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New Crown Compounds Derived from 1,2-Bis(2-hydroxybenzyl)benzene(I)

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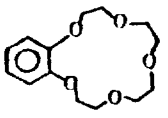
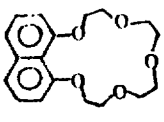
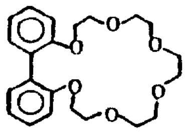
By cyclocondensation of 1,2-bis(2-hydroxybenzyl)benzene with oligoethylene glycol ditosylate, new crown ethers containing 1,2-dibenzylbenzene subunit were synthesized. By oxidation of the benzylic positions of them, carbonyl-containing crowns having 1,2-dibenzoylbenzene subunit were synthesized.

Introduction

Among various macrocyclic polyethers, many of them have aromatic hydrocarbon groups to which ethyleneoxy units are linked as the basic repeating structure, because they have been synthesized in general from di- or polyhydroxy aromatic compounds. For example, the benzocrown I$^{1-3}$, synthesized by C. J. Pedersen in his early work of crown ether synthesis, is a corand^{4} in which ethyleneoxy chain is separated by two carbon atoms in the *o*-phenylene group. In naphthaleno-crown II^{5}, the ethyleneoxy chain is separated by three carbon atoms in the naphthene unit. The biphenyl crown III^{3,6}, prepared by D. J. Cram *et al.*, is another corand in which ethyleneoxy chain is separated by four carbon atoms in the biphenyl moiety. These three corands have similarities in structural constitution and properties, though they contain different hydrocarbon units.


I


II

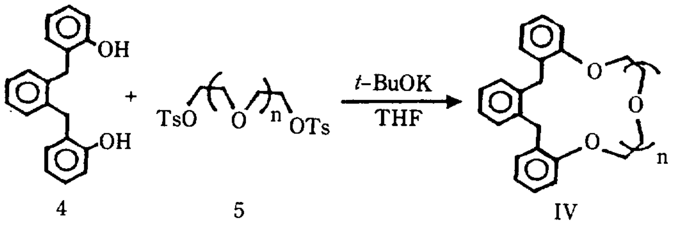

III

Now, we wish to report new crown ethers which are structurally related with the corands I-III, but in which ethyleneoxy chains are separated by eight carbon atoms in the aromatic hydrocarbon subunit. In this work, we also report novel crowns possessing ketonic carbonyl group as part of the macroring. We have been interested for many years in the synthesis of carbonyl crowns in which ether oxygens are substituted partially or completely for carbonyl groups, and this is one of the series of the investigation.

Results and Discussion

New crown ethers IV were synthesized by the condensation of 1,2-bis(2-hydroxybenzyl)benzene with oligoethylene glycol ditosylate in the presence of base. In this reaction, a small amount of side products were produced as well, which were known to be a symmetrical crown ethers having two or more 1,2-dibenzylbenzene subunits bound by ethyleneoxy units. The new corands IV are structurally related with the corands I-III, but IV are more flexible in a conformational sense, because the hydrocarbon unit in IV is flexible, wheras those in II and III are rigid. The molecular model shows that three benzene rings in IV are not neccessarily in a plane, but properly arranged rotating about the benzylic carbon between benzene rings to form a bent structue, which makes

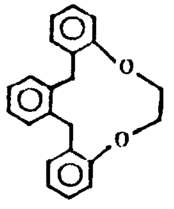
Table 1. Cyclocondensation of 1,2-Bis(2-hydroxybenzyl)benzene with Oligoethylene glycol ditosylate



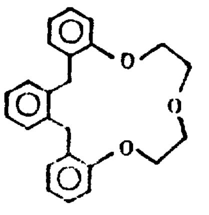
n	Products	Yield[a] (%)	m.p.[b] (°C)	MS *m*/*e*(M+)	IR[c] ν(cm^{-1})	^{1}H-NMR(TMS)[d] δ(ppm)
0	IVa	50-60	166-167	316	3070,3030,2960 2930,1600,1570 1490,1100,1050	7.22-6.67(m, 12H, arom.) 4.34(s, 4H, benzylic) 3.85(s, 4H, OCH_2)
1	IVb	70-80	158-159	360	3060,3025,2870 1600,1585,1300 1140,1105,1050	7.27-6.79(m, 12H, arom.) 4.07(s, 4H, benzylic) 4.19-3.74(m, 8H, OCH_2)
2	IVc	50-70	168-169	404	3080,3030,2870 1600,1585,1300 1240,1100,1050	7.24-6.74(m, 12H, arom.) 4.02(s, 4H, benzylic) 4.14-3.69(m, 12H, OCH_2)
3	IVd	70-80	166-167	448	3070,3030,2930 1600,1590,1300 1120,1100,1050	7.26-6.76(m, 12H, arom.) 4.01(s, 4H, benzylic) 4.12-3.45(m, 16H, OCH_2)

[a] Isolated yield based on 4. [b] Melting points were not corrected. [c] IR spectra were recorded with Perkin-Elmer Model 782 spectrometer. [d] NMR spectra were recorded on Bruker AC80 FT NMR spectrometer.

the two phenolic oxygens much closer.



