Cyclic Trimerization of Oxetanes

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Conditions for obtaining the optimum yield of the cyclic trimer in the cationic oligomerization of oxetanes have been determined. At moderate dilution (0.05 M) with catalytic quantities of BF_3 in CH_2Cl_2, the yield of the cyclic trimer (1,5,9-trioxacyclododecane) from oxetane could be increased to 50 % at the expense of the cyclic tetramer (1,5,9,13-tetraoxacyclohexadecane), 12 %, and polymer. In contrast, 3,3-dimethyloxetane consumed the BF_3 catalyst, which had to be renewed, producing, in a slow reaction, a homologous series of fluorohydrins, together with cyclic oligoethers. The fluorohydrins cyclized if treated with gaseous BF_3 before work-up, boosting the isolated yields to 20 % cyclic trimer and 8 % cyclic tetramer. With PF_5 in CH_2Cl_2 the catalyst was stable and the reaction fast, and no fluorohydrins were formed; no cyclic trimer but 73 % cyclic tetramer could be isolated.

Other solvents (benzene, $CHCl{=}CCl_2$, CH_2ClCH_2Cl), other catalysts (SbF_5, $AlEt_3$) and other oxetanes (3-methoxymethyl-3-methyloxetane, 3-halomethyl-3-methyloxetane) were also examined.

In 1956 Rose observed[1] the formation of substantial amounts of crystalline cyclic tetramers during the BF_3-catalysed polymerization of oxetane and of 3,3-dimethyloxetane. We have proposed[2] that the conformational homogeneity and high melting point of such 16-membered rings is due to the remarkable stability of a 'square' diamond-lattice conformation of D_{2d} symmetry, and this was subsequently confirmed by X-ray crystallography.[3] Both tetramers complex Li cation, but the ring in these complexes was shown by NMR[4] and subsequently by X-ray crystallography[5] to have an entirely different 'butterfly' conformation, also of D_{2d} symmetry and diamond-lattice type [Fig. 1(a)].

One can imagine the addition of two bridges to this structure to produce a beautifully symmetric cage structure providing six ether oxygens for octahedral coordination to small cations [Fig. 1(b)]. From Figs. 1(c) and (d) it can be seen how this can also be related to cyclic trimers of oxetane with and without ligating side arms. Since the 12-membered ring here is ready for complexation in its only diamond-lattice conformation, it occurred to us that cyclic trimers could be more interesting ligands for small cations. This proved to be correct, and the results have been briefly communicated.[6,7]

In this paper we report in more detail how the conditions in the cationic cyclooligomerization of oxetanes can be modified to give preparative quantities of the cyclic trimer at the expense of the cyclic tetramer and polymers. The cyclic trimer has been recognized analytically as a minor product in the polymerization of unsubstituted oxetane,[8,9] but never isolated. The only isolated trimer of this kind was obtained in a yield of 2 % by extraction of the crude polymer from the $AlEt_3$-catalysed bulk polymerization of 3,3-bis(chloromethyl)oxetane.[10] We also report the syntheses and cyclooligomerization of some oxetanes carrying potential ligating sites in one of the substituents.

Preparation of oxetanes. In spite of the difficulty in forming four-membered rings by ring-closure reactions, as compared with similar reactions leading to three- and five-membered rings,[11] the intramolecular Williamson synthesis has been widely applied. Fragmentation of the inter-

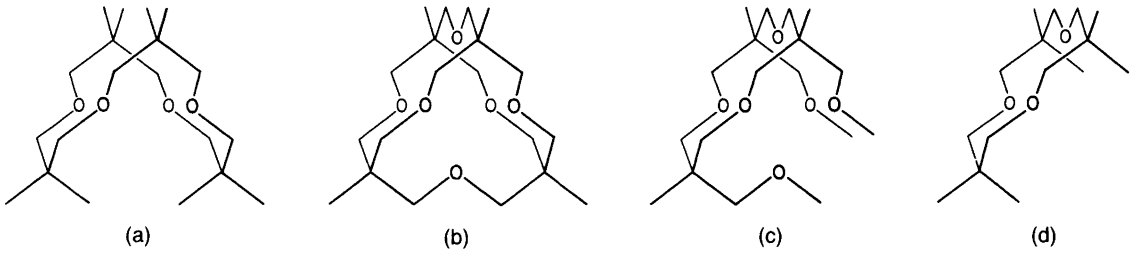

Fig. 1. Derivation of diamond-lattice ligand structures with complete or partial octahedral coordination geometry. Methyl substituents are drawn in all vacant '3-positions.'

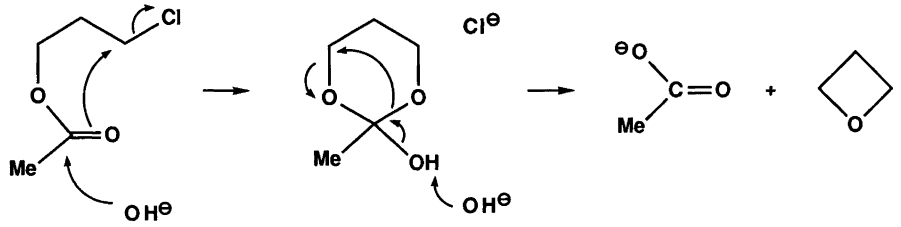

Fig. 2. Proposed mechanism for oxetane formation from 3-chloropropyl acetate.

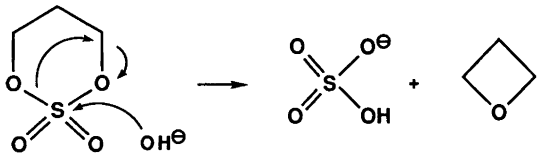

Fig. 3. Proposed mechanism for oxetane formation from 1,3-propanediol in sulfuric acid/strong alkali.

mediate alkoxide into alkene and carbonyl compounds,[12,13] as well as elimination and intramolecular reactions, often decrease the yield of oxetane. Alkyl substituents on the OH-carrying carbon increase the yield,[14] while an alkyl substituent on the carbon carrying the leaving group decreases the yield,[15] and no oxetane is formed when it is tertiary.[15,16] *gem*-Dialkyl substitution on the 2-carbon is expected to favour cyclization, but will also favour fragmentation.[12,13] It therefore became necessary to evaluate a number of the methods reported in the literature.[17]

Oxetane itself has been obtained in a yield of only 20–25 % by base-induced cyclization of 3-chloropropanol,[18] but, surprisingly, in a much better yield (44 %) from 3-chloropropyl acetate.[18,19] We can confirm this result and propose that the reaction proceeds via an initial facile cyclization to a six-ring 'ortho-ester,' which then fragments in a second step (Fig. 2). Sulfate ester formation from 1,3-propanediol and conc. H_2SO_4 followed by treatment with hot conc. alkali is another common method,[20] for which we propose a similar mechanism via fragmentation of a postulated cyclic sulfate ester (Fig. 3). However, in our hands only a poor yield of oxetane (<10 %) was obtained.

