Cyclic Oligo-ethers Related to Ethylene Oxide

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Summary The preparation of cyclic oligo-ethers consisting of five or more $-CH_2CH_2-O-$ units and the analysis by n.m.r. of oligomer mixtures is described.

CYCLIC ethers are useful for conformational studies of macrocyclic saturated compounds, since they contain geometrically well defined dipoles and resemble cycloalkanes conformationally; 16-membered cyclic tetra-ethers have already been studied.[1]

The simplest cyclic oligo-ethers belong to the series of general formula (I) of which the lowest members are ethylene oxide and 1,4-dioxan (n = 1 and 2). The cyclic tetramer (n = 4) has been reported to be formed in low yield by isomerization of ethylene oxide with triethylaluminium as catalyst.[2] Higher oligomers ("crown compounds") have been prepared by Pedersen[3] in two steps from a glycol component and a corresponding dichloride component in polyether solvents; yields were very low, the cyclic hexamer (n = 6) being obtained in an overall yield of only 0·2%.

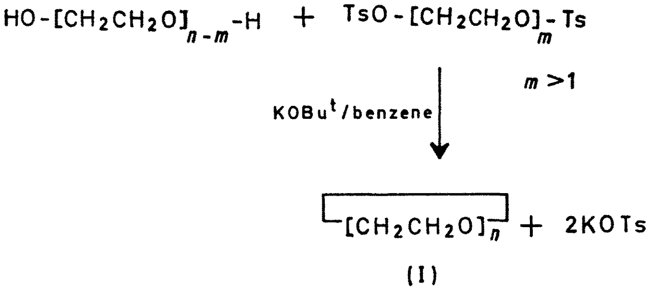
TABLE

n in (I)	M.p.	Yield of isolated product (%)	Mol. weight[a]	Chem. shift (p.p.m.) In $CDCl_3$ Alone	Chem. shift (p.p.m.) In $CDCl_3$ With $Eu(dpm)_3$[b]	Chem. shift (p.p.m.) In CCl_4 Alone	Chem. shift (p.p.m.) In CCl_4 With $Eu(dpm)_3$[b]	Dipole moment (D) Measured in benzene	Dipole moment (D) Calc. for free rel. orientation
2				3·70	5·75	3·58	4·83		
4						3·57[c]			
5	Liquid	20[d]	220	3·70	4·52	3·58	4·30	3·01	2·91
6	39°	33		3·70	5·97	3·57	6·78	2·65	3·18
7	Liquid	26[d]	308	3·68	7·05	3·58	7·77	2·84	3·44
8	19°	15[d]	358	3·69	6·30	3·57	6·93	3·04	3·68

[a] By vapour-pressure osmometry. [b] All rings together in solution saturated with respect to europium compound. [c] Ref. 5. [d] Actual yield shown by g.l.c. to be substantially higher.

We report a convenient one-step laboratory preparation of the cyclic pentamer and higher homologues in yields higher than those obtained in ref. 3.

In a modified Williamson ether synthesis an equimolar mixture of a diol component and the ditosylate of the same or another diol component are dissolved in benzene and added dropwise to a heated suspension of potassium t-butoxide in benzene. High-dilution techniques are not needed. Attempts to prepare the trimer and the tetramer gave the hexamer and octamer.



(I)

The complexing properties of these cyclic ethers[3] are used in their isolation. Thus, for the hexamer, a part of the potassium tosylate formed in the synthesis forms a complex (1:1) with the ring, the excess of potassium tosylate is filtered off, and the benzene solution concentrated until the complex crystallizes in needles, m.p. 164°. The salt-free cyclic ether is liberated by adsorbing the complex on an alumina column and eluted with benzene–chloroform

(2:1). If more chloroform is used (1:1) the complex is eluted unchanged.

All these ring compounds, including 1,4-dioxan, had identical n.m.r. shifts both in chloroform and in carbon tetrachloride (see Table). However, addition of the paramagnetic tris(dipivalomethanato)europium[4] caused a dramatic down-field displacement which was strikingly different for each ring (see Table) and allowed an easy analysis of mixtures. No spectral change was observed for any of these compounds even on cooling $CHFCl_2$ solutions down to −130°.

The dipole moments (see Table) were uninformative as to the ring conformations, unlike i.r. spectra which will be reported later and which are useful in the conformational studies of oligo-ethers as free molecules and in the complexed form.

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