ORGANIC
LETTERS

2004
Vol. 6, No. 13
2081−2083

Tetrabromobutatriene: Completing the Perhalocumulene Series

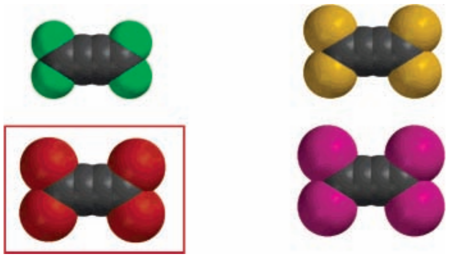
Pei-Hua Liu, Lei Li, Jeffrey A. Webb, Yi Zhang, and Nancy S. Goroff*

Department of Chemistry, State University of New York,
Stony Brook, New York 11794-3400

nancy.goroff@sunysb.edu

Received February 14, 2004 *(Revised Manuscript Received May 17, 2004)*

ABSTRACT



Tetrabromobutatriene, C_4Br_4, can be prepared directly from dibromobutadiyne by reaction with Br_2 at –25 °C in concentrated hexanes solution. The cumulene precipitates out of the reaction mixture as a yellow powder. Under palladium-catalyzed coupling conditions, C_4Br_4 can undergo allylic rearrangement, giving a mixture of products, including some with butenyne backbones. However, in furan solution, C_4Br_4 reacts cleanly at its central double bond to give the furan Diels–Alder adduct. Under Suzuki conditions, this adduct reacts at the furan double bond rather than at bromide.

The perhalocumulenes **1**−**4** are attractively simple compounds with unusual structures (Figure 1). Of these, tetrafluorobutatriene (**1**) was first reported in 1959 by Martin and Sharkey.[1] Heinrich and Roedig prepared compound **2** in 1968,[2] and in 2002, we reported the synthesis of tetraiodobutatriene (**4**),[3] bringing the number of known perhalocumulenes to three. Unlike the previous syntheses of **1** and **2**, we prepared **4** via electrophilic halogenation, starting from diiodobutadiyne. Here, we present the synthesis and properties of compound **3**, the last to be made in the series of perhalocumulenes.

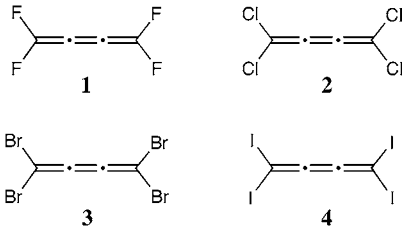


Figure 1. Perhalocumulenes **1**−**4**.

The perhalocumulenes have particular promise as starting materials for the synthesis of larger cross-conjugated molecules and materials. After preparing **4**, we searched for ways to use it as a substrate for Stille- or Sonagashira-type couplings. However, compound **4** is extremely unstable in most solvents, undergoing disproportionation to give 1,1,2,3,4,4-hexaiodobutatriene (C_4I_6, **5**) plus unknown carbon-rich byproducts.[3] Compound **4** is more stable in benzene or carbon tetrachloride, but its solubility in these solvents is too poor for effective reaction. We have not yet found reliable conditions for coupling **4** to either aryl or alkynyl compounds.

---

(1) Martin, E. L.; Sharkey, W. H. *J. Am. Chem. Soc.* **1959**, *81*, 5256−5258.

(2) Heinrich, B.; Roedig, A. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 375−376.

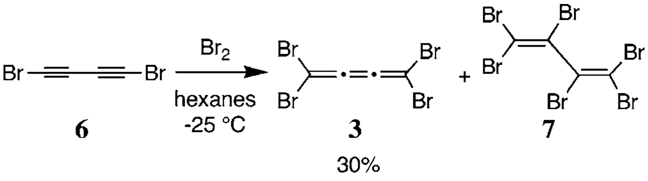
(3) Webb, J. A.; Liu, P.-H.; Malkina, O. L.; Goroff, N. S. *Angew. Chem., Int. Ed.* **2002**, *41*, 3011−3014.

