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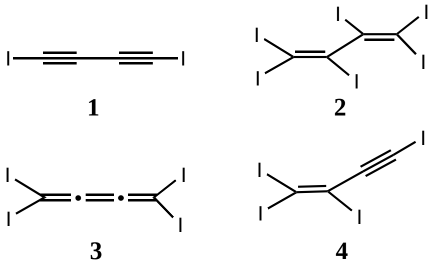
Tetraiodobutatriene: A New Cumulenic Carbon Iodide**

Jeffrey A. Webb, Pei-Hua Liu, Olga L. Malkina, and Nancy S. Goroff*

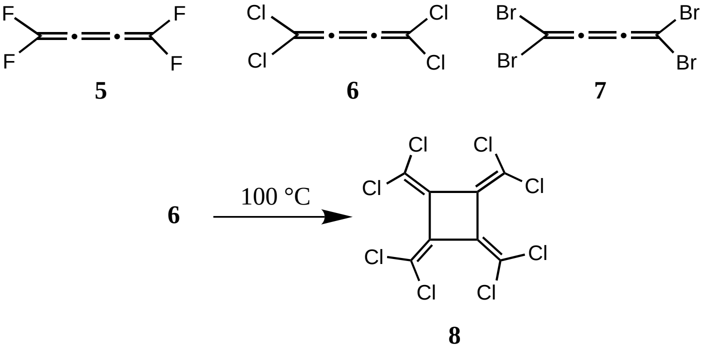
Diiodopolyynes such as **1** have attracted our attention as potential precursors to all-carbon molecules and materials. Lespieau and Prévost reported 75 years ago that diiodobutadiyne (**1**) reacts with molecular iodine to form hexaiodobutadiene (**2**).[1] Others repeated this experiment with similar results, each time obtaining a yellow solid that melted at about 165°.[2] We now present evidence that, under appropriate conditions, this same reaction can instead give cumulene **3**, which is stable, isolable, and fully characterized (Scheme 1).



Scheme 1. A family of carbon iodides C_4I_x.

We recently synthesized two longer diiodopolyynes, C_6I_2 and C_8I_2,[3] and began exploring methods for the ordered polymerization of such iodine-capped polyynes. As part of our studies, we collected X-ray data on a crystal from a previously pure sample of **1** which had been sitting on a benchtop for several months. Instead of the expected butadiyne **1**, the sample contained novel butatriene **3**. Evidently, **1** (C_4I_2) can disproportionate over time to yield **3** (C_4I_4), with unknown carbon-rich by-products. However, the majority of crystals in the sample still contained **1** instead of **3**; the decomposition reaction had occurred in low overall yield.

Compound **3** is one of only a handful of halogenated cumulenes that have been characterized. Perfluorobutatriene **5** (Scheme 2) is extremely unstable; it reportedly explodes above its boiling point of $-5\,^{\circ}C$ and decomposes even at $-80\,^{\circ}C$.[4] Perchlorobutatriene **6** is more stable (m.p. 59–60 °C), but like many cumulenes it dimerizes to form radialene **8** when heated.[5] Perbromobutatriene **7** has not been reported, and compound **3** is, to the best of our knowledge, the first known iodine-substituted cumulene of any sort.[6]



Scheme 2. Cumulenes **5** and **6** are known; **7** is not.

We have now found conditions which lead cleanly to **3** in good yield. Iodination of **1** in concentrated solution in hexanes produces a yellow precipitate after only a few minutes.[7] Filtration separates the solid from the solvent and any remaining I_2, leaving a yellow powder (m.p. 142–143 °C). As discussed below, mass spectrometry, IR and NMR spectroscopy, and X-ray diffraction studies all confirm that this material is cumulene **3**.

Without careful handling, however, compound **3** rapidly decomposes in solution to give **2**. The decomposition reaction occurs in pure solutions of **3**, suggesting a disproportionation mechanism, much like the observed decomposition of **1**. The simplest disproportionation of **3**, to give equal parts of **1** and **2**, would be endothermic by 9.1 kcal mol^{-1}, according to density-functional (B3LYP/LanL2DZ) calculations.[8] Furthermore, we found no evidence for the formation of **1** during the decomposition reaction. Thus far, we have been unable to identify the by-product(s) of this reaction.

