Macromolecules

Volume 10, Number 3 May–June 1977

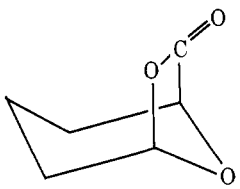
Preparation and Structures of Novel Macrocyclic Oligoesters from 6,8-Dioxabicyclo[3.2.1]octan-7-one

Masahiko Okada,* Hiroshi Sumitomo, and Ichiro Tajima

Faculty of Agriculture, Nagoya University, Chikusa, Nagoya, Japan.
Received December 28, 1976

ABSTRACT: Ten-, twenty-, and thirty-membered macrocyclic oligoesters consisting of alternating tetrahydropyran and ester moieties were prepared by the cationic oligomerization of 6,8-dioxabicyclo[3.2.1]octan-7-one (1). At low temperatures below −30 °C, these cyclic oligomers were selectively formed irrespective of the initiators (BF_3OEt_2, $SbCl_5$, $SnCl_4$, and CH_3COBF_4) and solvents (methylene chloride, 1-nitropropane, and toluene), whereas at higher temperatures only low molecular weight polymer was produced. Both the total yield and composition of the cyclic oligomers were markedly dependent not only upon the temperature but also upon the reaction time, solvents, and concentration of 1. On the basis of the ^1H and ^{13}C NMR data of the isolated cyclic oligomers, along with the x-ray analysis of the crystals of the cyclic dimer, the mechanism of the cationic oligomerization is discussed.

It is well recognized that cyclic oligomers of various ring sizes are inevitably formed in the cationic polymerization of cyclic ethers with three- and four-membered rings,[1-6] cyclic acetals,[7-10] cyclic sulfides,[11] and cyclic imines.[12] However, as far as we know, there has been no reference dealing with the formation of cyclic oligoesters in the cationic ring-opening polymerization of lactones. In the course of the studies on the cationic polymerization of bicyclic monomers containing a tetrahydropyran ring, it was found unexpectedly that the cationic polymerization of 6,8-dioxabicyclo[3.2.1]octan-7-one (1) at low temperatures gave rise to the cyclic oligoesters (2)



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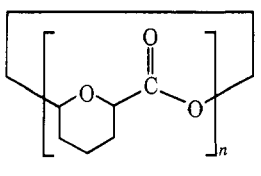

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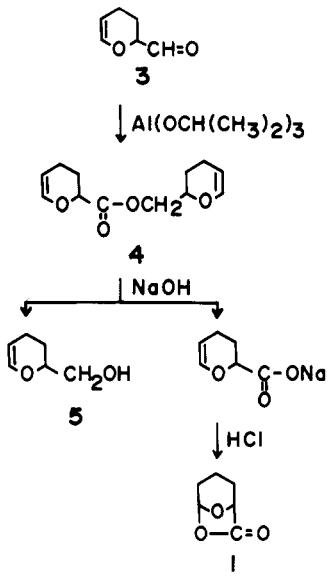
with degree of polymerization of 2, 4, and 6.[13] This interesting finding prompted us to investigate the effect of reaction conditions on the formation of such cyclic oligoesters and to characterize them, because it is expected that these macrocyclic esters could act as an ion carrier in a similar way as naturally occurring macrocyclic antibiotics, nonactin, and its analogues.[14] This paper describes the preparation and structures of the cyclic oligoesters from 1 and also the mechanism of this unique oligomerization.

Experimental Section

In the early stage of this study, the monomer 1 was prepared from 3,4-dihydro-2*H*-pyran-2-carbaldehyde (acrolein dimer) (3) through a series of the following reactions:[15] the oxidation of 3 with silver oxide to the corresponding silver carboxylate, its esterification with ethyl iodide, the alkaline hydrolysis of the ethyl ester, and finally the ring closure of the free carboxylic acid with a trace of hydrochloric acid. This method has a disadvantage of requiring tedious procedure for the regeneration of a large amount of silver oxide for repeated use. Therefore, we adopted an alternative route as illustrated in Scheme I.