10.1021/ol049734x CCC: $27.50

Like **4**, perbromocumulene **3** might also act as a substrate for palladium-catalyzed couplings, and it is an interesting target in its own right. We therefore decided to pursue the synthesis of compound **3**. The methodology used to make compound **4** can be applied to the preparation of **3**, with some caveats. First, the major difficulty in making **4** is overiodination to give hexaiodobutadiene (**5**). Because bromine addition occurs even more readily, overbromination of **3** is a greater problem. In addition, dibromobutadiyne (**6**) can explode at room temperature when neat, even under argon.[4] Thus, careful handling and low temperatures are required for any reactions using **6**, and it must be prepared shortly before use.

Despite these difficulties, we have now found conditions under which bromination of compound **6** will lead to cumulene **3** (Scheme 1). Dropwise addition of bromine to a concentrated solution of freshly prepared **6** (1.1 equiv) in hexanes at −25 °C leads to formation of a yellow precipitate, compound **3**. The remaining filtrate is a complex mixture that contains 1,1,2,3,4,4-hexabromobutadiene (**7**) as the major component.[5] Under these conditions, the yield of pure **3** is about 30−40%.

Scheme 1



Neat compound **3** is stable to above its melting temperature of 102−104 °C. (Unlike **2**,[2] compound **3** does not dimerize to form a [4]radialene.) Compound **3** decomposes in solution over time, but more slowly than compound **4**. The NMR spectrum of **3** in DMSO-d_6 includes only two peaks, at 65.5 and 153.6 ppm. By analogy to compound **4**, we assign the lower-frequency peak to C-1 and C-4, and the higher peak to C-2 and C-3. The IR absorptions of **3** match calculations well: 777 and 1634 cm^{-1} (KBr pellet) vs 771 and 1703 cm^{-1} calculated (B3LYP/6-31G*).[6]

Compound **3** does not readily form X-ray quality single crystals alone. However, by using phenazine as a cocrystallizing agent, we obtained suitable crystals for X-ray analysis. In these crystals, each phenazine nitrogen is 3.05 Å from a bromine atom, consistent with weak Lewis acid−base interactions between them (Figure 2).[7]

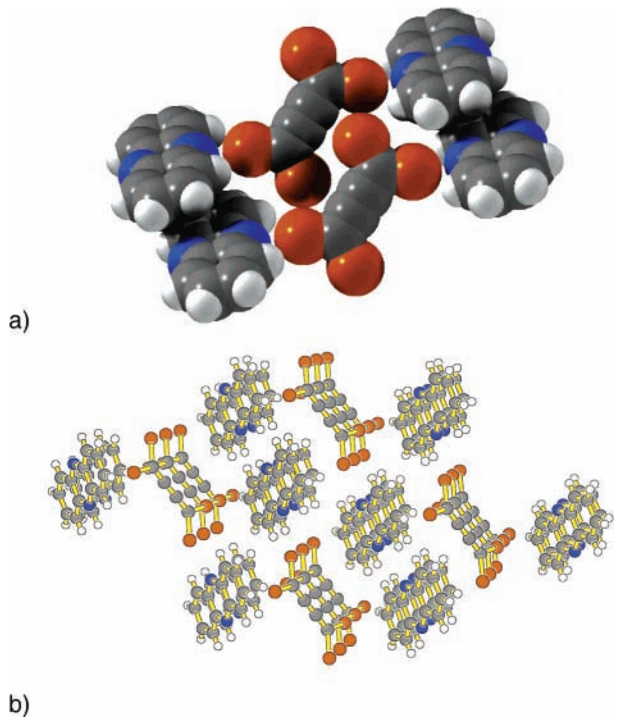


Figure 2. Crystal structure of **3** with phenazine, showing (a) the intermolecular N−Br interactions which provide order in the crystal and (b) the overall packing of the molecules.

