁹ have also reviewed this Glaser reaction, and this reaction yields product distributions depending upon the reaction conditions and catalysts used.^{20–24} We found no real difference in using degassed solvents or not, but use of N₂ did increase oligoenyne yields.

Furthermore, reactions involving desilylated ODA intermediates were typically accompanied by polymerization reactions, especially with increasing oligoenyne length, as evidenced by formation of intractable residues. The instability of short unprotected oligoenynes has been reported previously,¹³ and is expected to become more problematic with increased conjugation length. This is exemplified by the failure of desilylated dimers, viz. **5a** and **5b**, to yield the corresponding pentamers via Pd/Cu-catalyzed coupling with *t*DCE, in contrast to synthetic routes involving ionic intermediates.

Compounds **2a**,⁵ **2c**,¹⁸ **3a**,⁵ **3c**,⁵ **4a**,⁵ **5a**,⁵ **6a**,⁵ **7**,⁵ **8a**¹⁸ and **8c**¹⁸ had physical and spectroscopic characteristics consistent with those reported in the literature. New compounds **2b**, **3b**, **4b**, **5b**, **6b**, **6c** and **9** were fully characterized and afforded physical and spectroscopic data consistent with their molecular structures.

As expected, an increase of the number of enynic units leads to both higher extinction coefficients and red-shifting of absorption maxima (Fig. 1). Substituent

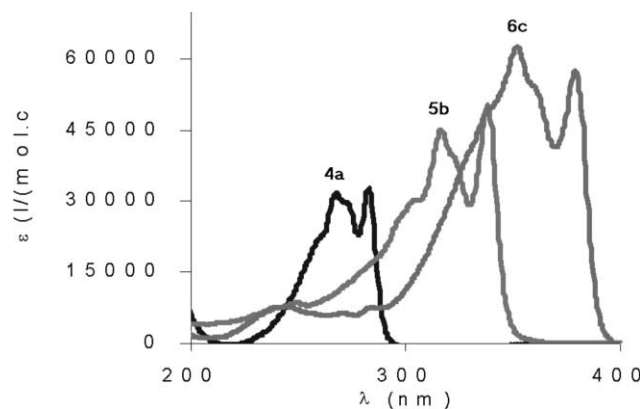


Figure 1. Absorption spectra of oligomers **4a**, **5b** and **6c**.

effects on the absorption properties are evident from higher ϵ values and greater red-shifting for ODAs bearing trimethylsilyl (TMS) substituents, a result of the better electron-donating ability of TMS relative to alkyl groups. The solvent-induced shift of the absorption band increased with increasing conjugation length, but even for the trimer **6c** $\Delta\lambda \approx 5$ nm, which is still small in comparison to PDAs ($\Delta\lambda \approx 20$ nm).²⁵ A detailed analysis of the photophysics of these materials will be published elsewhere.¹¹

In conclusion, Sonogashira-style synthesis provides a viable route towards oligoenynes and is superior to previously reported ionic routes for low molecular weight (monomeric and dimeric) ODA syntheses. This approach is thus complementary to ionic synthetic routes, due to the propensity of deprotected ODAs to undergo polymerization as the oligoenyne length increases, a complication that can be circumvented by employing an ionic synthetic approach in which no free $\text{C}\equiv\text{C}\text{--}\text{H}$ species are produced as intermediates at any stage.

General procedure for coupling of terminal acetylenes with *t*DCE, **3a, **3b** or **3c**:** To a solution of CuI (0.1 equiv.), Pd(PPh₃)₄ (0.05 equiv.), piperidine (2 equiv.) and *t*DCE (0.5 or 5 equiv.) or **3a**, **3b** or **3c** (1 equiv.) in THF, maintained at ca. 15–20°C under N₂, was added, dropwise with stirring, the appropriate acetylene (1 equiv.). After 2–3 h the reaction was quenched with saturated NH₄Cl and the aqueous layer separated and extracted with petroleum ether (bp 40–60°C) (PE) (3×30 mL). The combined organic extracts were washed with water (3×50 mL), dried over MgSO₄, concentrated by evaporation under reduced pressure and purified by distillation under vacuum, by column chromatography or by recrystallization.

General procedure for coupling of trimethylsilyl oligoenynes with *t*DCE or **3c:** To a solution of NaH (catalytic) and MeOH (1 equiv.) in THF was added the 1-(trimethylsilyl)substituted oligodiacetylene (1 equiv.). After complete desilylation (followed by TLC, GC or GC–MS) the same procedure as outlined previously was followed. Data for **6b** and **6c** are representative. **6b**: Mp 96.9–99.8°C; ν_{max} (KBr/cm^{−1}) 3021 (=CH- str, m), 2209 (C≡C str, v), 841 (=CH- def); δ_{H} (400 MHz, CDCl₃) 0.90 (6H, t, $J_{\text{H2-H1}}$ 8.00, -CH₃), 1.29–1.59 (24H, m, H₂–H₇, H₂₄–H₂₉), 2.34 (4H, t, $J_{\text{H7-H8}}$ 6.88, H₈, H₂₃), 6.00–6.18 (6H, m, =CH-); δ_{C} (100 MHz, CDCl₃) 14.50 (C₁, C₃₀), 20.14 (C₂, C₉), 23.04 (C₃, C₂₈), 28.91 (C₄, C₂₇), 29.30 (C₅, C₂₆), 29.47 (C₆, C₂₅), 29.56 (C₇, C₂₄), 32.22 (C₈, C₂₃), 79.70 (≡C-), 92.72 (≡C-), 94.60 (≡C-), 98.16 (≡C-), 119.41 (=CH-), 121.08 (=CH-), 122.94 (=CH-); EI: calculated for C₃₀H₄₀, 400.3130; measured, 400.3124. **6c**: mp 140.5–141.5°C; ν_{max} (CHCl₃/cm^{−1}) 3030 (=CH- str, m), 2159 (C≡C str, v), 830 (=CH- def, s); δ_{H} (400 MHz, CDCl₃) 0.22 (18H, s, -SiCH₃), 6.01–6.20 (6H, m, =CH-); δ_{C} (100 MHz, CDCl₃) 0.14 (-SiCH₃), 94.01 (≡C-), 94.48 (≡C-), 102.12 (≡C-), 103.50 (≡C-), 121.42 (=CH-), 121.71 (=CH-), 121.91 (=CH-); EI: calculated mass for C₂₀H₂₄Si₂, 320.1417; measured, 320.1417.

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