Scheme I
Synthetic Route of 6,8-Dioxabicyclo[3.2.1]octan-7-one (1)



This method should give the desired monomer 1 at most in 50% yield based on the starting material 3. Nevertheless, we prefer this route because not only does it not need a large quantity of expensive silver oxide, but also 2-hydroxymethyl-3,4-dihydro-2*H*-pyran (5), which is obtained in nearly quantitative yield by the alkaline hydrolysis of the intermediate ester (4), can be used as a precursor for 6,8-dioxabicyclo[3.2.1]octane or 6,8-dioxabicyclo[3.2.1]oct-3-ene, from which polysaccharide analogues have been prepared by cationic polymerization in our laboratory.[16-18]

Preparation of 3,4-Dihydro-2*H*-pyran-2-ylmethyl 3′,4′-dihydro-2′*H*-pyran-2′-carboxylate (4). Finely pulverized aluminum isopropoxide (4.0 g) was added to freshly distilled 3 (112 g), and the suspension was stirred for several hours at 30–35 °C with external

Table I
Polymerization of 6,8-Dioxabicyclo[3.2.1]octan-7-one (1)[a]

Exptl No.	Initiator (mol %)	Solvent[b]	Temp., °C	Time, h	Yield,[c] % Cyclic dimer	Cyclic tetramer + cyclic hexamer	Polymer	$\overline{M}_n$[d]
C-6	$SnCl_4$ (0.5)	MC	−30	18	62	~0	0	
C-24	CH_3COBF_4 (0.5)	MC	−30	24	48	~0	0	
C-23	CH_3COBF_4 (0.5)	MC	−78	72	0	0	0	
F-17	$SbCl_5$ (1.0)	MC	−40	48	45	~0	0	
C-25	BF_3Et_2O (1.0)	MC	−40	1	11	37	0	
F-4	BF_3Et_2O (1.0)	MC	−40	48	77	~0	0	
F-11	BF_3Et_2O (1.0)	NP	−40	48	50	26	0	
T-1	BF_3Et_2O (1.0)	TL	−40	48	16	15	0	
F-15	BF_3Et_2O (1.0)	MC	0	48	0	0	79	1900
F-32	BF_3Et_2O (1.0)	NP	0	48	0	0	71	1520
F-33	BF_3Et_2O (1.0)	TL	0	48	19	0	40	1410

[a] Monomer, 2.0 g; solvent, 2 mL. [b] MC, methylene chloride; NP, 1-nitropropane; TL, toluene. [c] Diethyl ether insoluble part; determined by NMR or liquid chromatography. [d] Number average molecular weight of polymer determined by vapor pressure osmometry in benzene at 37 °C.

cooling. The reaction mixture gradually became an orange yellow transparent solution. It was then allowed to stand overnight at room temperature. Distillation of the reaction mixture gave the ester 4 in 78% yield, bp 120–130 °C (2 mm) (lit.[19] bp 115–125 °C (0.5 mm)).

Preparation of 6,8-Dioxabicyclo[3.2.1]octan-7-one (1). Sodium hydroxide aqueous solution (2.5 N, 156 mL) was added dropwise to 4 (87 g) at room temperature with vigorous stirring. After a while, the turbid reaction mixture became homogeneous, with concomitant rise in the reaction temperature up to about 40 °C. The resultant orange colored solution was extracted several times with methylene chloride (total 450 mL). From the combined methylene chloride extract, 5 was obtained in 94% yield, bp 71 °C (5 mm) (lit.[20] bp 102 °C (45 mm)). The aqueous layer was transferred to a flask, to which cold 6 N hydrochloric acid (70 mL) was added in a few minutes with stirring below 10 °C. After adding a sufficient amount of sodium chloride to saturate the solution, it was extracted several times with diethyl ether (total 500 mL). The ether extract was washed three times with a saturated sodium chloride aqueous solution, dried over anhydrous sodium sulfate, and distilled to give 1 in 74% yield; bp 64–65 °C (4 mm) (lit.[15] bp 62–64 °C (3 mm)). It was purified by drying over calcium hydride and repeated fractional distillation before use.