3,3-Dimethyloxetane was prepared by cyclization of the chloro- or bromo-hydrin in yields of 59 and 54 %, respectively.[12] The chloro- and bromo-hydrin could be obtained in yields of 54 and 88 %, respectively, by monohalogenation of 2,2-dimethyl-1,3-propanediol using Cl_2 or Br_2 with triphenylphosphine,[21] the standard $SOCl_2$/pyridine method giving mainly cyclic sulfites.[22] Other cyclization methods were less successful, such as the sulfate ester method (<20 %), the alkali treatment of the monotosylate of the diol (which gave rearrangement products), and the fragmentation of the cyclic carbonate induced by nucleophilic catalysts (KCN, KCl, LiCl).[23]

3-Hydroxymethyl-3-methyloxetane has been reported to be formed in excellent yield from treatment of the cyclic carbonate of 2-hydroxymethyl-2-methyl-1,3-propanediol with alkali, the third hydroxy group acting as an internal catalyst.[24] We could confirm that yields of >80 % are easily obtained. This oxetane could be routinely methylated to give 3-methoxymethyl-3-methyloxetane, the potential monomer for the trimer with ligating side arms [Fig. 1(c)]. Attempts to prepare the corresponding chloromethyl derivative with $SOCl_2$/pyridine again resulted in the formation of a cyclic sulfite, but using Cl_2 or Br_2 with triphenylphosphine,[21] the chloromethyl and the bromomethyl derivatives were obtained in yields of 12 and 47 %, respectively.

Table 1. Cationic cyclooligomerization of oxetane.

Catalyst	Solvent	*T*/°C	Time for addition of catalyst[a]/h	Total reaction time[b]/h	Trimer yield by NMR/%	Isolated yields (%)	Yield of cyclics /%	Composition of volatiles by GLC–MS (%)				
								Trimer	Tetramer	Pentamer	Hexamer	Higher
BF_3	CH_2Cl_2	25	3	27 h	50	40 trimer 12 tetramer	72	75	19	2	1	3
BF_3	CH_2Cl_2	25	3[c]	(3)	–	–		94	6	–	–	–
BF_3	CH_2Cl_2	25	11[c]	(11)	–	–		85	13	2	–	–
BF_3	CH_2Cl_2	25	11[c]	35	65	50 trimer	75	72	15	4	2	7
BF_3	Benzene	25	–	24	2	–	8	25	56	9	–	–
PF_5	CH_2Cl_2	25	–	48	23	–	60	38	49	12	1	–
$AlEt_3$	Benzene	80	–	170	4	–	5	90	10	–	–	–
CF_3SO_3H	$MeNO_2$	65	–	120	<5	–	<15	36	42	21	1	–

[a]Catalyst solution added to monomer solution. [b]Reaction terminated when all monomer was consumed. [c]Parallel addition of catalyst and monomer solutions.

Cyclooligomerization of oxetane. As in the cyclooligomerization of oxirane,[25] CH_2Cl_2 was the favoured solvent and BF_3 the favoured catalyst (Table 1). Only cyclic oligomers and polymers were observed, and there was no sign that the catalyst was consumed during the reaction. In significant contrast with oxirane, there was no indication of secondary reactions of the products: once the strain-free cyclic oligomers (trimer and higher) were formed, they were not reincorporated into the growing chain intermediate and degraded to smaller rings, as was the case with oxirane.[25] The reason for this difference is not that the entropy-favoured cyclic dimer of oxetane would be a strained 8-membered ring, in contrast with the strain-free dimer of oxirane (1,4-dioxane), but rather that oxetane is *more* basic[26] than its oligomers and experiences no competition as the nucleophile in the growth of the chain. In contrast, oxirane is *less* basic[26] than its oligomers, and as these are produced, they become 'alkylated' by the growing chain, whereby degradation is initiated.[25] Thus the oxetane reaction is under kinetic control, and the use of dilution procedures becomes meaningful. Already at moderate dilution, the formation of the cyclic trimer could be favoured at the expense of the tetramer and higher members. Using ca. 0.05 M solutions of monomer (Table 1), the trimer constituted 75 % of the volatile cyclic oligomers, and when a catalyst solution and a monomer solution were dropped in parallel into a large volume of CH_2Cl_2, the initially formed volatile product consisted of 94 % of cyclic trimer.

Further experiments with other catalyst/solvent systems gave less interesting results. With PF_5 in CH_2Cl_2 the cyclic tetramer was produced in preference to the trimer (Table 1), while BF_3 in benzene gave mainly polymer. $AlEt_3$ in benzene also gave mainly polymer together with a small cyclic fraction interestingly dominated by the trimer (cf. the extraction of only cyclic trimer from the 3,3-bis(chloromethyl)oxetane polymer[10] produced with $AlEt_3$). The $AlEt_3$-catalysed reaction was very slow even in refluxing benzene, as was the CF_3SO_3H-catalysed reaction in refluxing nitromethane.

Cyclooligomerization of 3,3-dimethyloxetane. Under comparable conditions, this substituted oxetane showed chemical behaviour remarkably different from that of the unsubstituted oxetane. First, the reaction was much slower, and the BF_3 catalyst was consumed during the reaction and had to be replenished at intervals. Similar observations have been made in the BF_3-catalysed oligomerization of methyloxirane.[27] Secondly, a homologous series of fluorohydrins was formed as by-products, together with minor amounts of corresponding diols presumably arising from the intervention of moisture.

It was natural to connect the appearance of these fluorine compounds with the consumption of BF_3, and it was in fact found that when, at the end of the reaction, relatively large quantities of gaseous BF_3 were bubbled through the reaction mixture, all the fluorohydrins (except the dimeric) were converted into the corresponding cyclic oligomers (Table 2). In this way the isolated yield of cyclic trimer could be considerably improved and was higher than that of cyclic tetramer, as was also the case for oxetane. However, the absolute yield of cyclic oligomers was lower, since more polymer was produced from 3,3-dimethyl-

Table 2. Cationic cyclooligomerization of 3,3-dimethyloxetane.

