Available online at www.sciencedirect.com

ScienceDirect

Tetrahedron Letters 49 (2008) 1771–1772

Tetrahedron Letters

Simple and convenient one-pot synthesis of cyclooctatetraene

Supriyo Majumder, Aaron L. Odom *

Michigan State University, Department of Chemistry, East Lansing, MI 48824, United States

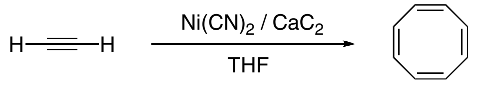
Received 6 December 2007; revised 4 January 2008; accepted 14 January 2008
Available online 19 January 2008

Abstract

Cyclooctatetraene is readily synthesized by the oxidation of in situ generated $[Li(TMEDA)]_2[C_8H_8]$ with 1,2-dibromoethane. The product is readily isolated and produced without the use of hazardous or toxic reagents.

1. Introduction

Cyclooctatetraene (COT, **1**) has seen wide application in both organic[1] and organometallic chemistry.[2] In 1911, Willstätter and Waser reported the first seven step synthesis of cyclooctatetraene starting from pseudopelletierine.[3] In 1948, Reppe's group at BASF reported a one step synthesis of COT involving tetramerization of acetylene in the presence of a nickel catalyst at high pressure (Eq. 1).[4]



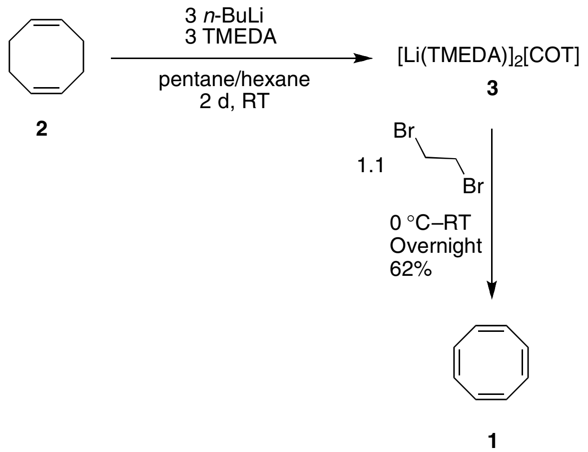
(1)

1

Though the one step synthesis of COT (**1**) was industrially viable, the handling of acetylene at high pressure makes this process unwieldy on laboratory scales.

Several groups have addressed this problem by focusing on the conversion of the $C_8H_8^{2-}$ dianion into cyclooctatetraene. The dianion can be readily obtained in high yield from 1,5-cyclooctadiene (**2**) by treatment with 3 equiv of *n*-butyllithium in the presence of *N*,*N*,*N′*,*N′*-tetramethylethylene-1,2-diamine (TMEDA) to produce $[Li(TMEDA)]_2C_8H_8$ (**3**) as shown by the Wilke group;[5] they oxidized $C_8H_8^{2-}$ dianion into **1** using cadmium chloride. Roesky and co-workers have converted $[Li(TMEDA)]_2C_8H_8$ (**3**) to COT (**1**) by employing mercuric chloride as an oxidizing agent.[6] Oxidation of $K_2C_8H_8$ by either dry oxygen or iodine to **1** has also been reported by Simons and Lagowski, but the yields of COT were low.[7] In a very recent paper, Edelmann and co-workers used di-*tert*-butylperoxide as an oxidizing agent for the conversion of **3** to C_8H_8.[8] Many of the routes used for COT synthesis involved potentially hazardous or less common reagents. We sought a straightforward and expedient method of COT (**1**) synthesis on the laboratory scale.

Here, we report that inexpensive and commercially available 1,2-dibromoethane is a very efficient reagent for the clean conversion of **3** into cyclooctatetraene (Scheme 1).



Scheme 1. Synthesis of cyclooctatetraene (**1**).

---

[*] Corresponding author.
E-mail address: odom@chemistry.msu.edu (A. L. Odom).

doi:10.1016/j.tetlet.2008.01.070

$[Li(TMEDA)]_2C_8H_8$ (**3**) was prepared according to the known literature procedure.[5] To the in situ generated lithium COT (**3**) cooled with an ice bath was added 1,2-dibromoethane. Further stirring at room temperature produced a yellow mixture, which upon acidic work-up followed by distillation produced COT (**1**) in 62% isolated yield.