Polymerization. Freshly distilled 1 and solvent were charged into a glass ampule, and an initiator solution was added to the monomer solution at −78 °C. All these manipulations were carried out under a nitrogen atmosphere. The ampule was chilled in liquid nitrogen, evacuated, sealed off, and allowed to stand in a constant temperature bath. After the addition of a small volume of pyridine to terminate the polymerization, the reaction mixture was poured into a large amount of diethyl ether to yield a white powdery precipitate. It was separated on a sintered glass filter, washed with cold diethyl ether, and dried under vacuum at 50 °C for a few days.

Characterization. The composition of the reaction products was determined by a Hitachi high-speed liquid chromatography Model 634A using chloroform as solvent (Column, Hitachi No. 3011, 4ϕ × 1500 mm for liquid chromatography (LC) or Shodex 802A, 8ϕ × 1000 mm for gel permeation chromatography (GPC)). LC analysis afforded only the total content of the cyclic tetramer and hexamer because of poor resolution of the peaks.

The molecular weight of the oligomers was determined by a Hewlett Packard vapor pressure osmometer on solutions in chloroform at 37 °C.

^1H NMR spectra were taken with a JEOL MH-100 spectrometer working at 100 MHz at room temperature. Proton-noise decoupled ^{13}C NMR spectra were recorded on a JEOL FX-100 Fourier transform spectrometer operating at 25 MHz. Deuteriochloroform and tetramethylsilane were used as solvent and internal standard, respectively.

Infrared spectra were measured on a JASCO IRG-5 spectrophotometer in chloroform solution.

Results and Discussion

Preparation of Cyclic Oligoesters from *1*. Polymerization of 1 was carried out in methylene chloride, 1-nitropropane, and toluene at different temperatures ranging from −78 to 0 °C with various initiators. Some of the results are presented in Table I. The most noticeable point is that only the cyclic oligomers were produced at lower temperatures irrespective of the initiators and solvents used here, while only the polymers with relatively low molecular weight were formed at higher temperatures, except that an appreciable amount of the cyclic dimer was obtained along with the low molecular weight polymer in the polymerization in toluene. In Table I, the yields of the cyclic tetramer and hexamer are given as their sum, but as will be seen later, the cyclic hexamer is the predominant product in all the runs.

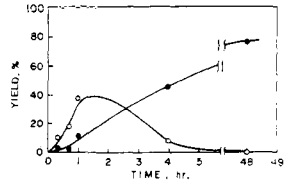


Figure 1. Time–yield curves of the oligomerization of 6,8-dioxabicyclo[3.2.1]octan-7-one (1). Monomer, 4 g; CH_2Cl_2, 4 mL; BF_3OEt_2, 1 mol % to monomer; temp, −40 °C: (●) cyclic dimer; (○) cyclic tetramer plus cyclic hexamer.

It is noteworthy that solvents affect the oligomer composition. For example, comparison of runs F-4 and F-11 shows that although the cyclic dimer was the major product in 1-nitropropane, the cyclic tetramer and hexamer (mostly the latter) were formed simultaneously, while the cyclic dimer was produced almost exclusively in the polymerization in methylene chloride under otherwise the identical reaction conditions. This remarkable difference must arise from the difference in the solubility of these cyclic oligomers in these solvents. This point will be discussed later.

Another important feature is the time dependence of the oligomer composition (runs C-25 and F-4). In the early stage of the reaction, the total yield of the cyclic tetramer and hexamer exceeded the yield of the cyclic dimer, while after the prolonged reaction time, the cyclic dimer was obtained nearly selectively. Such a peculiar behavior is clearly demonstrated in Figure 1.

