Syntheses of crown ether-esters with (benzyloxy)methyl side arms using SbPh$_3$ and BiPh$_3$ as templates [1]

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New crown ether-esters 3a, 3b, 4a, 4b, 4c and 5a with side arms are synthesized by the treatment of (benzyloxy)methyl-substituted diols (1 and 2) with acid chlorides [malonyl chloride and diglycolyl chloride (2,2'-oxydiacetyl chloride)]. SbPh$_3$ and BiPh$_3$ are effective templates for the synthesis of 14-crown-4 ether-esters with (benzyloxy)methyl side arms, and the template effect depends on the structures of both the diols and acid chlorides. Also, it was revealed that the key step in the template synthesis is the formation of a complex between 1 and MPh$_3$ (M = Sb and Bi) by IR and mass spectral studies. The order of complexing ability between 1 and MPh$_3$ is: 1 + BiPh$_3$ $\gg$ 1 + SbPh$_3$ > 1 + AsPh$_3$. In particular, BiPh$_3$ can form stable 1:1 and 2:1 complexes with 1.

It is well known that template syntheses are some of the most useful methods for the synthesis of macrocyclic compounds such as crown ethers and supramolecules.[2] Ogawa *et al.* reported[3] that triarylbismuthines were efficient dehydration reagents for the preparation of ester compounds such as the crown ether-esters by the reaction of a carboxylic acid or carboxylic acid anhydride with an aliphatic alcohol or polyethylene glycol in nonpolar solvents such as benzene. Also, Alcock *et al.*[4] and Takahashi *et al.*[5] reported that antimony(III) chloride (SbCl$_3$), which is unstable in air, formed stable 1:1 complexes with 12-crown-4, 15-crown-5 and 18-crown-6. These results have led us to use SbPh$_3$ as a template for the syntheses of crown ether-esters with side arms. SbPh$_3$ is a very convenient template, because (i) it is highly soluble in low polarity solvents such as benzene, (ii) it is stable in water and air, and (iii) it is easily recovered from the reaction mixture. Although a number of crown ethers having one or more side arms as additional binding sites have been extensively investigated,[6] no example has been reported on the synthesis of crown ether-ester derivatives with side arms. It is expected that these crown ether-esters may have specific selectivities for metal cations similar to crown ethers with side arms. Here, we report the synthesis of crown ether-esters with (benzyloxy)methyl side arms using MPh$_3$ (M = Sb and Bi) as the template.

Results and discussion

Syntheses of crown ether-esters with (benzyloxy)methyl side arms

(Benzyloxy)methyl-substituted 16-, 14- and 13-membered crown ether-esters were prepared by the treatment of diols 1 and 2[7] with the corresponding acid chlorides (malonyl chloride and diglycolyl chloride) under high dilution conditions (see Experimental section). For example, when 1 was treated with malonyl chloride, pure monomer 3a and dimer 3b were obtained as hygroscopic oils in 35 and 21% yield, respectively. On the other hand, when diglycolyl chloride was used, monomer 4a, dimer 4b and trimer 4c were obtained as cyclization products. Using 2 as a diol gave only the monomer 5a. Structures of these cyclization compounds were confirmed by elemental analyses, ^{1}H and ^{13}C NMR in CDCl$_3$ and EI-mass spectroscopy (20 eV). COSY and CHCORR (C-H Correlated 2D NMR) techniques were used for the assignment of the ^{1}H and ^{13}C NMR spectra. All peaks in the ^{1}H and ^{13}C NMR spectra were reasonably assigned. Although the molecular ion peaks of 3a, 3b, 4a and 5a in the EI-mass spectra were observed as [M + H]$^+$, those of 4b and 4c could not be

observed. We confirmed these structures by the fragment ion peaks arising from ([M − C$_6$H$_5$CH$_2$ − H]$^+$ at 700 (44%), [M − C$_6$H$_5$CH$_2$ − OCOCH$_2$O + H]$^+$ at 628 (10%) and [M/2]$^+$ at 396 (5%) in 4b and [M − C$_6$H$_5$CH$_2$ − CH$_2$COO-CH$_2$CH$_2$OCH$_2$CCH$_3$(CH$_2$OCH$_2$C$_6$H$_5$)CH$_2$OCH$_2$CH$_2$O]$^+$ at 774 (0.9%), [M − C$_6$H$_5$CH$_2$ − M/3]$^+$ at 701 (2%) and [M − M/3 − C$_6$H$_5$CH$_2$ − OCOCH$_2$O + H]$^+$ at 628 (0.5%) in 4c.

