

Two New Iodine-Capped Carbon Rods

Kunxiu Gao[†] and Nancy S. Goroff*Department of Chemistry, State University of New York
Stony Brook, New York 11794-3400

Received May 18, 2000

Baeyer first reported the synthesis of diiodoacetylene (**1**) and diiodobutadiyne (**2**) in 1885.¹ Heilbronner and co-workers reported the synthesis of **2** in pure form in the 1970s.² These two molecules (Figure 1) have received renewed interest recently as precursors to conjugated polymers, including carbyne,³ and as constituents in multicomponent conducting salts.⁴ In the 115 years since Baeyer's initial description of **1** and **2**, however, no other members of this family have been reported. We have now extended this series of carbon iodides by synthesizing diiodohexatriyne (**3**) and diiodooctatetrayne (**4**), two new iodine-capped carbon rods.

Developments in synthetic methodology since Baeyer's time have made compounds **3** and **4** accessible targets, despite their extreme reactivity. Walton's pioneering work⁵ provided routes to silyl-protected carbon rods based on copper-mediated reactions such as the Cadiot–Chodkiewicz⁶ and Hay⁷ couplings.⁸ Recent improvements in techniques for halogenating alkynes involve preparing them directly from trimethylsilyl-protected precursors,⁹ thereby allowing us to avoid both triacetylene and tetraacetylene as volatile and unstable intermediates in the preparation of **3** and **4**.

We chose **3** and **4** as targets because of our interest in preparing well-defined organic molecules that can fragment to form small neutral all-carbon compounds size-specifically. These precursor molecules will allow us to study the reactions of small C_n species that lead to fullerene formation.¹⁰ The relative weakness of carbon–iodide bonds makes **3** and **4** promising precursors to the linear species C₆ and C₈, respectively, as shown in Scheme 1.

To act as efficient C_n precursors, these compounds need to be stable enough for convenient handling, but unstable enough to fragment as desired upon pyrolysis or photolysis. In fact, triyne **3** explodes when heated in a melting point capillary to 100 °C, and decomposes over a few days' time at room temperature. At –10 °C, **3** can be kept for several months at least, either as a yellow crystalline solid or in solution, without noticeable decomposition. Tetrayne **4** is somewhat less stable, exploding at 85 °C. A yellow solution of **4** in acetone, kept in the dark at –10 °C, decomposed slowly, after a few weeks producing a black precipitate.

We prepared **3** and **4**, in 65% and 71% yield, respectively, directly from the silyl-protected polyynes **7** and **10** by reaction with *N*-iodosuccinimide and silver nitrate (Scheme 2).⁸ Com-

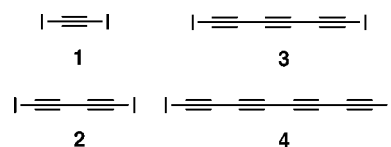
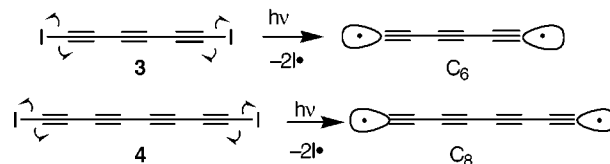
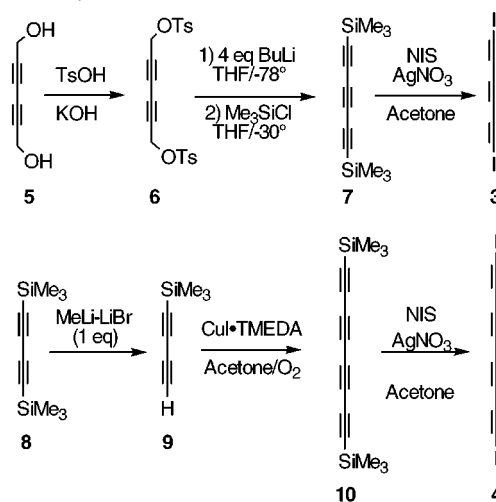


Figure 1. Diiodopolynes 1–4.