Interestingly, the total yield of the cyclic tetramer and hexamer passed through a maximum value of about 40% and then decreased to nearly zero after 48 h. On the other hand, the yield of the cyclic dimer increased rather sigmoidly with

Table II
Oligomerization of 6,8-Dioxabicyclo[3.2.1]octan-7-one (1) in 1-Nitropropane[a]

Exptl No.	Solvent, mL	Temp., °C	Time, h	Conversion,[b] %				
				Cyclic dimer	Cyclic tetramer	Cyclic hexamer	Other[c]	Total
N-1	2	−40	1	23.8	2.8	37.2	0	63.8
N-2	2	−40	48	60.7	2.0	25.6	0	88.3
N-3	2	−40	192	92.3	1.5	2.2	1.1	97.1
N-4	4	−40	48	13.0	2.0	51.0	0	66.0
N-5	4	−60	48	19.0	6.5	51.7	0	77.2
N-6	4	−60	192	30.9	0	55.5	0.1	86.5

[a] Monomer, 2 g; initiator, BF_3OEt_2, 1 mol % to monomer. [b] The whole reaction mixture was analyzed by GPC without separating the reaction products by precipitation with diethyl ether just after the reaction had been terminated by the addition of pyridine. [c] Unidentified oligomeric materials.

Table III
Effect of Temperature on the Polymerization of 6,8-Dioxabicyclo[3.2.1]octan-7-one (1) in Methylene Chloride[a]

Exptl No.	Temp, °C	Time, h	Yield,[b] %			$\overline{M}_n$[c]
			Cyclic dimer	Cyclic tetramer + cyclic hexamer	Polymer	
F-13	0	0.3	0	0	1	
C-40	−10	0.3	8	0	1	
T-9	−20	0.3	9	12	0	
C-36	−30	0.3	20	11	0	
C-27[d]	−40	0.3	3	10	0	
F-15	0	48	0	0	79	1900
C-41	−10	48	0	0	76	1300
C-39	−20	48	0	0	56	1300
C-37	−30	48	62	~0	4	
F-4[c]	−40	48	77	~0	0	

[a] Monomer, 4.0 g; initiator, BF_3Et_2O, 0.5 mol % to monomer; solvent, CH_2Cl_2, 4.0 mL. [b] Diethyl ether insoluble part; determined by NMR or liquid chromatography. [c] Number average molecular weight of polymer determined by vapor pressure osmometry in benzene at 37 °C. [d] Initiator, 1.0 mol % to monomer.

reaction time. This phenomenon seems to be closely related to the remarkable change in the appearance of the polymerization system: Under the conditions given in the caption of Figure 1 the whole reaction mixture became jelly-like after about 1 h, but as the reaction was allowed to proceed further, it liquefied again with concomitant precipitation of white crystals which were identified as the cyclic dimer. Therefore it seems adequate to say that the crystallization of the cyclic dimer out of the solution is an important driving force for its preferential formation especially in the later stage of the reaction, even though it may not be the sole factor.

A similar trend was observed in the oligomerization in 1-nitropropane, although the transformation of the cyclic tetramer and hexamer into the cyclic dimer was slower in this solvent than in methylene chloride (Table II). The solubilities of the cyclic oligomers in 1-nitropropane were found to be one or two orders lower than those in methylene chloride. Therefore it seems very likely that most of the cyclic tetramers and hexamers are precipitated out of the solution as they are produced, thus retarding their transformation to the cyclic dimer. It should be noticed in Table II that the yield of the cyclic hexamer was overwhelmingly higher than that of the cyclic tetramer in the early stage of the reaction.

