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Synthesis of a Novel Dicycloproparene

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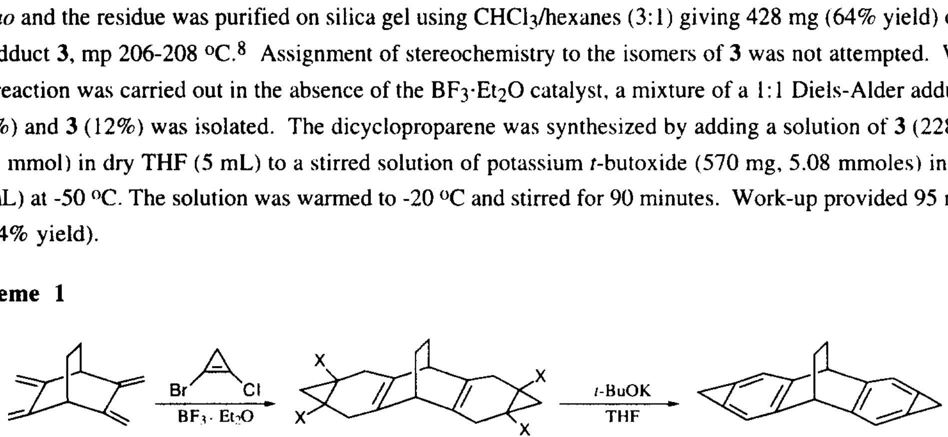
Abstract: A novel bridged dicycloproparene has been synthesized by treating the Diels-Alder adduct of 1-bromo-2-chlorocyclopropene and 2,3,5,6-tetramethylidene[2.2.2]bicyclooctane with potassium t-butoxide in tetrahydrofouran.

Cycloproparenes are the most highly strained members of the 1,2-bridged aromatic hydrocarbons.[1] A cycloproparene derivative was reported by Anet and Anet[2] in 1964, and the parent hydrocarbon was synthesized in 1965 by Vogel, Grimme, and Korte.[3] A dicycloproparene was described by Vogel and Ippen[4] in 1974, and two other dicycloproparenes were reported in 1991.[5] Our interest in the use of the dicycloproparenes as precursors to ladder polymers prompts us to describe the synthesis of the novel dicycloproparene **1**.

The synthesis of **1** is illustrated in Scheme 1. Thus a solution of 2,3,5,6-tetramethylidene[2.2.2]bicyclooctane **2**[6] (226 mg, 1.43 mmoles) in THF (2 mL) was added via a syringe to a freshly prepared solution of 1-bromo-2-chlorocyclopropene.[7] The mixture was warmed to -20 °C and $BF_3 \cdot Et_2O$ (0.1 mL) was added. The resulting solution was stored for 8 days at -20 °C. The solvent was then removed *in vacuo* and the residue was purified on silica gel using $CHCl_3$/hexanes (3:1) giving 428 mg (64% yield) of the bisadduct **3**, mp 206-208 °C.[8] Assignment of stereochemistry to the isomers of **3** was not attempted. When the reaction was carried out in the absence of the $BF_3 \cdot Et_2O$ catalyst, a mixture of a 1:1 Diels-Alder adduct(s) (27%) and **3** (12%) was isolated. The dicycloproparene was synthesized by adding a solution of **3** (228 mg, 0.49 mmol) in dry THF (5 mL) to a stirred solution of potassium *t*-butoxide (570 mg, 5.08 mmoles) in THF (8 mL) at -50 °C. The solution was warmed to -20 °C and stirred for 90 minutes. Work-up provided 95 mg of **1** (84% yield).

Scheme 1



2 3 X = Br or Cl 1

The ^1H NMR spectrum of **1** is displayed in Figure 1. ^{13}C NMR signals were observed at 20.6, 26.9, 45.4, 111.3, 123.8, and 145.8 ppm. IR (KBr, cm^{-1}) ν 3044, 2940, 1662, 1450, 1401, 1355, 1141, 1059, 881, 860, 832, 559, 423. HREIMS. Calculated for $C_{18}H_{14}$: 230.1096. found: 230.1110.

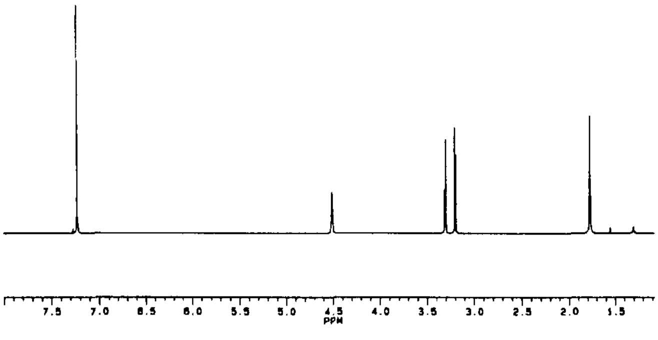
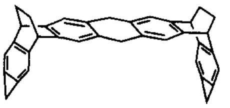


Figure 1. 250 MHz ^{1}H NMR spectrum ($CDCl_3$, ppm) of **1**.

Polymerization[9] of **1** was observed to occur rapidly when the dicycloproparene was added to a solution of $AgBF_4$ in $CHCl_3$. Although characterization of the insoluble polymers is still under investigation, dimers **4** and **5** could be isolated at an early stage of the oligomerization. A sharp singlet in the ^{1}H NMR spectrum at 3.80 ppm ($-CH_2-$) suggests that **5** is the major component.



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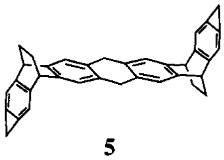

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9. A florisil column was used to separate the dimeric dicycloproparenes from the starting material and other oligomers.

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