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Partial Acetalization of Cyclic Imides Using an Intramolecular Oxetanyl Group

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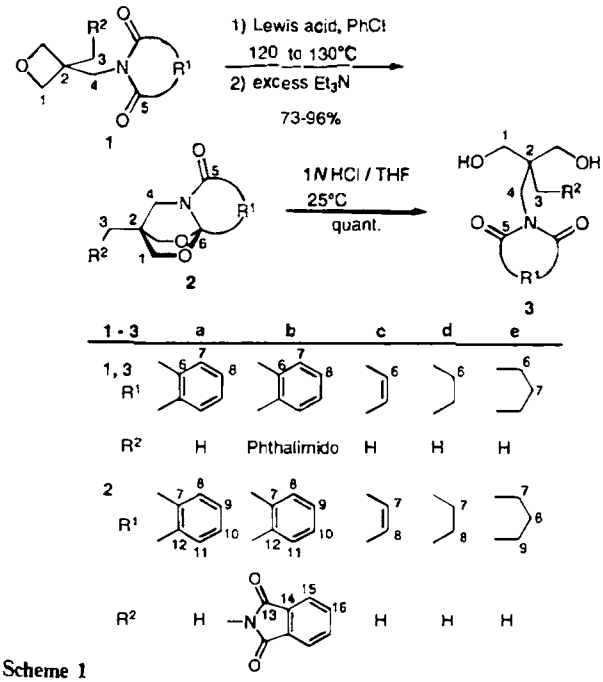
Acetalization of only one carbonyl group of cyclic imides has been achieved in good yields by the Lewis acid catalyzed isomerization of easily accessible *N*-(3-oxetanylmethyl)-substituted imides.

It is well known that carbonyl compounds can be protected from nucleophilic attack by transformation into acetals. Selective acetalization of either of the imide carbonyl groups would serve as a useful method for destroying the symmetry of the imide moiety. Here, we describe the partial cycloacetalization of cyclic imides using an intramolecular oxetanyl group as a propanediol equivalent.

Thus, the reaction of 3-methyl-3-(phthalimidomethyl)oxetane (**1a**) with boron trifluoride-diethyl ether gave exclusively 2-methyl-2-(phthalimidomethyl)propane-1,3-diol (**3a**) after quenching the reaction with MeOH (Scheme 1). In previous studies on polyether syntheses, we demonstrated that 3-functionalized oxetanes show excellent cationic ring-opening polymerizability.[1,2] According to these results, simple hydrolysis of the oxetane ring under the conditions leading to **3a** seemed unlikely. Thus, **3a** is probably formed via bridged acetal **2a** as an intermediate. The following results confirmed this assumption and led to a synthesis of bridged acetal lactams.

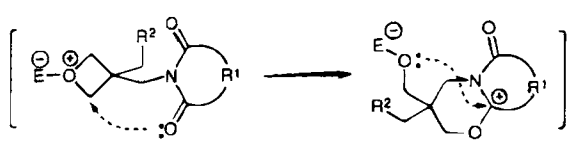


Scheme 1

It was found that quenching the Lewis acid catalyzed reaction of **1a** with anhydrous Et_3N prevented **2a** from undergoing hydrolysis. The oxetane **1a** was exposed to various Lewis acids and the product ratios were determined by NMR. The results are summarized in Table 1. Thus, with $BF_3 \cdot OEt_2$ and trimethylsilyl triflate, mixtures of **2a** and polymeric products were obtained from **1a** under different conditions. The acidity of the Lewis acid remarkably influenced the yield of **2a**. Weak Lewis acids such as triphenylboron and organoaluminums showed poor catalytic activities both for the polymerization and the isomerization to **2a** below 25°C. However, at high temperatures (120–130°C), trimethylaluminum (Me_3Al) and methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide) (MAD) produced **2a** in excellent yields.