The effect of the temperature on the polymerization of 1 in methylene chloride is presented in Table III. The upper half of the data in the table shows the temperature effect on the products in the initial stage of the reaction; and the lower half is that for the middle to final stages of the reaction. Obviously, there is a drastic change in the reaction products between −20 and −30 °C: Below −30 °C, the cyclic dimer is the predominant or even sole product after the reaction of 48 h, while above −20 °C, the low molecular weight polymer is formed exclusively. It is to be noted that the cyclic oligomers once formed in the initial stage of the reaction are converted to the polymer in the later stage of the reaction above −20 °C. Such a pronounced temperature dependence of the reaction products was observed more or less in the polymerization with any other initiators used. These phenomena are inconsistent with a usual equilibrium process if, as expected, the enthalpy of the polymerization is negative. Therefore, solubility and kinetic factors must play an important role.

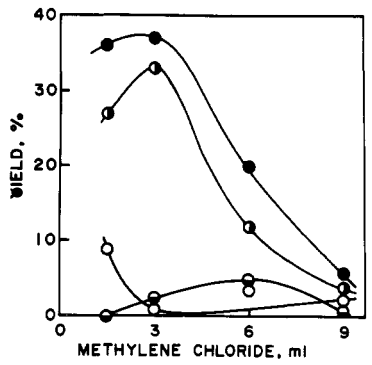


Figure 2. Effect of dilution on the oligomerization of 6,8-dioxabicyclo[3.2.1]octan-7-one (1). Monomer, 3 g; solvent, CH_2Cl_2; BF_3OEt_2, 1 mol % to monomer; temp, −40 °C; time, 1 h: (●) total; (◑) hexamer; (◒) tetramer; (○) dimer.

Figure 2 illustrates the dilution effect on the total yield and

Table IV
Characterization of Cyclic Oligomers of 6,8-Dioxabicyclo[3.2.1]octan-7-one (1)

		Cyclic dimer	Cyclic tetramer	Cyclic hexamer
C, %	Found	56.37	56.12	56.22
	Calcd	56.26	56.26	56.26
H, %	Found	6.36	6.43	6.27
	Calcd	6.31	6.31	6.31
Mol wt	Found[a]	259	518	762
	Calcd	256	512	768
Dec point,[b] °C		160	155	175

[a] Determined by vapor pressure osmometry in chloroform at 37 °C. [b] Determined by differential scanning calorimetry (heating rate, 1.25 °C/min). All these cyclic oligomers decompose quantitatively to 1.

composition of the cyclic oligomers. With increasing volume of the solvent, the formation of the cyclic hexamer was depressed significantly. The yield of the cyclic tetramer became maximum at moderate dilution, although it was still about half of that of the cyclic hexamer. The fall in the yield of the cyclic hexamer and conversely the appreciable rise in the yield of the cyclic dimer in the most concentrated solution are, at least partly, due to the heterogeneity of the reaction mixture from the beginning of the reaction. Such a dilution effect is understandable on the assumption that the propagation is a bimolecular process between the propagating active species and the monomer, while the cyclization is a unimolecular reaction, the former being retarded to a greater extent by dilution. The initiator concentration did not affect appreciably both the total yield and composition of the cyclic oligomers.

Structures of the Cyclic Oligomers of *1*. The cyclic oligomers of 1 described in the foregoing section were isolated by means of gel permeation chromatography. Some of their characterization data are presented in Table IV. Their elementary analytical data and molecular weights determined by vapor pressure osmometry were in good agreement with those calculated for $(C_6H_8O_3)_n$ within the accuracy of the measurements. In addition, no possible end groups (carboxyl, hydroxyl, olefinic double bond, etc.) could be detected in the infrared and ^1H and ^{13}C NMR spectra of these cyclic oligomers. The cyclic dimer dissolves in chloroform, methylene chloride, and tetrahydrofuran and is slightly soluble in acetonitrile and diethyl ether. The cyclic tetramer and hexamer are readily soluble in chloroform, methylene chloride, and acetonitrile and very slightly soluble in tetrahydrofuran and diethyl ether.