The decomposition of **3** can be monitored by thin-layer chromatography (TLC; AlO_3/hexanes).[9] When **3** is dissolved in a variety of solvents (e.g., THF, CS_2), the diyne disappears over several minutes, while a new TLC spot appears simultaneously, corresponding to **2**. In some solvents (acetone, benzene, CCl_4), TLC indicates that **3** is stable unless exposed

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[**] We thank J. Lauher for crystallography assistance, D. Salahub for use of the DeMon program at Stony Brook, and V. Malkin and M. Kaupp for helpful discussions. We also thank the Computing Center of the Slovak Academy of Sciences for computational resources. We acknowledge the National Science Foundation (CHE-9984937), the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Slovak Grant Agency VEGA (O.L.M., Grant No.2/7203/20) for support of this research.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

to light. In pyridine, compound **3** appears to form a stable solvent–solute complex and does not decompose.

The instability of **3** in many solvents makes spectroscopic characterization difficult. GC/MS experiments on the crude yellow precipitate indicate that it contains only one compound, with molecular formula C_4I_4, consistent with either cumulene **3** or enyne **4**. Density-functional (B3LYP/LanL2DZ) calculations place compound **4** higher in energy than **3** by 4.5 $kcal\,mol^{-1}$, but the B3LYP functional is known to overestimate the stability of cumulenes relative to acetylenic isomers.[10] Previous literature reports contain examples of both 1,4- and 1,2-addition to diynes, and often mixtures of the two.[11,12]

^{13}C NMR spectroscopy should distinguish between **3** and **4** easily, but initial NMR spectroscopic experiments were difficult to interpret. Figure 1a shows the ^{13}C NMR spectrum of starting diyne **1**, whereas Figures 1b–d show the NMR spectra of the yellow precipitate dissolved in various solvents.

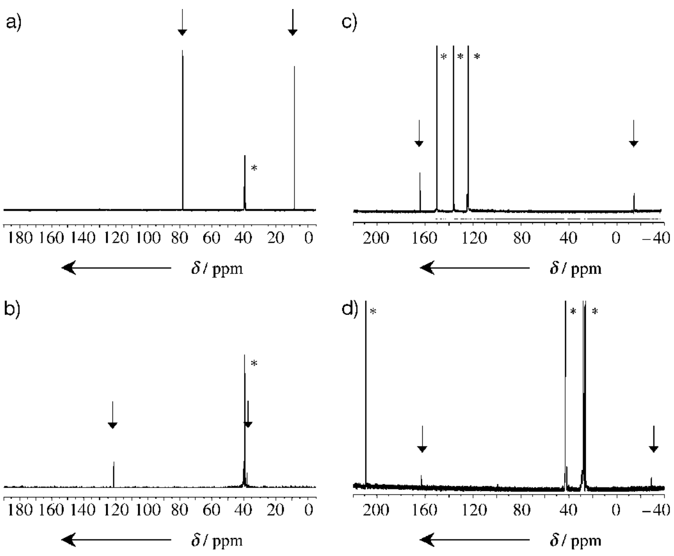

Figure 1. ^{13}C NMR spectra; ↓ denotes sample signal, * denotes solvent or deuterium lock. a) **1** in [D$_6$]DMSO; b) **3**, decomposed, in [D$_6$]DMSO; c) **3** in [D$_5$]pyridine; d) **3** in cyclohexanone with internal [D$_{12}$]cyclohexane lock.

The spectrum in Figure 1b was obtained first, with dimethyl sulfoxide (DMSO) as solvent. Initially, based on symmetry, we assigned the two peaks in this spectrum at $\delta = 37.7$ and 121.2 ppm to compound **3**.

To confirm the assignment, we calculated the ^{13}C NMR spectrum of **3**, including the spin-orbit coupling effect of the iodine atoms.[13–15] These calculations predict chemical shifts for C1 and C2 at $\delta = -48.9$ and 163.2 ppm, respectively, far from the observed spectrum in DMSO. This difference provided our first evidence for the decomposition of **3** in solution.

Figures 1c and d show the NMR spectra of freshly prepared samples of the yellow precipitate, dissolved in pyridine and in cyclohexanone, respectively. Each spectrum includes two peaks: $\delta = 163.5$ and -14.9 ppm in pyridine and $\delta = 162.9$ and -27.5 ppm in cyclohexanone. We assign both these spectra to compound **3**, despite the difference between the lower-frequency shifts and the calculated value of $\delta = -48.9$ ppm. The discrepancy most likely results, at least in part, from a Lewis acid–base interaction between **3** and the solvent.[3,16] The ≈12-ppm difference in the low-frequency peak in the spectra when in pyridine or in weakly basic cyclohexanone supports this hypothesis.

