β-Chlorovinylsilanes as masked alkynes in oligoyne assembly: synthesis of the first aryl-end-capped dodecayne†

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An aryl-end-capped dodecayne has been prepared using a four-fold fluoride-mediated dechlorosilylation of a masked dodecayne precursor containing four β-chlorovinylsilane residues that serve as masked alkynes; the unstable dodecayne product has been characterised by UV-vis absorption spectroscopy and 'matrix-free' MALDI-TOF mass spectrometry.

Poly(alk(2*n* + 1)yne), also known as carbyne (Fig. 1), represents the fourth allotrope of carbon, after diamond, graphite and the fullerenes.[1,2] The regular alternating sequence of single bonds and triple bonds in this polymer lends itself to an iterative synthesis involving oxidative coupling of alkyne fragments; however, a controlled synthesis of this form of carbon using this—or any other—approach is beset with problems associated with its relative instability and propensity to react further, especially in the solid state.[1,2]

Oligoynes represent clipped versions of carbyne and are a more tractable synthetic target.[3–6] That said, the preparation of systems beyond the hexayne still remains a challenging synthetic problem. Of the various approaches to oligoyne assembly, which have been disclosed, most rely on oxidative acetylenic coupling reactions to construct the oligoyne framework.[3,4,6,7] Whilst this strategy has met with appreciable success, especially for systems that can be stabilised by sterically demanding end-capping groups,[4,5,8] in particular metal-based units,[3,9] this approach becomes increasingly unsatisfactory as the length of the conjugated oligoyne increases. For this reason, a number of alternative approaches have been reported, which obviate the need to employ free oligoynes of any length in oxidative acetylenic coupling.[10] The work of Tykwinski and co-workers, who have pioneered the use of the Fritsch–Buttenberg–Wiechell reaction in oligoyne assembly, is particularly noteworthy.[5,11]

We postulated that β-chlorovinylsilanes would offer an attractive alternative alkyne masking strategy for oligoyne assembly, as the desired product should be accessible in a selective manner from its protected precursor through the action of fluoride (Scheme 1).[12] Drawing analogy with approaches, which have proved successful in the preparation of other non-aromatic, π-conjugated organic oligomers,[13] we initially considered enediyne **1**, in which the β-chlorovinylsilane masks a third alkyne, as a potential monomer for oligoyne assembly. However we argued that the unsymmetrical nature of this building block would necessarily lead to the formation of each masked oligoyne in the series as a mixture of constitutional isomers through head-to-head and head-to-tail couplings, something which would hinder compound characterisation of the intermediate oligo(enediyne) precursors, which are interesting targets in themselves. Differentially substituting the alkyne termini in **1**, and dimerising to a centrosymmetric masked hexayne **2**, would neatly circumvent this problem and provide a larger monomer unit, which would also allow a more rapid method for long-chain oligoyne assembly. To this end, we recently reported a completely selective synthesis of masked triyne **3** (Scheme 2).[14] Our method allows the incorporation of a range of silyl groups into the internal (*E*)-β-chlorovinylsilane, and significantly, the differentiation of the two alkyne termini. Masked triyne **3** provides our starting point for oligoyne assembly. Herein we report its application in the synthesis of an aryl-end-capped dodecayne, which represents the longest aryl-end-capped oligoyne reported to-date.

Masked triyne **3** was prepared according to our established methodology in nine steps and 52% overall yield from TMS-acetylene.[14] Dimerisation to the corresponding masked hexayne **4** using the standard Eglinton–Glaser–Hay oxidative coupling conditions,[7] however, provided the desired product in <10% yield. A range of Pd-mediated acetylenic coupling methods were also investigated,[15] although none offered any significant improvement. Returning to the more commonly used copper-mediated

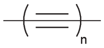
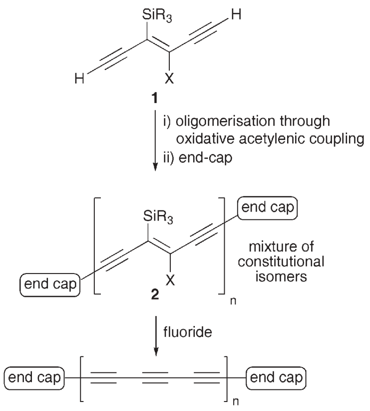


Fig. 1 Carbyne represents a fourth allotrope of carbon.



