Bis(5-carbomethoxy-1,3-phenylene)-30-crown-4: a macrocyclic monomer of predominantly hydrocarbon character

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A general route to 5,5′-difunctionalized bis(*m*-phenylene) macrocycles (**1**) is reported. Bis(5-carbomethoxy-1,3-phenylene)-30-crown-4 (**1e**) has been synthesized in one step from methyl 3,5-dihydroxybenzoate and 1,10-dibromodecane in the presence of sodium hydride in dimethylformamide. This monomer is suitable for synthesis of backbone polymacrocycles of predominantly hydrocarbon character.

(Keywords: macrocycle; hydrocarbon; synthesis)

Introduction

We have developed a synthetic methodology according to *Scheme 1* for the synthesis of bis(*m*-phenylene) crown ethers with different ring sizes and functionalities[1–6]. As opposed to the functionalization of preformed macrocycles by aromatic substitution reactions, this approach yields 1,3,5-substituted products free of regioisomeric impurities. Moreover, the 1,3,5-substitution of the two aromatic rings provides: (1) minimal steric hindrance to reactions of the functional groups; (2) axial symmetry for polymers produced from the macrocycles, giving higher glass transition temperatures and the possibility of liquid crystalline behaviour; and (3) spatial separation of the macrocyclic cavity from the backbone components attached at the functional groups. Indeed, we have reported the synthesis[3] of bis(5-carbomethoxy-1,3-phenylene)-32-crown-10 (**1a**) and its use in the syntheses of polyesters[3] and polyamides[7] having macrocyclic backbone components, i.e. 'polymacrocycles'. We have also made **1b**[1], **1c**[2] and **1d**[4] and its *para*-linked analogue[4]. The unsymmetrical macrocycle in which only one phenylene unit bore a 5-methyl substituent was made via a multistep method[1].

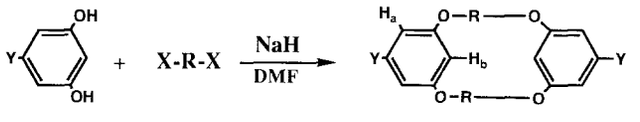
Incorporation of predominantly hydrocarbon linking units into crown ether structures will produce stiffer macrocycles in comparison to flexible ethyleneoxy analogues. Hence polymers derived from these macrocyclic monomers are expected to have higher glass transition temperatures. Moreover, enhanced hydrophobicity and thermal stability should result. For example, the melting point of **1d** (102–105°C) is 30°C higher than that of **1c**.

Therefore, we chose to use this methodology to prepare a predominantly hydrocarbon difunctional macrocyclic monomer. Bis(5-carbomethoxy-1,3-phenylene)-30-crown-4 (**1e**) was made in one step from inexpensive starting materials, methyl 3,5-dihydroxybenzoate and 1,10-dibromodecane, in the presence of sodium hydride in dimethylformamide (DMF). The yield was 5.5%. This yield is lower than those for **1a** (9%)[3], **1b** (25%)[1], **1c** (14%)[2] and **1d** (8%)[4]. Template effects[8] are not expected in this case. The lower yield in the present case probably represents a combination of two effects. First, the phenolate derived from the ester is less nucleophilic than that derived from resorcinol or methylresorcinol as can be deduced by comparing the yields of **1a** (9%), **1b** (25%) and **1c** (14%). Second, the decamethylene linkages are more rigid than tetraethyleneoxy units, causing less efficient cyclization to form the fourth ether linkage, as deduced from the yields of **1c** (14%) and **1d** (8%). Thus, the low yield of **1d** under similar conditions reflects the negative contributions of these two factors.

As expected, the less flexible **1e** has a higher melting point (134–135°C) than **1a** (106.5–107.5°C)[3]. The infra-red spectrum of **1e** displays the expected ester carbonyl and ether absorptions. In the proton n.m.r. spectrum H_a appears as a doublet because of coupling to H_b and H_b as a triplet because of *meta* coupling to two equivalent H_as. The chemical shift of H_b (6.66δ) of **1e** compared to that of **1a** (6.71δ)[3] reveals the effect of the alkylene R groups of **1e** *versus* the tetra(ethyleneoxy) R groups of **1a**. Mass spectrometry on **1e** yields a parent ion peak at $m/z = 612$.

Experimental

All materials except as noted were used as received from suppliers. Methyl 3,5-dihydroxybenzoate was made by esterification of the acid[3]. I.r. spectra were taken on a Nicolet MX-1 instrument. The n.m.r. spectra were taken on a Bruker 270 MHz machine. A VGA 7070E instrument was used to obtain the mass spectrum.



1

X = Br, Cl, OTs

a. R = $(CH_2CH_2O)_3CH_2CH_2$, Y=$COOCH_3$
b. R = $(CH_2CH_2O)_3CH_2CH_2$, Y=CH_3
c. R = $(CH_2CH_2O)_3CH_2CH_2$, Y=H
d. R = $(CH_2)_{10}$, Y=H
e. R = $-(CH_2)_{10}-$, Y=$COOCH_3$

Scheme 1

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Bis(5-carbomethoxy-1,3-phenylene)-30-crown-4 (***1e***). Following a general procedure developed in our laboratory for the synthesis of functionalized crowns[1–6], in a 1 l three-necked flask equipped with a magnetic stirrer and reflux condenser under nitrogen, methyl 3,5-dihydroxybenzoate (9.58 g, 57 mmol) was dissolved in DMF (225 ml) and sodium hydride (3.2 g, 133 mmol) was added slowly to this solution. Then 1,10-dibromodecane (17.1 g, 57 mmol) in DMF (250 ml) was added in one portion. The mixture was stirred vigorously at 85°C for 48 h, cooled, filtered and evaporated to give a viscous oily residue. This was dissolved in dichloromethane, filtered and then chromatographed on silica gel (7 g per 1 g crude product) with diethyl ether as eluent to produce **1e**, 0.96 g, (5.5%), m.p. 134–135°C. I.r. (thin film on NaCl) ν 1717 (C=O), 1607 (C=C), 1238 (C–O–C) and 1170 (O=C–O–C) cm^{-1}. ^1H n.m.r. ($CDCl_3$/tetramethylsilane) δ7.15 (4H, d, H_a, $J=2.4$), 6.66 (2H, t, H_b, $J=2.4$), 3.98 (8H, t, OCH_2, $J=6.2$), 3.89 (6H, s, OCH_3), 2.36 (8H, q, $OCCH_2$, $J=6.5$) and 1.46–1.25 (24H, m, $OCCCH_2$, $OCCCCH_2$ and $OCCCCCH_2$). *m/z* (EI^+): 612 (M^+, 30%), 168 ($C_8H_8O_4^+$, 30%), 137 ($C_{10}H_{17}^+$ or $C_7H_5O_3^+$, 25%), 95 (12%), 83 ($C_6H_{11}^+$, 20%), 55 (C_4H_7, 100%).

Conclusion

Difunctional macrocycle **1e** was readily made from inexpensive starting materials. This new macrocyclic monomer is a precursor to polymacrocycles with hydrophobic cavities, potentially useful in a number of applications.

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