The NMR spectroscopic data contain no evidence of enyne **4**. Furthermore, vibrational spectroscopy confirms the structure of **3**. The extremely simple experimental IR spectrum matches calculations well: 668 and 1678 cm^{-1} (calculated) compared to 603 and 1616 cm^{-1} (experimental). We have been unable to obtain Raman or UV spectra of **3** because of its swift decomposition upon irradiation in solution.

As final proof of the structure, we obtained X-ray diffraction data on a new crystal grown from the yellow powder. These data confirm that the yellow solid is tetraiodobutatriene (**3**), just like the initial material from decomposition of **1**. The two samples, prepared in very different ways, have indistinguishable crystal structures. The crystal packing is shown in Figure 2a. Figure 2b shows a crystal structure of **2**, prepared directly from **1** and then cocrystallized with 1,7-phenanthroline.[17]

As a solid, cumulene **3** is more stable than diyne **1**. Upon heating, compound **1** decomposes at 90 °C, but **3** melts at 142–

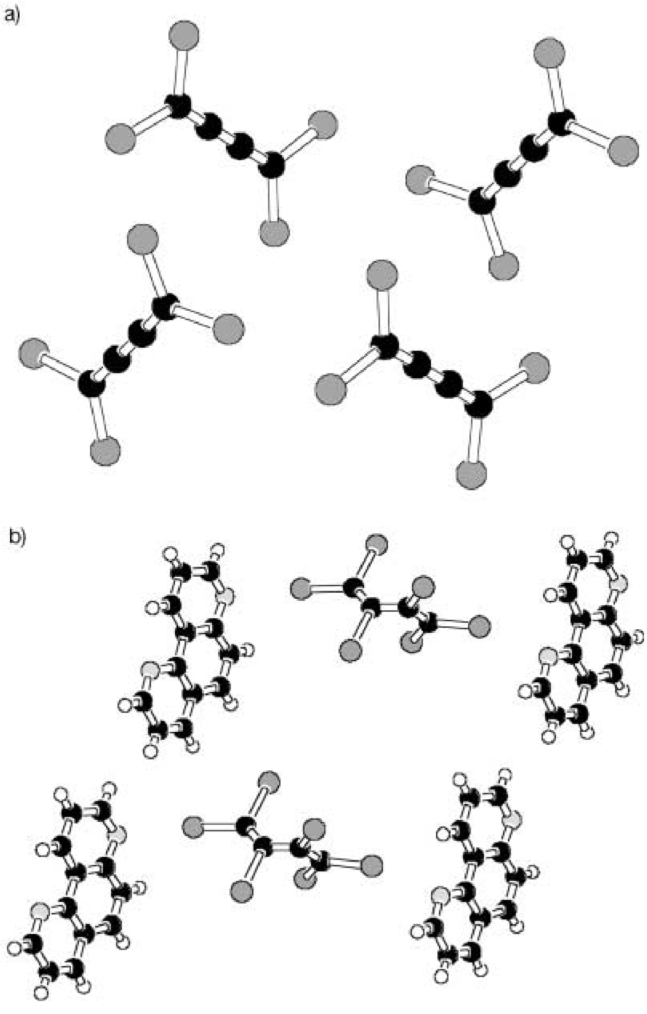

Figure 2. a) X-ray crystal structure of **3**; b) X-ray structure of 1:1 cocrystal of **2** and 1,7-phenanthroline.

143 °C. We have produced **3** in gram quantities without difficulty and can keep solid samples in the freezer indefinitely. Nonetheless, compound **3** decomposes much more readily in solution than **1**.

The weakness of carbon–iodine bonds makes compound **3** a promising precursor to all-carbon and carbon-rich molecules and materials. Compound **3** also offers another Lewis acid for the crystal engineer's toolbox. Carbon iodides have previously found use as components in designed materials by acting as Lewis acid templates. For example, diiodoacetylene and other carbon iodides can determine the spacing of ions in multicomponent conducting solids.[18] The stability of **3** in pyridine solution indicates that it can survive Lewis acid–base interactions without decomposition, making it a suitable candidate for such multicomponent systems.

Cumulene **3** is surprisingly easy to prepare and to isolate in a pure form, is surprisingly stable in the solid state, and disproportionates surprisingly readily in solution. It is one more example of the unusual chemistry of carbon and iodine.

