Syntheses of Armed Crown Ether-Esters using $SbPh_3$ as a Template

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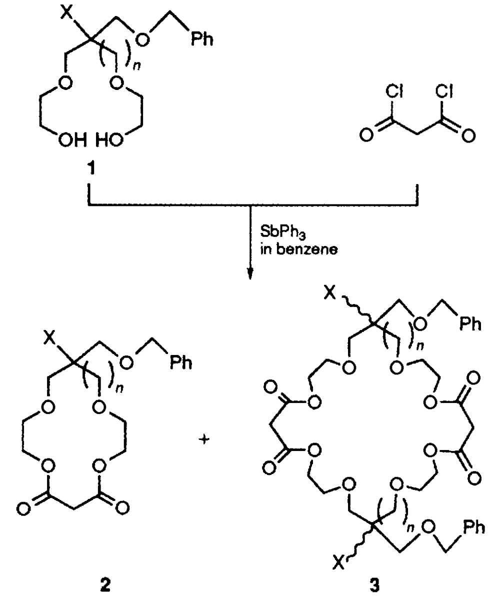
(Benzyloxy)methyl-13- and -14-crown-4 ether-esters and dimer thereof are synthesized by the reaction of the corresponding diol with malonylchloride in the presence of $SbPh_3$.

Although a number of crown ether-esters and crown esters, which have two or four ester groups in the macrocyclic ring, have been synthesized and examined for their complexing ability toward alkali, alkaline earth, and transition metal cations,[1] no example has been reported for armed crown ether-ester derivatives. It is expected that armed crown ether-esters may have specific selectivities for metal cations similar to the armed crown ethers. Recently, Ogawa *et al.*[2] reported that triarylbismuthines were efficient dehydration reagents for the preparation of ester compounds such as crown ether-esters by the reaction of carboxylic acids or carboxylic acid anhydrides with aliphatic alcohols or polyethylene glycols in nonpolar solvents such as benzene. Also, Takahashi *et al.*, and Alcock *et al.*[3] reported that $SbCl_3$, 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 employ triphenylantimony ($SbPh_3$) as a template for the syntheses of armed crown ether-esters. $SbPh_3$ is very convenient as a template, because (*i*) it is highly soluble in low polarity solvents such as benzene, (*ii*) is stable in water and air, and (*iii*) is easily recovered from the reaction mixture. Here, we report the syntheses of (benzyloxy)methyl substituted 14-crown-4 ether-ester **2a**, its dimer **3a** and 13-crown-4 ether-ester **2b** using $SbPh_3$ as the template.

(Benzyloxy)methyl substituted crown ether-esters were prepared by the reaction of the corresponding diol[4] with malonylchloride under high dilution conditions. For example, **1a** (17 mmol) in benzene (100 cm^3) and malonyl chloride (17 mmol) in benzene (100 cm^3) were added dropwise at the same rate (5 h) to refluxing benzene (500 cm^3) under a nitrogen atmosphere. The reflux was continued for 24 h. After separation and purification by silica-gel (benzene–ethylacetate) and then gel-permeation (ethanol) column chromatography, the pure monomer **2a** and dimer **3a** were obtained in 35 and 21% yields, respectively, as hygroscopic oils† (Table 1, run 1, condition A). The ratio of the yield of **2a** and **3a** was *ca.* 1.7 : 1. Using larger quantities of benzene enhanced the yield of **3a** but the yield of **2a** decreased under these conditions (**2a** : **3a** = 0.85 : 1, run 2, condition B). As shown in runs 3 and 4, in the presence of 1 equiv. of $SbPh_3$, the yield of **2a** increased, and **2a** and **3a** were obtained in 40 and 15% (**2a** : **3a** = 2.7 : 1, condition A) and 33 and 18% (**2a** : **3a** = 1.8 : 1 condition B) yields, respectively; the recovery of $SbPh_3$ was in the range of 86–89%. For the reaction of **1b** with malonylchloride, only the monomer **2b**† was obtained, and there was a slight increase in the yield of **2b** using $SbPh_3$ (runs 5 and 6). These results indicate that the effect of the $SbPh_3$ as a template depends on the structure of the crown ether-ester rings.

