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Cyclooctatetraene made easy

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Abstract—Cyclooctatetraene, C_8H_8, has been made readily available from 1,5-cyclooctadiene in 65% yield without the need of using hazardous or toxic reagents by the straightforward oxidation of the intermediate $[Li(tmeda)]_2C_8H_8$ (**3**, tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) with di-*tert*-butylperoxide.

Since its discovery by Willstätter in 1911,[1] cyclooctatetraene, C_8H_8 (**1**), has never lost its fascination and remains a highly valuable intermediate in organic synthesis as well as a useful sterically demanding ligand in organometallic chemistry.[2,3] The classical Reppe synthesis of cyclooctatetraene involves tetramerization of acetylene under high pressure in the presence of nickel catalysts.[4] However, the use of flammable and potentially explosive acetylene under pressure makes this method unsuitable for laboratory use. In addition, since industrial production has been discontinued, cyclooctatetraene has become a very expensive material in recent years.

Quite surprisingly, there is also a significant lack of straightforward laboratory methods for synthesizing **1**. Several attempts have been reported to convert the cheap and readily available 1,5-cyclooctadiene (**2**) via the $C_8H_8^{2-}$ dianion into cyclooctatetraene. According to Cloke and co-workers **2** can easily be metalated upon treatment with *n*-butyllithium in the presence of tmeda to afford the intermediate $[Li(tmeda)]_2C_8H_8$ (**3**) in high yield.[5] In a recently reported cyclooctatetraene synthesis mercury dichloride has been employed as an oxidizing agent for the conversion $C_8H_8^{2-} \rightarrow C_8H_8$.[6] The isolated yield of **1** is acceptable (45%), but a major disadvantage of this method is the use of large amounts of highly toxic $HgCl_2$. A more recent paper by Simons and Lagowski reports the oxidation of $K_2C_8H_8$ with either dry oxygen or iodine.[7] This method too is unsatisfactory for the purpose of making cyclooctatetraene on a preparative scale, as the starting material $K_2C_8H_8$ is highly explosive and therefore difficult to handle. In the case of the I_2 oxidation the isolated yield of **1** is only 22%. Thus there is a strong demand for a simple and straightforward cyclooctatetraene synthesis employing cheap starting materials and without the need of using hazardous and/or toxic reagents. We report here that di-*tert*-butylperoxide is the reagent of choice for cleanly converting **3** into cyclooctatetraene. The stable di-*tert*-butylperoxide is commercially available and its handling does not require any special safety precautions.

$[Li(tmeda)]_2C_8H_8$ (**3**) was prepared from 1,5-cyclooctadiene (**2**) in virtually quantitative yield following the procedure given by Cloke et al.[5] There is no need to isolate **3** as a solid material. When di-*tert*-butylperoxide was slowly added to a freshly prepared suspension of **3** in *n*-pentane a vigorous reaction was observed, which required cooling of the reaction mixture during the peroxide addition. Further heating for 4 h produced a yellow solution of cyclooctatetraene along with a white precipitate of LiO^{t}Bu. Standard hydrolytic work-up afforded pure cyclooctatetraene **1** in 65% yield (bp 142–143 °C). The overall one-pot reaction is illustrated in Scheme 1.

The method reported here provides an easy and straightforward access to preparative amounts of cyclooctatetraene. The new method combines several synthetic advantages: it uses cheap starting materials and can be carried out as a one-pot reaction. It is also clean as the oxidizing agent di-*tert*-butylperoxide yields only *tert*-butanol as a by-product, and there is no need of using hazardous (such as explosive $K_2C_8H_8$) and/or toxic (such as $HgCl_2$) reagents. Thus it makes laboratory

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Keywords: Cyclooctatetraene; Cyclooctadiene; di-*tert*-Butylperoxide.

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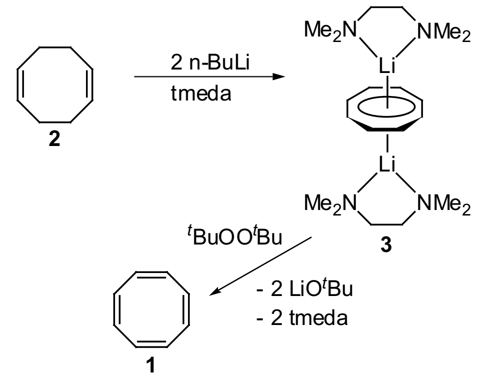

Scheme 1. Synthesis of cyclooctatetraene (**1**).

quantities of cyclooctatetraene readily available in a safe and straightforward manner.

Experimental procedure

To a stirred solution of 1,5-cyclooctadiene (45 mL, 0.367 mol) in *n*-pentane (370 mL) was added dropwise *n*-butyllithium (153 mL of a 1.6 M solution in *n*-hexane) followed by slow addition of tmeda (37 mL), and stirring was continued for 24 h. Di-*tert*-butylperoxide (67.4 mL, 0.796 mol) was added dropwise over 1 h at 0 °C. After stirring at room temperature for another hour, the resulting suspension was stirred at reflux temperature for 4 h. The mixture was added to 300 mL of ice water and diluted with *n*-pentane (200 mL). The organic layer was washed thoroughly with diluted acetic acid (1%, 6 × 150 mL), saturated $NaHCO_3$ solution (3 × 150 mL), and dried over anhydrous $MgSO_4$. Distillation under normal pressure afforded 24.85 g **1** (bp 142–143 °C) whose spectroscopic and analytical data were in excellent agreement with the published data.

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