Scheme 1 β-Chlorovinylsilanes as masked alkynes in oligoyne assembly.

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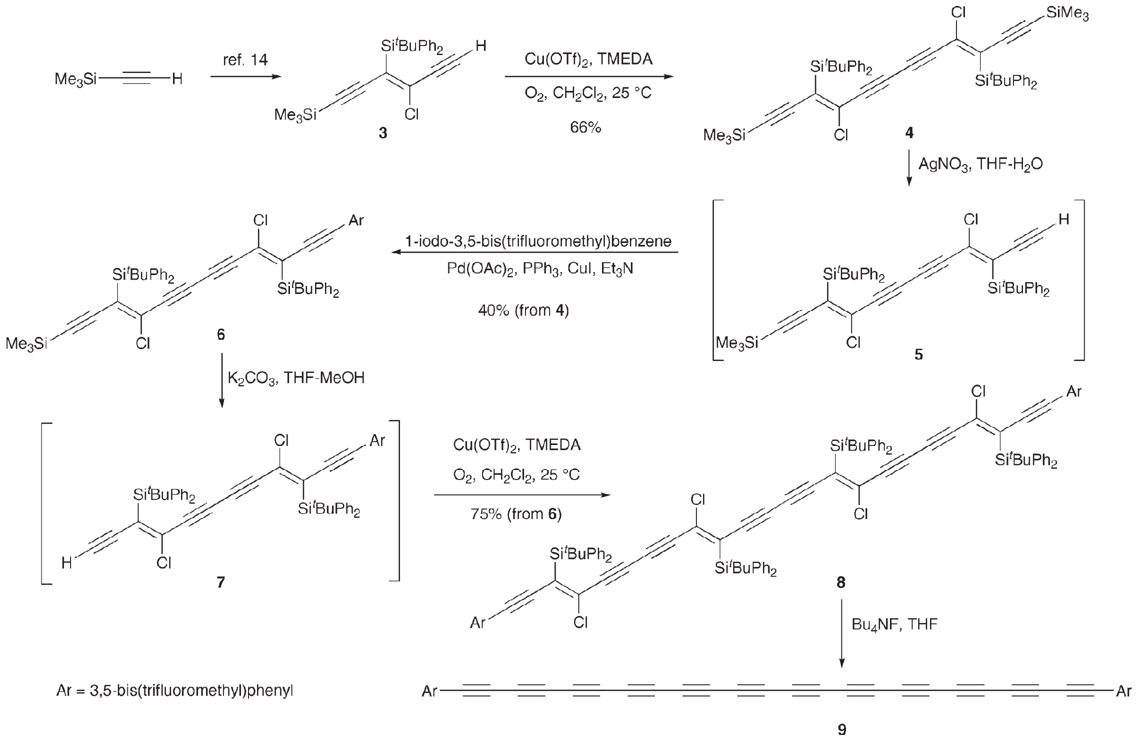

Scheme 2 Synthesis of dodecayne **9**.

coupling methodology, careful analysis of the reaction mixture by mass spectrometry revealed dimerisation was indeed proceeding; however the low yield of the desired hexayne **4** was a consequence of partial premature dechlorosilylation. We hypothesised that the relatively nucleophilic halide anion present in the reaction mixture (CuCl and CuI are the most common sources of copper in this type of coupling reaction) was responsible for effecting this elimination side-reaction, and therefore a range of alternative copper sources was investigated.‡ Gratifyingly, Cu(OTf)$_2$, which possesses a very weakly nucleophilic triflate counteranion, efficiently circumvented the problem of premature dechlorosilylation and now permitted the masked hexayne **4** to be obtained in a greatly improved 66% isolated yield.