Template effect by MPh$_3$ for the syntheses of the crown ether-esters

The yield and recovery of MPh$_3$ (M = As, Sb and Bi) from the reaction of diols with acid chlorides are summarized in Table 1. As shown in Run 3, using SbPh$_3$ for the reaction of 1 with malonyl chloride increased the yield of monomer 3a and decreased that of dimer 3b when compared with Run 1. The recovery of SbPh$_3$ was 86%. We also examined the effect of AsPh$_3$ and BiPh$_3$ as a template for the cyclization reaction, because As and Bi are also group XV metals. When AsPh$_3$ was used as the template (Run 2), the yields of 3a decreased and that of 3b remained the same as compared with Run 1. The recovery of AsPh$_3$ was quantitative. On the other hand, addition of one equivalent of BiPh$_3$ increased not only the yield of 3a but also that of 3b (Run 6). In this case, BiPh$_3$ could not be recovered because it decomposed under the reaction conditions. In order to investigate the effect on the structure of the acid chloride, diglycolyl chloride was used as the acid chloride. Runs 5–8 in Table 1 show the yield of the (benzyloxy)methyl substituted 16-crown-5 ether-ester 4a, the dimer 4b and the trimer 4c. A significant template effect by MPh$_3$ was not observed, although the yield of the dimer was slightly enhanced by using SbPh$_3$ (Run 6). Next, we examined the effect on the structure of the diol. The (benzyloxy)methyl-substituted tri(ethylene glycol)-derivative 2 was treated with malonyl chloride (Runs 7 and 8). In this system, monomer 5a was predominantly obtained. A significant template effect was not observed, although the yield of 5a was slightly increased using SbPh$_3$. These results show that the effect of SbPh$_3$ and BiPh$_3$ as templates depends on the structures of both the diols and acid chlorides under the given reaction conditions.

Complexing ability between diol 1 and MPh$_3$

Recently, Rogers *et al.*[8] reported the X-ray crystallography of complexes of ethylene glycols with M(NO$_3$)$_3$ (M = As, Sb and Bi). We believe that complex formation between the diol and MPh$_3$ is an important step in the cyclization reaction. In order to assess the complexing abilities of diol 1 with MPh$_3$ (M = As,
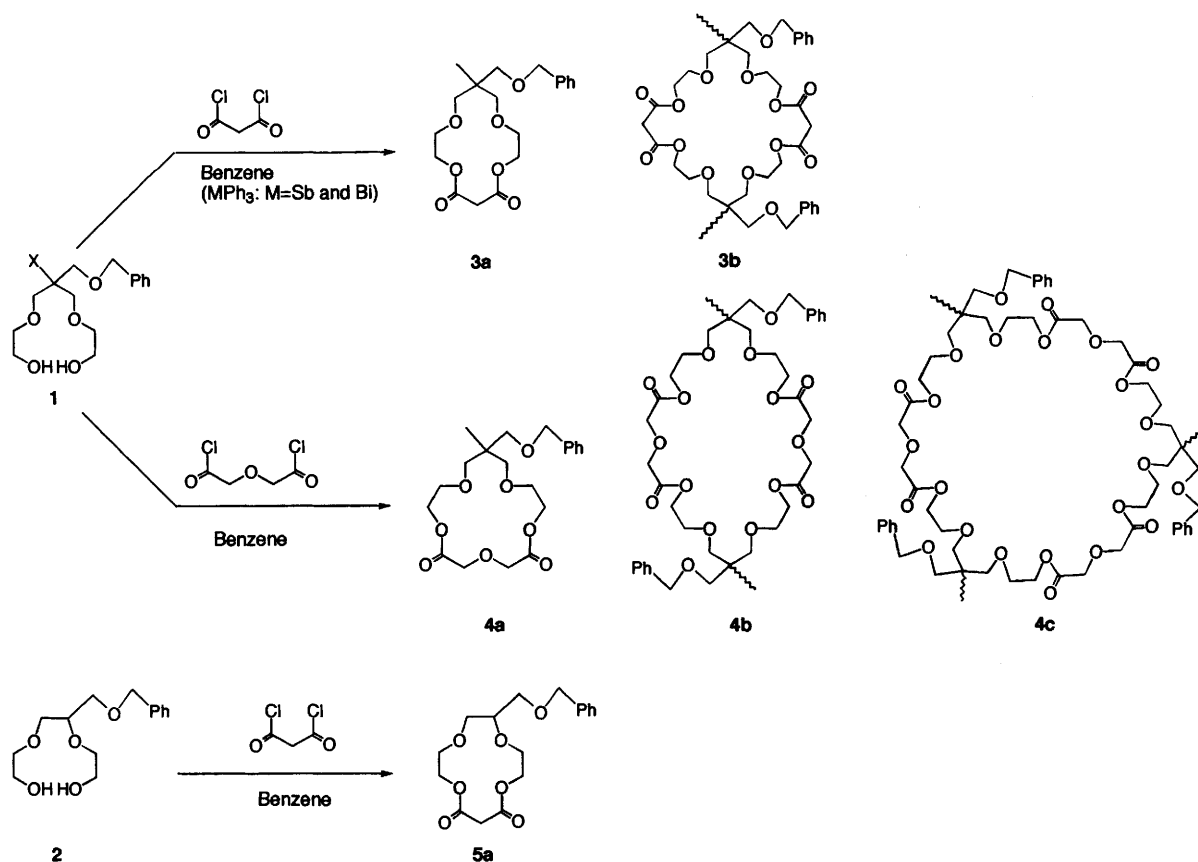
Table 1 Yield[a] of crown ether-ester and recovery of MPh₃ (M = As, Sb and Bi)

