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# The Synthesis of Chiral Crown Ethers 1-Phenoxymethyl-3,6,9,12,15,18-hexaoxocyclooctadecane

by

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# The Synthesis of Chiral Crown Ethers
# 1-Phenoxymethyl-3,6,9,12,15,18-Hexaoxacyclooctadecane

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## ABSTRACT

Starting from epoxides through their diglycols the synthesis of some derivatives af 18-Crown-6. such as 1-Phenoxymethyl- 3. 6. 9. 12. 15. 18- hexaoxacylooctadecane were synthesised by williamson method and reported.

## INTRODUCTION

Macrocyclic ethers exhibit very interesting and unusual ion binding properties. Their central hydrophilic cavities ringed with electropositive binding atoms and exterior flexible frame works exhibiting hydrophobic behavior. They show a perfect ability to bind a quite number cations they even undergo conformational changes during binding(1).

Their hydrophobic exteriors allow them to solublize ionic substance in nonaqueous solvents. Particularly the strong tendency shown by the macrocyclic ethers for alkaline and alkaline earth metal ions, their selective binding of these cations resulting in their use in many fields of chemistry(2,3).

Complexing of Crown Ethers is due to electrostatic attraction between the cation and the negative end of C–O dipoles. The stability of the polyether complexes depends primarly upon how well the cation fits into the polyether ring depending on the charge density of the cation and the solvating power of the medium in solution.

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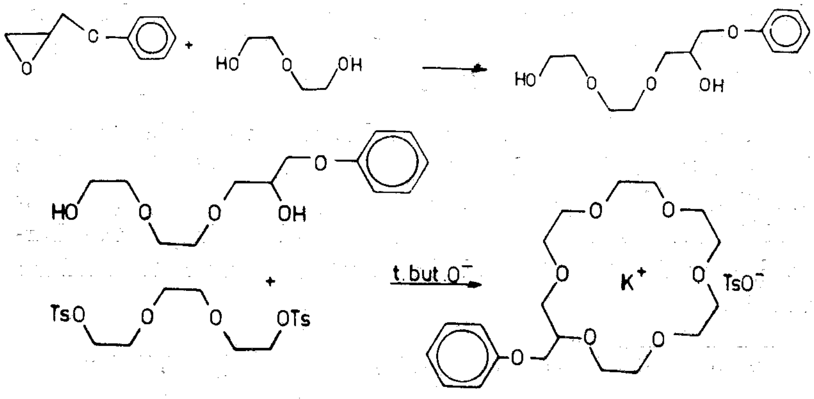
They have been first synthesised by Pedersen by the aid of Williamson synthesis, of dichlorides and cathecoles. Dale has tried diglycoles reacting with ditosylates of diglycols obtaining satisfactory yields(4). Green investigated the template effect and the solvent during the cyclication processes(5). Okahara Recently reportes the cyclication of monotosylates in the presence of KOH which improves the general methods(6).

Parsons first reported the synthesis of branched derivatives of 18-Crown-6(7). Stoddart synthesised Similar derivatives starting from saccarides(8).

We now report the synthesis of phenoxymethyl -18-Crown-6 from 1,3-dichlor-2-propanol which was first converted to 1-(phenoxy)-2, 3-epoxypropane in 63 % yield reacting with phenol in the presence of NaOH. Epoxydes were tried to react with glycols in order to obtain higher oligomers we therefore allowed to react the 1-(phenoxy)-2, 3-epoxypropane with diethylene glycol and 1-(phenoxy)-4,7-dioxononan-2,9-diol obtained in 70 % yield. Triethyleneglycol ditosylate was condansed with 1-(phenoxy)-4, 7-dioxononan-2,9-diol forming 1-phenoxymethyl-3, 6, 9, 12,15, 18-hexaoxacyclooctadecane in more than 30% yields. However in order to obtain the phenoxymethyl derivative we synthesied the 1-phenoxyethyl-4-oxohexane-2, 6-ditoluensulphonate it was then recated with tetraethyleneglycol in the presence of K$^+$ t-butoxide and it was observed that less then 30% cylic product formed in such a reaction.



The Generale scheme of the reaction is given above to form the macrocyclic ether.

## EXPERIMENTAL

1-(phenoxy)-2, 3-epoxypropane (I), was obtained according to Fairbourne. (9) sothat 188 g phenol (2M) was allowed to heat at 70–80°C with 1,3-dichlor-2-propanol of 258 g (2M) in the presence of 593 gr of 27 % NaOH-water solution organic layer of the reaction mixture was dried and purified through out the disstillation. 190 g of product (63–65 % yield) at 120 / 13 mmHg.

1-phenoxy-4, 7-dioxanonan- 2,9- diol (II), 30 g (0,2M) 1-(phenoxy)-2,3- epoxypropane were reacted with 66 gr (0,62M) diethyleneglycol at 160°C to 200°C for two hours and then at 200°C for 4 hours. Row product distilled at 180–200°C / 3 mm torr gave 14,6 g of pure compound of 28 % yield.

