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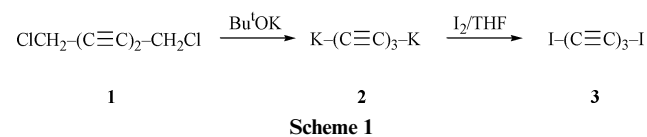
1,6-Diiodohexa-1,3,5-triyn-3-ene (**3**) and 1,8-diiodoocta-1,3,5,7-tetrayne (**5**) were prepared in yields of 64 and 75%, respectively, using a new method, allowing easy scale-up. Novel alkyne synthons, viz. 1-triisopropylsilyl-4-iodobuta-1,3-diyne (**7**) and 1-trimethylsilyl-4-iodobuta-1,3-diyne (**8**) were obtained in yields of 55 and 40%, respectively, from butadiyne in two-step reactions.

## Introduction

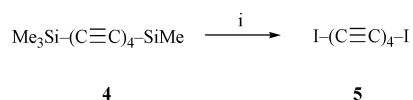
Linear carbon-chain molecules are a focus of modern acetylene chemistry<sup>1</sup> and materials science.<sup>2</sup> Higher homologues of conjugated oligoynes need to be stabilised by capping them with bulky protecting groups.<sup>1,3</sup> Such oligoynes have been prepared via oxidative coupling by Hay,<sup>4</sup> Glaser or by the Cadiot–Chodkiewicz reaction<sup>5</sup> up to dodecahexayne.<sup>6</sup> We have recently shown that the derivatives of hexatriyne are interesting precursors for the soft-chemical preparation of carbon nanotubes and carbon onions at room temperature.<sup>7</sup> The work described in this paper is aimed at the optimisation of the synthesis of several other promising precursors for such nanocarbons.

## Results and discussion

Gao and Goroff<sup>8</sup> have recently reported the syntheses of 1,6-diiodohexa-1,3,5-triyn-3-ene **3** and 1,8-diiodoocta-1,3,5,7-tetrayne **5** via iodination of bis(trimethylsilyl)alkynes with *N*-iodosuccinimide catalysed by AgNO<sub>3</sub>. On a small scale (0.3 mmol), these reactions proceed with good yields. However, the intermediate formation of explosive silver alkynides seems to be problematic for large-scale syntheses. Hence, we have developed a new safe synthesis of **3** and **5**, which allows easier scale-up. 1,6-Diiodohexa-1,3,5-triyn-3-ene **3** was synthesised by dehydrochlorination of 1,6-dichlorohexa-2,4-diyne<sup>9</sup> **1** according to Scheme 1.



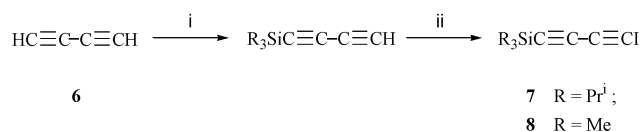
This procedure of direct iodination of hexatriynide **2** enabled the formation of 1,6-diiodohexa-1,3,5-triyn-3-ene **3** in a one pot reaction. 1,8-Diiodoocta-1,3,5,7-tetrayne **5** was synthesised according to Scheme 2 from 1,8-bis(trimethylsilyl)-1,3,5,7-octatetrayne<sup>10</sup> **4**.



Scheme 2 Reagents: i KOH–H<sub>2</sub>O, THF; I<sub>2</sub>–THF.

The preparations of diiodoalkynes **3** and **5** presented here give similar yields to those reported by Gao and Goroff<sup>8</sup> and moreover they enable the safe scale-up of the reaction. Our

<sup>13</sup>C-NMR data of **3** and **5** apparently match those reported<sup>8</sup> for the same substances. 1-Trialkylsilyl-4-iodobuta-1,3-diyne **7** and **8** were prepared from butadiyne **6** (Scheme 3).



Scheme 3 Reagents and conditions: i BuLi, THF, –78 °C; R<sub>3</sub>SiCl; ii BuLi, THF; I<sub>2</sub>–THF.

This two stage strategy allows new iodobutadiynes **7** and **8** to be obtained in medium yields due to the partial deprotection of trialkylsilyl intermediates during the iodination. When the temperature during the iodination is kept at –10 °C unwanted deprotection can be suppressed. <sup>13</sup>C-NMR spectra and elemental analysis confirm the identity of the capped iodobutadiynes **7** and **8**. All the products prepared are potential synthons for higher alkynes and carbonaceous polymers, including nanocarbons.<sup>7</sup>

## Experimental

### 1,6-Diiodohexa-1,3,5-triyn-3-ene (**3**)

14.8 g (0.1 mol) of dichlorohexadiyne **1** in 150 ml THF reacted with 0.4 mol of potassium *tert*-butoxide solution (Bu<sup>t</sup>OK) in 150 ml THF at –78 °C. The intermediate **2** formed was subsequently iodinated by addition of 50 g (0.4 mol) of iodine in 250 ml ether at –40 to –60 °C, and the reaction mixture was left overnight at –20 to –30 °C. The solution was washed with an aqueous solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and water and finally dried over anhydrous CaCl<sub>2</sub>. After partial evaporation of the solvents, a pale yellow product **3** precipitated (21 g, 64% yield). CAUTION: heating at 104–110 °C caused explosive decomposition (Found: C, 22.40%; I, 77.67%. Calc. for C<sub>6</sub>I<sub>2</sub>: C, 22.11%; I, 77.88%);  $\nu_{\text{max}}$  (KBr pellet)/cm<sup>–1</sup> 1260 (m), 2053 (m), 2164 (s);  $\delta_{\text{C}}$  (200 MHz, CDCl<sub>3</sub>) 78.8, 62.0, 58.8, 1.9; *m/z* (EI): 326 (M<sup>+</sup>, 100%), 254 (1), 199 (60), 163 (10), 127 (45), 72 (7).