Run	Diol	Acid chloride	Template	Yield (%) Monomer	Dimer	Trimer	Recovery of MPh₃ (%)
				3a	**3b**		
1	1	Malonyl chloride	—	35	21	—	
2	1	Malonyl chloride	AsPh₃	25	21	—	>99
3	1	Malonyl chloride	SbPh₃	40	15	—	86
4	1	Malonyl chloride	BiPh₃	40	44	—	b
				4a	**4b**	**4c**	
5	1	Diglycolyl chloride	—	43	22	4	
6	1	Diglycolyl chloride	AsPh₃	44	23	8	>99
7	1	Diglycolyl chloride	SbPh₃	42	28	8	84
8	1	Diglycolyl chloride	BiPh₃	43	18	4	b
				5a			
9	2	Malonyl chloride	—	48	—	—	
10	2	Malonyl chloride	SbPh₃	54	—	—	78

[a] Isolated yield. [b] BiPh₃ decomposed.

Sb and Bi), ¹H NMR titration studies in CDCl₃ solution were carried out by the addition of 1 to MPh₃ (Fig. 1). No chemical shift changes for the OH protons were observed for 1 + AsPh₃, 1 + SbPh₃ or 1 + BiPh₃, although there were slight chemical shift changes between 1 and the 1 + MPh₃ systems. Since we could not observe differences in the binding abilities using ¹H NMR spectral studies, we tried to estimate them by means of IR and EI-mass spectroscopy (20 eV). IR spectral data for the C–OH stretching band for 1, 1 + AsPh₃, 1 + SbPh₃ and 1 + BiPh₃ are shown in Table 2. There are remarkable differences between 1 and the 1 + MPh₃ (M = Sb and Bi) systems. The order of differences is as follows: 1 + BiPh₃ (−15 cm⁻¹) > 1 + SbPh₃ (−10 cm⁻¹) > 1 + AsPh₃ (±0 cm⁻¹). The same tendency was observed using EI-mass spectra. Table 3 shows the fragment ion peaks and intensities of MPh₃, Table 4 shows those of mixtures of 1 + MPh₃ (1:MPh₃ = 1:1, M = As, Sb and Bi) and Table 5 shows the peaks and intensities of a mixture of malonyl chloride + BiPh₃. In the EI-mass spectral

Table 2 IR spectral data (ν/cm⁻¹)[a] of 1, 1 + AsPh₃, 1 + SbPh₃ and 1 + BiPh₃ systems

	ν(C–OH)	Δ cm⁻¹
1	1065	—
1 + AsPh₃	1065	0
1 + SbPh₃	1055	−10
1 + BiPh₃	1050	−15

[a] Neat.

data of MPh₃, the fragment ion peaks and their intensities are compatible with the previously reported data.[9] On the other hand, there were significant intensity changes in the fragment ion peaks between mixtures of 1 + AsPh₃, 1 + SbPh₃ and 1 + BiPh₃. In the mixture of 1 + AsPh₃, the intensity of [1 + H]⁺ was 100%, while those of [1 + AsPh₂]⁺, [1 + AsPh₂ − H]⁺ and [1 + AsPh₂ − 2H]⁺ were very low (0.1–0.5%). Also, the intensities of [1 + SbPh₂]⁺, [1 + SbPh₂ − H]⁺ and [1 +