2. Experimental

Under nitrogen atmosphere a 2 L 2-neck round bottom flask was charged with *n*-BuLi (750 mL, 1.6 M solution in hexane, 1200 mmol) and 1,5-cyclooctadiene (**2**) (49 mL, 400 mmol) in 150 mL dry pentane. The mixture was cooled to 0 °C and TMEDA (182 mL, 1200 mmol) was added via syringe. The resulting solution was stirred at room temperature for 2 d. The solution turned red after an hour, and orange crystals had formed after a day. Then, the mixture was again cooled to 0 °C and 1,2-dibromoethane (82.7 g, 440 mmol) was added slowly over 30 min. The 1,2-dibromoethane reaction is quite exothermic and should be done slowly with care. The mixture was stirred overnight at room temperature. The solution was diluted with 300 mL of pentane, and the organic layer was washed with 5% acetic acid (250 mL × 2) followed by saturated $NaHCO_3$ (250 mL × 2). The organic layer was dried with Na_2SO_4, and the solvent was removed under rotary evaporation. The crude yield is quite high (80–90%) with the major impurity being a small amount of cyclooctadiene (**2**). The crude product was purified by distillation using a Vigreux column under nitrogen to yield 26.8 g (62%) of cyclooctatetraene (**1**). ^1H NMR ($CDCl_3$, 500 MHz): δ 5.77 (8H, s); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 132.10. MS: 104 (M^+).

Acknowledgements

The authors wish to thank the National Science Foundation and Petroleum Research Fund administered by the American Chemical Society for funding.

References and notes

1. (a) Fray, G. I.; Saxton, R. G. *The Chemistry of Cyclooctatetraene and its Derivatives*; Cambridge University: Cambridge, 1978; (b) Paquette, L. A. *Acc. Chem. Res.* **1993**, *26*, 57; (c) Huisgen, R.; Mietzsch, F. *Angew. Chem.* **1964**, *76*, 36; *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 83; (d) Spitler, E. L.; Johnson, C. A., II; Haley, M. M. *Chem. Rev.* **2006**, *106*, 5344. For a review on the synthesis of substituted derivatives see:(e) Wang, C.; Xi, Z. *Chem. Commun.* **2007**, 5119.
2. (a) *Comprehensive Organometallic Chemistry*, 2nd ed.; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1996; Vol. 4, (b) Edelmann, F. T. *New J. Chem.* **1995**, *19*, 535; (c) Avdeef, A.; Raymond, K. N.; Hodgson, K. O.; Zalkin, A. *Inorg. Chem.* **1972**, *11*, 1083. For some recent examples see: (d) Dunn, S. C.; Nazari, N.; Cowley, A. R.; Green, J. C.; Mountford, P. *Organometallics* **2006**, *25*, 1755; (e) Dunn, S. C.; Hazari, N.; Jones, N. M.; Moody, A. G.; Blake, A. J.; Cowley, A. R.; Green, J. C.; Mountford, P. *Chem. Eur. J.* **2005**, *11*, 2111; (f) Hill, A. F.; Smith, M. K. *Organometallics* **2007**, *26*, 3900.
3. Willstätter, R.; Waser, E. *Chem. Ber.* **1911**, *44*, 3423.
4. Reppe, W.; Schlichting, O.; Klager, K.; Toepel, T. *Justus Liebigs Ann. Chem.* **1948**, *560*, 1.
5. (a) Gausing, W.; Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 371. For a study on the nature and mechanism of formation for **3** see: (b) Hoye, T. R.; Kabrhel, J. E.; Hoye, R. C. *Org. Lett.* **2005**, *7*, 275.
6. Wetzel, T. G.; Dehnen, S.; Roesky, P. W. *Organometallics* **1999**, *18*, 3835.
7. Simons, L. H.; Lagowski, J. J. *Tetrahedron Lett.* **2002**, *43*, 1771.
8. Gottfriedsen, J.; Miloslavina, A.; Edelmann, F. T. *Tetrahedron Lett.* **2004**, *45*, 3583.