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The Synthesis of Chiral Derivatives of 1,4,7,10,13,16-Hexaoxacyclooctadecane

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SUMMARY

The asymmetrical poly glycoles obtained by the addition of epoxides to the poly ethylene glycoles condensed with the dihalo glycoles to form the chiral derivatives of 1,4,7,10,13,16-hexa oxacyclooctadecane.Macrocyclic ethers obtained performed the utility of our new procedure.

INTRODUCTION

Quite a number of papers appeared since the reported study of Pedersen$^{1)}$ regarding the synthesis of various type of Macro cyclic ethers. In general Williamson type of procedures have been mostly developed emphasizing the template effect and the role of reaction media. Dale$^{2)}$ has first prepared the ditosylates of polyethylene glycoles for the cyclisation process. Greene$^{3)}$ has examined the template effect depending on the solvent. Cram$^{4,5)}$ and his collaboraters have designed some chiral ethers utilised them for enantiomer discrimination. Recently Stoddart$^{6,7)}$ has tried some derivatives of 18-crown-6 and focused his studies on the stereochemical factors which could play remarkable role on the complexing behavior of the macrocyclic ethers.

It is clear that the hydrophobic character of the macrocyclic ether could be varied by the substituents on the ring. On the other hand the route of interconvertion of macrocyclic ring could be influenced by the nature of side groupings which affect the cation binding ability depending on the solvent.

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RESULTS

In our presented study we have synthesised the following compounds starting from epichlorhydrine. We first obtained some 1-chloro-3-alkoxy-2-propanols by the acid catalysed addition of some alcoholes to epichlorhydrine (Ia-If). Some of them were then converted into the asymmetrical epoxides in the presence of NaOH (IIa -IIc). The epoxides obtained were reacted with some of poly ethylene glycoles and their addition products were investigated[8)] (IIIa-IIIk).

Above glycoles were reacted with the dihalogen glycoles to

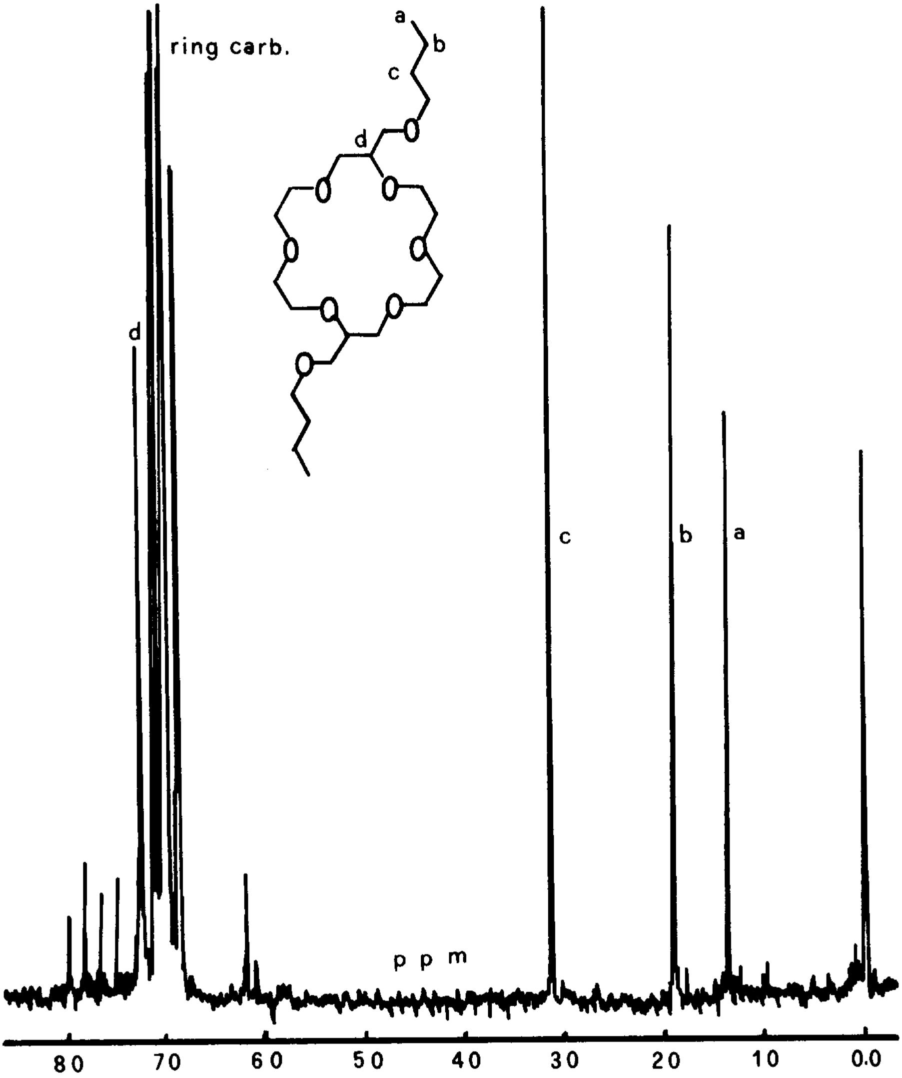
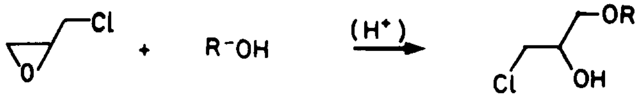
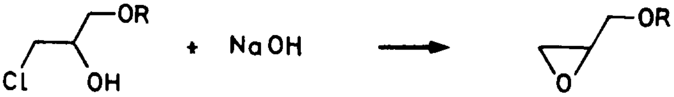