The isomerization can also be applied to the oxetane imides **1b–e** (Scheme 1). In contrast to **1a**, negligible amounts of polymeric products were formed independent of the reaction conditions. Furthermore, the isomerization of **1d** and **1e** with weak Lewis acids at 25°C proceeded in moderate rates, probably because of the enhanced nucleophilicity of the carbonyl oxygen atom. Good yields (73–84%) of acetals **2** were obtained at higher reaction temperatures (120–130°C). The optimized reaction conditions are described in the experimental section.

As has been reported earlier, a similar oxetane, containing a phthalimide group separated by the longer spacer $CH_2O(CH_2)_4$, does not isomerize under the influence of $BF_3 \cdot OEt_2$, but undergoes ring-opening polymerization.[1] The isomerization of the CH_2-separated oxetane imides **1**, therefore, can be explained by intramolecular carbonyl participation. The reaction begins with coordination of Lewis acid E to the oxetanyl oxygen atom. Intramolecular attack of one of the imide carbonyl oxygen atoms on an α-carbon atom of the oxetane causes ring opening followed by ring closure to the bridged acetal lactams **2** (Scheme 2). In the case of the complexed oxetane mentioned above, intramolecular nucleophilic attack is entropically less favorable. Instead, a polyether is formed by the ring-opening polymerization of the oxetanyl groups. A similar isomerization involving intramolecular carbonyl participation was published in a report on syntheses of bridged ortho esters from CH_2-separated oxetane esters.[3]



Scheme 2

In order to confirm the proposed mechanism, the reaction of **1d** with MAD (0.5 equiv) was studied by NMR spectroscopy. It is known that MAD complexes not only with carbonyl groups but also with cyclic ethers such as

Table 1. Lewis Acid-Catalyzed Isomerization of **1a**[a]

Entry	Lewis Acid[b]/Solvent	Solvent (mL)	Conditions		Yield[c] (%)		
			Temp. (°C)	Time (h)	**1a**	**2a**	Polymer
1	$BF_3 \cdot OEt_2/CH_2Cl_2$	CH_2Cl_2 (5.0)	25	2	0	72	28
2	$BF_3 \cdot OEt_2/CH_2Cl_2$	CH_2Cl_2 (5.0)	25	4	0	42	58
3	$BF_3 \cdot OEt_2/CH_2Cl_2$	CH_2Cl_2 (2.0)	25	2	0	60	40
4	$BF_3 \cdot OEt_2/CH_2Cl_2$	CH_2Cl_2 (2.0)	0	2	35	36	29
5	$BF_3 \cdot OEt_2/CH_2Cl_2$	CH_2Cl_2 (1.0)	25	2	0	44	56
6	$BF_3 \cdot OEt_2$/PhCl	PhCl (2.0)	25	2	0	56	44
7	$BF_3 \cdot OEt_2$/toluene	toluene (2.0)	25	2[d]	4	83	13
8	TMSOTf/CH_2Cl_2	CH_2Cl_2 (2.0)	25	2	0	57	43
9	Ph_3B/toluene	PhCl (2.0)	0	24	63	31	6
10	Ph_3B/toluene	PhCl (2.0)	130	12	0	94	6
11	Me_3Al/hexane	PhCl (2.0)	0	24	~100	0	0
12	Me_3Al/hexane	PhCl (2.0)	120	12	0	~100	0
13	MAD/toluene	PhCl (2.0)	0	24	84	10	6
14	MAD/toluene	PhCl (2.0)	130	12	0	~100	0

[a] 5 mol% of each Lewis acid was used for 0.5 g (2.2 mmol) of **1a**.
[b] The amounts of Lewis acids used are as follows: $BF_3 \cdot OEt_2$ (0.25 mL, 0.43 M), trimethylsilyl trifluoromethanesulfonte (TMSOTf) (0.25 mL, 0.43 M), Ph_3B (0.36 mL, 0.30 M), Me_3Al (0.11 mL, 1.0 M), methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide) (MAD) (0.22 mL, 0.50 M).
[c] Determined by ^1H NMR spectroscopy.
[d] The reaction mixture became gradually turbid.