Experimental Section

3: I_2 (340 mg, 1.32 mmol) was added to a solution of **1** (400 mg, 1.32 mmol) in hexanes (5 mL). Aluminum foil was used to wrap the reaction vessel. The reaction mixture was stirred vigorously at room temperature for 15 min, forming a yellow precipitate. The yellow powder was filtered and washed with hexanes to yield crude product (604 mg, 82 %). The crude products from three iterations were combined and recrystallized from cyclohexanone/hexanes to yield pure **3** as fine yellow needles (1.47 g, 67 % total). M.p. 143–144 °C; MS (EI): m/z (%): 556 (24) [M^+ (C_4I_4)], 429 (45) [M^+−I], 302 (100) [M^+−2(I)], 175 (28) [M^+−3(I)], 127 (27) [I^+].

2: Iodine (2.52 g, 9.93 mmol) was added to a solution of **1** (1.0 g, 3.3 mmol) in methanol (30 mL). After stirring at room temperature for 2 h, the precipitate was filtered and washed with hexanes to yield **2** as a yellow powder. The material left in solution was not recovered, and no yield was determined. M.p. 165–166 °C; MS (EI)[19]: m/z (%): 682 (22) [M^+−I], 556 (34) [M^+−2(I)], 429 (34) [M^+−3(I)], 302 (100) [M^+−4(I)], 175 (38) [M^+−5(I)], 127 (50) [I^+]. To prepare cocrystals of **2** and 1,7-phenanthroline, compound **2** (0.14 g, 0.25 mmol) was dissolved in acetone (3 mL). A solution of 1,7-phenanthroline (0.045 g, 0.25 mmol) in methanol (2 mL) was added dropwise to this solution with stirring. The solution, in a small vial, was cooled to −10 °C, forming small crystals.

X-ray structure analysis: X-ray intensity data were measured on a Bruker AXS diffractometer. The structures were solved by direct methods and refined by using full-matrix least-squares methods (SHELX97).[20] Empirical absorption corrections were applied. Compound **3** crystallizes in space group $P2_1/n$, with $a = 4.4362(4)$ Å, $b = 17.1459(14)$ Å, $c = 12.5217(10)$ Å, $\beta = 96.716(2)°$, $V = 945.90(14)$ Å^3, $Z = 2$, $\rho_{calcd} = 4.877$ g cm^{-3}, $T = 293(2)$ K, 4223 reflections measured, 1352 crystallographically independent ($R_{int} = 0.068$), and 1154 reflections with $I > 2\sigma(I)$, $Mo_{K\alpha} = 0.71073$ Å, $2\theta_{max} = 53°$, $R(F_{obs}) = 0.034$, $wR(F^2)_{all} = 0.113$. Compound **2** forms cocrystals with [1,7]-phenanthroline in the space group $P\bar{1}$, with $a = 7.4475(17)$ Å, $b = 10.609(2)$ Å, $c = 14.845(3)$ Å, $\alpha = 103.128(4)°$, $\beta = 103.840(4)°$, $\gamma = 91.510(4)°$, $V = 1105.0(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 2.974$ g cm^{-3}, $T = 293(2)$ K, 6417 reflections measured, 4390 crystallographically independent ($R_{int} = 0.174$), and 3591 reflections with $I > 2\sigma(I)$, $Mo_{K\alpha} = 0.71073$ Å, $2\theta_{max} = 53°$, $R(F_{obs}) = 0.120$, $wR(F^2)_{all} = 0.379$. Unit cells and ORTEP representations are available as supplementary material. CCDC-181226 and –181227 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Received: March 12, 2002 [Z18877]

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Atom-Transfer Tandem Radical Cyclization Reactions Promoted by Lewis Acids[**]

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Tandem radical cyclization reactions are powerful methods for the synthesis of a wide range of highly functionalized polycyclic natural products as multiple stereocenters can be constructed in one step under mild conditions.[1,2] However, no enantioselective tandem radical cyclization reactions have been reported.[3] Herein we describe a Lewis acid catalyzed atom-transfer tandem radical cyclization method for the formation of various bicyclic and tricylic ring skeletons. Furthermore, the first enantioselective tandem radical cyclization was achieved by using chiral Lewis acids as catalysts.

