

FLUORO-SUBSTITUTED BENZO-CROWN POLYETHERS

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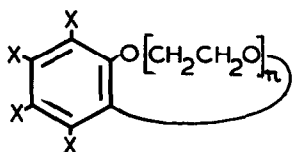
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Abstract 3',4',5',6'-Tetrafluorobenzo-15-crown-5 (1) and 3',4',5',6'-tetrafluorobenzo-18-crown-6 (2) are readily prepared by reaction of hexafluorobenzene with tetra- and pentaethylene glycol, respectively, and show markedly reduced salt-extraction capability compared to hydrocarbon analogues.

Controlled modification of the cation complexing properties of benzo-crown polyethers should be possible by introduction of substituents into the benzene ring. Measurements of complexation constants have indicated there is often an inverse relationship between electron withdrawing power of substituents and the complexing power of the ether,¹⁻⁴ but exceptions have been noted.²⁻⁴ Substituent effects can also play an important part in influencing the ability of benzo-crown polyethers to extract metal salts from aqueous to organic media.⁵ Despite this interest, relatively few halogen substituted compounds of this type have been reported. This note describes the facile preparation of 3',4',5',6'-tetrafluoro derivatives of benzo-15-crown-5 and benzo-18-crown-6, and extraction data obtained with them for the methylene chloride-water-metal picrate system.⁶

Addition of sodium hydride (40 mM), to a stirred solution of hexafluorobenzene (20 mM) and tetraethylene glycol (20 mM) in 1,2-dimethoxyethane at room temperature gave one major product, which was conveniently isolated by p.l.c. in 38% yield⁷ as an oil, and identified as 3',4',5',6'-tetrafluorobenzo-15-crown-5 (1), M^+ 340.0910 (calc. 340.0934); δ_H 3.66 (s, $-\underline{CH_2CH_2O}-$), 3.84 (t, J 5Hz, $ArOCH_2CH_2O-$), 4.24 (t, 5Hz, $ArOCH_2CH_2O-$); δ_C 70.17, 70.61, 70.95, 74.51 (CH_2) and 138.01, 138.26, 142.53 ($Ar-C$ showing C to F coupling); δ_F 158.4 and 165.3 ($AA'XX'$ pattern). A minor component forming 6% of the crude product was the di-ether 2.

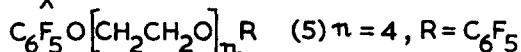
Similar reaction of hexafluorobenzene with pentaethylene glycol gave, after purification by p.l.c., 3',4',5',6'-tetrafluorobenzo-18-crown-6 (2) as an oil in 45% yield, M^+ 384.1226 (calc. 384.1196); δ_H 3.64, 3.68 (2xs, $-\underline{OCH_2CH_2OCH_2CH_2O}-$), 3.84 (t, J 5Hz, $ArOCH_2CH_2O-$), 4.26 (t, J 5Hz, $ArOCH_2CH_2O-$); δ_C 70.12, 70.66, 70.76, 74.36 (CH_2) and



(1) $n=4$, $X=F$

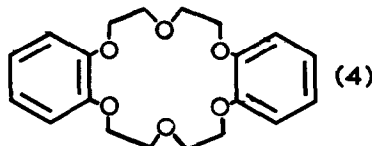
(2) $n=5$, $X=F$

(3) $n=4$, $X=H$



(5) $n=4$, $R=C_6F_5$

(6) $n=3$, $R=H$



137.53, 137.70, 142.01 (Ar-C showing C to F coupling); δ_F 158.4 and 165.2 (AA'XX' pattern).

Although 3',4',5',6'-tetrafluorobenzo-6-crown-2 (5,6,7,8-tetrafluoro-2,3-dihydro-1,4-benzodioxin) has been prepared³, attempted formation of the tetrafluoro-derivative of benzo-12-crown-4 from hexafluorobenzene, triethylene glycol, and either sodium hydride or *n*-butyl lithium was unsuccessful; in the first case polymeric material, and in the second case the mono-ether 6 was the main product.

Chloroform containing either 1 or 2 dissolved potassium permanganate. Data for the extraction of alkali metal picrates from water into dichloromethane solutions of 1, 2, benzo-15-crown-5 (3) and dibenzo-18-crown-6 (4), are recorded in the Table.

Table 9 Alkali Metal Picrate Extracted from Aqueous Solution into Dichloromethane Containing a Macrocyclic Polyether.^a

	Polyether			
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
K ⁺ picrate ^b	4	11	45	78 ^d
Na ⁺ picrate ^c	<1	2	26	7 ^d

a) Concentration of polyether 7×10^{-4} M. b) Original aqueous solution 7.5×10^{-5} M in K⁺ picrate, 0.1 M in KOH. c) Original aqueous solution 8.1×10^{-5} M in Na⁺ picrate, 0.1 M in NaOH. d) Reported⁷: K⁺ picrate, 75%; Na⁺ picrate, 5%.

The strength of complex formation is one factor governing this type of extraction equilibrium,⁹ the others being the magnitude of the partition coefficient of the polyether and of the complexed salt between the aqueous and organic phases. The poor extraction properties of 1 and 2 compared to 3 and 4, respectively, most probably result from the strong inductive effects of the fluorine substituents, which lower the basicity of the aromatic ether oxygen atoms; the strength of alkali ion interactions with ethers is known to depend on the basicity of ether oxygen.¹⁰

The method of preparation of 1 and 2 suggested that the crude reaction mixture might be a convenient source of "naked fluoride",¹¹ but the mixture was unable to bring about the replacement of chloride in 2,4-dinitrochlorobenzene by fluoride, even when potassium *t*-butoxide was used in place of sodium hydride.

REFERENCES AND NOTES

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7. All new compounds gave satisfactory elemental analysis except 5 which was identified by mass spectrometry [$m^+ + 1$ 527.09075 (calc. 527.0916)] and by its ¹³C-, ¹⁹F-, and ¹H-n.m.r. spectrum. N.m.r. spectra were recorded in CDCl₃; ¹H- and ¹³C-chemical shifts are from TMS, ¹⁹F-shifts from CFC1₃.
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