Table 2. Spectroscopic Data of Compounds 1–3 Prepared

Product[a]	IR (KBr) ν (cm^{-1})	^1H NMR ($CDCl_3$, 399.78 MHz) δ, J (Hz)	^{13}C NMR ($CDCl_3$, 100.54 MHz) δ, J (Hz)	HRMS M^+, m/z
1a	1769, 1763, 1720, 1707 (imide C=O), 975, 830 (C O)	1.36 (s, 3H, CH_3), 3.87 (s, 2H, NCH_2), 4.35, 4.72 (each d, J = 6.4, each 2H, *cis* and *trans* OCH_2), 7.74, 7.86 (each dd, J = 5.4, 2.9, each 2H, H_{arom})	22.2 (C-3), 41.6 (C-2), 44.3 (C-4), 80.5 (t, $^1J_{CH}$ = 150.7, C-1), 123.3 (C-7), 131.8 (C-6), 134.1 (C-8), 168.7 (C-5)	$C_{13}H_{13}NO_3$ Calc. 231.0896, Found 231.0893
1b	1771, 1719, 1710 (imide C=O), 984, 839 (C–O)	3.86 (s, 4H, NCH_2), 4.50 (s, 4H, OCH_2), 7.86 (s-like, 8H, ArH)[b]	41.5 (C-3/4), 44.5 (C-2), 76.1 (C-1), 123.0 (C-7), 131.4 (C-6), 134.4 (C-8), 168.5 (C-5)[b]	$C_{21}H_{16}N_2O_5$ Calc. 376.1060, Found 376.1072
1c	1766, 1709 (imide C=O), 1590 (C=C), 977, 834 (C–O)	1.27 (s, 3H, CH_3), 3.67 (s, 2H, NCH_2), 4.30, 4.59 (each d, J = 5.4, each 2H, *cis* and *trans* OCH_2), 6.73 (s, 2H, CH=CH)	22.0 (C-3), 40.3 (C-2), 44.3 (C-4), 80.4 (t, $^1J_{CH}$ = 150.8, C-1), 134.2 (C-6), 171.1 (C-5)	$C_9H_{11}NO_3$ Calc. 181.0738, Found 181.0747
1d	1774, 1764, 1703, 1697 (imide C=O), 972, 824 (C O)	1.31 (s, 3H, CH_3), 2.77 (s, 4H, $COCH_2$), 3.68 (s, 2H, NCH_2), 4.30, 4.66 (each d, J = 6.3, each 2H, *cis* and *trans* OCH_2)	22.7 (C-3), 28.6 (C-6), 41.0 (C-2), 45.6 (C-4), 81.0 (t, $^1J_{CH}$ = 148.9, C-1), 177.7 (C-5)	$C_9H_{13}NO_3$ Calc. 183.0896, Found 183.0897