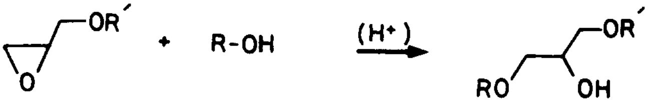
FIGURE-I. 20 MHz ^{13}C Spectrum of 2,11-di(2-oxo-n-hexyl)-1,4,7, 10,13,16-hexaoxacyclooctadecane(VIb) in $CDCl_3$.



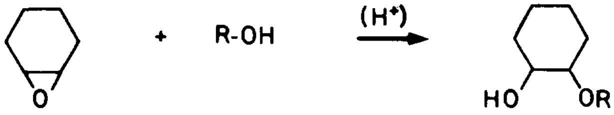
I.a. R:C_6H_{11}
I.b. R:i-C_4H_9
I.c. R:n-C_4H_9
I.d. R:ClC_2H_4
I.e. R:$ClC_2H_4OC_2H_4$
I.f. R:$BrC_2H_4OC_2H_4$



II.a. R:n-C_4H_9
II.b. R:i-C_4H_9
II.c. R:C_6H_{11}

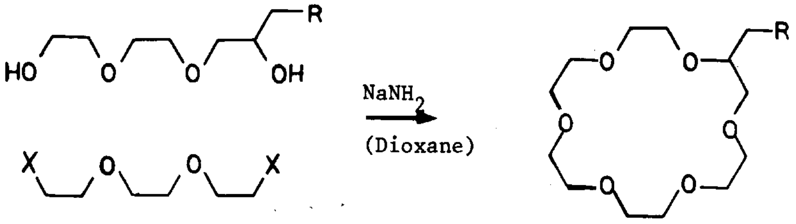


III.a.	R':C_6H_{11}	R:$HOC_2H_4OC_2H_4$
III.b.	R':n-C_4H_9	R:$HOC_2H_4OC_2H_4$
III.c.	R':i-C_4H_9	R:$HOC_2H_4OC_2H_4$
III.d.	R':C_6H_{11}	R:$ClC_2H_4OC_2H_4$
III.e.	R':n-C_4H_9	R:$ClC_2H_4OC_2H_4$
III.f.	R':i-C_4H_9	R:$ClC_2H_4OC_2H_4$
III.g.	R':C_6H_{11}	R:$BrC_2H_4OC_2H_4$
III.h.	R':n-C_4H_9	R:$BrC_2H_4OC_2H_4$
III.i	R':i-C_4H_9	R:$BrC_2H_4OC_2H_4$



