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Synthesis, Structure and Attempted Polymerization of a Diepoxide Macrocycle

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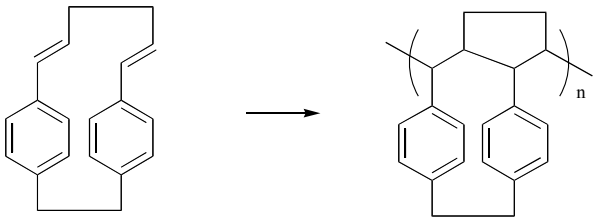
Abstract: A novel diepoxide containing paracyclophane was synthesized by peracid oxidation of a known paracyclophane diene. The resulting diepoxide was characterized. It was investigated as a potential monomer for a cyclophane containing polyether by cationic ring opening polymerization. None of the standard catalyst systems for such a polymerization were successful in producing polymer.

Keywords: Cationic polymerization, cyclophane, diepoxide, macrocycle.

INTRODUCTION

Cationic polymerization of olefins is one of the major routes to high molecular weight polymers [1]. The mechanism involves nucleophilic attack of the alkene functional group on the electron poor initiator (initiation) or the growing cationic chain end (propagation). Dienes have been demonstrated to undergo cationic polymerization to polymer chains containing newly formed rings (cyclopolymerization [2]). This technique has been extended to a cyclophane diene (**1**) providing a polymer containing stacked [3.2] paracyclophane groups (Scheme **1**) [3]. It was of interest to see if this diene could be epoxidized by standard epoxidation reagents (peracids) and what the resulting structure would be. It was also of interest to see if this compound could be polymerized in a manner analogous to the diene.

Polymerization of diepoxides to give ring containing polymers has been reported in the literature (Scheme **2**) [4]. This process is mechanistically similar to the cationic polymerization of alkenes or dienes. It was hoped that an analogous process could be used to polymerize the paracyclophane diepoxide **2**.



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Scheme 1.

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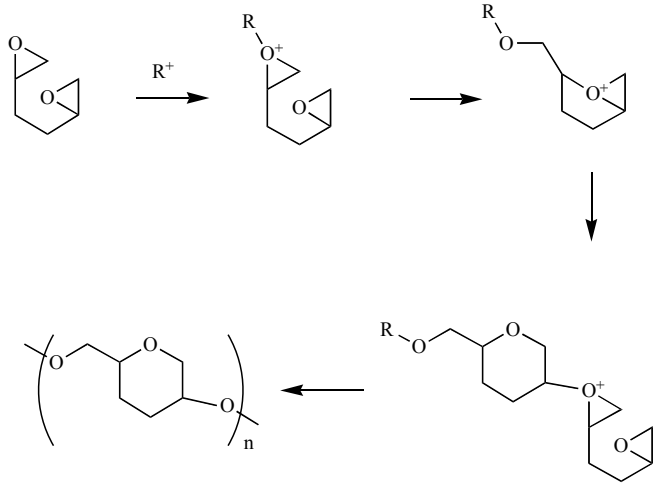

Scheme 2.

MATERIALS AND METHODS

All solvents and reagents were used as received from Sigma-Aldrich Chemical Co. unless otherwise specified. A JEOL-400 Eclipse spectrometer was used for NMR analysis. ^{1}H-NMR experiment settings included x-frequency = 399.8 MHz, x-points = 16k and total scans = 24. ^{13}C-NMR experiment settings included x-frequency = 100.5 MHz, x-points = 32k and total scans = 1024+. Data was processed using Delta version 4.3.4 software. IR analysis was conducted using a Perkin Elmer Spectrum One spectrometer. Solid samples were analyzed using a KBr pellet produced from a mixture containing 2 mg sample and 80 mg KBr.

Synthesis of (E,E)-[6.2]Paracyclophane-1,5-diene (1)

The diene was synthesized by Hofmann elimination of 3-(4-methylphenyl)-2-propenyltrimethylammonium bromide as described previously in the literature [3].

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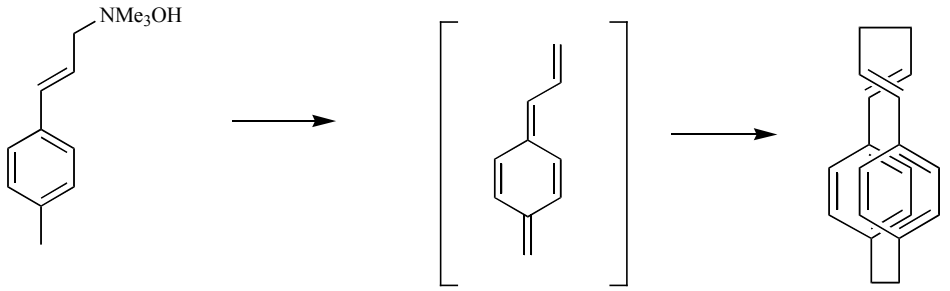

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Scheme 3.