Although compounds **1**−**4** have similar structures, they have distinctly different properties. Compound **1**, the earliest identified of the four, is the least stable.[1,8] At or near its boiling temperature of −5 °C, liquid **1** detonates violently. In the gas phase, it explodes in the presence of oxygen and slowly forms polymeric material in inert atmosphere. In contrast, compounds **2**−**4** are stable solids at room temperature. Compound **2** is also stable in solution and has been used as a starting material for reactions such as nucleophilic addition−elimination to make perthiocumulenes.[9] Our past efforts to carry out similar reactions using **4** as a substrate have been hampered by its poor solubility and stability in solution.

Compound **3** is soluble and moderately stable in solution. In examining its chemistry, we focused first on its potential as a substrate for palladium-catalyzed aryl couplings to make targets such as tetraphenyl cumulene **8**.[10] We have found, however, that Suzuki couplings give undesirable mixtures of products (Figure 3). The makeup of the product mixture

---

(4) Dembinski, R.; Bartik, T.; Bartik, B.; Jaeger, M.; Gladysz, J. A. *J. Am. Chem. Soc.* **2000**, *122*, 810−822.

(5) Straus, F.; Kollek, L.; Hauptmann, H. *Ber.* **1930**, *63B*, 1886−1899.

(6) (a) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheesemen, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Startmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanaykkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A.5; Gaussian, Inc.: Pittsburgh, PA, 1998. (b) Becke, A. D. *J. Chem. Phys.* **1996**, *104*, 1040−1046.

(7) Metrangolo, P.; Resnati, G. *Chem.*−*Eur. J.* **2001**, *7*, 2511−2519.

(8) Bach, A.; Lentz, D.; Luger, P.; Messerschmidt, M.; Olesch, C.; Patzschke, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 296−299.

(9) (a) Roedig, A.; Zaby, G.; Scharf, W. *Chem. Ber.* **1977**, *110*, 1484−1491. (b) Roedig, A.; Zaby, G. *Lieb. Ann. Chem.* **1979**, 1614−1625.

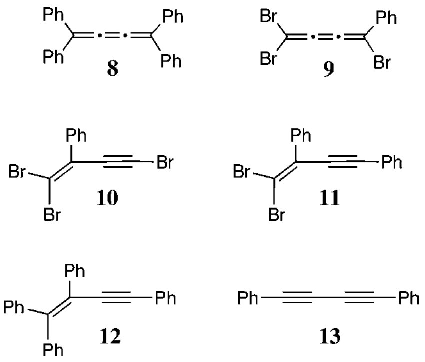


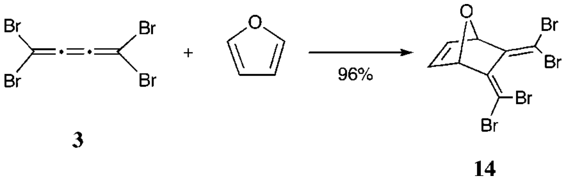
Figure 3. Desired product (**8**) and actual products (**9**−**13**) of the Suzuki coupling of phenyl boronic acid to **3**.

depends on the solvent, the temperature, and the amount of phenyl boronic acid used, but in all cases allylic rearrangement competes with the desired coupling reactions, leading to enynes such as **10**−**12**. Reaction in benzene provides a small amount of monophenylcumulene **9** (14%), in addition to **10** and **11**, but no other cumulenes. In THF/H_2O (4:1), diphenylbutadiyne (**13**) is a major product, along with the enynes **10**−**12**. In all cases, the reactions are not synthetically useful. Similarly, Stille coupling with phenyltributyltin at room temperature in toluene[11] gives a mixture of products, of which enyne **11** appears to be the major component, although no purification was attempted. Experimental details for these reactions are provided in the Supporting Information.