With a centrosymmetric masked hexayne **4** in hand, deprotection of one of the trimethylsilyl end-caps was best achieved under the very mild conditions afforded by AgNO$_3$ in THF–H$_2$O.[16] The use of K$_2$CO$_3$ in THF–MeOH was also effective for trimethylsilyl deprotection; however, the rapidity of reaction meant that it proved difficult to isolate the mono-deprotected product in significant quantities. Monodeprotected masked hexayne **5** was not particularly stable and hence was used directly without purification in a Sonogashira coupling with 1-iodo-3,5-bis(trifluoromethyl)benzene to provide mono-aryl-end-capped masked hexayne **6**. Usefully, the CF$_3$ groups in this aryl end-cap allowed the purity of the coupled product **6**, and all subsequent compounds in the sequence, to be assessed by ^{19}F NMR.§. Removal of the remaining TMS group in **6** with K$_2$CO$_3$ in THF–MeOH, and immediate oxidative coupling of the free alkyne intermediate **7** under our modified Eglinton–Glaser–Hay coupling conditions, afforded masked dodecayne **8** in good yield. Four-fold dechlorosilylation with TBAF in THF effected rapid reaction; however all attempts to isolate the oligoyne product **9** proved futile. Fortunately, as the UV-vis spectra of oligoynes are particularly characteristic in appearance,[4,11,17] and very different from the spectrum of the masked dodecayne precursor (Fig. 2), we were able to monitor the unmasking reaction and characterise the oligoyne product by UV-vis spectroscopy. After careful experimentation with varying quantities of TBAF, we found that treating a solution of masked dodecayne **8** with 4 equiv. of TBAF at room temperature, led to the formation of the dodecayne **9** over a period of a few min. Unfortunately, even at the low concentrations (10^{-6} M) required for recording UV-vis spectra, extensive decomposition of the product was evident as the UV spectrum of dodecayne **9** decayed when the solution was assayed after 1 h; in spite of the instability of the dodecayne we were pleased to observe the molecular ion for the product by MALDI-TOF

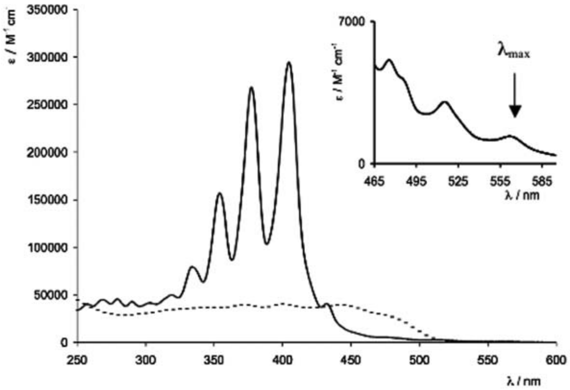

Fig. 2 UV-vis spectrum of masked dodecayne **8** (dashed line) and dodecayne **9**. Inset shows expansion of region II of spectrum for **9** highlighting the low intensity, long wavelength absorptions.

analysis of the reaction mixture. Interestingly, the best results were observed in the *absence* of a matrix (see ESI†).

The UV-vis data for the masked dodecayne **8** and the four-fold dechlorosilylation dodecayne product **9** are shown in Fig. 2.¶ The differences in the two spectra are immediately apparent with that for the dodecayne product showing the typical π–π^* absorptions of oligoynes. In the region between 330 and 405 nm (region I), several vibrational bands, exhibiting increasing intensity with increasing wavelength are clearly observable, reaching a maximum value of ε = 295000 M^{-1} cm^{-1} for the most intense band at 405 nm. At longer wavelengths (region II), a number of much weaker (ε <6000 M^{-1} cm^{-1}) absorption bands are present (see inset in Fig. 2). These low-intensity bands are characteristic of aryl-end-capped oligoynes.[4,11,17] The value of 562 nm for λ_{max} is higher than the values reported by Hirsch,[18] and Walton,[19] for shorter aryl end-capped decaynes. However, it remains to be seen as to whether saturation has been reached for this class of oligoyne.|| To probe whether this is the case, the octadecayne trimer will be our next target.