1e	1726, 1667 (imide C=O), 979, 828 (C O)	1.30 (s, 3H, CH_3), 1.99 (quint, J = 6.4, 2H, CH_2-7), 2.70 (t, J = 6.4, 4H, $COCH_2$), 3.93 (s, 2H, NCH_2), 4.20, 4.60 (each d, J = 6.1, each 2H, *cis* and *trans* OCH_2)	17.0 (C-7), 22.2 (C-3), 32.8 (C-6), 40.4 (C-2), 44.5 (C-4), 81.0 (t, $^1J_{CH}$ = 150.8, C-1), 173.0 (C-5)	$C_{10}H_{15}NO_3$ Calc. 197.1053, Found 197.1036
2a	1721, 1711 (lactam C=O), 1132, 1055–968 (acetal)	0.95 (s, 3H, CH_3), 3.63 (s, 2H, NCH_2), 3.94, 4.07 (each d, J = 8.3, each 2H, *equatorial* and *axial* OCH_2), 7.44–7.53 (m, 3H, 9,10,11-H_{arom}), 7.72 (d, J = 7.3, 1H, 8-H_{arom})	15.61 (C-3), 31.17 (C-2), 49.3 (C-4), 74.0 (t, $^1J_{CH}$ = 150.8, C-1), 101.2 (C-6), 121.8 (C-9), 123.2 (C-8), 130.5 (C-11), 132.0 (C-10), 132.9 (C-12), 139.6 (C-7), 163.9 (C-5)	$C_{13}H_{13}NO_3$ Calc. 231.0896, Found 231.0885
2b	1771, 1719, 1709 (imide and lactam C=O), 1122–990 (acetal)	3.73 (s, 2H, NCH_2-3), 3.80 (s, 2H, NCH_2-4), 4.14, 4.30 (each d, J = 8.8, each 2H, *equatorial* and *axial* OCH_2), 7.54 7.55 (m, 3H, 9,10,11-H_{arom}), 7.75 (d, J = 6.8, 1H, 8-H_{arom}), 7.78, 7.90 (each dd, J = 5.6, 3.2, each 2H, 15,16-H_{arom})	37.7 (C-3), 39.4 (C-2), 46.8 (C-4), 71.6 (t, $^1J_{CH}$ = 150.8, C-1), 101.5 (C-6), 122.0 (C-9), 123.5 (C-8), 123.7 (C-15), 130.8 (C-11), 131.4 (C-14), 132.3 (C-10), 132.9 (C-12), 134.6 (C-16), 139.3 (C-7), 154.1 (C-5), 168.1 (C-13)	$C_{21}H_{16}N_2O_5$ Calc. 376.1060, Found 376.1071
2c	1711 (lactam C=O), 1596 (C=C), 1152, 1064–975 (acetal)	1.00 (s, 3H, CH_3), 3.53 (s, 2H, NCH_2), 3.93, 4.03 (each d, J = 8.3, each 2H, *equatorial* and *axial* OCH_2), 6.17, 6.73 (each d, J = 5.9, each 1H, CH-8 and 7)	15.9 (C-3), 31.5 (C-2), 49.3 (C-4), 73.8 (t, $^1J_{CH}$ = 148.9, C-1), 103.0 (C-6), 131.5 (C-8), 140.4 (C-7), 165.6 (C-5)	$C_9H_{11}NO_3$ Calc. 181.0738, Found 181.0723

