Journal of Chromatography, 107 (1975) 380-382
© Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

CHROM. 8134

Note

Column and thin-layer chromatography of some nitrogen crowns

J. R. BLACKBOROW, J. C. LOCKHART, D. E. MINNIKIN, A. C. ROBSON and M. E. THOMPSON

Departments of Inorganic and Organic Chemistry, The University, Newcastle-upon-Tyne, NE1 7RU (Great Britain)

(Received October 31st, 1974)

Crown compounds have become increasingly important in areas ranging from physiology to electrochemistry as a result of their specific complexing abilities for alkali and alkaline earth cations[1]. Synthesis of a number of nitrogen-containing crowns derived from *o*-aminophenol and *o*-phenylenediamine by condensation with dichloropolyethers has been reported[2] (eqn. 1).

$$o\text{-}NH_2(C_6H_4)XH + ClCH_2CH_2(OCH_2CH_2)_nCl \rightarrow C_6H_4\{NHCH_2CH_2(OCH_2CH_2)_nX-\} \quad (1)$$

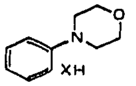
Initial attempts to purify nitrogen-containing crowns by column chromatography were hampered by the relative insolubility of the reaction products in non-polar solvents. The crude reaction products were readily soluble in chloroform but if such mixtures were applied to silica gel or alumina columns made up in chloroform, elution with this solvent resulted in a series of fractions containing partially resolved crowns heavily contaminated with coloured impurities. To avoid this difficulty the crowns were separated from other components in the oily product by adsorption on Celite, which was then packed on an alumina column and eluted with light petroleum (b.p. 60–80°) diethyl ether mixtures. The crown content of each fraction was monitored by thin-layer chromatography (TLC). The Celite method was also used to separate mixtures of crowns obtained from a mixture of polyethers (eqn. 1), where *n* in the product ranged from 2 to 8, and X was O or NH*.

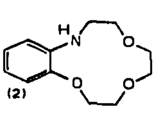
EXPERIMENTAL AND RESULTS

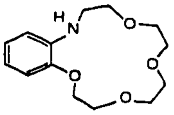
The synthesis in eqn. 1 provided an oil containing unreacted polyether and by-products in addition to the desired crown compound. This oil was adsorbed on to 30–80 mesh Celite (BDH, Poole, Dorset, Great Britain) from a chloroform solution; approximately equal weights of Celite and oil were required. The chloroform was evaporated and the residue then pumped at 100° under vacuum (1 mm Hg) for several hours to give a free-running solid. This was packed on top of an alumina column (20 g

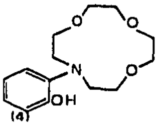
---

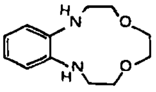
* Pederson's scanning system is used throughout (*cf.* ref. 1).

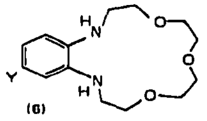

(1)
a: X = O
b: X = NH

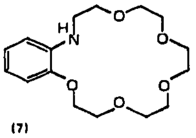

(2)

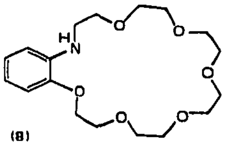

(3)

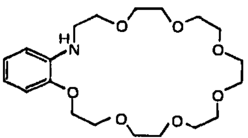

(4)

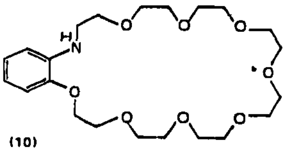

(5)


(6)
a: Y = H
b: Y = CH_3


(7)


(8)


(9)


(10)

alumina per gram of oil) activity IV, prepared from BDH Brockman Grade I by addition of water. Elution with light petroleum containing increasing amounts of diethyl ether effected a separation. Fractions were collected, evaporated and monitored for crown content via TLC using ethanol or acetone–light petroleum (40:60) eluant on Polygram SIL G precoated silica plates. Distinctive coloured spots (Table I) were obtained from fractions containing the nitrogen crowns when the plates were developed in a tank of iodine vapour. These fractions were combined and recrystallised as described previously[2]. R_F values are quoted in the table for pure samples of several crowns.

The method was also used to separate a mixture of crowns obtained from eqn. 1, where the starting material was a mixture of dihalides obtained from the reaction of $SOCl_2$ upon BDH Polyethylene Glycol 400 (n = 2–10, average 7–8). Crown-containing fractions from a preliminary alumina column were analysed by mass spectroscopy to show a preliminary fractionation with crowns (where n = 2–10) eluting in order of ring-size, smallest first. A second column was required to separate each crown in reasonable purity, and the new crowns (7, 8, 9 and 10) were first successfully characterised from these mixtures (by elementary analysis, mass spectroscopy and NMR consistent with literature assignments for the smaller analogous crowns[2]).

TABLE I

R_F VALUES AND SPOT COLOURS OF NITROGEN CROWNS*

No.	Compound	R_F**	Spot colour***
	o-Aminophenol	0.79 (0.38)	brown-orange
1a	2-Morpholinophenol	0.77 (0.52)	grey
1b	2-Morpholinoaniline	0.73 (0.39)	grey-pink
	o-Phenylenediamine	0.58 (0.32)	orange
2	Benzo-12-azacrown-4	0.69 (0.46)	purple-pink
3	Benzo-15-azacrown-5	0.70 (0.43)	blue
4	N-(2-Hydroxyphenyl)-12-azacrown-4	0.51	brown-pink
5	Benzo-12-diazacrown-4	0.57	purple-pink
6a	Benzo-15-diazacrown-5	0.58 (0.3)	maroon
6b	4-Methylbenzo-15-diazacrown-5	0.49	red-brown

* Pure compounds on plates coated with Merck silica gel G (0.4 mm thick).

** R_F values for ethanol as eluant, figures in brackets for acetone–light petroleum (b.p. 60–80°) (40:60).

*** Fresh spot after development in an iodine-vapour tank; colours faded on long exposure.

ACKNOWLEDGEMENTS

We are grateful for financial support from SRC (SRC CASE studentship to M.E.T. in collaboration with Albright and Wilson) and from Lithium Corporation of America (A.C.R.) and Albright and Wilson.

REFERENCES

1 C. J. Pedersen, *J. Amer. Chem. Soc.*, 89 (1967) 7017.
2 J. C. Lockhart, A. C. Robson and M. E. Thompson, *J. Chem. Soc. Perkin I*, (1973) 577.