Dodecayne **9** represents the longest oligoyne possessing aryl termini reported to-date. Although it may be possible to improve the stability of the dodecayne by increasing the steric bulk of the aryl end-caps, this mode of stabilisation alone is unlikely to provide sufficient stability for the trimer in the series, namely the octadecayne. Instead, we are currently investigating molecular encapsulation methods, which will provide insulation along the entire length of the conjugated framework,[20,21] rather than relying solely on stabilising groups at the oligoyne termini.

In summary, the synthesis of an aryl-end-capped dodecayne has been achieved for the first time, in a controlled fashion from a masked hexayne building block in which two of the internal alkynes are protected as β-chlorovinylsilanes. This novel approach to oligoyne assembly differs from the majority of previous strategies: by using such a large monomer unit, only one oxidative acetylenic coupling is required to access what is the longest aryl end-capped oligoyne reported to-date. Furthermore, our approach does not rely on oxidative coupling of long-chain terminal oligoynes to afford the end-product; rather, the *entire* carbon chain, 24 carbons in the case of dodecayne **9**, is already installed *before* the oligoyne is released, which prevents the formation of shorter oligoynes resulting from loss of acetylene fragments that is sometimes observed when traditional approaches are taken.[4,5]

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Notes and references

‡ $Cu(OAc)_2$, $Cu(NO_3)_2$, CuI, CuCl, $CuCl_2$, CuBr, $CuBr_2$ and $Cu(OTf)_2$ were investigated.

§ See ESI† for full characterisation data.

¶ See ESI for a full breakdown of absorption peaks and their associated molar extinction coefficients.†

|| See ESI for a more detailed analysis.†

1 S. Szafert and J. A. Gladysz, *Chem. Rev.*, 2006, **106**, PR1; S. Szafert and J. A. Gladysz, *Chem. Rev.*, 2003, **103**, 4175.

2 X. Y. Chaun, T. K. Wang and J. B. Donnet, *New Carbon Mater.*, 2005, **20**, 83; A. Lamperti and P. M. Ossi, *Chem. Phys. Lett.*, 2002, **376**, 662; A. Scemama, P. Chaquin, M. C. Gazeau and Y. Benilan, *Chem. Phys. Lett.*, 2002, **361**, 520; Y. P. Kudryavtsev, S. Evsyukov, M. Guseva, V. Babaev and V. Khvostov, *Chem. Phys. Carbon*, 1997, **25**, 1; F. Cataldo, *Polym. Int.*, 1997, **44**, 191; L. Kavan and J. Kastner, *Carbon*, 1994, **32**, 1533.

3 Q. L. Zheng, J. C. Bohling, T. B. Peters, A. C. Frisch, F. Hampel and J. A. Gladysz, *Chem.–Eur. J.*, 2006, **12**, 6486.

4 T. Gibtner, F. Hampel, J.-P. Gisselbrecht and A. Hirsch, *Chem.–Eur. J.*, 2002, **8**, 408.

5 S. Eisler, A. D. Slepkov, E. Elliott, T. Luu, R. McDonald, F. A. Hegmann and R. R. Tykwinski, *J. Am. Chem. Soc.*, 2005, **127**, 2666.

6 R. Eastmond, D. R. M. Walton and T. R. Johnson, *Tetrahedron*, 1972, **28**, 4601.

7 P. Siemsen, R. C. Livingston and F. Diederich, *Angew. Chem., Int. Ed.*, 2000, **39**, 2633.

8 W. A. Chalifoux, M. J. Ferguson and R. R. Tykwinski, *Eur. J. Org. Chem.*, 2007, 1001.

9 R. Dembinski, T. Bartik, B. Bartik, M. Jaeger and J. A. Gladysz, *J. Am. Chem. Soc.*, 2000, **122**, 810.

10 A. Orita and J. Otera, *Chem. Rev.*, 2006, **106**, 5387; Y. Tobe, I. Ohki, M. Sonoda, H. Niino, T. Sato and T. Wakabayashi, *J. Am. Chem. Soc.*, 2003, **125**, 5614; G. A. Adamson and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 1996, 1535; F. Diederich and Y. Rubin, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1101.