Catalyst	Solvent	*T*/°C	Total reaction time/days	Trimer yield by NMR (%)	Isolated yields (%)	Composition of volatiles by GLC–MS[a] (%)									
						Dimers		Trimers			Tetramers		Pentamers		Higher
						FOH	OHOH	Cycl.	FOH	OHOH	Cycl.	FOH	Cycl.	FOH	
BF_3	CH_2Cl_2	25	15	20	10 Trimer 3 Tetramer	–	–	49	31	–	14	2	2	1	1
BF_3	CH_2Cl_2	25	15+BF_3[b]	30	20 Trimer 8 Tetramer	–	0.5	75	–	0.5	24	–	1	–	<1
BF_3	CH_2Cl_2	40	3	19	–	–	–	45	42	–	8	–	2	2	1
BF_3	CH_2Cl_2	40	3+BF_3[b]	25	–	–	–	85	–	–	12	–	2	–	1
BF_3	CH_2Cl_2	25	5[c]	17	–	–	–	34	23	–	32	5	4	–	3
BF_3	$CHCl{=}CCl_2$	25	1	[d]	–	[e]	–	5	3	–	42	–	6	–	4
BF_3	$CH_2Cl{-}CH_2Cl$	84	1	[d]	–	7	3	16	17	7	20	2	2	2	24
BF_3	Benzene	80	2	17[d]	–	1	3	36	57	–	3	–	–	–	–
BF_3	Benzene	80	2+BF_3[b]	[d]	–	–	3	93	–	–	4	–	–	–	–
PF_5	CH_2Cl_2	25	1	~0	73 Tetramer 1 Tetramer	–	–	<1	–	–	88	–	11	–	0.5
SbF_5	CH_2Cl_2	25	2	[d]	–	–	–	–	–	–	100	–	–	–	–

[a]Cycl. = cyclic oligomer; FOH = fluorohydrin; OHOH = diol. [b]Treatment with gaseous BF_3 before work-up. [c]Parallel addition of catalyst and monomer solutions. [d]Mostly polymers. [e]Unidentified products (40 % by GLC).

oxetane. In refluxing benzene, BF_3 gave selective cyclization to the trimer (via the fluorohydrin) to the highest degree (93 % of all cyclic oligomers). The use of higher-boiling chlorinated solvents offered no advantage except shorter reaction times, and polymers were mainly produced (Table 2).

We interpret these observations on the basis of the increased conformational restriction due to the *gem*-dimethyl groups, which are known[2] to be strongly favoured at $g^{\pm}\ g^{\pm}$ corners both in the cyclic tetramer and polymer. In the S_N2-like transition state for cyclization in each step of a growing chain (Fig. 4), a linear geometry is required so that the 'ring' of the transition state should preferably be 11-membered or higher.[25] Thus, considering trimerization (Fig. 4), one can understand why direct cyclization via a 10-ring transition state becomes difficult, and is replaced by transfer of fluoride via a 12-ring transition state. This intermediate contains a neutral boron atom that has lost some of its Lewis acidity and catalytic effect, and neutralization at this stage gives the fluorohydrin. However, activation of the primary fluoride function with BF_3 will lead to cyclization, since the oxygen nucleophile can now attack via a 12-ring transition state (Fig. 4). The way in which BF_3 exerts its role may be as depicted in Fig. 5.

It can be further seen from Fig. 4 that the dimeric chain should not be able to cyclize directly, and also fluoride transfer should be difficult (8-ring transition state). Some fluorohydrin was formed at high temperature (Table 2), however, cyclization also requires an 8-ring transition state and did not occur. Finally, the tetrameric chain should be able to cyclize directly via a 14-ring transition state without difficulty, and fluoride transfer should be negligible, and this was also observed experimentally (Table 2).

Using, as the catalyst, PF_5 or SbF_5 in CH_2Cl_2, the picture was much simpler (Table 2). The reaction was faster, there was practically no formation of cyclic trimer, the catalyst was not consumed, and no fluorine-containing by-products were observed. PF_5 gave the cyclic tetramer in excellent yield, but SbF_5 produced mostly polymer, with tetramer as the exclusive cyclic product.

Other oxetanes. 3-Chloromethyl-3-methyloxetane was reacted under the same conditions as for 3,3-dimethyloxetane with BF_3 in refluxing CH_2Cl_2. The reaction was very slow, and fresh catalyst had to be supplied several times. Even after 24 days only 20 % of the monomer had been converted. Fluorohydrins were observed and their precursors could be cyclized by treatment with gaseous BF_3. Both cyclic trimer (two isomers possible) and tetramer (four isomers possible) were formed.

3-Bromomethyl-3-methyloxetane, after being refluxed with BF_3 in CH_2Cl_2 for one day, gave less than 3 % of cyclic trimer as the only product, the rest being unchanged monomer. With PF_5 in CH_2Cl_2 for two days at room temperature, less than 2 % had reacted to give unidentified products.

3-Methoxymethyl-3-methyloxetane was treated with BF_3 in CH_2Cl_2 at room temperature for three days to give 80% unchanged monomer, 11 % cyclic trimer, and 9 % cyclic tetramer.

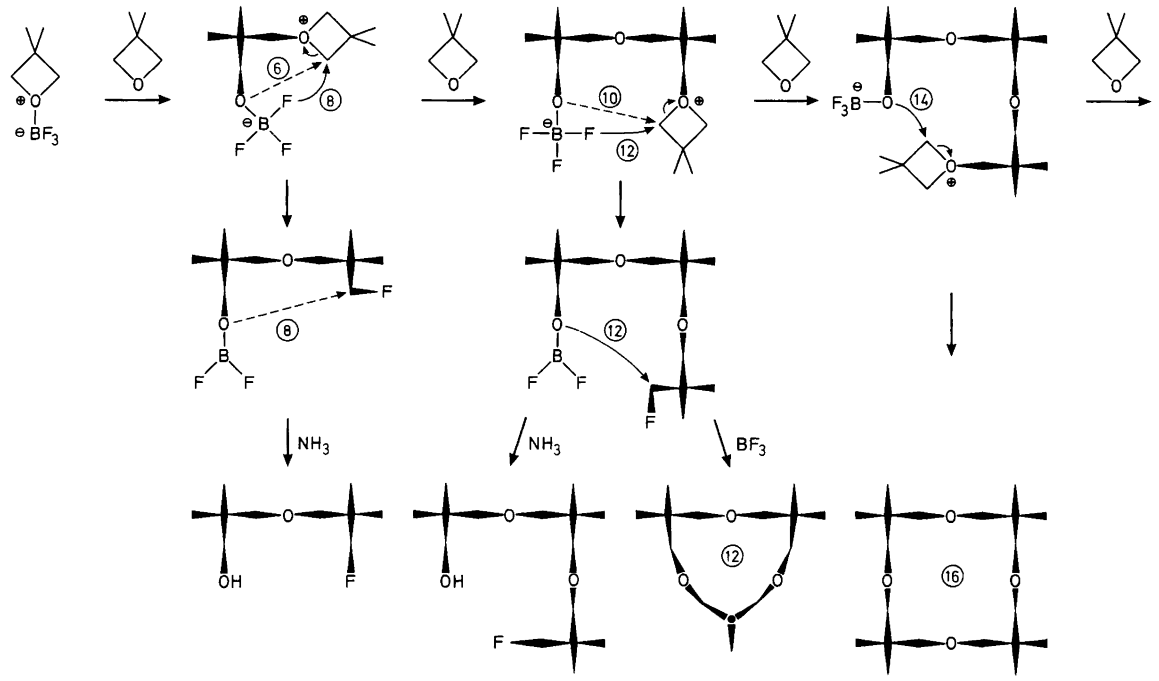

Fig. 4. Reaction scheme for 3,3-dimethyloxetane/BF_3.