Scheme 1. Predicted Fragmentation of **3** and **4** To Form C₆ and C₈



Scheme 2. Synthetic Route to **3** and **4**



pounds **7** and **10** were prepared by literature methods, starting from the propargyl alcohol and TMS–acetylene dimers **5** and **8**.^{11,12}

Preliminary mass-spectrometry data on compound **3** demonstrate its promise as a precursor to C₆. Direct electron-impact (EI)

(6) Cadiot, P.; Chodkiewicz, W. In *Chemistry of Acetylenes*; Viehe, H.-G., Ed.; Marcel Dekker: New York, 1969; Chapter 9.

(7) Hay, A. S. *J. Org. Chem.* **1962**, *27*, 3320.

(8) Hirsch and co-workers have also made dicyanopolyynes rods of up to 18 carbon atoms by vaporization of graphite in the presence of (CN)₂: (a) Grösser, T.; Hirsch, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1340–1342. (b) Schermann, G.; Grosser, T.; Hampel, F.; Hirsch, A. *Chem. Eur. J.* **1997**, *3*, 1105–1112. (c) Schermann, G.; Vostrowsky, O.; Hirsch, A. *Eur. J. Org. Chem.* **1999**, 2491–2500.

(9) Nishikawa, T.; Shibuya, S.; Hosokawa, S.; Isobe, M. *Synlett* **1994**, 485–486. For a recent review of halogenated alkynes, see: Hopf, H.; Witulski, B. In *Modern Acetylene Chemistry*; Stang, P. J., Diederich, F., Eds.; VCH: Weinheim, 1995; pp 33–66.

(10) Goroff, N. S. *Acc. Chem. Res.* **1996**, *29*, 77–83.

(11) When characterizing **10** by ¹³C NMR, we were surprised to find that our measured spectrum contained only three of the four reported and expected alkynyl carbon peaks. The spectrum reported by Weng et al. (ref 12c) includes peaks at 88.0, 87.8, 68.0, and 62.1 ppm for the alkynyl carbons, in addition to a peak at –0.6 ppm corresponding to the trimethylsilyl groups. In contrast, a 75-MHz ¹³C NMR of our sample of **10** showed peaks at 88.0, 87.8, 62.2, and –0.6 ppm, but no signal at 68.0 ppm. Recognizing that THF could be responsible for the signal at 68.0 ppm in the published spectrum (taken in THF-*d*₆), we took a new ¹³C NMR spectrum at 125 MHz which resolved the signal at 62.2 MHz into two visible peaks, at 62.167 and 62.179 ppm, each with a full width at half-height of <0.01 ppm. To confirm our assignment of these two signals as two separate peaks, we also measured the ¹³C NMR spectrum at 75 MHz in the presence of the relaxation agent chromium (III) acetylacetonate. Integration of the three peaks observed, at 88.0, 87.8, and 62.2 ppm, gave relative intensities of 1:1:2.

[†] Current address: Wayne State University, Detroit, MI 48202

(1) Baeyer, A. *Chem. Ber.* **1885**, *18*, 2269–2281.

(2) (a) Heilbronner, E.; Hornung, V.; Maier, J. P.; Kloster-Jensen, E. *J. Am. Chem. Soc.* **1974**, *96*, 4252–62. (b) Klabeo, P.; Kloster-Jensen, E.; Bjarnov, E.; Christensen, D. H.; Nielsen, O. F. *Spectrochim. Acta, Part A* **1975**, *31A*, 931–43.

(3) (a) Peregodova, S. M.; Denisovich, L. I.; Ustyniuk, N. A.; Leonteva, L. I.; Vinogradova, V. N.; Filatova, T. V. *Russ. Chem. Bull.* **1995**, *44*, 1973–1975. (b) Hlavaty, J.; Kavan, L. *Angew. Makromol. Chem.* **1998**, *254*, 75–78. (c) Hlavaty, J.; Kavan, L. *Angew. Makromol. Chem.* **1998**, *259*, 83–85. (d) Kijima, M.; Sakai, Y.; Shirakawa, H. *Synth. Met.* **1995**, *71*, 1837–1840.