Table 3 Fragment ion peaks and intensities of MPh₃ (M = As, Sb or Bi)[a]

Compound	MPh₃⁺	MPh₂⁺	MPh⁺	M⁺
AsPh₃	306 (31.7%)	229 (7.3%)	152 (100.0%)	
SbPh₃[b]	352 (10.8%)	275 (14.9%)	198 (100.0%)	121 (0.4%)
	354 (7.9%)	277 (7.4%)	200 (74.3%)	123 (0.3%)
BiPh₃		363 (4.5%)	286 (100.0%)	209 (89.5%)

[a] Measured by the EI method (20 eV). [b] Natural abundances of ¹²¹Sb and ¹²³Sb are 57.25 and 42.75%, respectively (100 : 74.7).

**Table 4** Fragment ion peaks and intensities of mixtures of 1 with MPh₃ (M = As, Sb or Bi)[a]

Mixture	[1 + H]⁺	[1 + MPh₂]⁺	[1 + MPh − H]⁺ or [1 + MPh]⁺	[1 + M − 2H]⁺ or [1 + M]⁺	[2 × 1 + M − 2H]⁺
1 + AsPh₃[c]	299 (100.0%)	527 (0.1%)	449 (0.1%)	371 (0.5%)	
1 + SbPh₃[b,c]	299 (100.0%)	573 (1.8%)	495 (5.5%)	417 (4.6%)	
		575 (1.3%)	497 (4.4%)	419 (3.6%)	
1 + BiPh₃[c]	299 (82.3%)	661 (26.1%)	584 (23.4%)	507 (100.0%)	803 (3.3%)

[a] Measured by the EI method (20 eV). [b] Natural abundances of ¹²¹Sb and ¹²³Sb are 57.25 and 42.75%, respectively (100 : 74.7). [c] The intensity of each peak was normalized based on that of [1 + H]⁺ for 1 + AsPh₃ and 1 + SbPh₃, and [1 + M]⁺ for 1 + BiPh₃ systems.

Table 5 Fragment ion peaks and intensities of a mixture of BiPh₃ with malonyl chloride[a]

Mixture	Fragment ions, peaks and intensities				
Malonyl chloride + BiPh₃	BiPh₂⁺	BiPh⁺	Bi⁺		
	363 (4.3%)	286 (12.8%)	209 (95.1%)		
	BiCl₃⁺	BiCl₂⁺	BiCl⁺	BiPhCl₂⁺	BiPhCl⁺
	314 (0.8%)	279 (3.7%)	244 (85.9%)	356 (0.6%)	321 (14.5%)
	316 (0.7%)	281 (2.4%)	246 (26.6%)	358 (0.4%)	323 (4.7%)
	318 (0.2%)	283 (0.4%)		360 (0.1%)	
	320 (0.1%)				

[a] Measured by the EI method (20 eV).
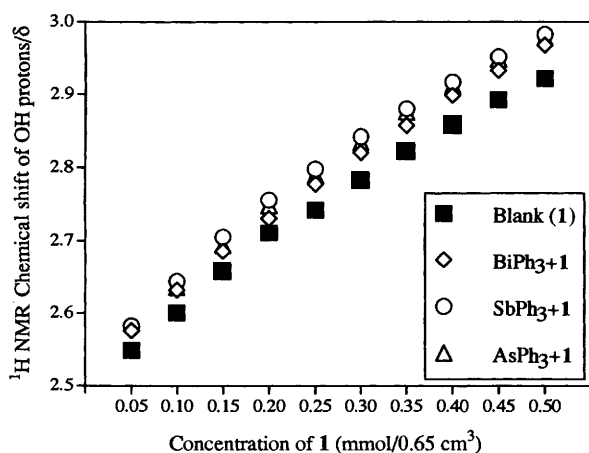
Fig. 1 ¹H NMR shift changes of OH protons of 1 ([MPh₃] = 0.05 mmol/0.65 cm³)

