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THE PREPARATION OF MACROCYCLIC DI- OR TETRAESTER/ETHER COMPOUNDS FROM GLYCOLS WITH DIACID CHLORIDES BY THE USE OF DIBUTYLTIN OXIDE

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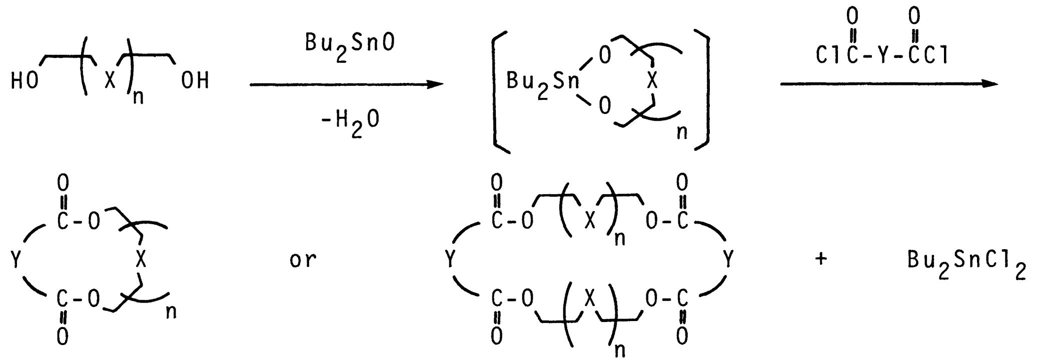
Several macrocyclic di- or tetraester/ether compounds were readily prepared by reacting various oligoethylene glycols with aliphatic and aromatic diacid chlorides, and hetero atoms-containing diethylene glycols with adipoyl chloride by the use of dibutyltin oxide in good yields.

The synthesis and unique cation complexing characteristics of cyclic polyethers were first reported by Pedersen.1) Since that time a large variety and number of macrocyclic compounds have been prepared and their cation complexation properties have been studied extensively. Similarly, macrocyclic ester/ether compounds display some unusual metal- and water-bonding properties,2) in that they may form complexes through either the ether oxygens or the carbonyl groups, or both. The macrocyclic di- and tetraester/ether compounds have been prepared by treating various glycols and diacid chlorides in dilute solutions,3) thermolysis of *o*-phthalate polyester of glycols,4) cyclotransesterification with use of an ion template,5) catalytic cyclization by metal salts of oligoethyleneglycol monosuccinates,6) and sublimation from poly(diethyleneglycol terephthalate).7) Recently, macrocyclic tetraester compounds were prepared by reacting cyclic stannoxanes, as templated diol precursors with diacid chlorides.8)

This work reports the preparation of the macrocyclic di- or tetraester/ether compounds from the reaction of glycols with dibutyltin oxide, and successively with diacid chlorides via the route of Eq. 1.

The following reaction procedure was typical; A mixture of 1.49 g (6 mmol) of dibutyltin oxide, 0.63 g (6 mmol) of diethylene glycol, and 100 ml of dry benzene was refluxed with stirring for 1 h in a 300 ml flask equipped with a Dean and Stark water collector. After completion of the dehydration, a solution of 1.10 g



Diester Tetraester (1)

(6.9 mmol) of adipoyl.chloride in 100 ml of dry benzene was added dropwise to the mixture during 30 min. Reflux was then continued for 2.5 h and the reaction mixture allowed to cool. Then 1 ml of pyridine was added, and the reaction mixture was concentrated under vacuum, and separated by column chromatography on silica gel(Wako-gel C-200; developing solvents, benzene and then ethyl acetate). Dibutyltin oxide was recovered as dibutyltin dichloride from the benzene fraction. The ethyl acetate fraction was recrystallized from hexane to give 1,4,7,14,17,20-hexaoxacyclohexacosane-8,13,21,26-tetrone in 58% yield. The experimental results are summarized in Tables 1 and 2. The structures of these products were consistent with IR, NMR, and Mass spectra and elemental analyses.

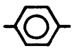
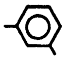
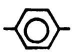
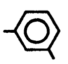
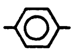
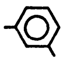
Table 1 shows the results of glycols with adipoyl chloride. 1,5-Pentanediol gave cyclic tetraester compound in 80% yield, but other glycols, containing hetero atoms such as oxygen, nitrogen, and sulfur gave cyclic diester compounds, and the yields of the diesters decrease in the following order O > N-CH_3 > S. It seems that the structure and coordinate bond energies of cyclic pentacoordinated organotin compounds,[9)] which are prepared from the reaction of glycols with dibutyltin oxide contribute to the formation of the diester compounds.

Table 1. Reaction products of glycols($HOCH_2CH_2XCH_2CH_2OH$) with adipoyl chloride

Glycol X	Product[a)]	Yield %	Mp °C
CH_2	T[b)]	80	82-84
O	D	58	76-77
N-CH_3	D[b)]	41	53-54
S	D[b)]	27	63-64

a) D and T mean di- and tetraester compounds shown in Eq. 1, respectively. b) New product.

Table 2. Reaction products of oligoethylene glycols($HOCH_2(CH_2OCH_2)_nCH_2OH$) with diacid chlorides(ClCO-Y-COCl)

Glycol n	Diacid chloride Y	Product a)	Yield %	Mp °C
1	—	T	34	155-158
	CH_2	T	32	67- 69
	$(CH_2)_2$	D	36	32- 35
	$(CH_2)_3$	D b)	35	Oil
	$(CH_2)_4$	D	58	76- 77
		T	57	200-204
		T b)	27	168-170
2	$(CH_2)_2$	D	19	Oil
	$(CH_2)_3$	D b)	29	Oil
	$(CH_2)_4$	D	45	56- 58
		D b)	37	170-172
		T b)	64	108-111
3	CH_2	D	29	65- 67
	$(CH_2)_3$	D	32	Oil
	$(CH_2)_4$	D	29	Oil
		D	64	94- 96
		D	51	93- 94

a) and b) See Table 1.

Table 2 shows the results of oligoethylene glycols with aliphatic and aromatic diacid chlorides. The yields of cyclic di- or tetraester/ether compounds were higher than those of the high dilution technique used hitherto.3) In the case of aliphatic diacid chlorides, minimum ring size of cyclic diester/ether compounds was 11 membered ring. Eight of the products shown in Tables 1 and 2 have not been known previously. Further works on the scope of the reaction are in progress.

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