Table 2. (continued)

Product[a]	IR (KBr) ν (cm^{-1})	^1H NMR ($CDCl_3$, 399.78 MHz) δ, J (Hz)	^{13}C NMR ($CDCl_3$, 100.54 MHz) δ, J (Hz)	HRMS M^+, m/z
2d	1706 (lactam C=O), 1067–900 (acetal)	0.95 (s, 3 H, CH_3), 2.17, 2.48 (each d, 2 H, CH_2-8 and 7), 3.45 (s, 2 H, NCH_2), 3.87, 3.95 (each d, J = 8.1, each 2 H, *equatorial* and *axial* OCH_2)	15.6 (C-3), 28.8 (C-8), 29.7 (C-7), 30.9 (C-2), 49.8 (C-4), 74.0 (t, $^1J_{CH}$ = 149.8, C-1), 104.9 (C-6), 171.4 (C-5)	$C_9H_{13}NO_3$ Calc. 183.0896, Found 183.0886
2e	1649 (lactam C=O), 1098–943 (acetal)	0.94 (s, 3 H, CH_3), 1.80 (quint, J = 6.2, 2 H, CH_2-8), 1.94 (t, J = 6.1, 2 H, CH_2-9), 2.37 (t, J = 6.4, 2 H, CH_2-7), 3.48 (s, 2 H, NCH_2), 3.78, 3.90 (each d, J = 7.8, each 2 H, *equatorial* and *axial* OCH_2)	16.1 (C-3), 17.1 (C-8), 30.6 (C-2), 31.8 (C-7), 32.3 (C-9), 50.7 (C-4), 72.7 (t, $^1J_{CH}$ = 145.3, C-1), 99.8 (C-6), 168.8 (C-5)	$C_{10}H_{15}NO_3$ Calc. 197.1053, Found 197.1047
3a	3403 (OH), 1769, 1703, 1692 (imide C=O), 1056, 1032 (C–O)	0.88 (s, 3 H, CH_3), 3.38, 3.49 (each dd-like, J_1 = 11.1, J_2 = 7.2 and 5.9, each 2 H, OCH_2), 3.53 (dd-like overlapping OCH_2 signals, J = 7.2, 5.9, 2 H, OH), 3.82 (s, 2 H, NCH_2), 7.78, 7.89 (each dd, J = 5.4, 2.9, each 2 H, H_{arom})	17.9 (C-3), 40.4 (C-4), 42.2 (C-2), 67.6 (t, $^1J_{CH}$ = 143.4, C-1), 123.7 (C-7), 131.6 (C-6), 134.8 (C-8), 170.0 (C-5)	$C_{13}H_{15}NO_4$ Calc. 249.1002, Found 249.1017
3b	3504 (OH), 1768, 1704 (imide C=O), 1058 (C–O)	3.47 (d, J = 7.6, 4 H, OCH_2), 3.77 (t, J = 7.6, 2 H, OH), 3.90 (s, 4 H, NCH_2), 7.78, 7.88 (each dd, J = 5.5, 3.1, each 4 H, H_{arom})	39.4 (C-3/4), 47.8 (C-2), 63.2 (C-1), 123.7 (C-7), 131.6 (C-6), 134.5 (C-8), 169.7 (C-5)	$C_{21}H_{18}N_2O_6$ Calc. 394.1165, Found 394.1147
3d	3344 (OH), 1769, 1703, 1687 (imide C=O), 1054 (C–O)	0.83 (s, 3 H, CH_3), 2,82 (s, 4 H, $COCH_2$), 3.29, 3.40 (each dd-like, J_1 = 11.9, J_2 = 8.3 and 5.7, each 2 H, OCH_2), 3.48 (dd-like, J = 8.3, 5.7, 2 H, OH), 3.64 (s, 2 H, NCH_2)	18.0 (C-3), 28.0 (C-6), 41.3 (C-4), 42.0 (C-2), 67.3 (C-1), 179.1 (C-5)	$C_9H_{16}NO_4$[c] Calc. 202.1080, Found 202.1087
3e	3378 (OH), 1719, 1660 (imide C=O), 1049, 1037 (C–O)	0.80 (s, 3 H, CH_3), 1.99 (quint, J_1 = 6.6, 2 H, CH_2-7), centered at 2.75 (m, 4 H, $COCH_2$), 3.24, 3.33 (each d-like, J = 12.0, each 2 H, OCH_2), 3.48 (br s, 2 H, OH), 3.92 (s, 2 H, NCH_2)	16.9 (C-7), 18.1 (C-3), 32.9 (C-6), 41.1 (C-4), 41.9 (C-2), 67.5 (C-1), 174.6 (C-5)	$C_{10}H_{17}NO_4$[d]

[a] Satisfactory microanalyses obtained: C ± 0.30, H ± 0.24, N ± 0.19. Exception: **2c**, C – 0.40.
[b] Measured in DMSO-d_6.
[c] For MH^+.
[d] EIMS: m/z (%) = 215 (M^+, 1.8), 167 (100), 152 (49.6), 139 (55.3), 114 (46.3).

propylene oxide and oxetane.[4,5] In $CDCl_3$ at 0–25°C, separate sets of signals for free and MAD-complexed **1d** were observed, indicating a slow or negligible exchange of MAD. For the **1d** complex, maximum downfield shifts were observed for the hydrogens in the neighborhood of the oxetane oxygen atom; +0.63 and +0.57 ppm for *cis* and *trans* OCH_2, respectively, and none for NCH_2 and $COCH_2$. This clearly indicated that complexation of **1d** with MAD had occurred at the ether function. The **1d**-complex was gradually transformed into the **2d**-MAD complex. In contrast, **2d** itself was found to complex with MAD at the carbonyl site as indicated by the maximum down-field shift of +0.24 ppm for 6-CH_2 adjacent to the lactam carbonyl group.