SbPh₂ − 2H]⁺ were about 1–4% in the mixture of 1 + SbPh₃, although the intensity of [1 + H]⁺ was 100%, the same as in the 1 + AsPh₃ system. Surprisingly, in the mixture of 1 + BiPh₃, the intensities of [1 + H]⁺, [1 + BiPh₂]⁺, [1 + BiPh − H]⁺ and [1 + Bi − 2H]⁺ were 82.3, 26.1, 23.4 and 100.0%, respectively, and [2 × 1 + Bi − 2H]⁺ arising from the 2 : 1 (1 : BiPh₃) complex also appeared (3.3%) under these conditions. The results imply an order for the complexing abilities between 1 and MPh₃ of 1 + BiPh₃ ≫ 1 + SbPh₃ > 1 + AsPh₃, and in particular that BiPh₃ can form stable 1 : 1 and 2 : 1 complexes with 1. The increase and decrease in the yields of 3a and 3b using SbPh₃ and BiPh₃ (Runs 3 and 4, Table 1) can be explained by the trend in the complexing abilities between 1 and 1 + MPh₃ (M = Sb and Bi). That is, when SbPh₃ was used, the formation of a 1 : 1 complex between 1 and SbPh₃ enhanced the yield of monomer 3a and reduced that of dimer 3b. On the other hand, when BiPh₃ was used, the

formation of the 1 : 1 and 2 : 1 complexes enhanced the yield of both compounds. Therefore, it is reasonable to speculate that enhancement of the yields of 3a by SbPh₃ and that of 3a and 3b by BiPh₃ is due to the template effect as shown in Fig. 2. When AsPh₃ was used as a template for the treatment of 1 with acid chlorides, the yield of 3a (Run 2) decreased compared with the template-free conditions (Run 1), although there is no effect on the yield of 4a (Runs 5 and 6). The results may indicate that AsPh₃ inhibits monomer formation by 1 and malonyl chloride. In order to analyse the decomposition products of BiPh₃, the mass spectrum of the mixture of malonyl chloride + BiPh₃ was measured. As shown in Table 5, several ion peaks such as BiCl₃⁺ and BiPhCl₂⁺ arising from the Cl substituted compounds of BiPh₃ together with the fragment ion peaks arising from BiPh₃ were detected. However, the ion peaks arising from the malonyl chloride–bismuth compound were not detected at all. The experimental results show that (i) the decomposed products of BiPh₃ are mixtures of the Cl substituted compounds of BiPh₃ and (ii) the formation of the complex of BiPh₃ with malonyl chloride can be ruled out in the cyclization mechanisms. The second suggestion strongly supports our postulated cyclization mechanisms.

In conclusion, we have demonstrated that SbPh₃ and BiPh₃ are effective templates for the syntheses of 14-crown-4 ether-esters with (benzyloxy)methyl side arms and that the template effect depends on the structures of both diol and acid chloride. Also, we showed that the key step in the template synthesis is the formation of a complex between the diol and MPh₃ based on IR and mass spectral data.

Experimental

Mass spectra were obtained on a Hitachi M80 Mass spectrometer. ¹H and ¹³C NMR spectra were obtained on a Bruker AC 250 spectrometer with Me₄Si as the internal stand-
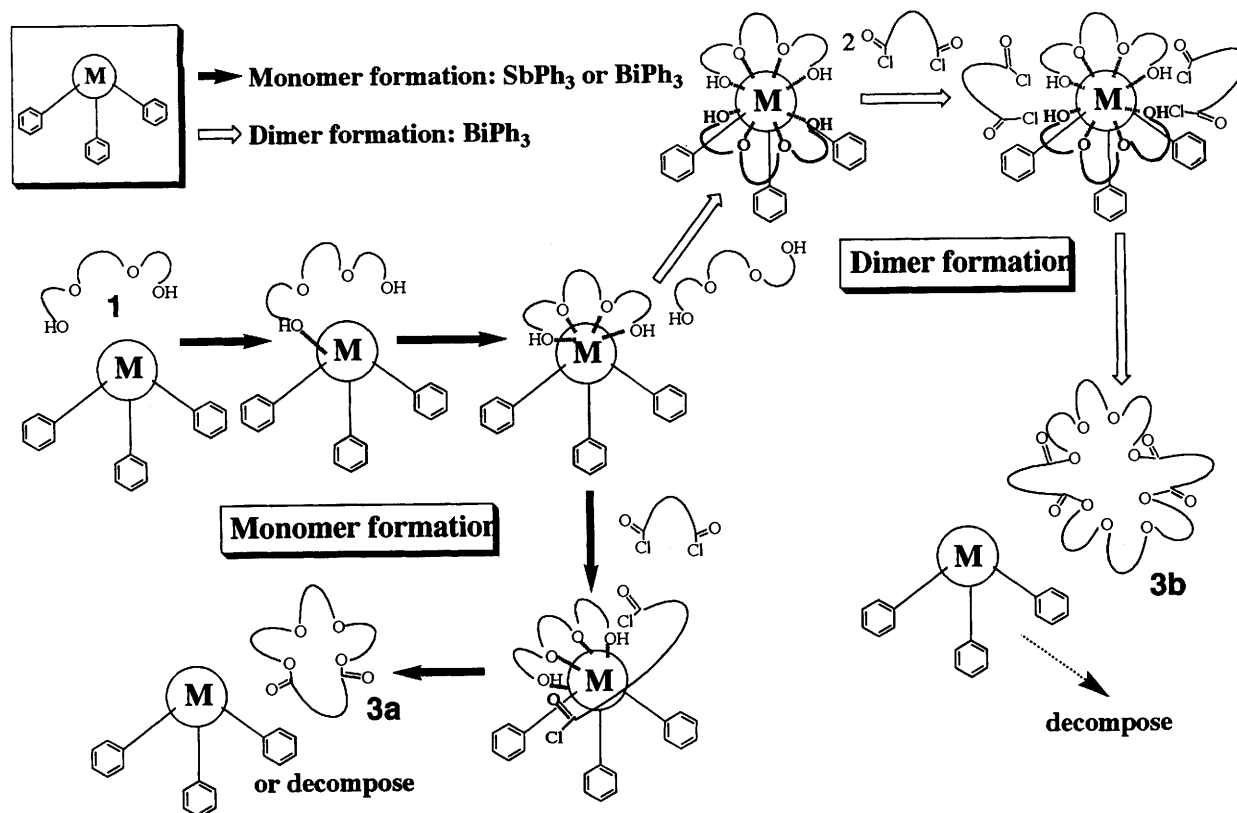
Fig. 2 Postulated cyclization mechanisms for **3a** and **3b** by the template effect