We recently reported an enantioselective atom-transfer radical monocyclization catalyzed by a chiral Lewis acid to prepare cyclic 2,3-disubstituted ketones.[4] $Yb(OTf)_3$ (OTf = trifluoromethanesulfonate) and $Mg(ClO_4)_2$ were found to be the best Lewis acids in these monocyclization reactions. Therefore, the two Lewis acids were further used to promote tandem cyclization of α-bromo β-keto esters **1a**–**f** with Et_3B/O_2 as the radical initiator (Table 1). Substrates **1a** and **1b** with two C=C bonds in the same carbon chain exclusively underwent 6-*endo* and then 5-*exo* cyclization for **1a** and 6-*exo* cyclization for **1b** in the presence of a Lewis acid to give the fused ring products 6,5-*cis*-**2a** and 6,6-*trans*-**2b**, respectively (Table 1, entries 1–4). In each case, four stereocenters of the cyclization products **2a**/**2b** were set up in one step. Furthermore, as little as 0.3 equivalents of $Yb(OTf)_3$ was sufficient to catalyze the cyclization of **1a** to give **2a** in 69% yield (Table 1, entry 2), and a decrease in the amount of $Mg(ClO_4)_2$ (to 0.5 equiv) did not decrease the yield of **2b** in the cyclization of **1b** (Table 1, entry 4). For substrates **1c**—**e**,[5] which have an allyl substituent in the α-position, 6-*endo* (6-*exo* for substrate **1d**) followed by 5-*exo* cyclization gave the corresponding bicyclic products **2c**–**e** in moderate yields in the presence of a stoichiometric amount of $Mg(ClO_4)_2$ (Table 1, entries 5–7). Furthermore, triple cyclization of **1f** gave product **2f** as one of 16 possible stereoisomers in 26% yield (Table 1, entry 8). When $Yb(OTf)_3$ was used as the Lewis acid catalyst, no more than 16% yield can be obtained in the cyclization of substrates **1b**–**f**. For all the substrates investigated, no atom-transfer radical cyclization was observed in the absence of Lewis acids. These results demonstrate that the Lewis acids not only promote tandem radical cyclization reactions, but also control the stereoselectivities of the cyclization products.[6] The major side products of those tandem cyclization reactions were the corresponding reductive debromination products (< 12% yield), monocyclization products (< 30% yield), and even a bicyclization product (for **1f** only; 12% yield).[7] Especially for substrate **1b**, the 1,3-diaxial interaction of two methyl groups made the second ring cyclization unfavorable, and as a result the radical chain process was partially terminated in the monocyclization stage with the isolation of a monocyclization product in up to 30% yield.

Then we investigated the enantioselective tandem cyclization of **1a** and **1b** by using $Mg(ClO_4)_2$ and bisoxazoline ligand **L1** as a chiral catalyst (Table 2). Poor *ee* values were observed in the cyclization of **1a** (Table 2, entry 1). Although the addition of activated 4-Å molecular sieves[4,8] improved the *ee* value, it decreased the yield dramatically (Table 2, entry 2). High *ee* values (82–84%) were observed in the cyclization of **1b** at higher temperature, despite lower yields (Table 2, entries 3 and 4). With $Yb(OTf)_3$ as the catalyst,[9] the effects of chiral ligands,[10] additives,[11] and solvents on the enantioselective tandem cyclization of **1a** were evaluated. As shown in Table 3, the **L3**/Yb complex gave the best results (60% yield and 66% *ee*; Table 3, entry 4). Dichloromethane was found to be a better solvent than toluene in this tandem cyclization system (Table 3, entry 4 vs. 6). The addition of Et_2O or water had negative effects on these reactions (Table 3, entries 2 and 3). Surprisingly, the addition of molecular sieves led to reversed enantiofacial selectivity of the cyclization[11e] (Table 3, entry 5).

The stereochemistry of tandem radical cyclization reactions in the presence of the chiral complex $[Yb(Ph\text{-}pybox)(OTf)_3]$ (pybox = 2,6-bis(2-oxazolin-2-yl)pyridine) can be explained using the transition-state model shown in Scheme 1. Similar to the chiral complex $[Sc(Ph\text{-}pybox)(ethyl\ glyoxylate)(OTf)]^{2+}$ proposed by Evans et al.,[12] the ytterbium center adopts a square-pyramidal geometry with the ester carbonyl group

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[**] This work was supported by The University of Hong Kong and the Hong Kong Research Grants Council. D.Y. acknowledges the Bristol-Myers Squibb Foundation for an Unrestricted Grant in Synthetic Organic Chemistry and the Croucher Foundation for a Croucher Senior Research Fellowship.

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