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Some Aromatic Derivatives of 1,4,7,10,13,16-Hexaoxacyclooctadecane

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SUMMARY

Some of the derivatives of polyglycoles were obtained just by reacting the α-chlorhydrines with phenols, α-naphtol and β-naphtols in the presence of NaOH. Derivatives obtained were condensed with the ditosylates of polyethyleneglycoles in the presence of potassium tert-butoxide in THF and some asymmetrical mono and disubstituted hexaoxacyclooctadecanes were formed.

INTRODUCTION

Syntheses of various type of substituted macrocyclic ethers were reported by Stoddart (1) and similar type of studies was outlined by Cram (2). Such results revealed a rather interesting field of macrocyclic ethers These studies mostly deal with the behaviour of such compounds to bind the respective cations and with the stereoselectivity of the systems (1,2).

Regarding the studies reported, Stoddart synthesized some chiral cryptands from l-tartaric acid and d-mannitol (1). Kenji has developed the preparation of some sulfur containing enzyme models designed with Crown ethers (3). As we have reported previously from our laboratory we have developed a quite favourable method to obtain some polyglycoles in order to synthesize some polyoxalactones and macrocyclic ethers (4,6).

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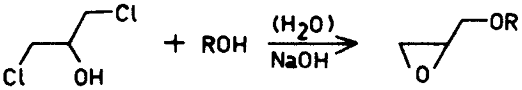
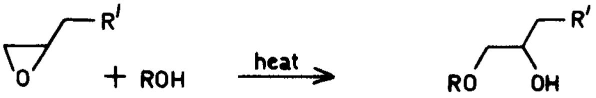
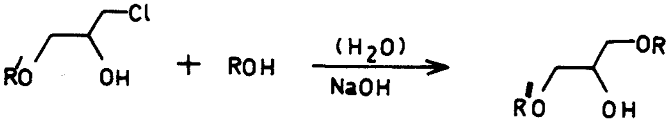


I.a. (R:C_6H_5)
I.b. (R:p-$NO_2C_6H_4$)
I.c. (R:α-$C_{10}H_7$)
I.d. (R:β-$C_{10}H_7$)



II.a. (R': Cl ..., R: $HOCH(CH_2R')$)
II.b. (R': Cl ..., R: $HOCH(CH_2R')CH_2OC_2H_4$
II.c. (R': C_6H_5O., R: $HOCH(CH_2R')CH_2OC_2H_4$
II.d. (R': α-$C_{10}H_7O$, R: HOC_2H_4
II.e. (R': α-$C_{10}H_7O$, R: $HOCH(CH_2R')CH_2OC_2H_4$



III.a. R': HOC_2H_4...., ..,
R : β-$C_{10}H_7$..., .., R": HOC_2H_4

III.b. R': $HOC_2H_4OC_2H_4$...,
R : β-$C_{10}H_7$...,..., R": $HOC_2H_4OC_2H_4$

III.c. R': $HOCH(CH_2Cl)CH_2$,
R : β-$C_{10}H_7$...,..., R": $HOCH(CH_2OR)CH_2$

III.d. R': $HOCH(CH_2Cl)CH_2OC_2H_4$
R : β-$C_{10}H_7$...,..., R": $HOCH(CH_2OR)CH_2OC_2H_4$

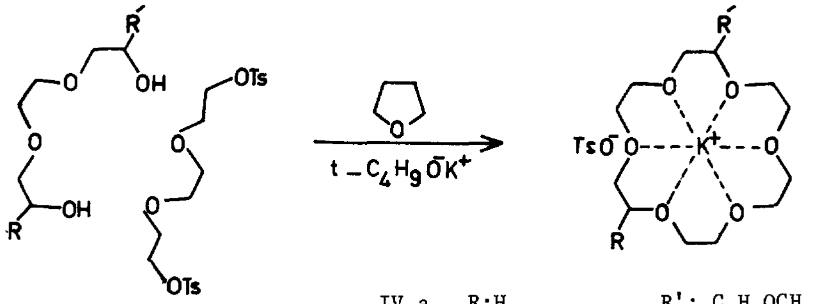
III.e. R': $HOCH(CH_2Cl)CH_2OC_2H_4$
R : α-$C_{10}H_7$...,..., R": $HOCH(CH_2OR)CH_2OC_2H_4$

RESULTS

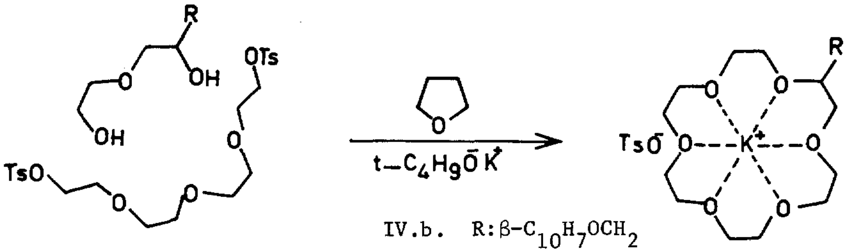
In the present study, some of the epoxides to be condensed were prepared by reacting the 1,3-dichloro-2-propanol with some of the phenols and naphtols in the presence of NaOH in water solution (I.a-I.d). However, some of the glycoles to be derived were then reacted with epoxydes obtained as cited above by warming without a catalyst(II.a-II.c).