The cyclic dimer possesses four asymmetric carbon atoms, and hence, there are sixteen possible structures, considering that the cyclic dimer involves two ester linkages, in other words, it is formed by either consecutive acyl–oxygen fissions or consecutive alkyl–oxygen fissions of the first and second monomers. Acyl–oxygen fission of the first monomer followed by alkyl–oxygen fission of the second monomer, or vise versa, would lead to the cyclic dimer with one ether and one anhydride linkage. Actually, however, the ^1H and ^{13}C NMR and infrared data of the cyclic dimer are in conflict with such a structure. X-ray analysis of the crystals of the cyclic dimer which were obtained by recrystallization from its chloroform solution revealed that it consisted of a pair of different enantiomers of 1 and that all of the four substituents attached to the two tetrahydropyran rings occupied the axial position as illustrated in Figure 3. The details of the x-ray analysis will be reported elsewhere.[21]

However, there is anxiety that the cyclic dimer examined might be the one which is most readily crystallizable among various cyclic dimers and that there might exist some other

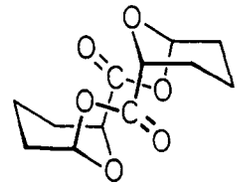


Figure 3. Structure of the cyclic dimer of 6,8-dioxabicyclo[3.2.1]-octan-7-one (1).

cyclic dimers of different steric structures. In order to check this point, the cyclic dimer as separated from a reaction mixture was subjected, without further purification, to ^1H and ^{13}C NMR spectroscopy. The spectra were found to be in complete agreement with those of the recrystallized sample used for x-ray analysis, thus excluding the possibility of the coexistence of two or more cyclic dimers of different configurations.

The steric structures of the cyclic tetramer and hexamer have not yet been fully elucidated, because their reluctance to form crystals makes x-ray technique unavailable. Nevertheless, valuable information concerning their structures is obtainable from their ^1H and ^{13}C NMR data. The ^1H and ^{13}C NMR spectra of 1 and its cyclic oligomers are given in Figures 4 and 5, respectively, and their chemical shift values are summarized in Table V for comparison.

The acetal proton signals of the cyclic tetramer and hexamer as well as that of the cyclic dimer are relatively sharp, that is, the coupling constants between the acetal protons and their vicinal hydrogens are small. This means that in any of these cyclic oligomers the acetal hydrogens occupy the equatorial position of the tetrahydropyran ring. The methine proton signal adjacent to the carbonyl group of the cyclic dimer shows a narrow doublet, while those for the cyclic tetramer and hexamer exhibited rather widely separated doublets. This difference implies that the methine hydrogens are located in the equatorial position in the cyclic dimer as proved by x-ray analysis, and conversely they are in the axial position in the cyclic tetramer and hexamer.

The ^{13}C NMR signals f of the central methylene carbon atom of the tetrahydropyran ring of the cyclic tetramer and hexamer appeared at 17.9 and 17.4 ppm downfield from tetramethylsilane, whereas the corresponding signal for the cyclic dimer appeared at 13.8 ppm. Such a remarkable higher field shift of the latter is presumably due to the steric compression effect[22] encountered in the cyclic dimer in which both substituents of the tetrahydropyran ring are located in the axial positions, although the magnetic anisotropy effect of the carbonyl group cannot be ruled out. In other words, this implies that the carbonyl groups in the cyclic tetramer and hexamer are situated in the equatorial position of the te-

Table V
^{1}H and ^{13}C NMR Data for 6,8-Dioxabicyclo[3.2.1]octan-7-one (1) and Its Cyclic Oligomers

	Peak[a]	Chemical shift,[b] ppm			
		Monomer	Dimer	Tetramer	Hexamer
^{1}H NMR[c]	a	6.01	6.36	6.58	6.50
	b	4.45	4.39	4.45	4.60
	c	1.91[d]	1.57–2.39[e]	1.90[d]	1.85[d]
^{13}C NMR[f]	a	173.7	171.1	168.5	168.8
	b	104.6	91.7	90.9	91.8
	c	72.9	70.3	69.5	69.4
	d	27.2	27.3	27.4	27.9
	e	24.6	24.7	27.4	27.9
	f	15.8	13.8	17.9	17.4

