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Polyoxo Lactones and their Solvation Properties

by

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Polyoxo Lactones and their Solvation Properties

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ABSTRACT

Some polyoxo lactones prepared by condensing polyetyleneglycoles with their correpsonding diaciddichlorides in satisfactory yields.

In order to investigate their solvating ability for cations in aprotic media we also examined the effect to polyoxo lactones on optical spectra of α- (2, 4-dinitrophenyl) actophenone in the presence of $N(C_2H_5)_3$ in THF.

Results were found in accordance with observations on Cyclicpolyoxo compounds of similar nature reported earlier.

INTRODUCTION

It has been shown that the macrocyclic ethers considerably increase the solubility of inorganic salts in non polar media and can form crystalline stochiometric complexes with a variety of alkaline and alkalinearth salts (1–3). However certain macrocyclic antibiotics, such as nonactin, enniatin, etc are known to exhibit a high degree specifity in metabolic bahevior in the presence of such cations. It has been reported that in CH_2CI_2 the macrocyclic antibiotic nonactin binds the K^+ ion more efectively than dicyclohexyl–18–Crown–6(4–6)

In our study we prepared the lactones of polyethylen glycols with polyglycolic acid dichlorides in order to investigate the solvation properties of macrocyclic lactones as "bridge" compounds between the Crown ethers and macrocyclic antibiotics (Table-1)

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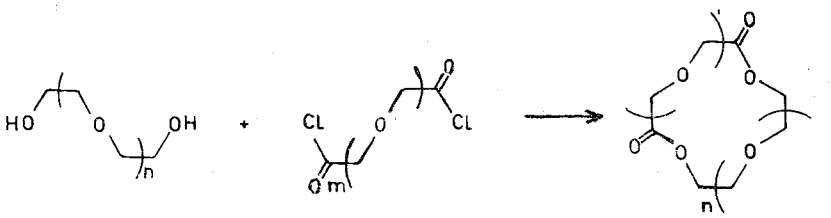

Cyclization was carried out in the presence of equimolar amount of pyridin of dichlorides in satisfactory yields. 0,1–0,2 M solutions of dichlorides and glycoles in benzen were reacted through a peristaltic pump. Corresponding cyclic esters were quite stable and easily purified by crystallization or distillation (Table-1) Some of polyoxo lactones obtained exhibited satisfactory results regarding to their solvating properties.

Various spectroscopic methods have been used to study structures of İon pairs and their solvates in aprotic solvents (7,8). Smid and his co-workers proved that specific cation solvent interactions in a variety of aprotic media give rise to the formation of various type of ion pairs which could be quantitatively determined from their optical absorbtion spectra (8). They have also proved that, complexation of certain Crown ethers in aprotic media give rises crown–separated ion pairs (9).

RESULTS AND DISCUSSIONS

In our study, in order to determine the cation binding properties of macrocyclic lactones we investigated optical spectrum of some carbanions in the presence of polyoxo lactones. We obserwed that THF solutions of *a*-(2,4–dinitrophenyl) acetophenone give an absorption of 430 nm which drasticaly changes with, temperature indicating the existance of ion pairs in equilibrium.

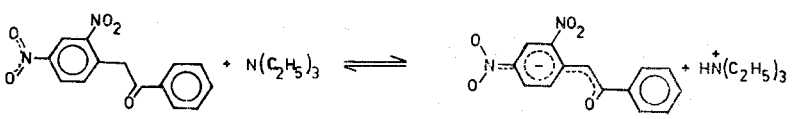

Table 1. Some polioxo lactones (▽)

n	m	Name	M.p °C	B.p °C	% yield	$\delta_1(COCH_2O)$ (ppm)	$\delta_2(OC_2H_4O)$ (ppm)	δ_1/δ_2
0	2	1, 4, 7, 10–tetraoxocyclododeca–2,3–dion	59	—	70–75	4,45	3,75	1:2
0	3	1, 4, 7, 10, 13–pentaoxocyclopentadeca–2,3–dion	84	—	75–80	4,45	3,75	1:3
1	2	1, 4, 7, 10, 13–pentaoxo–15–chlormethlcyclopentadeca–2,6–dion	86	—	80–85	4,35	3,65	2:3
1	2	1, 4, 7, 10, 13–pentaoxocyclopentadeca–2,6–dion	98	—	80–85	4,35	3,70	1:1
1	3	1, 4, 7, 10, 13, 16–hexaoxocyclooctadeca–2,6–dion	79	—	35–40	4,25	3,70	3:2
2	2	1, 4, 7, 10, 13,16–hexaoxocyclooctadeca–2,9–dion	(x)	180/0,02	45–40	4,25	3,70	3:2
2	3	1, 4, 7, 10, 13, 16, 19–heptaoxocycloheneicosa–2,9–dion	oil	210/0,0,2	35–45	4,25	3,70	8:3

(x) Hygrouscopic material

(V) Pmr spectrums were obtained with a 60 MHz spectrometer of Varian model T 60A in $CDCl_3$, (δ) Values given in ppm internal reference to TMS.