IV.a ($HOC_2H_4OC_2H_4$)R

IV.b. ($ClC_2H_4OC_2H_4$)R

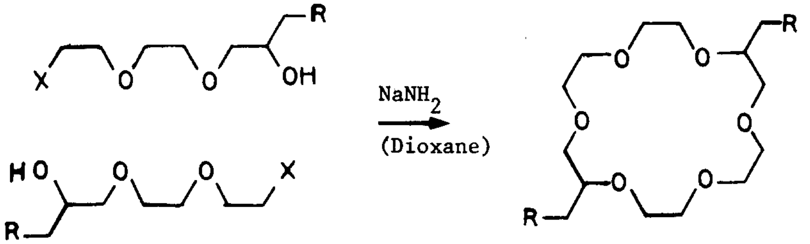


V.a. R:$C_6H_{11}O$

V.b. R:i-C_4H_9O

V.c. R:n-C_4H_9O

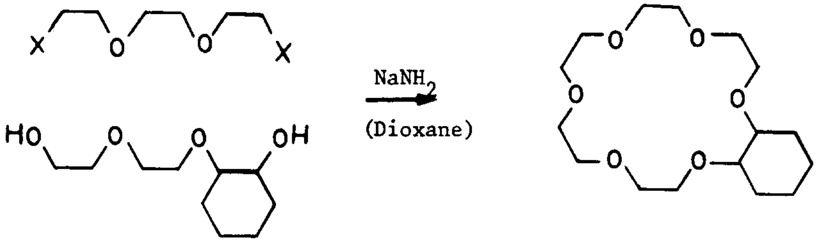
X(Cl,Br)



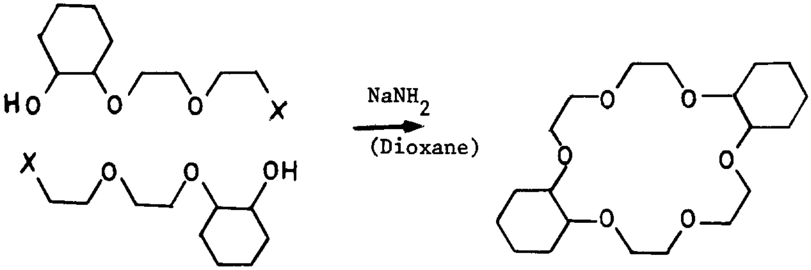
VI.a. R:i-C_4H_9O

VI.b. R:n-C_4H_9O

X(Cl,Br)



VII.a. X(Cl,Br)



VII.a. X(Cl)