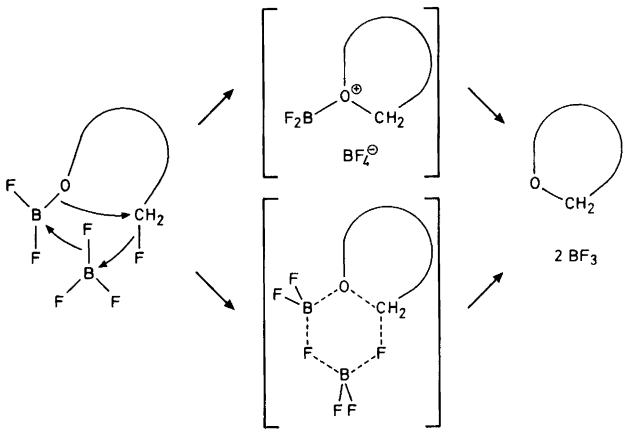

Fig. 5. Mechanisms for the cyclization of fluorohydrin precursors assisted by BF_3.

Experimental

General methods. Solvents were purified by standard procedures.[28] The catalyst solutions were made as follows. BF_3/dichloromethane: dry dichloromethane (1 l) was placed in a round-bottomed, three-necked flask and kept under a nitrogen atmosphere. BF_3 (Merck) was bubbled into the solution for 3 h at room temperature, and stirring was then continued for 12 h. The concentration of BF_3 was determined to be 0.035 M by titration with NaOH. The colourless catalyst solution could be stored for weeks. The BF_3/benzene catalyst solution, which became dark and inactive on storage, and the PF_5/dichloromethane catalyst solution were made in the same way. Catalyst solutions (0.035 M) of $AlEt_3$/benzene, SbF_5/dichloromethane and CF_3SO_3H/nitromethane were made by pipetting out appropriate volumes of the catalyst and dissolving them in the dry solvents. All catalyst solutions were stored under nitrogen.

Oxetane. Solid KOH (171 g, 3.0 mol) and water (20 ml) were placed in a 750 ml three-necked round-bottomed flask equipped with a mechanical stirrer and a Vigreux column with distillation head and condenser. 3-Chloropropyl acetate (136.6 g, 1.0 mol) was added dropwise to the preheated solution (temp. in oil bath 150 °C), and the product distilled out as it was formed. The crude product was redistilled over KOH in a Vigreux column. Yield 23.3 g (40 %), b.p. 45–52 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.71 (2 H, quint, *J* 7.8 hz), 4.76 (4 H, t, *J* 7.8 Hz).

3-Bromo-2,2-dimethyl-1-propanol. 2,2-Dimethyl-1,3-propanediol (52.1 g, 0.5 mol), triphenylphosphine (131.2 g, 0.5 mol) and pyridine (39.5 g, 0.5 mol) were dissolved in dry chloroform (250 ml) and cooled in an ice–water bath. Bromine (79.9 g, 0.5 mol) dissolved in chloroform (50 ml) was slowly added to the solution, and the reaction mixture was then stirred for 12 h at room temperature. The reaction mixture was poured into ice/HCl, and the phases were separated. The organic phase was washed with dilute hydrogencarbonate solution and then with water. After drying ($MgSO_4$), the solvent was evaporated in a Rotavapor, and the residue was distilled in a Vigreux column. Yield 73.6 g (88 %), b.p. 73–82 °C/8 mmHg. ^{1}H NMR (60 MHz, $CDCl_3$): δ 0.95 (6 H, s, CH_3), 2.30 (1 H, br s, OH), 3.30 (2 H, s, CH_2Br), 3.40 (2 H, s, CH_2OH).

3-Chloro-2,2-dimethyl-1-propanol. Triphenylphosphine (131.2 g, 0.5 mol) was dissolved in dry chloroform (200 ml), and Cl_2 (34.5 g, 0.5 mol) was bubbled into the solution for 2 h. The resulting solution of triphenylphosphine dichloride was slowly added to a stirred and cooled solution of 2,2-dimethyl-1,3-propanediol (52.1 g, 0.5 mol) and pyridine (39.5 g, 0.5 mol) dissolved in chloroform (200 ml). The reaction mixture was then stirred at room temperature for 12 h. Work-up was as described for 3-bromo-2,2-dimethyl-1-propanol. The crude product was distilled through a Vigreux column. Yield 33.3 g (54 %), b.p. 75–84 °C/14 mmHg. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.95 (6 H, s, CH_3), 1.82 (1 H, br s, OH), 3.42 (2 H, s, CH_2Cl), 3.43 (2 H, s, CH_2OH).

3,3-Dimethyloxetane. Method A: cyclization of 3-chloro-2,2-dimethyl-1-propanol. Solid KOH (51.2 g, 0.9 mol) was dissolved in ethylene glycol (49.7 g, 0.8 mol) by heating to 60 °C. 3-Chloro-2,2-dimethyl-1-propanol (36.8 g, 0.3 mol) was slowly added, and the reaction mixture was stirred for 1 h at 60 °C. The temperature was then raised to 110–120 °C, and volatile reaction products were codistilled with water (22 g, temp. in distillation head 75–82 °C). GLC–MS analysis of the crude product showed that it contained 77 % of the oxetane and 23 % methanol (due to fragmentation to isobutene and formaldehyde, then Cannizzaro reaction.[13]) The crude product was dried over $CaCl_2$ and thereafter Na, then chromatographed on neutral alumina, and finally distilled through a Vigreux column. Yield 15.2 g (59 %), b.p. 75–77 °C. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.27 (6 H, s), 4.33 (4 H, s).

Method B: cyclization of 3-bromo-2,2-dimethyl-1-propanol. The experimental procedure was as described above, using 3-bromo-2,2-dimethyl-1-propanol (33.4 g, 0.2 mol), KOH (56.9 g, 1.0 mol) and ethylene glycol (49.7 g, 0.8 mol). GLC–MS analysis of the crude distillate (12.3 g) showed that it consisted of 87 % oxetane and 13 % methanol. Drying and distillation was as described above. Yield 9.3 g (54 %), b.p. 79–82 °C.

