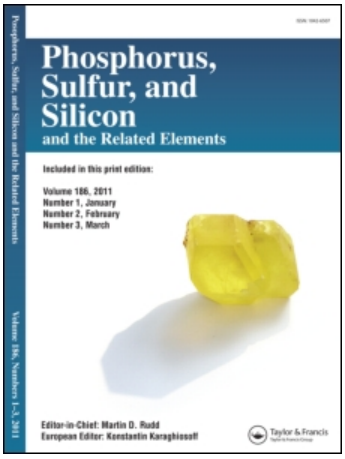

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Facile and Rapid Synthesis of Some Crown Ethers Under Microwave Irradiation

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Facile and Rapid Synthesis of Some Crown Ethers Under Microwave Irradiation

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A series of crown ethers were synthesized from the reaction of 1,8-dichloro-3,6-dioxaoctane with the appropriate hydroxy compound under microwave irradiation in short times and high yields.

Keywords Synthesis of crown ethers

Since the pioneering work of Pederson on the preparation and properties of macrocyclic polyethers (crown ethers),[1] there have been waves of interest concerning the synthesis of a wide variety of oxygen-, sulfur- and nitrogen-containing crowns.[2] The crown ethers have proved to be enormously popular and extremely useful ligands (host) for a startling range of metal ions and neutral or ionic organic species.[3] Indeed, it seems as if they bend into the majority of the elements of the periodic table. The highly flexible crown ethers have proved to be capable of adopting themselves to a wide variety of a coordination requirements and media.[4] Furthermore, immobilization of the crown ethers onto polymers allows for the ease of handling recyclability and the adoption to continuous processes for this important set of complexants.[5]

Crown ether derivatives can be useful as potential chiral selectors in capillary electrophoresis for the chiral separation of amino acids.[6] Crown ethers have been developed to increase the metal selectivity and complex stability in analytical separation methods as well as in

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biological membranes.[7] Considerable attention also has been paied to crown ether dyes containing a chromophore.[8] The increasing interest to rapidly provide highly pure large molecules is driving the development of new technologies. Microwave-assisted organic chemistry is a relatively new technology that has been shown to significantly improve productivity in the rapid generation of complex molecules.[9] Microwave irradiation has been demonstrated not only to significantly accelerate many organic reactions, but also to improve yields and selectivity.[10]

As a result of the work performed in our laboratories concerning the synthesis of organic compounds under microwave irradiation,[9] interest has developed in the synthesis at variety of crown ethers by this technique.[11]

While several syntheses for substituted derivatives of 12-crown-4 and 15-crown-5[12] have been reported, only a few syntheses of unsubstituted crown ethers have appeared in the literature.[2d] Cook and colleagues[2d] prepared 12-crown-4 in 13% yields and 15-crown-5 in 14% yields. Here we wish to report the facile and rapid modified Williamson syntheses of 12-crown-4, 15-crown-5, 18-crown-6, and 21-crown-7 in good yields using easily prepared 1,8-dichloro-3,6-dioxaoctane **1** in the presence of a base under microwave irradiation. Compound **1** was easily prepared from the reaction of triethylene glycol with thionyl chloride in benzene in the presence of piperidine.[1a]

Compound **1** was caused to react with an appropriate hydroxy compound in the presence of potassium hydroxide under microwave irradiation to afford the corresponding crown ether (Scheme 1).

Dibenzo-14-crown-4 was synthesized from the reaction of cathacol with 1,3-dichloropropane in the same manner in the presence of sodium hydroxide (Scheme 2).

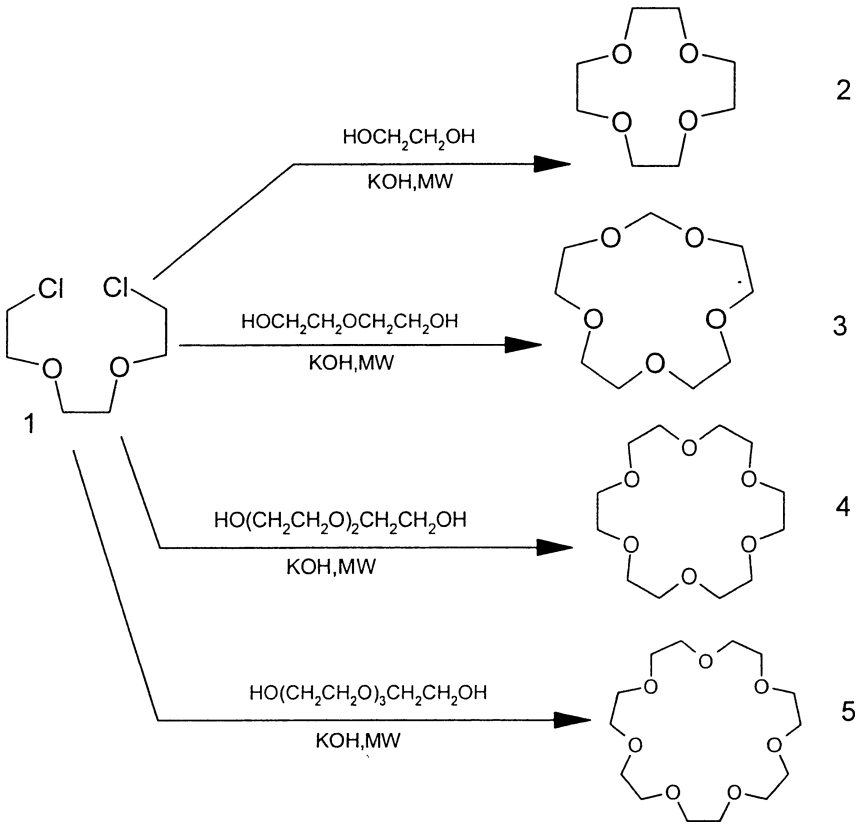
In conclusion, we have developed a modified Williamson synthesis for the rapid preparation of crown ethers under microwave irradiation in good yields.