In order to obtain information on the template effect, ^{13}C NMR spectra‡ of **2a** and **2b** upon the addition of 1.3 equiv. of $SbPh_3$ were measured in $CDCl_3$ (25 °C). As shown in Fig. 1, the ring and the side-arm carbons attached to the oxygen



Scheme 1 **1a**–**3a** n = 1, X = Me; **1b**, **2b** n = 0, X = H

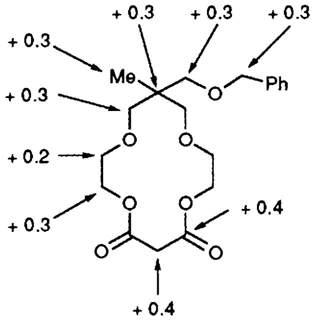


Fig. 1 Chemical shift changes of **2a** upon the addition of 1.3 equiv. of $SbPh_3$

Table 1 Yield, ratios of monomer/dimer, and recovery of $SbPh_3$

Run	Diol	Condition[a]	Template	Yield (%) Monomer	Yield (%) Dimer	Ratio of monomer/dimer	Recovery of $SbPh_3$ (%)
				2a	**3a**		
1	**1a**	A	—	35	21	1.7	—
2	**1a**	B	—	22	26	0.85	—
3	**1a**	A	$SbPh_3$	40	15	2.7	86
4	**1a**	B	$SbPh_3$	33	18	1.8	89
				2b	**3b**		
5	**1b**	A	—	48	0	—	—
6	**1b**	A	$SbPh_3$	54	0	—	78

[a] Condition A: the diol (17 mmol) in benzene (100 cm^3) and malonyl chloride (17 mmol) in benzene (100 cm^3) were added to benzene (500 cm^3). Condition B: the diol (17 mmol) in benzene (200 cm^3) and malonyl chloride (17 mmol) in benzene (200 cm^3) were added to benzene (2.5 l).

atoms of **2a** shifted downfield by ca. +0.2–0.4 ppm, while all ring and arm carbons of **2b** shifted downfield by less than +0.1 ppm. These results suggest that **2a** forms a more stable complex with $SbPh_3$ than does **2b**, and $SbPh_3$ may effectively act as a template in the preparation of **2a**, although the detailed structure of these complexes are not clear at present.

The structure of the $SbPh_3$ complex with **2a** and application of $SbPh_3$ for the synthesis of the crown ether-esters having other ring sizes and side arms are now in progress.

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Footnotes

† Selected spectral data for compounds **2a**, **3a** and **2b**: **2a**; ^1H NMR (250 MHz, $CDCl_3$, $SiMe_4$) δ 7.30 (s, 5H), 4.48 (s, 2H), 4.27–4.24 (m, 4H), 3.64–3.61 (m, 4H), 3.40 (s, 2H), 3.34 (d, J = 16.6 Hz, 2H), 3.30 (d, J = 16.6 Hz, 2H), 3.30 (s, 2H), 0.97 (s, 3H); m/z (20 eV) 367 (M^+ + 1, 18%); IR (neat) $\tilde{\nu}$/cm^{-1} 1750, 1730 (C=O). **3a**: ^1H NMR (250 MHz, $CDCl_3$, $SiMe_4$) δ 7.32 (s, 10H), 4.47 (s, 4H), 4.24 (t, J = 4.6 Hz, 8H), 3.59 (t, J = 4.6 Hz, 8H), 3.38 (s, 4H), 3.35 (s, 4H), 3.34 (s, 4H), 3.31 (s, 4H), 0.95 (s, 6H); m/z (20 eV) 733 (M^+ + 1, 18%). **2b**: ^1H NMR (250 MHz, $CDCl_3$, $SiMe_4$) δ 7.34–7.27 (m, 5H), 4.52 (s, 2H), 4.42–4.18 (m, 4H), 3.94–3.61 (m, 7H), 3.52–3.24 (m, 2H), 3.40 (d, J = 4.9 Hz, 2H); m/z (20 eV) 339 (M^+ + 1, 41%); IR (neat) $\tilde{\nu}$/cm^{-1} 1760–1740 (C=O).

‡ Assignments of the ^{13}C NMR spectra were carried out using COSY and CHCORR spectroscopy.

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