Method C: from 1,3-propanediol with H_2SO_4. 3,3-Dimethyl-1,3-propanediol (104 g, 1.0 mol) was dissolved in cold conc. H_2SO_4 (75 ml) and added over 5 h to a vigorously stirred hot solution of KOH (55 %, 200 ml) (temp. in oil bath 140 °C). Codistillation with water produced two layers. The organic phase was collected. The water phase was salted out with K_2CO_3 and extracted with CH_2Cl_2. The combined organic phases were dried (Na_2SO_4), and the

solution was distilled through a Vigreux column. Yield 13.7 g (16 %), b.p. 80–83 °C.

Method D: pyrolysis of the carbonate ester of 2,2-dimethyl-1,3-propanediol. A mixture of 2,2-dimethyl-1,3-propanediol (52.1 g, 0.50 mol), diethyl carbonate (65.0 g, 0.55 mol) and KOH (0.4 g) was refluxed for 1 h. The ethanol formed was distilled out of the reaction mixture. The residue was taken up in dichloromethane and washed with water. After drying ($MgSO_4$), the solvent was evaporated in a Rotavapor and the cyclic carbonate *(5,5-dimethyl-1,3-dioxan-2-one)* was distilled in a Claisen flask. Yield 58.5 g (45 %), b.p. 110–112 °C/0.2 mmHg, m.p. 112 °C. ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.13 (6 H, s, CH_3), 4.10 (4 H, s, CH_2O).

A mixture of the cyclic carbonate (45 g), KCl (3 g) and KCN (6 g) was heated to 230 °C for 2 h. Volatile products (10.8 g) were then distilled out (70–80 °C). 3,3-Dimethyloxetane was the main component in the distillate (67 %), but GLC–MS analysis showed that several other products were also formed. The oxetane was not further purified.

3-Hydroxymethyl-3-methyloxetane. A mixture of 2-hydroxymethyl-2-methyl-1,3-propanediol (180 g, 1.5 mol), diethyl carbonate (177 g, 1.5 mol), absolute ethanol (1.5 ml) and solid KOH (0.5 g) was refluxed for 2 h. The ethanol formed was distilled out of the reaction mixture. The pressure was then gradually reduced to 10 mmHg allowing CO_2 evolution, and the oxetane was distilled out of the mixture. The crude product was redistilled in a packed column. Yield 124 g (81 %), b.p. 105–107 °C/10 mmHg. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.29 (3 H, s, CH_3), 3.63 (2 H, d, *J* 4.9 Hz, CH_2OH), 4.04 (1 H, t, *J* 4.9 Hz, OH), 4.37 (2 H, d, *J* 5.9 Hz, CH_2 ring), 4.52 (2 H, d, *J* 5.9 Hz, CH_2 ring).

3-Chloromethyl-3-methyloxetane. 3-Hydroxymethyl-3-methyloxetane (10.0 g, 97.6 mmol), triphenylphosphine (25.7 g, 97.6 mmol) and pyridine (7.74 g, 97.6 mmol) were dissolved in dry chloroform (200 ml). The solution was cooled in an ice–water bath, and Cl_2 (6.9 g, 97.6 mmol) was bubbled into the mixture for 2 h. Stirring was continued at room temperature for 12 h. The reaction mixture was washed with dilute sodium hydrogencarbonate solution and with water and then dried ($MgSO_4$), and the solvent was evaporated in a Rotavapor. Ether was added to the residue, and precipitated triphenylphosphine oxide was filtered off. After evaporation of the ether, the crude product was distilled in a columnless distillation flask. Yield 2.0 g (12 %), b.p. 56 °C/22 mmHg. ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.40 (3 H, s, CH_3), 4.75 (2 H, s, CH_2Cl), 4.43 (4 H, br s, CH_2 ring). MS (CI, isobutane, $m/z > 100$, rel. int. > 3 %): 121/123 (100/32, MH^+, 1 Cl), 103/105 (7.7/2.4, 1 Cl).

3-Bromomethyl-3-methyloxetane. To a stirred and cooled solution of 3-hydroxymethyl-3-methyloxetane (5.0 g, 49 mmol), triphenylphosphine (12.8 g, 49 mmol) and pyridine (3.9 g, 49 mmol) in chloroform (60 ml) was added bromine (7.78 g, 49 mmol). Stirring was then continued at room temperature for 2 h. Work-up was as described for 3-chloromethyl-3-methyloxetane. The crude product was distilled in a columnless distillation flask. Yield 3.8 g (47 %), b.p. 65–67 °C/14 mmHg. ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.5 (3 H, s, CH_3), 3.6 (2 H, s, CH_2Br), 4.5 (4 H, br s, CH_2 ring).

3-Methoxymethyl-3-methyloxetane. 3-Hydroxymethyl-3-methyloxetane (3.5 g, 34 mmol) was dissolved in dry THF (75 ml) under a nitrogen atmosphere. Sodium (0.79 g, 34 mmol) was added, and the mixture was refluxed until all of the sodium had reacted. Methyl iodide (7.5 g, 53 mmol) dissolved in THF (10 ml) was then added at 35 °C, and the reaction mixture was stirred at this temp. for 2 h. Solvent and excess methyl iodide were evaporated off in a Rotavapor. Ether was added to the residue, and precipitated sodium iodide was filtered off. The ether solution was washed with water and dried ($MgSO_4$). The ether was evaporated in a Rotavapor, and the crude product was distilled through a Vigreux column. Yield 3.5 g (88 %), b.p. 140–141 °C. ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.30 (3 H, s, CH_3), 3.43 (3 H, s, CH_3O), 3.47 (2 H, s, CH_2O), 4.38 (2 H, d, *J* 6 Hz, ring CH_2), 4.55 (2 H, d, *J* 6 Hz, ring CH_2).

Catalytic cyclooligomerization of oxetane with BF_3: catalyst solution added to monomer solution. Oxetane (4.0 g, 69.0 mmol) was dissolved in dry dichloromethane (1.3 l) under a nitrogen atmosphere in a flask equipped with a magnetic stirrer. The BF_3 catalyst solution (0.035 M, 300 ml) was added to the monomer solution over 3 h. Stirring was then continued at room temperature, and the reaction mixture was analysed by ^{1}H NMR spectroscopy and GLC–MS at regular intervals. The ratio between unchanged monomer and reaction products (cyclic oligomers and polymers) was estimated using the signals for the α-methylene protons. GLC–MS analysis of the volatiles showed that the ratios between individual cyclic oligomers changed very little from the beginning to the end of the reaction, and that no other volatile products were formed. After a total reaction time of 24 h, all monomer had been consumed, and the reaction mixture was neutralized with gaseous NH_3. The solvent was evaporated in a Rotavapor, and the semisolid crude product was distilled through a short Vigreux column to give pure *1,5,9-trioxacyclododecane* (cyclic trimer). Yield 1.6 g (40 %), b.p. 103–106 °C/8 mmHg. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.77 (6 H, quintet, *J* 5.4 Hz), 3.58 (12 H, t, *J* 5.3 Hz). ^{13}C NMR [75 MHz, CD_3CN/CD_3OD (95:5)]: δ 28.7, 67.2. MS[29] (CI, isobutane $m/z > 110$, rel. int. > 1 %): 175 (100), 173 (3), 117 (8), 115 (2).