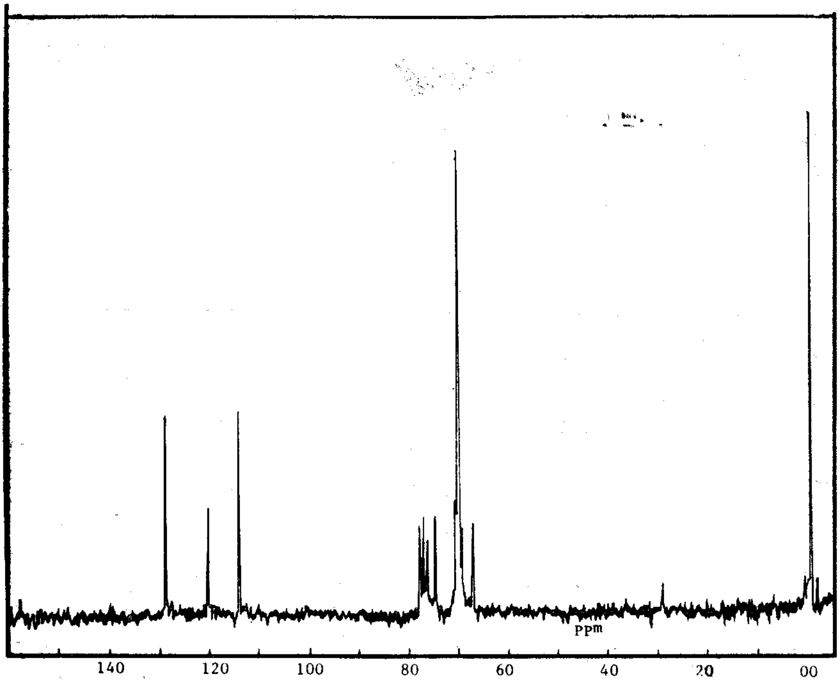
Table–1. Synthesis of Some glycoles for the 1-phenoxymethyl-18-Crown-6

| Name | Formule | B.p. °C | m.p. °C | yield |
|---|---|---|---|---|
| 1-(phenoxy)-2,3-epoxypropane | $C_9H_{10}O_2$ | 120°/13 mmHg | — | 63 |
| 1-phenoxy-4, 7-dioxononan-2, 9-diol | $C_{13}H_{20}O_5$ | 180–200°/3mmHg | — | 28 |
| 1-chlor-4-oxohexane-2,6-diol | $C_5H_{11}O_3Cl$ | 120–116°/1mmHg | — | 55 |
| 1-chlor-4,7-dioxononan-2,9-diol | $C_7H_{15}O_4Cl$ | 130–140°/1mmHg | — | 50 |
| 1-chlor-4-oxohexane-2,6-ditoluensulphonate | $C_{19}H_{23}O_7ClS_2$ | oil | — | 70 |
| 1-phenoxymethyl-3, 6, 9, 12, 15, 18-hexaoxacyclo octadecane | $C_{19}H_{30}O_7$ | oil | — | 30 |

1-chlor-4-oxohexane-2, 6-diol(III) was obtained by Kharasch's method... 278 gr (3,0M) epichlorhydrin and 379 g (6,0M) 1,2-ethandiol were placed in 2 1 round bottomed flask which was mounted in a fume cubroad. While the mixture was cooled and mixed regularly 10 ml of conc. $H_2SO_4$ was added dropwise (COUTION). After heating the mixture 12 hours on a steam bath it was treated with 38 gr $BaCO_3$ than filtered. Distillation at 110–120°C / 1 mmHg gave the product of 55 % yield.

1-chlor-4,7-dioxanonan-2,9-diol (IV) was obtained according to the method given above. So 92,6 g (1M) epichlorhydrin and 212 gr (2M) diethyleneglycol were reacted in the presence of 4,33 ml ml $H_2SO_4$ (8,5 mM) during 12 hours. Row product distilled after neutralisation.

1-chlor-4-oxohexane-2,6-ditoluensulphonate (V), 15,5 g (0,1M) of 1-chlor-4-oxohexane-2,6-diol and 80 ml of pyridin were placed into the 250 ml flask The cooled mixture was then reacted with 38,5 g (0,2 M) toluen sulphochloride with in the three hours, row product was extracted by $CHCl_3$ and dried, then purified on $Al_2O_3$ column before use.



Figure–I. 20MHz $^{13}$C spectrum of 1-phenoxymethyl-3, 6, 9, 12, 15, 18-hexaoxocyclooctadecane in CDCI$_3$ reference to TMS.

1-(phenoxymethyl)-3,6,9,12,15,18-hexaoxocyclooctadecane (VI), 259 gr (0,07 M) potassium was disolved in a 250 ml THF solution of 6.75 ml t-buthanol. The mixed solution of 9.21 g (0,036 M) 1-phenoxy-4,7-dioxanonan-2,9-diol and 26,4 g (0,036 M) triethylenglycolditosylate was added to the potassium buthoxide solution gradually during the boilling. Reaction mixture was then refluxed for 24 hours and filtered. Evaporated solution gave an oily mixture which was then refluxed for 24 hours and filtered. Evaporated solution gave an oily product which was than purified on acidic $Al_2O_3$. Hygrouscopic material was obtained 4.0 gr of 30 % yield.

## ACKNOWLEDGEMENT

Spectrums were obtained by Analytical Chemistry Department of Ankara University with a Varian T60–A model spectrometer. 20 MHz $^{13}C$-spectrum was obtained by Research Institute of Organic Chemistry of Ankara University with a Varian CFT–20 model spectrometer therefore greatly acknowledged.

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## ÖZET

Bazı asimetrik yapılı 18-Crown-6 sentezlerinin yapılması maksadı ile asimetrik glikoller elde edilmiş ve bunlar glikolerin ditoluen sulfonat türevleri ile etkileştirilmişlerdir. Bu yoldan 1- (fenoksimetil) - 3, 6, 9, 12, 15, 18-heksaoksasiklooktadekan'ın sentezi yapılmıştır.

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