11 T. Luu, E. Elliott, A. D. Slepkov, S. Eisler, R. McDonald, F. A. Hegmann and R. R. Tykwinski, *Org. Lett.*, 2005, **7**, 51; S. Eisler and R. R. Tykwinski, *J. Am. Chem. Soc.*, 2000, **122**, 10736.

12 C. Schmitz, A.-C. Rouanet-Dreyfuss, M. Tueni and J.-F. Biellmann, *J. Org. Chem.*, 1996, **61**, 1817; R. Yamaguchi, H. Kawasaki, T. Yoshitome and M. Kawanisi, *Chem. Lett.*, 1982, 1485; R. L. Danheiser and D. J. Carini, *J. Org. Chem.*, 1980, **45**, 3925; R. F. Cunico and E. M. Dexheimer, *J. Am. Chem. Soc.*, 1972, **94**, 2868.

13 Y. Takayama, C. Delas, K. Muraoka, M. Uemura and F. Sato, *J. Am. Chem. Soc.*, 2003, **125**, 14163; M. J. Edelmann, M. A. Estermann, V. Gramlich and F. Diederich, *Helv. Chim. Acta*, 2001, **84**, 473; R. E. Martin, U. Gubler, J. Cornil, M. Balakina, C. Boudon, C. Bosshard, J.-P. Gisselbrecht, F. Diederich, P. Günter, M. Gross and J.-L. Brédas, *Chem.–Eur. J.*, 2000, **6**, 3622.

14 S. M. E. Simpkins, B. M. Kariuki, C. S. Aricó and L. R. Cox, *Org. Lett.*, 2003, **5**, 3971.

15 A. S. Batsanov, J. C. Collings, I. J. S. Fairlamb, J. P. Holland, J. A. K. Howard, Z. Y. Lin, T. B. Marder, A. C. Parsons, R. M. Ward and J. Zhu, *J. Org. Chem.*, 2005, **70**, 703; J.-H. Li, Y. Liang and Y.-X. Xie, *J. Org. Chem.*, 2005, **70**, 4393; J.-H. Li, L. Yun and X.-D. Zhang, *Tetrahedron*, 2005, **61**, 1903; A. W. Lei, M. Srivastava and X. M. Zhang, *J. Org. Chem.*, 2002, **67**, 1969.

16 A. Carpita, L. Mannocci and R. Rossi, *Eur. J. Org. Chem.*, 2005, 1859; A. Orsini, A. Vitérisi, A. Bodlenner, J. M. Weibel and P. Pale, *Tetrahedron Lett.*, 2005, **46**, 2259.

17 T. R. Johnson and D. R. M. Walton, *Tetrahedron*, 1972, **28**, 5221; J. B. Armitage, N. Entwistle, E. R. H. Jones and M. C. Whiting, *J. Chem. Soc.*, 1954, 147.

18 λ_{max} for a dendronised aryl end-capped decayne is 546 nm: see ref. 4.

19 λ_{max} for a phenyl end-capped decayne is 549 nm; see ref. 17.

20 S. M. E. Simpkins, B. M. Kariuki and L. R. Cox, *J. Organomet. Chem.*, 2006, **691**, 5517.

21 See also: C. Klinger, O. Vostirowsky and A. Hirsch, *Eur. J. Org. Chem.*, 2006, 1508; J. Stahl, J. C. Bohling, E. B. Bauer, T. B. Peters, W. Mohr, J. M. Martin-Alvarez, F. Hampel and J. A. Gladysz, *Angew. Chem., Int. Ed.*, 2002, **41**, 1872.