On the other hand the glycoles with the aromatic side chain were synthesised just by developing the method of Fairborne(7). We therefore reacted some α-halohydrine attached glycoles with phenols and naphtols in the presence of NaOH in water as solvent.

α- and β-naphtoxymethyl substituted 1,4,7,10,13,16-hexaoxacyclooctadecanes were obtained mostly in crystalline form reacting the corresponding glycoles and ditoluensulfonates of di- or tri- ethylene glycoles in the presence of potassium tert-butoxide in THF by warming for about 24-48 hours.



IV.a. R:H.........., R': $C_6H_5OCH_2$
IV.b. R:α-$C_{10}H_7OCH_2$, R': α-$C_{10}H_7OCH_2$
IV.c. R:β-$C_{10}H_7OCH_2$, R': β-$C_{10}H_7OCH_2$



IV.b. R:β-$C_{10}H_7OCH_2$

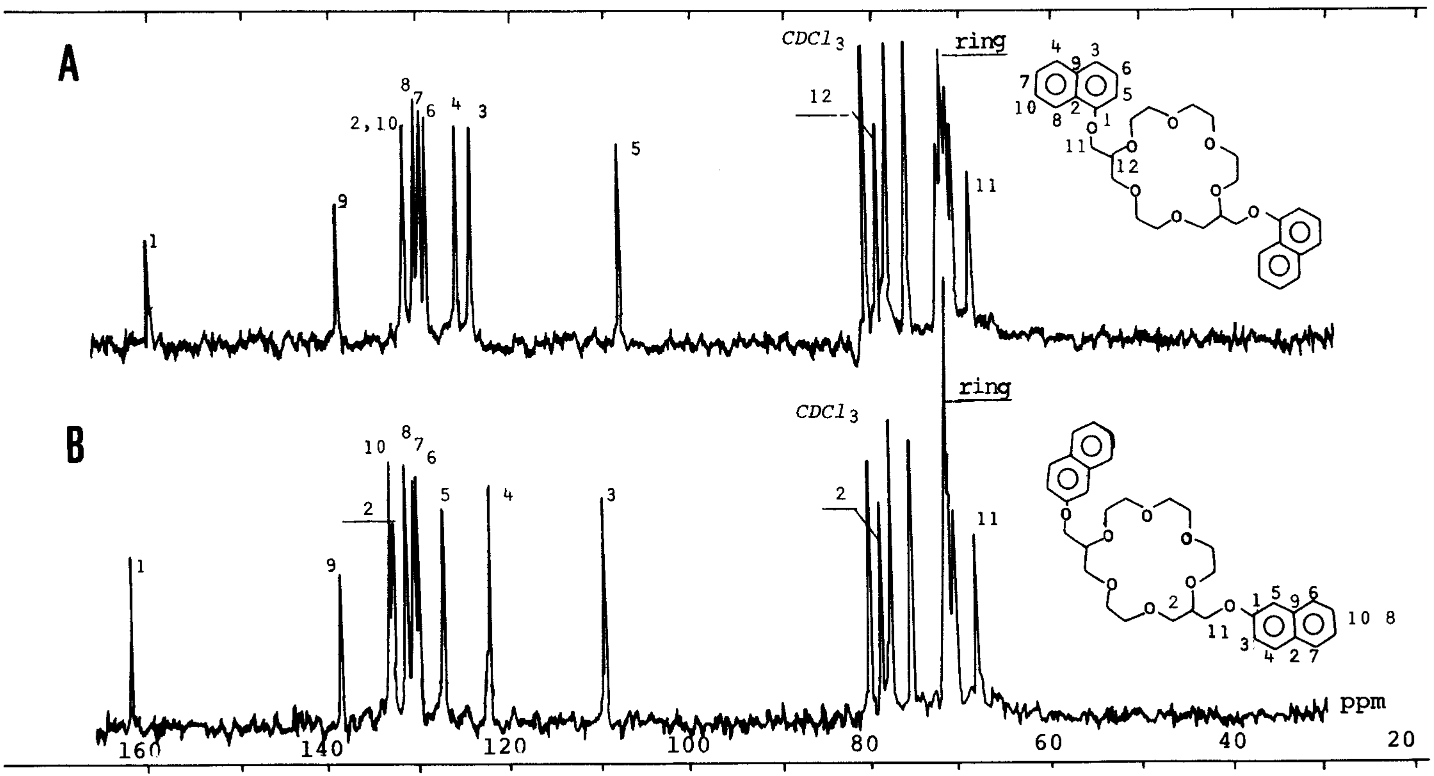


Figure-I.A. 15 MHz ^{13}C spectrum of 1,4,7,10,13,16-hexaoxa-2,9-di-α-naphtoxymethylcyclooctadecane in CDCl$_3$

I.B. 15 MHz ^{13}C spectrum of 1,4,7,10,13,16-hexaoxa-2,9-di-β-naphtoxymethylcyclooctadecane in CDCl$_3$

purifications were carried out by eluations of raw material on Al_2O_3 columns with benzene (IV.a-IV.c). However, regarding the earlier results THF as a solvent seems rather suitable and tert-buthyl potassium could be considered as a'soft' base forming less alkene type of side products (4) (Fig.I.A-I.B). ^{13}C analyses were conducted by 15 MHz JEOL NMR Spectrometer, model FX-60Q.

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