EXPERIMENTAL

IR spectra were obtained on a 4300 Shimdzu spectrometer. The ^{1}HNMR spectra were recorded on a Bruker Ac 100 unless otherwise stated using TMS as a standard reference. Mass spectra were scanned on a Varian CH-7 instrument at 70 ev.

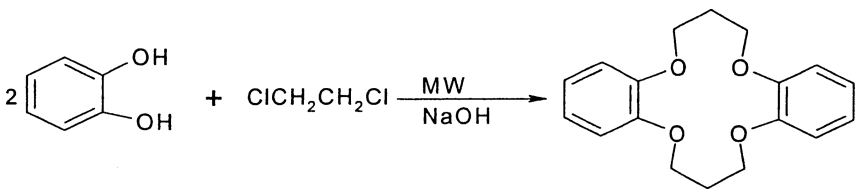
SYNTHESIS OF CROWN ETHERS UNDER MICROWAVE IRRADIATION: GENERAL PROCEDURE

Compound **1** (1 mmol) and an appropriate dihydroxy compound (1 mmol) were mixed with potassium hydroxide (0.02 mol) and water



SCHEME 1

(1 mL). The mixture was placed in an unmodified microwave oven for the indicated time. Progress of the reaction was monitored by TLC. After completion of the reaction, the resulting thick, brown slurry was diluted with dichloromethane (10 mL) and filtered. The filtrate was dried over $MgSO_4$ and evaporated to dryness to afford the corresponding crown ether. The final product was purified by vacuum distillation.



SCHEME 2

SELECTED DATA FOR 2

Irradiation time 6 min, yield 37%, b.p. 176 at 33 mmHg lit.[1b] 60–70 at 0.5 mmHg, IR (KBr disc) 2930, 1460, 1365, 1285, 1250, 1130, 1100, 920 cm^{-1}, ^{1}HNMR, δ(CDCl^3), 3.65 (sharp s) MS, m/z, M^+, 176.

SELECTED DATA FOR 3

Irradiation time, 8 min, yield 40%, b.p. 220–225 at 33 mmHg, IR (KBr disc) 2870, 1440, 1350, 1285, 1255, 1185, 980 cm^{-1}, ^{1}HNMR, δ ($CDCl_3$), 3.63 (sharp s) MS, m/z, M^+, 220.

SELECTED DATA FOR 4

Irradiation time 8 min, yield 54%, b.p. 264 at 33 mmHg, lit.[1c] mp 36.5–38.0°C, IR (KBr disc) 2870, 1450, 1350, 1120, 920 cm^{-1}, ^{1}HNMR, δ($CDCl_3$), 3.65 (sharp s) MS, m/z, M^+, 264.

SELECTED DATA FOR 5

Irradiation time 10 min, yield 68%, b.p. 308–310 at 33 mmHg, IR (KBr disc) 2860, 1500, 1460, 1250, 920, 910 cm^{-1}, ^{1}HNMR, δ($CDCl_3$), 3.65 (sharp s), MS, m/z, M^+, 308.

SYNTHESIS OF DIBENZO-14-CROWN-4.6

1,2-dihydroxybenzene (1.21 g, 0.011 mol), sodium hydroxide (0.8 g, 0.02 mol), and 1,3-dichloropropane (1.12, 0.01 mol) were mixed in DMSO (1 mL). The mixture was placed in a household microwave oven for 8 min. The crude product was taken up in conc. HCl (2 mL) and filtered. The filtrate was extracted with $CHCl_3$, dried, and evaporated to afford a crude residue, which was crystallized from n-heptane to afford the title compound. Yield 72%, m.p. 150, 150–152 lit.[1a] IR (KBr disc) 3000, 1600, 1450, 1420, 1300, 900 cm.$^{-1}$ ^{1}HNMR, δ($CDCl_3$) 2.25 (s, 4H, CH_2), 4.25 (t, 8H, CH_2), M, m/z, M^+, 300.

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