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SYNTHESES OF HYDROXY GROUP-CONTAINING CROWN ETHERS AND POLYMER-SUPPORTED CROWN ETHERS

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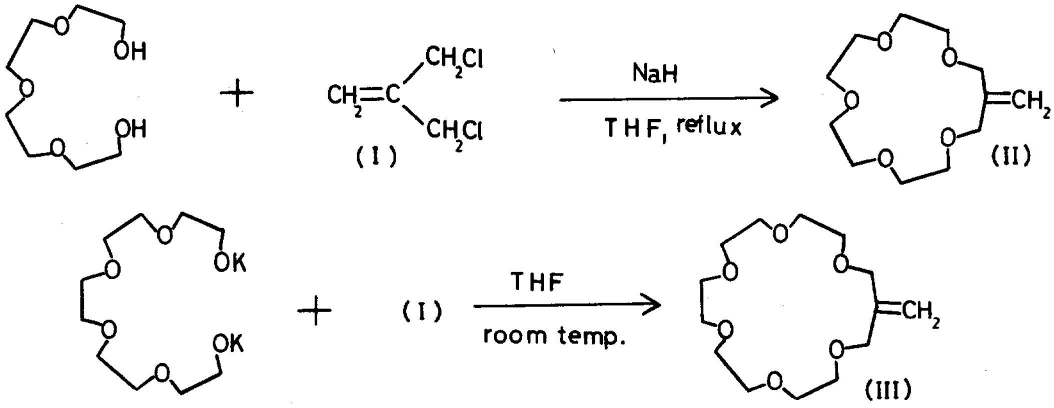
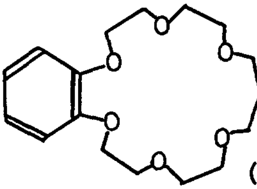
Since pioneering works by Pedersen[1)] a large variety of macrocyclic compounds have been prepared and their cation complexation properties have been investigated extensively[2)]. Moreover, the macrocyclic compounds have been found very useful as catalysts for various organic reactions[3)].

We wish to report the synthesis of new crown ethers containing functional groups such as vinylidene, hydroxy, or carbonyl groups and the preparation of polymer-supported crown ethers which can be used as phase-transfer catalysts. The crown ethers with vinylidene group were prepared by the reaction of 3-chloro-2-chloromethyl-1-propene (I)[4)] with appropriate glycols. Methylene-16-crown-5 (II) was synthesized by slow, dropwise addition of a solution of (I) (0.1 mol) and tetraethylene glycol (0.1 mol) in tetrahydrofuran (THF) (150 ml) to a stirred suspension of sodium hydride (0.3 mol) in THF (150 ml) at a reflux temperature under a nitrogen atmosphere. In the case of the synthesis of methylene-19-crown-6 (III), a solution of (I) (0.1 mol) in THF (100 ml) and a solution of potassium salt[5)] of pentaethylene glycol (0.1 mol) in THF (100 ml) were added simultaneously, dropwise with vigorous stirring, to THF (300 ml) at room temperature under a nitrogen atmosphere. These crowns could be purified by distillation under reduced pressure.



In the same manner, benzomethylene-19-crown-6 (IV) and methylene-19-diazacrown-6 (V) were prepared from (I) and potassium salts of 1,2-bis[2′-(2″-hydroxyethoxy)ethoxy]benzene[6] or 6,9-dioxa-3,12-diazatetradecane-1,14-diol[7], respectively. Dibenzomethylene-16-crown-5 (VI) was synthesized by the reaction of (I) (0.1 mol) with sodium salt of 1,5-bis(2-hydroxyphenoxy)-3-oxapentane[8] (0.1 mol) in a n-butanol—water mixture (700 ml : 30 ml) at 90°C.



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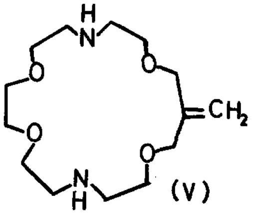

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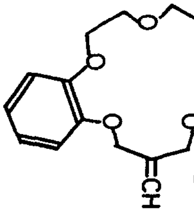
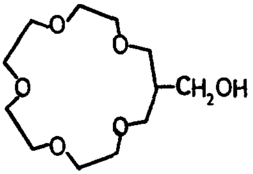


(VI)

These new crowns with vinylidene group could be successfully converted to the corresponding crowns with hydroxy or carbonyl groups, as described below. On hydroboration—oxidation[9], compound (II) yielded hydroxymethyl-16-crown-5 (VII). On ozonation followed by reduction with sodium borohydride[10], compound (II) gave sec-hydroxy-16-crown-5 (VIII). On oxymercuration—demercuration[11], compound (II) gave tert-hydroxy-16-crown-5 (IX). Oxo-16-crown-5 (X) was prepared by the decomposition of the ozonide from crown (II) with zinc and water in the presence of acetic acid[12]. Compound (VI) could be converted to compound (XI), hydroxymethyl-dibenzo-16-crown-5, by hydroboration—oxidation[9]. The yields and physical properties of these crowns are summarized in Table I.