(4) (a) Uji, S.; Terakura, C.; Terashima, T.; Aoki, H.; Yamamoto, H. M.; Yamaura, J.; Kato, R. *Synth. Met.* **1999**, *103*, 1978–1978. (b) Yamamoto, H. M.; Yamaura, J. I.; Kato, R. *Synth. Met.* **1999**, *102*, 1448–1451. (c) Yamamoto, H. M.; Yamaura, J.; Kato, R. *Synth. Met.* **1999**, *102*, 1515–1516. (d) Yamamoto, H. M.; Yamaura, J. I.; Kato, R. *J. Am. Chem. Soc.* **1998**, *120*, 5905–5913. (e) Yamamoto, H. M.; Yamaura, J. I.; Kato, R. *J. Mater. Chem.* **1998**, *8*, 15–16.

(5) (a) Eastmond, R.; Walton, D. R. M. *Tetrahedron* **1972**, *28*, 4591–4599. (b) Eastmond, R.; Johnson, T. R.; Walton, D. R. M. *Tetrahedron* **1972**, *28*, 4601–4616.

Table 1. ^{13}C NMR Chemical Shifts of **3** and **4** (in ppm)

	3			4			
	A	B	C	A	B	C	D
compound 3 in	$\delta(\text{A})$			$\delta(\text{A})$	$\delta(\text{B})$	$\delta(\text{C})$	
CDCl_3	0.9			78.5			59.7
$\text{DMSO}-d_6$	14.6			76.3			58.8
compound 4 in	$\delta(\text{A})$			$\delta(\text{A})$	$\delta(\text{B})$	$\delta(\text{C}, \text{D})$	
CDCl_3	1.9			78.8		58.8, 62.0	
$\text{DMSO}-d_6$	17.9			77.4		58.3, 62.7	

mass spectrometry of **3** gives the parent ion at m/z 326, as well as major fragment ions at m/z 199, 127, and 72. These peaks correspond to $[\text{C}_6\text{I}]^+$, $[\text{I}]^+$, and $[\text{C}_6]^+$, respectively. There is also a smaller fragment at m/z 254, presumably corresponding to $[\text{I}_2]^+$ formed in a secondary reaction.

The ^{13}C NMR spectra of **3** and **4** change significantly with solvent, as shown in Table 1. For instance, the peak assigned to carbon A, bonded directly to iodine, moves from 0.9 ppm in CDCl_3 to 14.6 ppm in $\text{DMSO}-d_6$. We attribute this almost 14-ppm displacement in chemical shift to a Lewis acid–base interaction between the iodine and the oxygen of DMSO. Interactions of this sort between iodoalkynes and Lewis bases are well documented, but the effect of this interaction on the chemical shift has to our knowledge not been noted previously.

Both the strength and the direction of this change in the chemical shift of carbon A are surprising. We have confirmed that the observed displacement in chemical shift is a general phenomenon of iodoalkynes. For example, the carbon bonded to iodine in iodophenylacetylene has a chemical shift of 6.1 ppm in CDCl_3 , but it resonates at 20 ppm in pyridine- d_5 . We are currently investigating this interaction further, both computationally and experimentally.

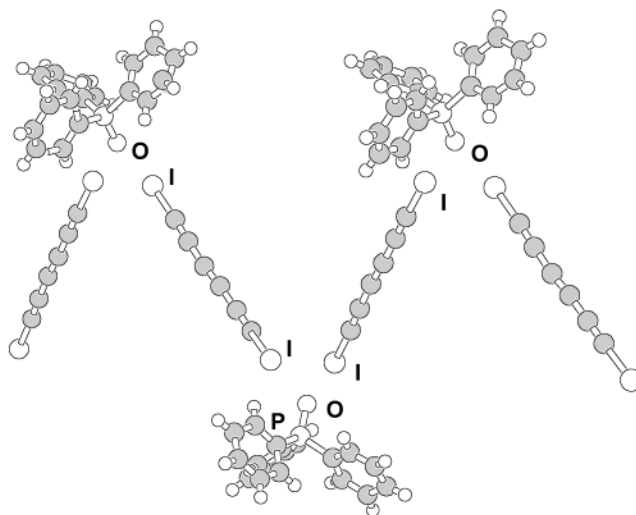
Attempts to obtain a single crystal of **3** suitable for X-ray diffraction studies proved unsuccessful. From chloroform, **3** forms fibrous bundles that are disordered along two dimensions. We therefore sought to take advantage of the Lewis acid–base interactions of **3** to prepare more highly ordered crystals using either diazabicyclooctane (DABCO) or triphenylphosphine oxide (PPh_3O) as a cocrystallizing agent, in a variation of the method established by Etter for crystallizing hydrogen bond donors.¹³

Mixing a dilute solution of DABCO in chloroform with a dilute solution of **3** or **4** resulted in instantaneous formation of a precipitate. This precipitate proved insoluble in chloroform, ethyl acetate, or dichloromethane, but soluble in methanol, 2-propanol, and DMSO. However, we were unable to obtain crystals of the DABCO-**3** coprecipitate, which when redissolved in methanol formed an oil upon slow evaporation of solvent. These observations are consistent with formation of a one-dimensional network polymer of DABCO and **3**.