The rearrangement of **1** to **2** is operationally simple: a mixture of the easily accessible oxetane imide and the Lewis acid in chlorobenzene was heated in a sealed tube, followed by addition of excess of Et_3N. Compounds **2** are stable under non-acidic conditions, and can be purified by column chromatography and recrystallization to afford the pure products. Compound **2a** can be obtained on a preparative scale of 8 g (experimental section). Hydrolysis of **2** by dilute hydrochloric acid led to the imide-alcohols **3** in almost quantitative yields.

The IR spectra of the polymeric products obtained in the rearrangement of **1a** showed characteristic bands assignable to amide and/or imide groups. We are presently studying the structure of the polymers formed and the polymerization mechanism.

CH_2Cl_2, PhCl, and toluene were purified by distillation from CaH_2 or BuLi under a dry N_2 atmosphere. $BF_3 \cdot OEt_2$ and trimethylsilyl trifluoromethanesulfonate (TMSOTf) were purified by fractional distillation in vacuo under a dry N_2 atmosphere. Benzylthiolanium hexafluoroantimonate (BnTA) was prepared according to Lit.[6]; yield: 60%, mp 112–113°C (Lit.[6] mp 121.5–122°C). Methylaluminium bis(2,6-di-*tert*-butyl-4-methylphenoxide) (MAD) was synthesized according to Lit.[4] and purified by recrystallization from hexane under a N_2 atmosphere; yield: 60%. Commercially available BPh_3 and Me_3Al were used without further purification.

Column chromatography was carried out on EM aluminium oxide 90 (70–230 mesh ASTM). All melting points are uncorrected. IR spectra (Table 2) were recorded on a JASCO FT/IR-3 IR spectrometer in KBr. ^1H and ^{13}C NMR spectra (Table 2) were measured in $CDCl_3$ using TMS as an internal standard on JEOL JNM GX-400, JEOL JNM FX-100S and JEOL JNM EX-500 spectrometers. Coupling constants ($^1J_{CH}$) were estimated from INEPT spectra, and the assignment of the OCH_2 proton signals were based on phase sensitive NOESY or NOE differential spectra: *cis*/*trans* to CH_3 at C-3 in **1a,c–e** and *axial*/*equatorial* position in the boat-type 1,3-

dioxane ring of **2a–e**. Mass spectra were performed on a HITACHI M-90 mass spectrometer (70 eV) (Table 2).

3-Methyl-3-(phthalimidomethyl)oxetane (**1a**):

From 2-(hydroxymethyl)-2-methylpropane-1,3-diol according to Lit.[1]; yield: 64%; mp 107–109°C (acetone/Et_2O, 1:1).

3,3-Bis(phthalimidomethyl)oxetane (**1b**):

From pentaerythritol as described for **1a**; yield: 30%; colorless needles; mp 264–266°C (toluene). [3,3-Bis(hydroxymethyl)oxetane; bp 120–135°C/0.3 Torr (Lit.[7] bp 122–124°C/0.15 Torr). Ditosylate; mp 108–110°C (precipitated from H_2O)].

3-(Maleimidomethyl)-3-methyloxetane (**1c**):

From 3-(hydroxymethyl)-3-methyloxetane[1] (1.14 g, 11.3 mmol), maleimide (1.00 g, 10.3 mmol), Ph_3P (2.70 g, 10.3 mmol), diisopropyl azodicarboxylate (2.08 g, 10.3 mmol), and neopentyl alcohol (0.50 g, 5.7 mmol) in anhyd THF (80 mL) according to Lit.[8]. Chromatography (eluent, EtOAc hexane, 1:2) followed by distillation in vacuo afforded a colorless semi-solid (0.47 g, 25%); bp 120–160°C/0.1 Torr. Crystallization from $CHCl_3/Et_2O$ gave colorless needles; mp 64–66°C.