IV a



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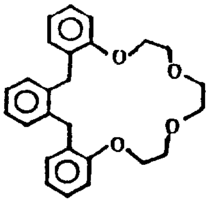
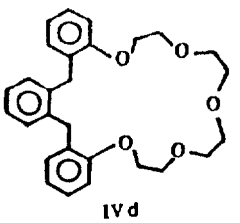


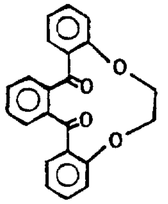
IV c



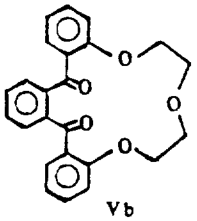
IV d

For the synthesis of corands IVa-d, the main reactant 1,2-bis(2-hydroxybenzyl)benzene (**4**)[7] was prepared by the reaction of 2-bromoanisole Grignard (**1**) with 1,2-bis(bromomethyl) benzene (**2**) in the presence of copper(I) iodide to obtain the coupling product, 1,2-bis(2-methoxybenzyl)benzene (**3**), followed by cleaving the ether linkages of **3** with HBr-AcOH to give **4**. The corands IV could be synthesized by the reaction of the bisphenolic compound **4** with oligoethylene glycol ditosylate **5** in the presence of base catalyst. The double Williamson reaction led to the formation of cyclocondensation product. The physical and spectral data are summarized in Table 1. Each of these corands is expected to show different binding properties to cations in crown complexation, since they have different numbers of ligating oxygen atoms to form different sizes of cavities. The complexation study will be continued.

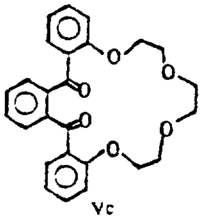
Now, it is of interest to synthesize crown ethers, containing carbonyl groups by the oxidation of IV. For this purpose various published methods was examined, in which benzyl-to-carbonyl conversion were investigated by R. Rathore[8] (PCC in benzene), B. Finucane[9] (NBS, hν, $CaCO_3$ in THF), A. Peason[10] ($Cr(CO)_6$, t-BuO_2H, in MeCN), J. Muzart[11] (CrO_3, t-BuO_2H, in CH_2Cl_2), H. Sugimoto[12] ($FeCl_3$, H_2O_2, in MeCN), and G. Morrison[13] (NBS, O_2, in CCl_4). But, it was not easy to oxidize benzylic positions of IV to carbonyl groups, for it was always accompanied by the cleavage of ether linkages. The most effective oxidation of IV was accomplished with ammonium cerium nitrate (CAN)[14], which afforded new corands Va-d in fairly good yields. The physical and spectral data are summarized in Table 2.



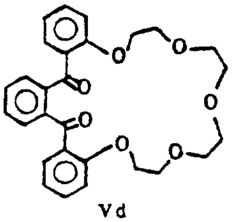
Va



Vb

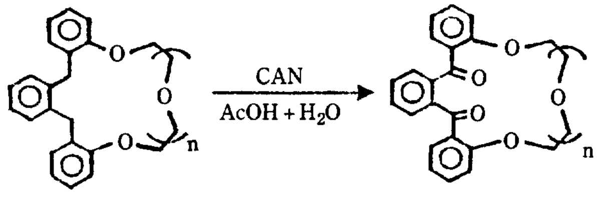


Vc



Vd

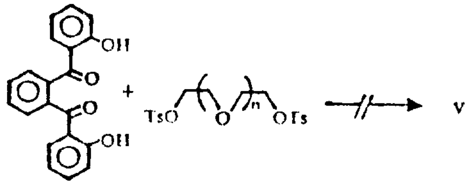
Table 2. Oxidation of Crown IV to Carbonyl-containing Crown V



IV V

n	Products	Yield^a (%)	m.p.^{b} (°C)	MS *m/e*(M$^+$)	IR^c ν(cm^{-1})	^{1}H-NMR(TMS)^d δ(ppm)
0	Va	41	211-222	344	3100,2930,1650 1600,1575,1300 1160,1105,1030	7.95-6.80(m, 12H, arom.) 3.98(s, 4H, OCH_2)
1	Vb	50	201-202	388	3070,2970,1670 1650,1600,1490 1300,1145,1060	7.88-6.60(m, 12H, arom.) 4.00-3.29(m, 8H, OCH_2)
2	Vc	70	133-134	432	3090,2910,1680 1660,1600,1490 1300,1110,1060	7.70-6.65(m, 12H, arom.) 4.05-3.45(m, 12H, OCH_2)
3	Vd	57	124-125	476	3075,2950,1685 1650,1600,1490 1300,1100,1040	7.63-6.67(m, 12H, arom.) 4.11-3.53(m, 16H, OCH_2)

