Synthesis of 2,6-Dimethyl-18-crown-6† *via* Oxymercuration

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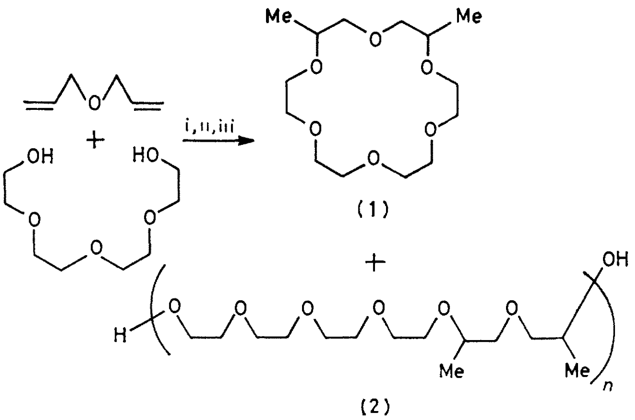
Summary 2,6-Dimethyl-18-crown-6 has been prepared in 11% yield by reaction of diallyl ether and tetraethylene glycol with mercury(II) acetate in the presence of perchloric acid and potassium perchlorate, followed by reductive demercuration with alkaline sodium borohydride.

Their potential as phase transfer catalysts and ion separation agents continues to stimulate the preparation of new crown ethers and related macroheterocycles.[1] However, new methods for bringing about closure of the macroring are rare; indeed most syntheses depend upon variations of nucleophilic displacement under basic conditions, *i.e.* modifications of the Williamson ether synthesis. Oxymercuration–demercuration has proved a versatile technique for converting olefinic substrates into oxygenated compounds.[2] It has been used to prepare ethers, including simple cyclic examples, and we felt that it could provide the basis of a new approach to the construction of macrocyclic polyethers. We now report the successful application of this strategy to the synthesis of a simple but previously unknown derivative of 18-crown-6.

To a well stirred suspension of $Hg(OAc)_2$ (0·2 mol), $KClO_4$ (0·1 mol), and 60% $HClO_4$ (4 mmol) in dichloromethane (1 l) was added diallyl ether (0·1 mol) and then tetraethylene glycol (0·1 mol). The resultant clear solution was stirred for 24 h. To remove perchlorate the organomercurial was treated with aqueous KCl and the organomercury chloride isolated. This was dissolved in dichloromethane and reduced with alkaline sodium borohydride at 0—5 °C to afford a pale yellow oil (12 g).



Reagents, i, $Hg(OAc)_2$–$KClO_4$–$HClO_4$, ii, KCl, iii, $NaBH_4$–NaOH.

This oil had a ^1H n.m.r. spectrum and mass spectrum consistent with 2,6-dimethyl-18-crown-6 (**1**), but an average molar mass (osmometry) of 625 [(**1**) requires 292] and a signal at δ 61·5 p.p.m. in the ^{13}C n.m.r. spectrum indicating the presence of CH_2OH groups. From these data we concluded that the oil contained methyl-substituted polyethylene glycols of composition (**2**) (*n* mainly 2 or 3), arising from competing linear polymerisation.

Distillation gave (**1**) (3·2 g; 11%) as a colourless hygroscopic oil, b.p. 120—130 °C at 0·05 mmHg, δ_H 1·15 (d, 6H) and 3·4—3·9 (m, 22H); δ_C 16·88, 17·13, 68·67, 70·66, 70·84, 71·06, 74·80, 75·23, and 75·98 p.p.m.; ν_{max} 2950, 1460, 1380, 1360, 1300, 1260, and 1150 cm^{-1}, osmometric

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† 2,6-Dimethyl-1,4,7,10,13,16-hexaoxacyclo-octadecane.

molar mass 315, M^+ 292·1885, $C_{14}H_{28}O_6^+$ requires 292·1886. The ^{13}C n.m.r. spectrum confirmed that (**1**) is obtained as a mixture of *meso* and (±) diastereoisomers, a 2:1 ratio being indicated by the intensities of the two methyl signals.

The presence of $KClO_4$ had a significant effect upon the oxymercuration, the yield of (**1**) being markedly lower (3·8% instead of 8·8% for a 4·5 h reaction) if it was omitted. Short reaction times for the oxymercuration also had a deleterious effect upon the yield of (**1**) (5·5% after 1 h) but it remained at 11% when the oxymercuration was allowed to run for 72 h.

A preliminary study of (**1**) as a phase transfer catalyst in organic synthesis indicates that it has an efficiency comparable with that of the commonly used commercial crowns. For example using (**1**) a 90% yield of 3,5-di-t-butyl-*o*-benzoquinone was obtained in the permanganate oxidation of 3,5-di-t-butylpyrocatechol (92% using 18-crown-6)[3], and the dichlorocyclopropanation of styrene proceeded in 89% yield (87% using dibenzo-18-crown-6)[3].

Whereas the modified Williamson procedures require the initial preparation of a suitable halide or tosylate and prolonged refluxing of the reaction mixture, this oxymercuration-based crown synthesis uses only commercially available starting materials and proceeds at room temperature.

Financial support by the S.R.C. and (to R.A.S.) by A. and K. Savva, P. and M. Aloupas, and J. Clarke is gratefully acknowledged.

(*Received, 3rd July* 1980; *Com.* 721.)

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