3-Methyl-3-(succinimidomethyl)oxetane (1d):

A solution of (3-methyl-3-oxetanyl)methyl *p*-toluenesulfonate[1,9] (10.00 g, 36.8 mmol) in DMF (100 mL) was mixed with an aqueous (7.0 mL) solution of succinimide (4.01 g, 40.4 mmol) and KOH (2.27 g, 40.4 mmol). After stirring at 80°C for 30 min additional solutions of succinimide (2.01 g, 20.24 mmol) and KOH (1.14 g, 20.2 mmol) in H_2O (3.5 mL) were added. Stirring at 80°C was continued for further 30 min and then the solvents were evaporated. The residue was suspended in $CHCl_3$ and the insoluble part was removed by filtration. Distillation of the soluble part gave a colorless semi-solid; bp 95–100°C/0.1 Torr. Chromatography (eluent, EtOAc) followed by crystallization from CH_2Cl_2/hexane afforded colorless needles (3.98 g, 59%); mp 105–106°C.

3-(Glutarimidomethyl)-3-methyloxetane (**1e**):

From (3-methyl-3-oxetanyl)methyl *p*-toluenesulfonate (10.0 g, 36.8 mmol), glutarimide (5.41 g, 47.8 mmol), and NaH (2.21 g, 60% in mineral oil, 55.3 mmol) in a similar manner to that described for **1d**; yield: 3.36 g (46%); colorless needles; mp 48–49°C (THF/hexane).

Bridged Acetal Lactams 2; General Procedure:

In a 25-mL ampule equipped with a stopper was placed **1** (0.5 g) and the ampule was repeatedly evacuated and filled with N_2. The content was dissolved in an anhyd solvent (Table 1), if necessary, by warming, and then a solution of Lewis acid (0.05 equiv to **1**, Table 1) was charged with the help of a hypodermic syringe under a N_2 stream. The ampule was sealed and the resulting solution was allowed to stand for 12 h at the given temperature (Table 1). After the reaction was quenched by adding anhyd Et_3N (0.1 mL), the cooled mixture was diluted with CH_2Cl_2 (10 mL). When Me_3Al was used as a Lewis acid, a small amount of insoluble materials which separated was removed by vacuum filtration. After the solvents were evaporated, the residue was dried over P_2O_5 in vacuo at 80°C and then an aliquot was subjected to NMR analysis for determining the product ratio. Purification by column chromatography (eluent, CH_2Cl_2) gave **2**.

5,6-Benzo-1-methyl-8,11,3-dioxazatricyclo[5.2.2.0^{3,7}]undecan-4-one (**2a**):

From **1a** (0.50 g, 2.2 mmol) and Me_3Al (0.11 mL, 0.11 mmol, in hexane) in PhCl (2.0 mL) at 120°C for 12 h (Table 1, entry 12); yield: 0.48 g (96%). In the preparative scale experiment starting from **1a** (8.00 g), **2a** was obtained as colorless needles after decolorization with charcoal followed by crystallization from CH_2Cl_2/hexane; yield: 7.30 g (91%); mp 172–174°C.

5,6-Benzo-1-(phthalimidomethyl)-8,11,3-dioxazatricyclo[5.2.2.0^{3,7}]undecan-4-one (**2b**):

From **1b** (0.75 g, 2.0 mmol) and TMSOTf (0.23 mL, 0.10 mmol, in PhCl) in PhCl (22.5 mL) at 130°C for 12 h; yield: 0.56 g (75%); colorless plates; mp 235–236°C (CH_2Cl_2/hexane).

1-Methyl-8,11,3-dioxazatricyclo[5.2.2.0^{3,7}]undeca-5-en-4-one (**2c**):

From **1c** (150 mg, 0.82 mmol) and BnTA (17 mg, 0.04 mmol) in PhCl (1.1 mL) at 120°C for 24 h; yield: 110 mg (73%); colorless needles; mp 78–79°C ($CHCl_3/Et_2O$).