The residue was then distilled in a Kugelrohr apparatus and *1,5,9,13-tetraoxacyclohexadecane* (cyclic tetramer) was isolated. Yield 0.48 g (12 %), oven temp. 150–175 °C/8 mmHg, m.p. 70–73 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.81 (8 H, quint, *J* 5.2 Hz), 3.55 (16 H, t, *J* 5.3 Hz). ^{13}C NMR [75 MHz, CD_3CN/CD_3OD (95:5)]: δ 31.4, 67.2.

MS^{29} (CI, isobutane, $m/z > 110$, rel. int. > 1 %): 233 (100), 231 (1), 175 (9), 173 (3), 117 (6), 115 (4).

The residue after Kugelrohr distillation was chromatographed on neutral alumina (Fluka Type 507 C) with CH_2Cl_2/MeOH (95:5) as the eluant. Two fractions were obtained. The first contained the higher cyclic oligomers (pentamer to undecamer, yield 0.8 g), which were analysed by GLC–MS. The second fraction consisted of 'polymers' (1.12 g, white powder, m.p. > 300 °C). (The oligomer fraction could also be separated from the polymers by dissolution in hexane, which leaves the polymers as an insoluble oil.) MS (CI, isobutane) of higher cyclic oligomers: *Pentamer:* 291 (100), 289 (0.6), 233 (4), 175 (11), 173 (7), 117 (9), 115 (6). *Hexamer:* 349 (100), 291 (2), 289 (7), 233 (5), 231 (2), 175 (9), 173 (7). *Heptamer:* 407 (5), 349 (18), 291 (100), 289 (1), 233 (15), 231 (3). *Octamer:* 465 (37), 407 (100), 349 (72), 291 (70), 289 (3). *Nonamer:* 523 (54), 465 (100), 407 (67), 349 (55). *Decamer:* 581 (7), 523 (50), 465 (100), 407 (70). *Undecamer:* 639 (14), 581 (34), 523 (82), 465 (76).

Catalytic cyclooligomerization of oxetane with BF_3: parallel addition of monomer solution and catalyst solution. The reaction was run under a nitrogen atmosphere. Dry dichloromethane (1.1 l) was placed in a three-necked round-bottomed flask equipped with two dropping funnels, a reflux condenser and a magnetic stirrer. A solution of oxetane (4.00 g, 69.0 mmol) dissolved in dichloromethane (300 ml) and an equal volume of BF_3 catalyst solution (0.035 M) were added in parallel from the funnels over 11 h. The reaction mixture was then stirred at room temperature until ^1H NMR analysis showed that all monomer had been consumed (24 h). The reaction mixture was neutralized with gaseous NH_3, and the solvent was evaporated in a Rotavapor. The semicrystalline material was distilled in a Kugelrohr apparatus to give the cyclic trimer, yield 2.0 g (50 %), oven temp. 140–150 °C/8 mmHg, a tetramer–undecamer fraction, yield 1.0 g, oven temp. 150–200 °C/8 mmHg, and a distillation residue (1.0 g).

Catalytic cyclooligomerization of oxetane with other catalyst / solvent systems. The reaction conditions and the results from ^1H NMR and GLC–MS analysis of the reaction mixtures are summarized in Table 1. The initial monomer concentration was 0.05 M, and the amount of oxetane used was 50–100 mg. No work-up or product isolation was done in these cases. The PF_5-catalysed reaction favoured formation of the tetramer over the trimer. None of the other reactions were suitable for preparative syntheses of cyclic oligomers, as mainly polymers were formed.

Catalytic cyclooligomerization of 3,3-dimethyloxetane with BF_3: optimization with respect to the cyclic trimer. The reaction was run under a nitrogen atmosphere. 3,3-Dimethyloxetane (6.0 g, 69.7 mmol) was dissolved in dry dichloromethane (1.4 l), and BF_3 catalyst solution (0.035 M, 550 ml) was added over 4 h at room temperature. Stirring was continued at room temperature, and the reaction was followed by GLC–MS and ^1H NMR spectroscopy. Further conversion of monomer required supplies of fresh catalyst solution; five portions of 100 ml were therefore added at regular intervals during the total reaction time of 15 days. ^1H NMR spectroscopy showed that 5–10 % monomer was still present, but further conversion into products was not possible. Analysis of the volatile reaction products by GLC–MS showed the presence of cyclic oligomers (trimer–hexamer), but in addition also acyclic, homologous fluorohydrins were formed. Gaseous BF_3 was bubbled through the solution for 1–2 h, and the mixture (which had now become intensely yellow) was then stirred at room temperature for 5 h. GLC–MS analysis during this treatment showed the gradual disappearance of the fluorohydrins and at the same time an increase in the amount of the corresponding cyclic oligomers. After neutralization with NH_3, the solvent was evaporated, and the semisolid material was chromatographed on an alumina column (Woelm, neutral alumina). With ether as the eluant, a fraction (2.50 g after evaporation of the solvent) containing all of the cyclic oligomers was collected. The cyclic trimer and tetramer were isolated by crystallization. (For the cyclic pentamer and hexamer, see the PF_5-catalysed reaction described below.)

3,3,7,7,11,11,15,15-Octamethyl-1,5,9,13-tetraoxacyclohexadecane (cyclic tetramer) was crystallized from the oligomer mixture in ether/ethanol. Yield 0.48 g (8 %), m.p. 152–154 °C. ^1H NMR (300 MHz, CD_2Cl_2): δ 0.85 (16 H, s, CH_2O), 3.10 (24 H, s, CH_3). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 22.7, 36.4, 75.8. MS^{29} (CI, isobutane, $m/z > 170$, rel. int. > 3 %): 345 (100), 343 (18), 277 (4), 259 (3), 257 (5), 173 (7), 171 (7).

3,3,7,7,11,11-Hexamethyl-1,5,9-trioxacyclododecane (cyclic trimer) was then isolated by concentration of the mother liquor and crystallization from ethanol. Yield 1.20 g, (20 %), m.p. 57 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 0.78 (12 H, s, CH_2O), 3.16 (18 H, s, CH_3). ^{13}C NMR (75 MHz, CD_3CN): δ 22.9, 36.3, 79.1. MS^{29} (CI, isobutane, $m/z > 84$, rel. int. > 1 %): 259 (100), 257 (9), 191 (1), 173 (2), 171 (6), 87 (18), 85 (31).

