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DIAXIAL CONFORMATION OF CYCLOHEXANE FRAGMENTS IN DICYCLOHEXANOTRITHIA-12-CROWN-4

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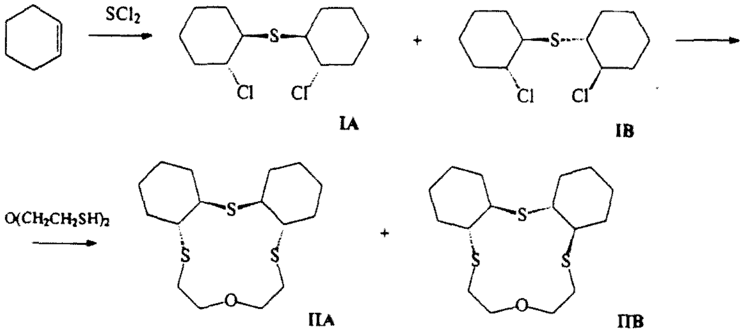
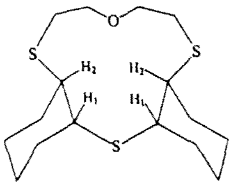
Tricrown ethers have attracted considerable attention as selective complexing agents for heavy metal ions [1, 2]. In a study of methods for the synthesis of these macroheterocycles by the addition of sulfur dichloride to alkenes [3], we obtained *trans*-5,6-*trans*-8,9-dicyclohexano-1-oxa-4,7,10-trithiacyclododecane (II) as a 1:1.2 mixture of diastereomers IIA and IIB, which could not be resolved.



Tricrown ethers IIA and IIB were synthesized by heating dichlorides IA and IB with 2,2'-dimercaptodiethyl ether in ethanol at reflux for 5 h with subsequent purification by chromatography on a silica gel column using 3:2 ether–hexane as the eluent.

The formation of a mixture of diastereomeric dichlorides I was studied by Tolstikov et al. [4]. Only adducts with *trans* configuration are formed. This configuration is retained upon the replacement of chlorine by the acetoxy or hydroxy group. Acetolysis or hydrolysis leads to identical diastereomer mixtures starting from dichlorides IA, IB, or their mixture. These observations were attributed to the formation of an episulfonium ion in the first solvation step. Two possible pathways for opening of this ion lead to stereoisomers [4]. Our present data support this scheme. The 1:1.2 mixtures of diastereomers IIA and IIB was obtained starting both from a mixture of dichlorides IA and IB and from diastereomer IIB isolated by crystallization from 1:1 ether–petroleum ether.

An unexpected result was obtained in a study of the PMR spectra of IIA and IIB on a Varian VXR-400 spectrometer for $CDCl_3$ solutions. The signals for 1-H and 2-H are poorly resolved quartets with width at half-height of 12-13 Hz (3.11 and 3.58 ppm) for IIA and 8.5-9.0 Hz (3.29 and 3.38 Hz) for IIB. Thus, the coupling constants with the vicinal protons are about 4 and 3 Hz, respectively, which indicates virtually complete predominance of the diaxial conformation in the cyclohexane fragments [4, 5].



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To our knowledge, this is the first example of the existence of two consecutive transoid S–C–C–S fragments in a relatively small 12-membered ring.

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