[a] Assignments of the peaks are given in Figures 4 (^{1}H NMR) and 5 (^{13}C NMR), respectively. [b] From tetramethylsilane. [c] Solvent, $CDCl_3$; room temperature; 100 MHz. [d] Chemical shift at the maximum of the broad peak. [e] Peak range is given because of the very complex multiplets. [f] Solvent, $CDCl_3$; room temperature; 25 MHz.

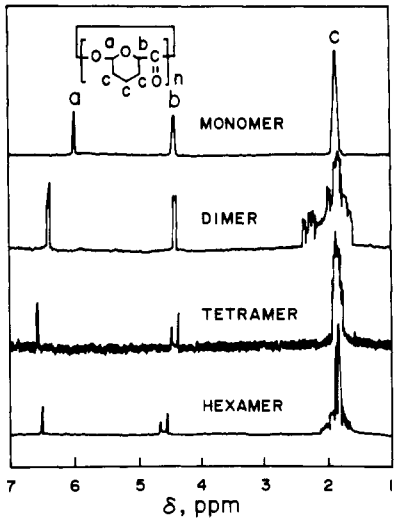


Figure 4. ^{1}H NMR spectra of 6,8-dioxabicyclo[3.2.1]octan-7-one (1) and its cyclic oligomers: solvent, $CDCl_3$; room temperature; 100 MHz.

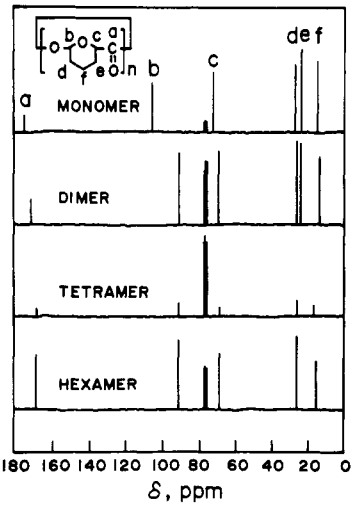
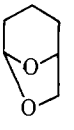


Figure 5. Proton-noise decoupled ^{13}C NMR spectra of 6,8-dioxabicyclo[3.2.1]octan-7-one (1) and its cyclic oligomers: solvent, $CDCl_3$; room temperature; 25 MHz.

trahydropyran rings as it is deduced from ^{1}H NMR spectra. Moreover, the signal e of the cyclic tetramer and hexamer shifted downfield compared with that of the cyclic dimer to coincide with the signal d. Such a downfield shift is consistent with, although not conclusive evidence for, the equatorial orientation of the carbonyl groups in the cyclic tetramer and hexamer, because there is a general rule that in cyclohexane derivatives an equatorial substituent makes the signal of the carbon atom in the β position from the substituent appear at a lower magnetic field than its axial counterpart.[23]

Mechanism of the Formation of the Cyclic Oligomers. As described in the introductory section, it is not unusual but rather common phenomenon that cyclic oligomers of various ring sizes are formed in the cationic polymerization of a variety of cyclic monomers. The formation of cyclic oligomers has been interpreted generally in terms of back-biting reaction of the growing chain ends. In the case of cyclic acetals, however, Plesch and his co-workers[7–9] claim that the cyclic oligomers are produced by ring-expansion mechanism.