Ether with increasing amounts of ethanol (5–25 %, step gradient) was then used as the eluant, and a fraction containing acyclic, homologous diols in addition to polymers was collected. The solvent was evaporated, and the dimeric and trimeric diols were isolated by fractional crystallization.

2,2,6,6-Tetramethyl-4-oxa-1,7-heptanediol (dimeric diol) was crystallized from ether/acetone. Yield 100 mg, m.p. 90–91 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 0.91 (12 H, s, CH_3), 2.68 (variable) (2 H, br s, OH), 3.26 (4 H, s,

CH_2O), 3.43 (4 H, br s, CH_2OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.8 (CH_3), 36.4 (C), 70.8 (CH_2O), 79.7 (CH_2OH). MS (CI, isobutane, *m/z* > 85, rel. int. > 1 %): 191 (85), 189 (2), 173 (3), 117 (10), 87 (100).

2,2,6,6,10,10-Hexamethyl-4,8-dioxa-1,11-undecanediol (trimeric diol) crystallized from the concentrated mother liquor on standing and was recrystallized from hexane/benzene. Yield 170 mg, m.p. 68–70 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 0.89 (6 H, s, CH_3), 0.90 (12 H, s, CH_3), 3.16 (4 H, s, CH_2O), 3.25 (4 H, s, CH_2O), 3.33 (2 H, s, OH), 3.42 (4 H, s, CH_2OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.0, 22.6, 36.3, 36.5, 71.8, 71.9, 80.5. MS (CI, isobutane, *m/z* > 170, rel. int. > 1 %): 277 (98), 259 (2), 257 (3), 203 (2), 191 (27), 189 (3), 187 (1), 173 (28), 171 (6).

The following diols were identified by GLC–MS analysis of the concentrated diol/polymer mixture. MS (CI, isobutane, *m/z* > 170, rel. int. > 1 %): *tetrameric diol:* 363 (55), 345 (1), 277 (10), 259 (6), 257 (6), 191 (17), 189 (4), 187 (3), 173 (22), 171 (9); *Pentameric diol:* 449 (1), 259 (1), 257 (1), 191 (2), 173 (3), 171 (2).

Catalytic cyclooligomerization of 3,3-dimethyloxetane with BF_3: isolation of fluorohydrins. The reaction was repeated as described above. The composition of the volatile part of the reaction mixture (analysed by GLC–MS) after 15 days was similar to the above reaction. The reaction mixture was neutralized with gaseous NH_3 (without previous treatment with gaseous BF_3). The solvent was evaporated in a Rotavapor, and the semisolid crude product was chromatographed (Woelm neutral alumina). With chloroform as the eluant, a fraction containing the cyclic oligomers (1.8 g after evaporation of the solvent) was collected. The cyclic tetramer was crystallized from ether/ethanol, yield 0.20 g (3 %). The cyclic trimer was thereafter crystallized from acetone and from ethanol, yield 0.60 g (10 %). No attempts were made to optimize these yields or to isolate the pentamer and hexamer. With chloroform/methanol (step gradient 5–30 %) as the eluant, a fraction containing acyclic fluorohydrins (dimer–pentamer), acyclic diols (dimer–pentamer, total amount <15 % by GLC) and polymers was obtained. The main component in the volatile part of this fraction was the trimeric fluorohydrin. The polymeric material was removed by dissolution in dichloromethane and filtering off of the white powder (m.p. > 230 °C). Several attempts to isolate the fluorohydrin by chromatography failed. Instead, the fluorohydrin/diol mixture was acetylated by treatment with an excess of acetyl chloride in chloroform, and the acetyl derivative of the trimeric fluorohydrin was isolated by repeated distillations in a Kugelrohr apparatus (oven temp. 70–100 °C/0.5 mmHg). Pure *11-fluoro-2,2,6,6,10,10-hexamethyl-4,8-dioxaundecanol* was finally recovered by hydrolysis (KOH, MeOH, reflux), yield 0.33 g (oil). Other homologues of fluoroacetates and fluorohydrins were identified by GLC–MS analysis of product mixtures.

Trimeric fluoroacetate. ^{1} NMR (300 MHz, $CDCl_3$): δ 0.87 (6 H, s, CH_3), 0.92 (12 H, s, CH_3), 2.05 (3 H, s, CH_3CO_2), 3.13 (8 H, m, CH_2O), 3.89 (2 H, s, CH_2OAc), 4.18 (2 H, s, *J* 47.9 Hz, CH_2F). ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.0, 21.9, 22.2, 35.6, 36.7 (d, *J* 17.2 Hz), 70.1, 76.0, 76.1, 77.2, 77.3, 88.8 (d, *J* 171.8, CH_2F), 130.0, 171.2. MS (CI, isobutane, *m/z* > 170, rel. int. > 2 %): 321 (26), 261 (3), 193 (3), 175 (18).

Tetrameric fluoroacetate. MS (CI, isobutane, *m/z* > 170, rel. int. > 1 %): 407 (100), 347 (2), 261 (8), 233 (12), 215 (7), 205 (5), 214 (5), 193 (6), 187 (3), 175 (40).

Dimeric fluorohydrin. MS (CI, isobutane, *m/z* > 100, rel. int. > 1 %): 193 (22), 191 (12), 175 (2), 173 (3), 121 (4), 119 (2), 107 (8).

Trimeric fluorohydrin: ^1H NMR (300 MHz, $CDCl_3$): δ 0.88 (6 H, s, CH_3), 0.92 (6 H, s, CH_3), 0.93 (6 H, s, CH_3), 2.8 (1 H, br s, OH), 3.14 (2 H, s, CH_2O), 3.16 (2 H, d, *J* 1.6 Hz, CH_2O), 3.18 (2 H, s, CH_2O), 3.26 (2 H, s, CH_2O), 3.45 (2 H, s, CH_2O), 4.18 (2 H, d, *J* 47.9 Hz, CH_2F). ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.9 (d, *J* 5.2 Hz, CH_3), 21.9, 22.2, 36.2, 36.4, 36.6 (d, *J* 16.9 Hz), 72.3, 76.1, 77.1, 77.7, 81.2, 88.6 (d, *J* 171.6 Hz, CH_2F). MS (CI, isobutane, *m/z* > 100, rel. int. > 1 %): 279 (100), 277 (4), 261 (1), 259 (3), 205 (2), 203 (1), 193 (16), 191 (6), 175 (22), 174 (12), 173 (11), 107 (3), 105 (10).

Tetrameric fluorohydrin. MS (CI, isobutane, *m/z* > 100, rel. int. > 1 %): 365 (15), 363 (2), 279 (2), 277 (2), 205 (2), 203 (1), 193 (5), 191 (5), 175 (6), 173 (6), 107 (5), 105 (8).