ard and *J* values are given in Hz. IR spectra were recorded with a JASCO FT/IR-230 spectrometer.

General procedure for the treatment of (benzyloxy)methyl substituted diols with acid chlorides

A solution of the diol (17 mmol) in benzene (100 cm³) and a solution of acid chloride (17 mmol) in benzene (100 cm³) were added dropwise over 5 h to refluxing benzene [500 cm³, containing MPh₃ (17 mmol) as appropriate] under a nitrogen atmosphere. After addition was complete, the mixture was heated under reflux for a further 24 h. The solvent was then removed under reduced pressure and the residual oil was purified by silica gel column chromatography (benzene–ethyl acetate). The first and the second fractions were the triphenylmetal and a mixture of the cyclization compounds, respectively. The second fraction was concentrated and the residual oil was separated and purified by gel-permeation column chromatography (Sephadex LH-20, ethanol as eluent). The pure monomer, dimer and trimer were obtained as hygroscopic oils.

13-(Benzyloxy)methyl-13-methyl-1,4,8,11-tetraoxacyclo-tetradecane-5,7-dione 3a. Oil; δ_H(CDCl₃) 7.30 (5 H, s), 4.48 (2 H, s), 4.27–4.24 (4 H, m), 3.64–3.61 (4 H, m), 3.40 (2 H, s), 3.34 (2 H, d, *J* 16.6), 3.30 (2 H, d, *J* 16.6), 3.30 (2 H, s) and 0.97 (3 H, s); δ_C(CDCl₃) 165.9 (C-5, C-7, C=O), 138.6 (phenyl, bridgehead carbon), 128.1 (phenyl), 127.2 (phenyl), 127.1 (phenyl), 73.1 (PhCH₂), 73.6 (BzOCH₂), 72.2 (C-12, C-14), 68.3 (C-2, C-10, OCH₂CH₂OCO), 64.4 (C-3, C-9, OCH₂-CH₂OCO), 42.1 (C-6), 40.3 (C-13) and 17.6 (13-Me); *m/z* (20 eV) 367 ([M + H]⁺, 18%); ν_max/cm⁻¹ 1750 and 1730 (C=O) (Found: C, 62.0; H, 7.25. Calc. for C₁₉H₂₆O₇: C, 62.28; H, 7.15%).