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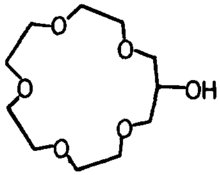
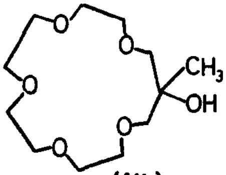


(VIII)



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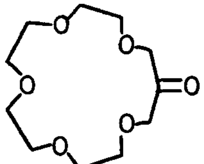
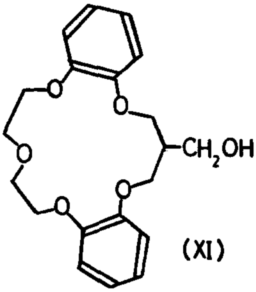
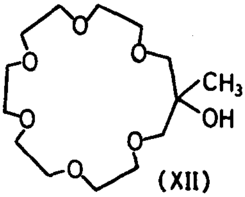


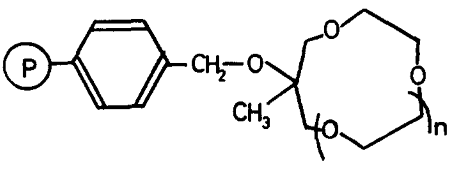
(X)



(XI)



(XII)



(XIII) n=3 ; (XIV) n=4

The hydroxy group-containing crown ethers were used for the preparation of immobilized phase-transfer catalysts[13]. The immobilized catalysts are easily separated from the reaction mixture and are reusable. In practice compounds (XIII) and (XIV) were prepared by the reaction of chloromethylated polystyrene resin cross-linked with 10% divinylbenzene (macroreticular type; 5.6 mequiv. of Cl per g of polymer) with sodium salts of crown (IX) or tert-hydroxy-19-crown-6 (XII) in

Table I. Yields and Physical Properties of Crowns

Crown	Yield %	bp(mp) °C	NMR spectra (60 MHz) ppm in CCl_4 or $CDCl_3$	IR spectra cm^{-1}, neat
II	45	115-120 (5–8x10^{-3}mmHg)	4.98(2H,s,CH_2=), 3.99(4H,s,OCH_2C=), 3.52(16H,s,CH_2CH_2)	1655(C=C), 1120(C-O-C)
III	66	120-125 (4–8x10^{-3}mmHg)	5.00(2H,s,CH_2=), 3.98(4H,s,OCH_2C=), 3.56(20H,s,CH_2CH_2)	1650(C=C), 1100(C-O-C)
IV	39	oil[a)]	6.77(4H,m,ArH), 5.03(2H,s,CH_2=), 3.99(4H,s,OCH_2C=), 3.60(16H,m,CH_2CH_2)	1640(C=C), 1120(C-O-C)
V	35	140-142 (5x10^{-3}mmHg)	5.05(2H,s,CH_2=), 3.97(4H,s,OCH_2C=), 3.52(12H,m,OCH_2CH_2O and OCH_2CN), 2.70(8H,t,CH_2N), 1.98(2H,s,NH)	3320(NH), 1650(C=C), 1110(C-O-C)
VI	40	(94-95)[b),c)]	6.85(8H,m,ArH), 5.37(2H,s,CH_2=), 4.66(4H,s,OCH_2C=), 3.97(8H,m,CH_2CH_2)	1655(C=C), 1250(=C-O-), 1110(c-O-C) (KBr disk)
VII	88	oil[a)]	3.58(6H,d,$OC\underline{H}_2CH$), 3.30(16H,s,CH_2CH_2), 2.55(1H,br.s,OH), 2.05(1H,m,CH) (in C_6H_6)	3400(OH), 1100(C-O-C)
VIII	63	oil[a)]	3.50(21H,m,CH_2CH_2 and $CHCH_2O$), 2.90(1H,br.s,OH)	3300(OH), 1100(C-O-C)
IX	78	oil[a)]	4.10(1H,s,OH), 3.50(16H,s,CH_2CH_2), 3.25(4H,s,OCH_2C), 0.94(3H,s,CH_3)	3350(OH), 1390($C-CH_3$), 1100(C-O-C)
X	98	oil[a)]	4.27(4H,s,OCH_2CO), 3.52(16H,m,CH_2CH_2)	1730(C=O), 1120(C-O-C)
XI	75	(110-111)[b),d)]	6.83(8H,m,ArH), 4.24(4H,d,$OC\underline{H}_2CH$), 3.95(8H,m,CH_2CH_2), 2.92(1H,t,OH), 2.50(1H,m,CH)	3450(OH), 1250(=C-O-C), 1120(C-O-C) (KBr disk)

a) Crude products, generally 90-95 % pure by gel permeation chromatography.

b) Uncorrected. c) From n-heptane. d) From n-heptane–benzene.

Table II. Reaction of n-$C_8H_{17}Br$[a] with KI[b] Catalyzed by Polymer-Supported Crown Ethers[c]

Catalyst	[Crown unit]/[$C_8H_{17}Br$]	Time, hr	Yield[d], %
None	—	24	<5
XIII	0.08	2	>95
XIV	0.08	3	95
XIII	0.01	8	86
XIV	0.01	8	79

a) No solvent was used for the substrate.
b) Saturated aqueous solution, 5.0 mol equiv.
c) Reaction temp, 80°C; internal standard, tetralin.
d) By g.l.c. analysis.

THF at a reflux temperature. Compounds (XIII) and (XIV) contained 2.0 and 1.8 mmol of crown unit per g of polymer,respectively. This is a convenient method for the immobilization of crown ethers. The solid phase catalysts obtained were found to catalyze the halogen exchange reaction of n-octyl bromide with potassium iodide (Table II).

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