Pentameric fluorohydrin. MS (CI, isobutane, *m/z* > 100, rel. int. > 1 %): 451 (1), 259 (1), 257 (1), 193 (3), 191 (2), 175 (3), 173 (2), 105 (5), 103 (3).

Catalytic cyclooligomerization of 3,3-dimethyloxetane with PF_5 in dichloromethane. A PF_5 catalyst solution (100 ml) was added to a solution of the oxetane (0.70 g, 8.1 mmol) in dry dichloromethane (160 ml) over 2 h, and stirring was continued at room temperature until ^1H NMR spectroscopy showed that all of the monomer had reacted. The total reaction time was 24 h. The reaction mixture was neutralized with gaseous NH_3. The solvent was evaporated in a Rotavapor, and the crude product was chromatographed on neutral alumina (Fluka Type 507 C). With ether as the eluant, a fraction of cyclic oligomers (0.60 g), mainly tetramer and pentamer, was obtained. Further elution with ether/ethanol (4:1) gave a fraction of polymers (0.1 g, white powder, m.p. > 300 °C).

3,3,7,7,11,11,15,15-Octamethyl-1,5,9,13-tetraoxacyclohexadecane (cyclic tetramer) was crystallized from ether/ethanol and from acetone/water. Yield 0.51 g (73 %), m.p. 152–154 °C. Spectroscopic data are given in the BF_3-catalysed reaction above.

3,3,7,7,11,11,15,15,19,19-Decamethyl-1,5,9,13,17-pentaoxacycloicosane (cyclic pentamer) was isolated by preparative GLC of the concentrated mother liquor. Yield 9 mg, m.p. 30–31 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.87 (30 H, s, CH_3), 3.16 (20 H, s, CH_2O). ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.3, 36.9, 77.6. MS (CI, isobutane, *m/z* > 80, rel. int. > 1 %): 431 (47), 363 (1), 345 (2), 343 (2), 259 (2), 257 (1), 173 (5), 171 (4), 87 (26), 85 (100).

Cyclic hexamer was not isolated. MS (CI, isobutane, *m/z* >80, rel. int. > 0.5 %): 517 (4), 515 (1), 343 (0.5), 279 (100), 259 (0.6), 257 (0.9), 173 (1), 171 (1), 85 (55).

Other cyclooligomerization experiments. Reaction conditions and results of catalytic cyclooligomerizations of 3,3-dimethyloxetane with other catalyst/solvent systems are summarized in Table 2. The reactions were performed on an analytical scale with 0.05 M solutions (initial concentration) of the oxetane monomer, and were followed by ^{1}H NMR spectroscopy and GLC–MS. No work-up or isolation of reaction products was carried out in these cases, as polymers were mostly formed, and none of the reactions were suitable for preparative syntheses of any of the cyclic oligomers. The BF_3-catalysed reaction was also carried out with one equivalent of $LiBF_4$ suspended in the monomer solution. This had no effect at all on the individual distribution of volatile reaction products. The reaction was faster at reflux temperature than at room temperature, and more of the cyclic trimer was then formed at the expense of cyclic tetramer. However, a greater amount of polymers was also formed. Complete conversion of the oxetane monomer was still not achieved. ^{1}H NMR spectroscopy showed about 15 % unchanged monomer when the reaction was terminated, and prolonged reaction time (7 days, reflux) gave no further conversion into products. Parallel addition of the monomer and BF_3 catalyst solution gave no improvement in the ratio cyclic trimer/tetramer. A higher reaction temperature was necessary when benzene was the solvent, as no conversion of the monomer took place at room temperature. Although all of the monomer was consumed in the remaining reactions in Table 2, only traces of the cyclic trimer and tetramer were detected, and mainly polymers were formed.

Catalytic cyclooligomerization of 3-chloromethyl-3-methyloxetane with BF_3. A BF_3 catalyst solution (25 ml, 0.035 M) was added dropwise to a refluxing solution of the monomer (208 mg, 173 mmol) in dichloromethane. Fresh catalyst had to be supplied several times throughout the total reaction time of 24 days (reflux). GLC–MS analysis revealed that conversion of the monomer was still incomplete (80 % unchanged monomer), and that the cyclic trimer (8 %) and tetramer (3 %), as well as their corresponding fluorohydrins (9 %, <0.5 %), were the volatile reaction products. The reaction mixture was treated with BF_3, which caused the disappearance of the fluorohydrin and a slight increase in the amount of trimer. After neutralization with gaseous NH_3, the solvent was evaporated in a Rotavapor, and the crude product was chromatographed on alumina (preparative TLC, Woelm neutral alumina) with chloroform/hexane (2:1) as the eluant. A fraction (<10 mg after evaporation of the solvent) containing a mixture of cyclic trimer and tetramer was obtained. No further attempts to separate these oligomers were made. MS (CI, isobutane, *m/z* > 120, rel. int. > 1 %).

Cyclic trimer. 361/363/365/367 (100/97/30/3, MH^+, 3 Cl), 325/237/329 (17/13/3, 2 Cl), 241/243/245 (11.8/7.6/2, 2 Cl), 121/123 (21.6/7.8, 1 Cl).

Cyclic tetramer. 481/483/485/487 (16/18/8/2, MH^+, 4 Cl), 361/363/365 (6.6/5.2/1.5, 2 Cl).

Trimer fluorohydrin. 381/383/386/387 (61.0/61.2/3.3/2.2) (MH^+, 3 Cl).

Catalytic cyclooligomerization of 3-bromomethyl-3-methyloxetane: with BF_3/CH_2Cl_2. A standard procedure was followed. To a stirred solution of the monomer (0.05 M) was added slowly an equal volume of the catalyst solution and the reaction was followed by GLC–MS analysis. No conversion of monomer had taken place after 72 h at room temperature. The reaction mixture was then refluxed for 24 h, whereafter the cyclic trimer (<3 %) was the only volatile reaction product. MS (CI, isobutane, *m/z* > 400, rel. int. > 1 %): 493/495/497/499 (3.8/11.8/11.1/2.9, MH^+, 3 Br), 413/415/417 (1.2/4.3/3.7, 2 Br).

With PF_5/CH_2Cl_2. The procedure was similar to that described above. The total reaction time was 48 h (room temp.), and GLC–MS analysis showed that conversion of the monomer (into unidentified products) was <2 %.

Catalytic cyclooligomerization of 3-methoxymethyl-3-methyloxetane with BF_3/CH_2Cl_2. The procedure described above was followed. The total reaction time was 3 days (room temp.), and GLC–MS analysis showed unchanged monomer (80 %), cyclic trimer (11 %) and cyclic tetramer (9 %). MS (CI, NH_3, *m/z* > 115, rel. int. > 1 %).

Trimer: 349 (100, MH^+), 233 (2), 117 (2).

Tetramer: 465 (100, MH^+), 349 (6), 233 (3).

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