In the presence of excess of base the formation of salts is almost completed, and the concentration of the ion pairs could be altered by the polyoxo lactones added. We therefore found that the system was a convenient probe to study complexing ability of polyoxo lactones.

A mixture of the keton and lactone in a certain ratio was prepared in THF. The concentration of the two sepcies was kept around 10^{-3}M due to tbe limited solubilities. Recorded absorbances ploted versus amount of polyoxo pactones for relative binding effects. A chracteristic result obtained is displayed an Figure-1. Which proves that polyoxo lactones provides better mediums even for alkil amonium salts of lower electropositivity.

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ÖZET

Bazı poliokso laktonlar, polietilenglikoller ve bunların diasitlerinin diklorürleri ile kondanse edilerek uygun verimler ile elde edilmiştir:

Bunların protonsuz ortamda katyon çözme etkilerini incelemek üzere, THF'li çözücülerde ve $N(C_2H_5)_3$ bulunan ortamda α-(2,4-dinitrofenil) asetofenon'un optik spektrumuna etkisini inceledik.

Elde edilen sonuçlar halkalı poliokso bileşikler üzerinde daha önce yapılan çalışmalardaki sonuçlara uymaktadır.

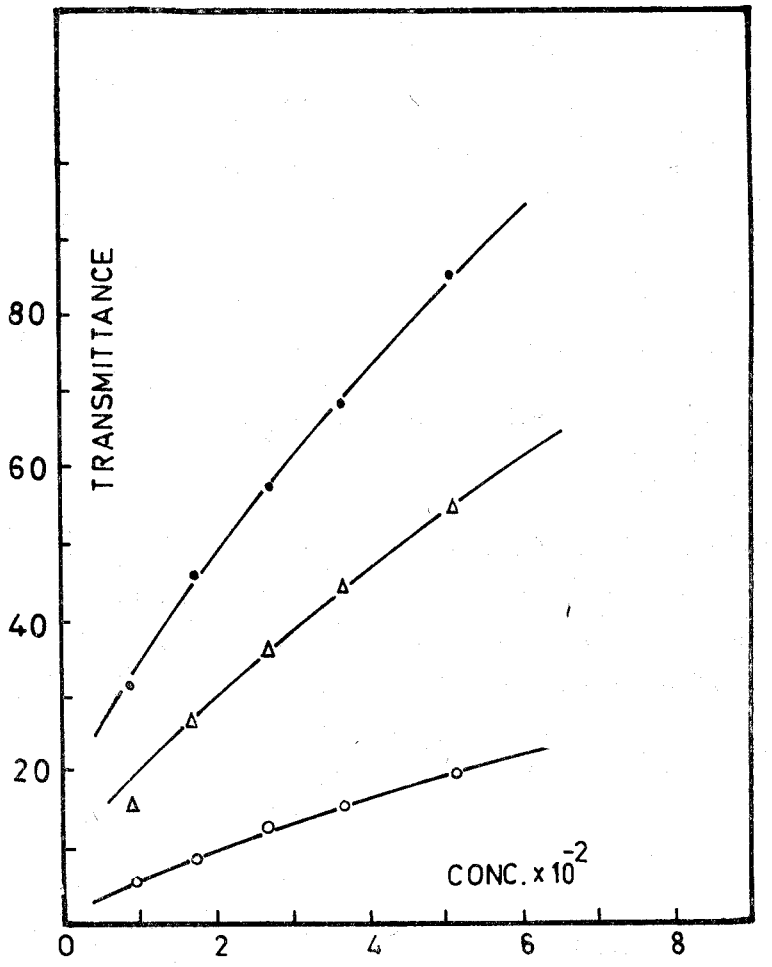

Figure 1. Dependance of formation of complexed ion pairs on concentration of macrocyclic compounds in THF solutions in The presence of 2,69 M triethylamine. Concentration of α-(2,4-dinitrophenyl) acetophenone is kept $3.75.10^{-4}$ M. (Eq.-1)
(A) 1, 4, 7, 10, 13, 16-hexaoxocyclohexadeca-2,6-dion.
(.) Hexaethyleneglycoldimethyl ether.
(o) 1, 4, 7, 10– tetraoxocyclododecane (10).

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