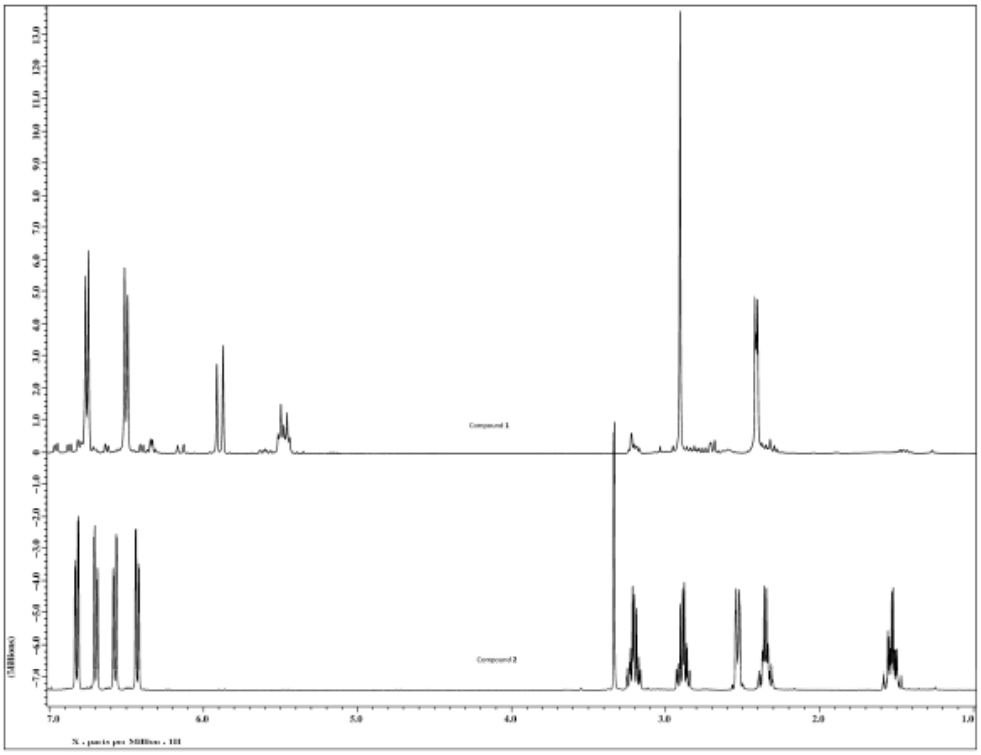


Fig. (1). ^{1}H NMR of Diene **1** and Diepoxide **2**.

Synthesis of 1,2:5,6-Diepoxy-[6.2]Paracyclophane (2)

A sample of **1** (544 mg, 2.09 mmol) in methylene chloride was treated with 1.12 g (5.01 mmol) of 3-chloroperoxybenzoic acid (77% max. by weight). This was stirred for 2.5 h at room temperature and then quenched with 20 mL of 10% sodium sulfite solution. The organic phase was washed with 10% sodium bicarbonate, brine and water. The solution was dried ($MgSO_4$) and reduced *via* rotary evaporation producing 604 mg (2.07 mmol, 99% yield) of crude **2**.

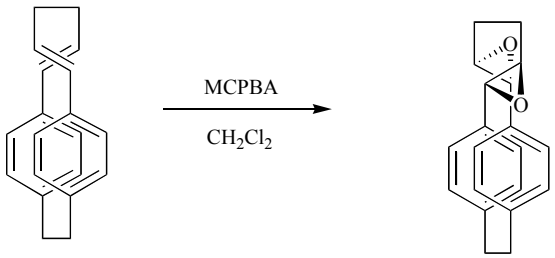
Compound **2** was recrystallized from chloroform to give 429 mg (1.47 mmol, 71% yield) of white, crystalline **2**: mp 286-288 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.82 (d·d, 2 H), 6.69 (d·d, 2 H), 6.57 (d·d, 2 H), 6.42 (d·d, 2 H), 3.33 (d, 2 H), 3.21 (m, 2 H), 2.87 (m, 2 H), 2.53 (m, 2 H), 2.35 (m, 2 H), 1.53 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.2, 134.0, 132.5, 130.1, 126.9, 122.1, 62.8, 61.5, 34.1, 27.4; IR (KBr) 2927, 1449, 909, 798, 555 cm^{-1}. Elemental Analysis Calculated for $C_{20}H_{20}O_2$: C, 82.16; H, 6.90. Found: C, 81.78; H, 6.89. All attempts to produce crystals for x-ray crystallographic analysis were unsuccessful due to the poor solubility of the compound.

