Lipophilic Crown Phosphonic Acid Monoalkyl Esters. Synthesis and Solvent Extraction

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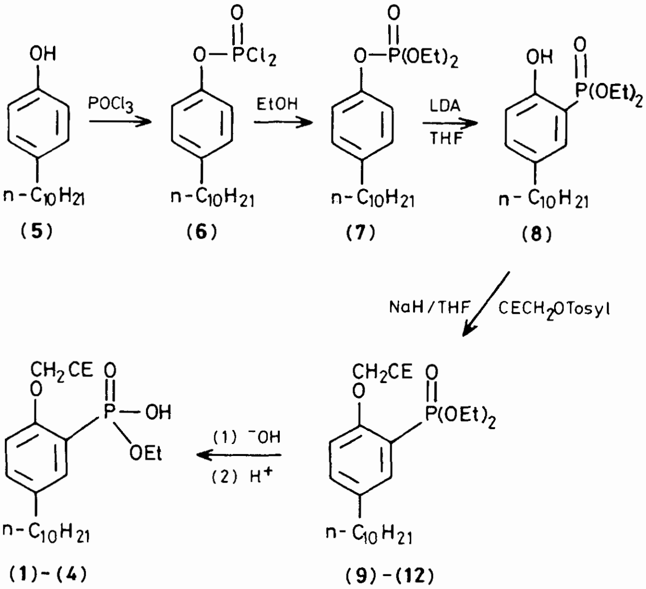
Lipophilic crown phosphonic acid monoalkyl esters capable of anion-independent metal ion transport from acidic and neutral aqueous solutions into organic media have been synthesized and tested in competitive alkali metal solvent extraction.

Lipophilic crown carboxylic acids are novel complexing agents for the transport of alkali metal and alkaline earth cations from aqueous solutions into organic media in solvent extraction and liquid membrane transport processes.[1] Compared with crown ether (macrocyclic polyether) compounds which do not possess pendant ionizable groups, these ionizable crown compounds have the special advantage that transport of the metal cation into the organic phase does not require concomitant transfer of the aqueous phase anion. Since ionization of the lipophilic crown carboxylic acid is required for efficient metal ion complexation, the aqueous phase from which the metal ions are extracted must be alkaline. This restricts the use of such complexing agents to metals with soluble hydroxides. To circumvent this problem, ionizable crown compounds of greater acidity are needed. To this end, lipophilic crown phosphonic acid monoethyl esters (**1**)—(**4**) have now been prepared (Scheme 1) and tested in competitive solvent extraction of alkali metal cations.[2]

The synthesis of compound (**2**) illustrates the preparative route. Refluxing 4-n-decylphenol[3] (**5**) with 6 mol. equiv. of $POCl_3$ in the presence of KCl for 7 hours formed the dichlorophosphate (**6**) (92%, b.p. 168 °C, 0.25 Torr). Treatment of (**6**) with anhydrous EtOH for 18 hours at 0—5 °C gave the diethyl phosphate (**7**) (88%, b.p. 176—178 °C, 0.25 Torr). Reaction of (**7**) with lithium di-isopropylamide (LDA) in tetrahydrofuran (THF) at −78 °C produced diethyl 2-hydroxy-5-n-decylphenylphosphonate (**8**) (80%, m.p. 28—29 °C). Attachment of the crown unit to form (**10**) (71%, oil after column chromatography, alumina, AcOEt) was accomplished by condensation of (**8**) with the toluene-*p*-sulphonate of hydroxymethyl-18-crown-6[4] in THF (NaH, reflux, 72 h). Hydrolysis of (**10**) (10% NaOH, reflux, 4 h) followed by acidification gave (**2**) in 96% yield as a viscous oil.

Similarly, the coupling of (**8**) with toluene-*p*-sulphonates of the appropriate hydroxymethyl crowns[4—6] gave (**9**), (**11**), and (**12**) in yields of 61, 61, and 69%, respectively. Basic hydrolysis of the lipophilic crown diethyl phosphonates followed by acidification produced 90, 91, and 89% yields of



	CE
(**1**),(**9**)	15-Crown-5
(**2**),(**10**)	18-Crown-6
(**3**),(**11**)	21-Crown-7
(**4**),(**12**)	24-Crown-8

Scheme 1

(**1**), (**3**), and (**4**) respectively. Structures of compounds (**1**)—(**4**), (**6**)—(**12**) were verified by elemental analysis and by ^{1}H n.m.r. and i.r. spectroscopy.

Competitive extractions of aqueous solutions which were 0.25 M in each alkali metal chloride with 0.050 M solutions of (**1**)—(**4**) in chloroform were conducted in the usual manner.[2]

Although the highest metals loading of the organic phase was observed when the contacting aqueous phase was somewhat alkaline, very substantial metals loading was noted at slightly acidic and neutral pH values [metals loading ≥70% at pH 7 for (**1**)—(**4**)]. Based upon the complexing agent concentration in the chloroform phase the organic phase metals with the aqueous phase at pH 9 were: Na^+ (50%), K^+ (21), Rb^+ (14), Li^+ and Cs^+ (5) with (**1**); K^+ (57%), Rb^+ (24), Cs^+ (5), Na^+ and Li^+ (undetectable) with (**2**); Rb^+ (31%), Cs^+ (30), K^+ (17), Na^+ (12), Li^+ (10) with (**3**); and K^+ (23%), Na^+ (22), Cs^+ (20), Rb^+ (18), Li^+ (11) with (**4**). Thus, for (**1**)—(**3**) the best extracted alkali metal cation was that which would be predicted from the crown ring size.

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References

1 W. Wierenga, B. F. Evans, and J. A. Woltersom, *J. Am. Chem. Soc.*, 1979, **101**, 1334; L. S. Frederick, T. M. Fyles, V. A. Malik-Diemer, and D. M. Whitfield, *J. Chem. Soc., Chem. Commun.*, 1980, 1211; J. Strzelbicki and R. A. Bartsch, *Anal. Chem.*, 1981, **53**, 2251; W. A. Charewicz, G. S. Heo, and R. A. Bartsch, *ibid.*, 1982, **54**, 2094; W. A. Charewicz and R. A. Bartsch, *ibid.*, p. 2300; S. Shinkai, H. Kinda, Y. Araragi, and O. Manabe, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 559.

2 J. Strzelbicki and R. A. Bartsch, *Anal. Chem.*, 1981, **53**, 1894.

3 E. C. Armstrong, R. L. Bent, A. Loria, J. R. Thirtle, and A. Weissberger, *J. Am. Chem. Soc.*, 1960, **82**, 1928.

4 B. Czech, B. Son, and R. A. Bartsch, *Tetrahedron Lett.*, 1983, **24**, 2923.

5 D. M. Dishong, C. J. Diamond, M. I. Cinoman, and G. W. Gokel, *J. Am. Chem. Soc.*, 1983, **105**, 586.

6 B. Czech, A. Czech, and R. A. Bartsch, *Tetrahedron Lett.*, 1983, **24**, 1327.