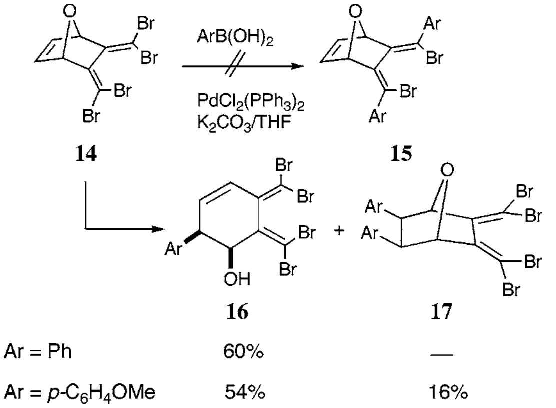
To use compound **3** as a starting material for making substituted cumulenes requires a method to protect the central double bond from allylic rearrangment. For this purpose, we turned to the Diels−Alder reaction. Calculations (B3LYP/6-31G*) indicate that the LUMO of **3** is located almost entirely on the central double bond, and it is lower in energy than the LUMO of dimethyl acetylenedicarboxylate. Diels−Alder addition, followed by palladium coupling and then a retro-Diels−Alder reaction, would provide a potential synthetic route to substituted cumulenes such as **8**.

In practice, the Diels−Alder reaction works well. Unlike the palladium-coupling reactions of **3**, Diels−Alder addition of furan to **3** is clean and high yielding (Scheme 2). This reaction, carried out at room temperature over 48 h, gives adduct **14** in 96% yield. With adduct **14** in hand, we attempted the Suzuki coupling with phenylboronic acid (Scheme 3). Unfortunately, we isolate compounds **16** and **17** from this reaction, instead of the desired **15**, indicating palladium insertion at the “wrong” double bond of **14**.[12]

Scheme 2



Scheme 3



Appropriate conditions for preparing tetraaryl cumulenes from **3** remain elusive. Nonetheless, compound **3** persists as an attractive substrate for further synthetic manipulation because of its solubility and relative stability. The Diels−Alder reaction of **3** with furan gives a single product in high yield. Efforts will continue toward finding a synthetic route from **3** to larger cumulene derivatives.

Acknowledgment. We acknowledge the National Science Foundation (CHE-9984937 and CHE-0131146) for support of this research. We thank R. Tykwinski for helpful discussions and O. Nduka for help in identifying compounds **16** and **17**.

Supporting Information Available: Experimental procedures and spectroscopic characterization for all new compounds, computational details, and crystallographic data for the cocrystals of **3** and **16** (Ar = p-C_6H_5OMe) with phenazine. This material is available free of charge via the Internet at http://pubs.acs.org.

OL049734X

---

(10) (a) Zweig, A.; Hoffmann, A. K. *J. Am. Chem. Soc.* **1962**, *84*, 3278−3284. (b) Sisenwine, S. F.; Day, A. R. *J. Org. Chem.* **1967**, *32*, 1770−1773. (c) Jasiobedzki, W.; Kujda, J.; Wozniak-Kornacka, J.; Zelechowski, K. *Bull. Pol. Acad. Sci. Chem.* **1996**, *44*, 215−234. (d) Dyker, G.; Borowski, S.; Henkel, G.; Kellner, A.; Dix, I.; Jones, P. G. *Tetrahedron Lett.* **2000**, *41*, 8259−8262.

(11) Littke, A. F.; Schwarz, L.; Fu, G. C. *J. Am. Chem. Soc.* **2002**, *124*, 6343−6348.

(12) For previous reports of similar reactions, see: (a) Duan, J.-P.; Cheng, C.-H. *Tetrahedron Lett.* **1993**, *34*, 4019−4022. (b) Moinet, C.; Fiaud, J.-C. *Tetrahedron Lett.* **1995**, *36*, 2051−2052. (c) Montalbetti, C.; Savignac, M.; Genêt, J.-P.; Roulet, J.-M.; Vogel, P. *Tetrahedron Lett.* **1996**, *37*, 2225−2228.