13,27-Bis[(benzyloxy)methyl]-13,27-dimethyl-1,4,8,11,15,-18,22,25-octaoxacyclooctacosane-5,7,19,21-tetraone 3b. Oil; δ_H 7.32 (10 H, s), 4.47 (4 H, s), 4.24 (8 H, t, *J* 4.6), 3.59 (8 H, t, *J* 4.6), 3.38 (4 H, s), 3.35 (4 H, s), 3.34 (4 H, s), 3.31 (4 H, s) and 0.95 (6 H, s); δ_C 166.1 (C-5, C-7, C-19, C-21, C=O), 138.6

(phenyl, bridgehead carbon), 128.2 (phenyl), 127.2 (phenyl), 127.1 (phenyl), 73.0 (PhCH₂), 72.8 (BzOCH₂), 73.3 (C-12, C-14, C-26, C-28), 68.7 (C-2, C-10, C-16, C-24, OCH₂CH₂-OCO), 64.4 (C-3, C-9, C-17, C-23, OCH₂CH₂OCO), 41.2 (C-6, C-20), 40.8 (C-13, C-27) and 17.2 (13-Me, 27-Me); *m/z* (20 eV) 733 ([M + H]⁺, 18%); ν_max/cm⁻¹ 1760–1730 (C=O) (Found: C, 61.6; H, 7.2. Calc. for C₃₈H₅₂O₁₄ + 1/2H₂O: C, 61.53; H, 7.20%).

15-(Benzyloxy)methyl-15-methyl-1,4,7,10,13-pentaoxacyclo-hexadecane-5,9-dione 4a. Oil; δ_H 7.31 (5 H, s), 4.48 (2 H, s), 4.35–4.31 (4 H, m), 4.23 (4 H, s), 3.66–3.63 (4 H, m), 3.39 (2 H, d, *J* 16.8), 3.36 (2 H, d, *J* 16.8), 3.31 (2 H, s) and 0.96 (3 H, s); δ_C 169.4 (C-5, C-9, C=O), 138.8 (phenyl, bridgehead carbon), 128.3 (phenyl), 127.5 (phenyl), 127.4 (phenyl), 73.3 (PhCH₂), 73.1 (BzOCH₂), 74.2 (C-14, C-16), 69.0 (C-2, C-12, OCH₂CH₂OCO), 64.8 (C-3, C-11, OCH₂CH₂OCO), 68.0 (C-6, C-8), 40.9 (C-15) and 17.4 (15-Me); *m/z* (20 eV) 397 ([M + H]⁺, 17%) and 204 ([CH₂CH₂OCOCH₂OCH₂COOCH₂-CH₂O]⁺, 100%); ν_max/cm⁻¹ 1750 and 1738 (C=O) (Found: C, 59.9; H, 7.2. Calc. for C₂₀H₂₈O₈ + 1/4H₂O: C, 59.76; H, 7.23%).

15,31-Bis[(benzyloxy)methyl]-15,31-dimethyl-1,4,7,10,13,-17,20,23,26,29-decaoxacyclodotriacontane-5,9,21,25-tetraone 4b. Oil; δ_H 7.31 (10 H, s), 4.47 (4 H, s), 4.27 (8 H, t, *J* 4.6), 4.24 (8 H, s), 3.60 (8 H, t, *J* 4.6), 3.33 (8 H, s), 3.31 (4 H, s) and 0.94 (6 H, s); δ_C 169.7 (C-5, C-9, C-21, C-25, C=O), 138.8 (phenyl, bridgehead carbon), 128.3 (phenyl), 127.4 (phenyl), 127.3 (phenyl), 73.3 (PhCH₂), 73.0 (BzOCH₂), 73.5 (C-14, C-16, C-30, C-32), 69.0 (C-2, C-12, C-18, C-28, OCH₂-CH₂OCO), 64.0 (C-3, C-11, C-19, C-27, OCH₂CH₂OCO), 68.0 (C-6, C-8, C-22, C-24), 41.0 (C-15, C-31) and 17.4 (15-Me, 31-Me); *m/z* (20 eV) 700 ([M − C₆H₅CH₂ − H]⁺, 44%), 628 ([M − C₆H₅CH₂ − OCOCH₂O + H]⁺, 10%), 396 ([M/2]⁺, 5%), 252 ([M/2 − COCH₂OCH₂COOCH₂CH₂]⁺, 32%) and 204 ([CH₂CH₂OCOCH₂OCH₂COOCH₂CH₂O]⁺, 100%); ν_max/cm⁻¹ 1755–1735 (C=O) (Found: C, 60.5; H, 7.1. Calc. for C₄₀H₅₆O₁₆: C, 60.59; H, 7.12%).

