

## Intramolecular Bromoalkoxylation: Synthesis of 2-Bromomethyl-2-methyl Crown Ethers

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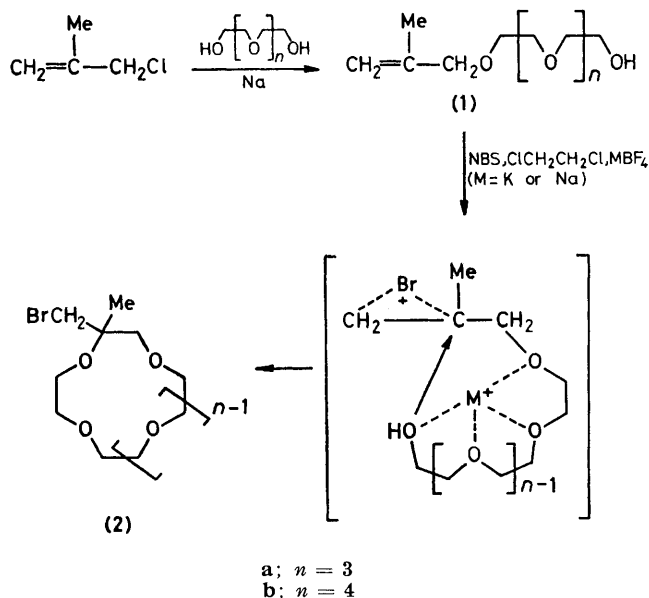
**Summary** 2-Bromomethyl-2-methyl crown ethers were prepared by intramolecular bromoalkoxylation of oligoethylene glycol monomethylallyl ethers using *N*-bromosuccinimide.

CROWN compounds having reactive substituents are potentially useful in preparing functionalized derivatives and in introducing the crown ring to a polymer chain. We have previously attempted the synthesis of crown ethers bearing chloromethyl<sup>1</sup> or hydroxymethyl groups<sup>2</sup> via the cyclization of the corresponding oligoethylene glycol derivatives.

Although the halogenoalkoxylation of olefins has been studied extensively, intramolecular halogenoalkoxylation has not been widely used, except in the case of terpene cyclizations,<sup>3</sup> when tetrahydrofuran derivatives were obtained from compounds possessing both double bonds and hydroxy-groups in the same molecule.

We now report a novel synthesis of 2-bromomethyl-2-methyl crown ethers by intramolecular bromoalkoxylation of the oligoethylene glycol mono-2-methylallyl ether (**1**) (prepared by the reaction of 2-methylallyl chloride with the sodium alkoxide of the corresponding oligoethylene glycol) in the presence of a template ion.

2-Bromomethyl-2-methyl-18-crown-6 (**2b**) was prepared by adding (**1b**) to a stirred suspension of  $\text{KBF}_4$  and *N*-bromosuccinimide (NBS) in 1,2-dichloroethane at 45–50 °C. The crude (**2b**) was distilled under reduced pressure using a kugelrohr apparatus (b.p. 130–135 °C at 0.05 Torr) to give a slightly yellow liquid, which was further purified by column chromatography on silica gel with hexane–acetone (97:3) as eluant and distilled (b.p. 125 °C at 0.05 Torr) to afford pure (**2b**) in 45% yield as a slightly yellow liquid:  $\delta$  ( $\text{CCl}_4$ ) 1.24 (s, 3H) and 3.44–3.66 (m, 24H);  $\nu_{\text{max}}$  (neat) 2900, 1470, 1360, 1250, 1120, and 940  $\text{cm}^{-1}$ ;  $m/e$  372, 370, 291, 277, 145(6%), 133(20), 101(18), 87(30), 73(30), 59(27), and 45(100). For 2-bromomethyl-2-methyl-15-crown-5 (**2a**),  $\text{NaBF}_4$  was used as the template: yield, 30%;



b.p. 100 °C at 0.01 Torr (kugelrohr);  $\delta$  ( $\text{CCl}_4$ ) 1.20 (s, 3H) and 3.44–3.68 (m, 20H);  $\nu_{\text{max}}$  (neat) 2900, 1460, 1350, 1250, 1120, and 940  $\text{cm}^{-1}$ ;  $m/e$  328, 326, 247(1%), 233(2), 145(11), 133(18), 101(19), 89(31), 87(28), 73(27), 59(29), and 45(100).

The temperature is crucial in determining the success of the reaction; at  $> 50$  °C substantial amounts of undesirable by-products are formed, and at lower temperatures the reaction hardly proceeds. The presence of a template ion ( $\text{K}^+$  or  $\text{Na}^+$ ) is also necessary for good results and  $\text{K}^+$  was superior to  $\text{Na}^+$  in the synthesis of (**2b**) [g.l.c. yield: 65% ( $\text{K}^+$ ), 45% ( $\text{Na}^+$ ), 30% (no metal ion)].

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