Our first attempts at cocrystallizing **3** with PPh_3O were also unsuccessful. However, redissolving a mixture of **3** and PPh_3O in toluene and then allowing the solvent to evaporate slowly led to formation of crystals suitable for X-ray crystallography. In addition, these crystals are significantly more stable than **3** alone,

(12) (a) Rubin, Y.; Lin, S. S.; Knobler, C. B.; Anthony, J.; Boldi, A. M.; Diederich, F. *J. Am. Chem. Soc.* **1991**, *113*, 6943–9. (b) Walton, D. R. M.; Waugh, F. *J. Organomet. Chem.* **1972**, *37*, 45–56. (c) Weng, W.; Bartik, T.; Brady, M.; Bartik, B.; Ramsden, J. A.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1995**, *117*, 11922–11931.

(13) Etter, M. C.; Baures, P. W. *J. Am. Chem. Soc.* **1988**, *110*, 639–640.

**Figure 2.** Cocrystal of **3** and triphenylphosphine oxide. (For clarity, only three PPh_3O molecules are shown.)

slowly turning brown at 125 °C, well above the explosion temperature of **3**. The **3**· PPh_3O crystals survive for weeks at room temperature with no apparent decomposition.

The crystal structure of **3** with PPh_3O is shown in Figure 2.¹⁴ As predicted, the iodine atoms of **3** are in close contact with the Lewis-basic oxygen atoms. The stoichiometry of the crystal is 1:1, with two iodine atoms interacting with each oxygen. Compound **3** is linear, with alternating bond lengths appropriate for the expected polyene structure ($\text{C}_\text{A}-\text{C}_\text{B} = \text{C}_\text{C}-\text{C}_\text{C}' = 1.20 \text{ \AA}$, $\text{C}_\text{B}-\text{C}_\text{C} = 1.38 \text{ \AA}$). The carbon–iodine bond length is 1.96 Å, similar to those observed in alkynylidonium salts.¹⁵

In conclusion, we have synthesized two new carbon iodides. Compounds **3** and **4** combine several interesting properties: Lewis-acidic sites suitable for molecular assembly, extended linear conjugation, and the potential to fragment in a predictable way. On the basis of these properties, they have potential as constituents in neutral-salt multicomponent conducting materials and promise to serve as useful precursors to linear all-carbon molecules. After 115 years, diiodoacetylene and diiodobutadiyne have some company.

Acknowledgment. We thank Prof. J. W. Lauher for extensive help with the crystallography of **3**. The mass spectrum of **3** was taken at the UC-Riverside Mass Spectrometry Facility. We also acknowledge the National Science Foundation (CHE-9809683 and CHE-9984937) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Supporting Information Available: Experimental procedures for preparation of **3** and **4**, characterization data for **3** and **4**, and crystallographic data for the $\text{PPh}_3\text{O}\cdot\text{3}$ crystal (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA001722T

(14) X-ray intensity data for the cocrystal of **3** and PPh_3O were measured on a Bruker AXS diffractometer. Samples were stored at $-10 \text{ }^\circ\text{C}$ and were mounted in the diffractometer within 30 min after removal from the freezer. **3** and PPh_3O crystallize together in space group $P2_1/n$ with $a = 10.915(1) \text{ \AA}$, $b = 14.051(1) \text{ \AA}$, $c = 15.399(2) \text{ \AA}$, $\beta = 97.84(1)^\circ$, $R_w = 5.3\%$, $R = 5.7\%$ for 253 variables and 1342 unique observations with ($I > 3\sigma$).

(15) Stang, P. J. In *Modern Acetylene Chemistry*; Stang, P. J., Diederich, F., Eds.; VCH: Weinheim, 1995; pp 67–98.