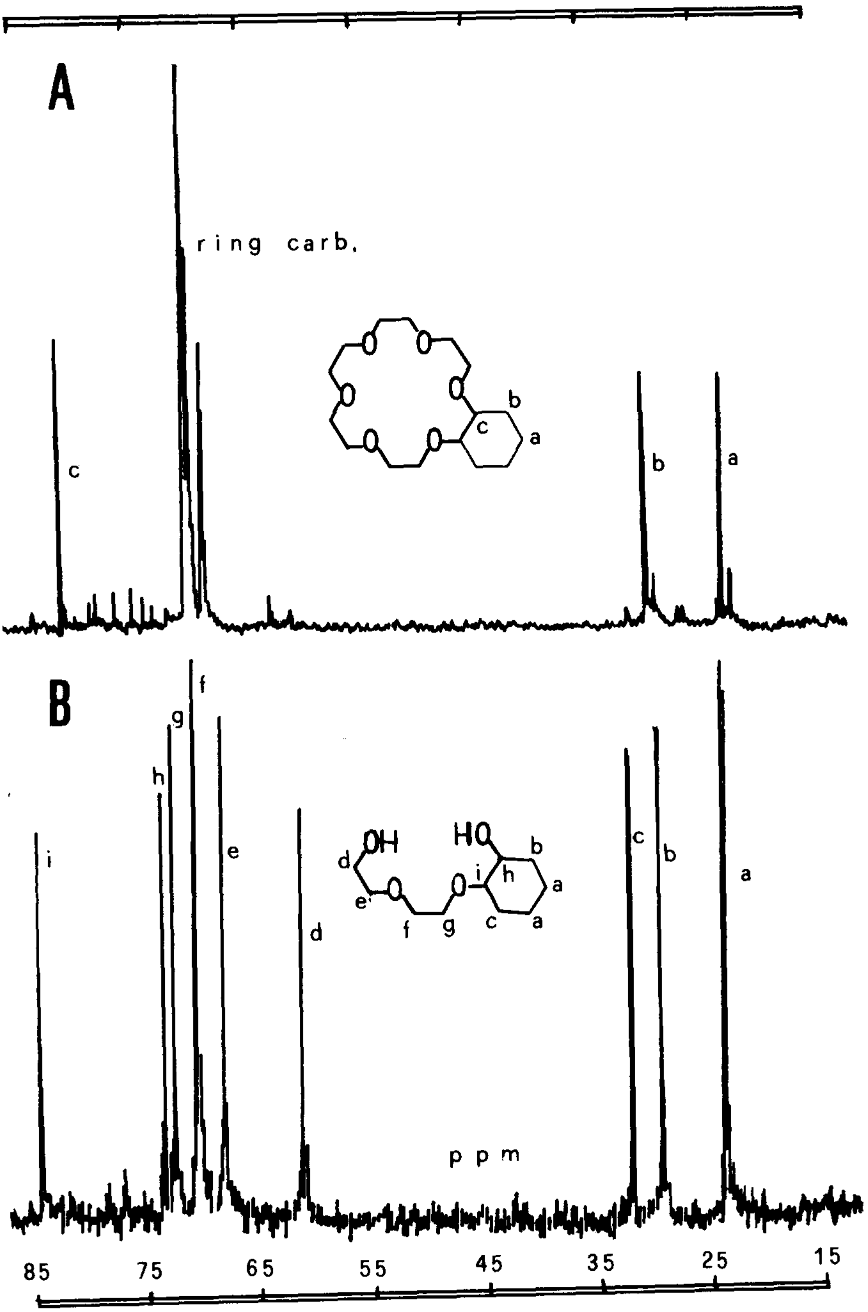


FIGURE.IIA.20 MHz ^{13}C spectrum of 1,4,7,10,13,16-hexaoxabicyclo [4.0.16]docosane in $CDCl_3$. Raw product(VII.a.).

FIGURE.IIB.20 MHz ^{13}C spectrum of 2-[β-(2-hydroxycyclohexyloxy) ethoxy]ethanol. Twice distilled product (V.a.).

form the mono substituted derivatives of 1,4,7,10,13,16-hexaoxa cyclooctadecan in the presence of $NaNH_2$ in dioxane solutions. (Va-Vc). Disubstituted derivatives were prepared trough the dimerisations of mono halogen derivatives of glycoles under the similar conditions given above(Va-Vb).Figure-I.

In connected with the method described above we could obtain the cyclohexyl and dicyclohexyl-18-crown-6 starting from cyclo hexeneoxide which was first reacted with glycoles. The poly ethylene glycoles derived (IVa-IVb) were reacted under the above given conditions in order to obtain the cyclohexyl derivatives of 18-crown-6 (VIIa-VIIIa).Figure-IIA,IIB.

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