In our present system, only three kinds of the cyclic oligomers (DP = 2, 4, and 6) are formed selectively, except in the later stage of the reaction where some other unidentified oligomeric products, although in minor amounts, are formed (Table II). It is very peculiar, and hence difficult to explain, that competitive formation of neither polymer nor cyclic oligomers of other sizes were observed at low temperatures, if the cyclic oligomers mentioned above were formed by back-biting mechanism. Probably, it would appear that the growing chain takes a particular conformation suitable for the formation of the cyclic tetramer and hexamer, especially the latter, under the reaction conditions used. The alternating arrangement of a 2,6-disubstituted tetrahydropyran ring and an ester linkage of the growing chain seems to be responsible for the ease of its taking the conformation favorable for the ring closure, because 6,8-dioxabicyclo[3.2.1]octane (6) having the same skeleton as that of 1 polymerizes readily to high polymers under similar conditions,[17,18] and 5-methyl-1,3-dioxolan-4-one (7) which has a partial structure of 1 forms neither cyclic oligomer nor linear polymer.[24]



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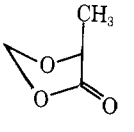

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Alternative, but less plausible, explanation for the formation of the even-membered cyclic oligomers would be that they are brought about by the polymerization of the cyclic dimer. However, the cyclic dimer isolated from the reaction mixture was found not to polymerize under the reaction conditions

used here for the oligomerization of **1**. Furthermore, the cyclic dimer with the configurations shown in Figure 3 cannot be converted directly to the cyclic tetramer and hexamer having the configurations described in the foregoing section by any simple mechanism. Therefore, if the above concept were correct, other cyclic dimer with different configuration and higher reactivity must have been formed during the reaction. However, its presence could not be verified by experiment.

Two different interpretations may be possible for the conversion of the cyclic tetramer and hexamer into the cyclic dimer. The first one is that the cyclic tetramer and hexamer depolymerize rapidly to the monomer, which anew dimerizes. The second one is that the cyclic tetramer decomposes directly to two molecules of the cyclic dimer, and that the cyclic hexamer decomposes to a molecule of the cyclic dimer and a molecule of the cyclic tetramer. However, the former interpretation appears more appropriate, in view of the fact that in the cyclic tetramer and hexamer, one substituent, the ester oxygen, in the tetrahydropyran ring lies in the axial position, and the other, the carbonyl group, lies in the equatorial position, while in the cyclic dimer both substituents are located in the axial positions as shown in Figure 3.

With regard to the mode of bond cleavage of 1 during the reaction, available data on the acid-catalyzed hydrolysis of aliphatic acetal esters would be informative. The acetal esters of the type $RCOOCH_2OR'$ are, in general, hydrolyzed in the presence of an acid catalyst by the normal unimolecular alkyl–oxygen fission designated by $A_{AL}1$,[25,26] but in some cases unimolecular and bimolecular reactions occur simultaneously.[27] In the acid-catalyzed hydrolysis of 1,3-dioxolan-4-ones (five-membered cyclic acetal esters), two mechanisms have been proposed on the basis of kinetic data:[28] Unsubstituted 1,3-dioxolan-4-one undergoes acid-catalyzed hydrolysis by bimolecular acyl–oxygen fission ($A_{AC}2$, mechanism), while an introduction of one or two methyl groups at the carbon 2 changes the mechanism to $A_{AL}1$-like mechanism.

From the structures of the cyclic oligomers described in the preceding section, along with the hydrolysis data above, it would be deducible that the oligomers, at least tetramer and hexamer, are formed via a mechanism involving the alkyl–oxygen fission of the monomer. However, there is still some uncertainty in the mechanism of the oligomerization, because it is also conceivable that the cyclic dimer as depicted in Figure 3 may be produced via another mechanism involving the acyl–oxygen fission. Therefore, some other independent experiments will be required to decide which mode of bond cleavage actually takes place in this oligomerization.

Further structural analysis of the cyclic tetramer and hexamer of **1**, and evaluation of the properties of these novel cyclic oligoesters, particularly of their complexing ability toward metal ions, are the objects of our continuing studies.

Acknowledgment. We are very grateful to Professor T. Ashida and his co-workers of Nagoya University for the x-ray analysis of the cyclic dimer. Also, we wish to express our gratitude to Mr. O. Fujii for his help in experiments.

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