### 1,8-Diiodoocta-1,3,5,7-tetrayne (**5**)

0.5 g KOH (9 mmol) in 0.5 ml of water was added to 1.2 g (5 mmol) of protected octatetrayne **4** in 20 ml THF. Stirring for 30 minutes at room temperature completed the deprotection. Subsequently, 2.5 g (20 mmol) of iodine in 20 ml of THF was added dropwise at –30 °C, and the solution was kept for 6 hours at –20 °C. The product was isolated after processing with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and water, as in the case of diiodohexatriyne **3**. A pale yellow precipitate **5** was formed (1.3 g, 75% yield). CAUTION: heating at 85–95 °C caused explosive decomposition.  $\nu_{\text{max}}$  (KBr pellet)/cm<sup>–1</sup> 1260 (m), 2045 (m), 2177 (m), 2940 (m);  $\delta_{\text{C}}$  (200 MHz, CDCl<sub>3</sub>) 78.89, 77.2, 77.00, 76.68, 62.10, 58.93, 1.01; *m/z* (EI) 350 (M<sup>+</sup>, 100%), 302 (10), 223 (45), 187 (5), 175 (15), 96 (70).

### 1-Triisopropylsilyl-4-iodobuta-1,3-diyne (7)

The first substitution-step was carried out as follows: 15 ml of 5.35 M BuLi (80 mmol) was added dropwise to 160 ml of THF containing 4 g (80 mmol) of butadiyne<sup>9</sup> **6** at  $-78\text{ }^{\circ}\text{C}$ . After 1.5 hours, 15.3 g (80 mmol) of triisopropylsilylchloride was added dropwise, and the solution was left at  $-20\text{ }^{\circ}\text{C}$  overnight. The second substitution step consisted of the addition of 15 ml of 5.35 M BuLi at  $-60\text{ }^{\circ}\text{C}$ , and the mixture was kept for 3 hours at  $-20\text{ }^{\circ}\text{C}$ . Subsequently, 11 g (87 mmol) of iodine in 50 ml THF was added and the reaction mixture was stored at  $-5\text{ }^{\circ}\text{C}$  overnight. The solution was then washed with aqueous  $\text{Na}_2\text{S}_2\text{O}_3$  and water and dried over  $\text{MgSO}_4$ . Finally, the solvents were removed *in vacuo*, and the remaining yellow-brown oil was purified chromatographically on silica (50 g Merck) in *n*-hexane. (The main impurity was diiodobutadiyne, which was apparently formed as a by-product during the second substitution step.) The end product (14.7 g, yield 55%) was a pale yellow-brown oil, which decomposed during attempts to distil it *in vacuo* (Found: C, 46.88%; H, 6.34%; I, 37.85%. Calc. for  $\text{C}_{13}\text{H}_{21}\text{SiI}$ : C, 46.98%; H, 6.36%; I, 38.18%;  $\nu_{\text{max}}$  (KBr pellet)/ $\text{cm}^{-1}$  1480 (m), 2077 (m), 2152 (w), 2214 (w), 2950 (s);  $\delta_{\text{C}}$  (200 MHz,  $\text{CDCl}_3$ ) 90.4, 80.5, 79.2, 77.3, 76.6, 18.4, 11.2,  $-2.4$ ;  $m/z$  (EI) 332 ( $\text{M}^+$ , 6%), 289 (100), 261 (49), 247 (34), 233 (55), 219 (100), 127 (4).

### 1-Trimethylsilyl-4-iodobuta-1,3-diyne (8)

1-Trimethylsilyl-4-iodobutadiyne (**8**) was prepared in a similar way to **7** from 4 g (80 mmol) of **6**, but instead of the triisopropylsilylchloride trimethylsilylchloride was used (Scheme 3). The reaction mixture was also processed in the same way as in the case of triisopropylsilyl derivative **7**. The pale yellow crystals of

**8** precipitated (7.9 g, 40%), mp  $49\text{--}50\text{ }^{\circ}\text{C}$  (Found: C, 34.20%; H, 3.77%; I, 51.56%. Calc. for  $\text{C}_7\text{H}_9\text{SiI}$ : C, 33.95%; H, 3.65%; I, 51.16%;  $\nu_{\text{max}}$  (KBr pellet)/ $\text{cm}^{-1}$  1480 (s), 2073 (m), 2144 (w), 2215 (m);  $\delta_{\text{C}}$  (200 MHz,  $\text{CDCl}_3$ ) 88.6, 83.1, 78.8, 77.3, 76.6,  $-0.01$ ,  $-0.4$ ;  $m/z$  (EI) 248 ( $\text{M}^+$ , 30%), 233 (100), 203 (9), 155 (4), 127 (5), 121 (30).

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