15,31,47-Tris[(benzyloxy)methyl]-15,31,47-trimethyl-1,4,7,-10,13,17,20,23,26,29,33,36,39,42,45-pentadecaoxacycloocta-tetracontane-5,9,21,25,37,41-hexaone 4c. Oil; δ_H 7.31 (15 H, s), 4.47 (6 H, s), 4.26 (12 H, t, J 4.6), 4.22 (12 H, s), 3.59 (12 H, t, J 4.6), 3.33 (12 H, s), 3.30 (6 H, s) and 0.94 (9 H, s); δ_C 169.7 (C-5, C-9, C-21, C-25, C-37, C-41, C=O), 138.8 (phenyl, bridge-head carbon), 128.3 (phenyl), 127.4 (phenyl), 127.3 (phenyl), 73.3 (PhCH_2), 72.9 (BzOCH_2), 73.6 (C-14, C-16, C-30, C-32, C-46, C-48), 69.1 (C-2, C-12, C-18, C-28, C-34, C-44, OCH_2CH_2OCO), 63.9 (C-3, C-11, C-19, C-27, C-35, C-43, OCH_2CH_2OCO), 68.0 (C-6, C-8, C-22, C-24, C-38, C-40), 41.0 (C-15, C-31, C-47) and 17.4 (15-Me, 31-Me, 47-Me); m/z (20 eV) 774 {[M $-$ C$_6$H$_5$CH$_2$ $-$ CH$_2$COOCH$_2$CH$_2$OCH$_2$CCH$_3$-(CH$_2$OCH$_2$C$_6$H$_5$)CH$_2$OCH$_2$CH$_2$O]$^+$, 0.9%}, 701 ([M $-$ C$_6$-H$_5$CH$_2$ $-$ M/3]$^+$, 2%), 628 ([M $-$ M/3 $-$ C$_6$H$_5$CH$_2$ $-$ OCOCH$_2$O $+$ H]$^+$, 0.5%), 252 ([M/3 $-$ COCH$_2$OCH$_2$CO-OCH$_2$CH$_2$]$^+$, 30%), 204 ([CH$_2$CH$_2$OCOCH$_2$OCH$_2$COO-CH$_2$CH$_2$O]$^+$, 32%) and 91 ([C$_6$H$_5$CH$_2$]$^+$, 100%); ν_{max}/cm^{-1} 1755–1735 (C=O) (Found: C, 61.0; H, 7.2. Calc. for C$_{60}$H$_{84}$O$_{24}$: C, 60.59; H, 7.12%)

5-(Benzyloxy)methyl-1,4,7,10-tetraoxacyclotridecane-11,13-dione 5a. Oil; δ_H 7.34–7.27 (5 H, m), 4.52 (2 H, s), 4.42–4.18 (4 H, m), 3.94–3.61 (7 H, m), 3.52–3.24 (2 H, m) and 3.40 (2 H, d, J 4.9); δ_C 166.1 (C-11, C-13, C=O), 137.9 (phenyl, bridgehead carbon), 128.4 (phenyl), 127.7 (phenyl), 127.6 (phenyl), 73.4 (PhCH_2), 69.9 (BzOCH_2), 71.0 (C-6), 68.8 and 68.6 (C-3, C-8, OCH_2CH_2OCO), 64.9 and 64.0 (C-2, C-9, OCH_2CH_2OCO), 42.4 (C-12) and 78.1 (C-5); m/z (20 eV) 339 (M$^+$ $+$ H, 41%); ν_{max}/cm^{-1} 1760–1740 (C=O) (Found: C, 60.3; H, 6.8. Calc. for C$_{17}$H$_{22}$O$_7$: C, 60.35; H, 6.55%).

Titration experiments

Titration experiments were carried out at 298 K upon the addition of 1.0–10.0 equiv. of **1** to the MPh$_3$ solution. Conditions: [**1**] = 0.05 mmol 10 mm^{-3} in CDCl$_3$; [MPh$_3$] = 0.05 mmol 0.65 cm^{-3} in CDCl$_3$.

Preparation of samples for IR and mass spectral studies

Samples for the IR and mass spectral studies were prepared as follows: 0.1 mmol of MPh$_3$ (M = As, Sb and Bi) was added to 0.1 mmol of **1** in 2 cm^3 of CHCl$_3$. After the mixture was concentrated under reduced pressure, the residual oil was dried

with an Abderhalden's dryer (0.1 Torr, 100 °C) for 1 h. The residual oil was used directly for the IR and mass spectral studies. Also, for sample of malonyl chloride with BiPh$_3$, 0.1 mmol of BiPh$_3$ was added to 0.1 mmol of malonyl chloride in a mixture of benzene (1 cm^3) and CHCl$_3$ (1 cm^3). After removal of the solvent, the residual solid was used directly for the mass spectral study.

References

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