1-Methyl-8,11,3-dioxazatricyclo[5.2.2.0^{3,7}]undecan-4-one (**2d**):

From **1d** (2.0 g, 10.9 mmol) and TMSOTf (1.26 mL, 0.55 mmol, in PhCl) in PhCl (8.0 mL) at 120°C for 3 h; yield: 1.67 g (84%); colorless needles; mp 100–101°C (CH_2Cl_2/hexane). Its sensitivity towards moisture often caused hydrolysis to **3d** throughout the purification.

1-Methyl-9,12,3-dioxazatricyclo[6.2.2.0^{3,8}]dodeca-4-one (**2e**):

From **1e** (0.5 g, 2.5 mmol) and TMSOTf (0.29 mL, 0.13 mmol, in PhCl) in PhCl (2.0 mL) at 120°C for 12 h; yield: 0.42 g (84%); colorless plates; mp 113–114°C (CH_2Cl_2/hexane).

Hydrolysis of Bridged Acetal Lactams 2; General Procedure:

The hydrolysis of **2** (each 0.1 g) was carried out by stirring in THF (5 mL) containing a few drops of 1 N HCl at 0 or 25°C and was complete at least within 0.5 h. After evaporation of the solvents, the alcohols **3** were obtained in nearly quantitative yields. Moisture-sensitive **2d** was hydrolyzed in boiling aqueous THF (3 mL) for 3 h. As an exception **2c** gave a complex mixture, which probably contained HCl adducts.

2-Methyl-2-(phthalimidomethyl)propane-1,3-diol (**3a**): Colorless plates; mp 117–118°C (CH_2Cl_2/CCl_4).

2,2-Bis(phthalimidomethyl)propane-1,3-diol (**3b**): Colorless needles; mp 223–225°C (THF).

2-Methyl-2-(succinimidomethyl)propane-1,3-diol (**3d**): Colorless plates; mp 106–107°C (CH_2Cl_2/hexane).

2-(Glutarimidomethyl)-2-methylpropane-1,3-diol (**3e**): Colorless needles; mp 107–108°C (CH_2Cl_2/hexane).

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(1) Motoi, M.; Sekizawa, S.; Asakura, K.; Kanoh, S. *Polym. J.* **1993**, *25*, 1283.
(2) Motoi, M.; Noguchi, K.; Arano, A.; Konah, S.; Ueyama, A. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 1778.
Motoi, M.; Saito, E.; Kyoda, S.; Takahata, N.; Nagai, S.; Arano, A. *Polym. J.* **1991**, *23*, 1225.
Motoi, M.; Nagahara, S.; Yokoyama, M.; Saito, E.; Nishimura, O.; Kanoh, S.; Suda, H. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 1572, and references cited therein.
(3) Corey, E.J.; Raju, N. *Tetrahedron Lett.* **1983**, *24*, 5571.
(4) Maruoka, K.; Itoh, T.; Yamamoto, H. *J. Am. Chem. Soc.* **1985**, *107*, 4573.
Adachi, T.; Sugimoto, H.; Aida, T.; Inoue, S. *Macromolecules* **1993**, *26*, 1238.
(5) Takeuchi, D.; Aida, T. *Macromolecules* **1996**, *29*, 8096.
(6) Endo, T.; Uno, H. *J. Polym. Sci.: Polym. Lett. Ed.* **1985**, *23*, 359.
(7) Vandenberg, E.J.; Mullis, J.C.; Juvet Jr., R.S. *J. Polym. Sci.: Part A: Polym. Chem.* **1989**, *27*, 3083.
(8) Walker, M.A. *J. Org. Chem.* **1995**, *60*, 5352.
(9) Kawakami, Y.; Takahashi, K.; Hibino, H. *Macromolecules* **1991**, *24*, 4531.