RESULTS AND DISCUSSION

The previously reported synthesis of [6.2]-paracyclophane-1,5-diene [3] was used to prepare our starting material. Epoxidation was carried out using m-chloro-perbenzoic acid (MCPBA) in methylene chloride. The resulting product was purified by recrystallization. The purified product (**2**) had a somewhat more complicated ^{1}H NMR spectrum than might at first be expected based on structural symmetry (Fig. **1**). As epoxidation by peracids is proposed to go by a concerted mechanism [5] it was expected that the overall ring structure would not be significantly changed during reaction.

The synthesis of the diene is *via* a Hoffman elimination that involves a concerted cycloaddition (Scheme **3**). Using

orbital symmetry considerations it is expected that the product would be the "crossed diene" shown. This has been confirmed by x-ray diffraction analysis in a closely related compound [6]. Since epoxidation is a concerted reaction it is expected that this "crossed" conformation would be retained. The steric constraints within the cyclophane structure keep the "crossed" and "parallel" conformers from interconverting, both in the diene and the diepoxide.



1 **2**

Scheme 4.

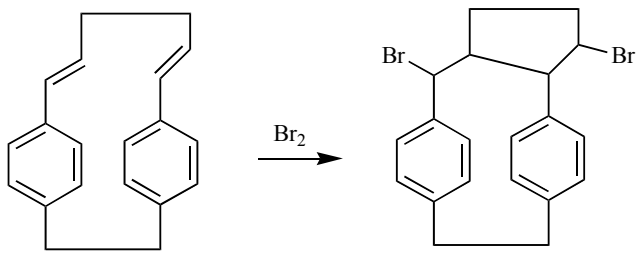
In the ^{1}H NMR spectrum of the starting diene **1** the aromatic protons appear as a doublet of doublets (AA'XX'), the vinylic proton adjacent to the aromatic ring appear as a doublet and the other vinylic proton as a multiplet. The isolated methylene bridge appears as a singlet and the methylene bridge adjacent to the alkenes appears as a doublet. The spectrum shows the two halves of the paracyclophane as being chemically equivalent as only one set of resonances is seen. A similar symmetry is seen in the ^{13}C NMR.

Careful analysis of the ^{1}H and ^{13}C NMR spectra of diepoxide **2** as well as COSY and HETCOR 2-D NMR spectra allowed us to assign all of the peaks in the ^{1}H NMR spectrum. In the ^{1}H NMR spectrum the aromatic region appears as four doublets of doublets. The benzylic methylene bridge is now split into two equally sized multiplets as is the methylene bridge adjacent to the epoxides. The epoxide proton adjacent to the aromatic ring is seen as a single doublet. The other epoxide proton appears as a single multiplet.

Upon epoxidation the aromatic ring as well as the methylene bridges shows an increase in complexity in the NMR. The most likely explanation of this is due to the presence of four new asymmetric centers in the diepoxide that are not present in the starting diene. These new asymmetric centers will make previously equivalent protons diastereotopic and lead to an overall increase in the complexity of the spectrum. An analogous increase in complexity can be seen in the previously reported model compound **3** (Scheme **5**) which shows a series of doublets in the aromatic regions as well multiplicities for the bridge protons in the ^{1}H NMR [3]. All attempts to produce crystals of the diepoxide **2** appropriate for x-ray crystallography were unsuccessful.

A number of cationic polymerization catalysts that have been previously reported to polymerize epoxides were tried. These included; 1:1 Et_2Zn-H_2O [7], Vandenberg's catalyst [8], $SnCl_2$ [9], and BF_3-Et_2O [10].

It was found however that none of these catalysts were effective in polymerizing diepoxide **2**. A small amount of rearrangement and/or dimerization was observed in a few



1 **3**

Scheme 5.

cases, but recovered monomer constituted the majority of all reaction products. In hindsight this might have been expected. Cationic polymerization of epoxides involves nucleophilic attack of the epoxide on the cation (either the initiator or the growing chain end). The resulting oxonium ion is attacked nucleophilicly by another epoxide oxygen (Scheme **2**). This attack must come from the back side of the epoxide cation [4].

Ring forming polymerizations of diepoxides proceed *via* an intra-intermolecular mechanism. Steric constraints within this macrocyclic system do not allow the incipient cation to 'reach around' to the 'inside' of the ring system to begin reaction with the second epoxide moiety.

CONCLUSIONS

The diepoxide macrocycle (*E,E*)-1,2:5,6-diepoxy-[6.2]paracyclophane was synthesized by peracid oxidation of the (*E,E*)-[6.2]paracyclophane-1,5-diene. The resulting compound showed an unexpectedly high number of resonances in both the ^{1}H and ^{13}C NMR spectra. Careful analysis of these spectra as well as the COSY and NOESY NMR spectra confirm that the expected product was produced. This compound was not successfully polymerized by cationic initiators due to the constrained geometry of the macrocyclic ring system.

ACKNOWLEDGEMENTS

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CONFLICT OF INTEREST

The author(s) confirm that this article content has no conflicts of interest.

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