To synthesize the carbonyl-containing corands V, we tried first the reaction of 1,2-bis(2-hydroxybenzoyl)benzene (**6**)[15] with oligoethylene glycol ditosylate (**5**) in the presence of base, but the cyclocondensation product, V, could not be obtained.



6 5

The corands V are expected to show characteristic ligating properties for cations, for they contain additional carbonyl groups, compared with the mother crown IV, which will probably participate in crown complexation. The influence of carbonyl group in ligating cations will be continued.

Experimental Part

All reactions involving organometallic reagent were carried out with the usual precautions for rigorous exclusion of air and moisture. The solvents, Et_2O and THF, were purified by refluxing several hours in the presence of sodium metal and benzophenone until the solution colored purple, followed by distillation under nitrogen.

Oligoethylene glycol ditosylate (5).

General procedure. Oligoethylene glycol (20 mmol) and *p*-toluenesulfonyl chloride (7.6 g, 40 mmol) were dissolved in tetrahydrofuran (100 m*l*). The solution was cooled in an ice bath, and 40% aqueous sodium hydroxide solution (40 m*l*) was added dropwise with stirring, followed by stirring at room temperature for 4 h. The usual work-up gave the ditosylate in more than 95% yield.

1,2-Bis(2-methoxybenzyl)benzene (3)

A Grignard reagent prepared from 5.7 g(30 mmol) of *o*-bromoanisole and 2g of magnesium turnings in THF (50 m*l*) was added, at -30 °C under nitrogen, to a solution of 2.3 g (8.7 mmol) of 1,2-bis(bromomethyl)benzene and catalytic amount of CuI (0.6 g) in THF (20 m*l*), followed by stirring overnight at room temperature. Normal hydrolytic workup and chromatography (silica gel) afforded a colorless crystalline solid, m.p. 122-113 °C, in 94% yield. IR(KBr): 3060, 2960, 1600, 1587, 1460, 1160, 1105 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 7.2-6.7 (m,12H, arom.), 3.95 (s, 4H, benzylic), 3.75 (s, 6H, OCH_3). MS (*m/e*): 318 (M$^+$).

1,2-Bis(2-hydroxybenzyl)benzene (4).

The ether linkage of 1,2-bis(2-methoxybenzyl)benzene (**3**) was cleaved by refluxing a solution of 1.0 g of **3** in 50 m*l* of HBr-AcOH (1:1, v/v) for 5 h. Water (150 m*l*) was added, extracted with dichloromethane, washed with aq. $NaHCO_3$ and water successively, and dried over anhydrous magnesium sulfate. After solvent removal, the crude product was chromatographed (silica gel) to give a colorless crystalline compound, m.p. 108-109 °C, in 75-80% yield. IR (KBr): 3430-3300 (broad), 3060, 2920, 1600, 1585, 1490, 1455, 1200, 1160 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 7.2-6.5 (m, 12H, arom.), 5.3 (s, 2H, OH), 3.9 (s, 4H, benzylic); MS (*m/e*): 290 (M$^+$).

Cyclocondensation; Corand IV a-d

General procedure. In a three-necked round-bottomed flask, fitted with a reflux condenser and a dropping funnel, were dissolved 0.67 g (6 mmol) of potassium *t*-butoxide and 0.87 g (3 mmol) of 1,2-bis(2-hydroxybenzyl)benzene (**4**) in THF (30 m*l*), and stirred for 30 min. To this mixture, was added dropwise with stirring a solution of 3 mmol of oligoethylene glycol ditosylate (**5**) in THF (40 m*l*) during the course of

3 h, and refluxed for 10 h. After normal work up, the crude product was chromatographed on silica gel using *n*-hexane-dichloromethane (3:1-2:1), and recrystallized to give colorless crystalline solid IV (Table 1).

Oxidation of IV to V

General procedure. To a solution of 2 mmol of corand IV in acetic acid (40 m*l*), was added a solution of 11 g (20 mmol) of ammonium cerium nitrate(CAN) in 50 m*l* of AcOH-H_2O (40 m*l*:10 m*l*) and stirred for 24 h. After normal work up, the crude product was chromatographed on silica gel (CH_2Cl_2 or Et_2O) and recrystallized from mixed solvent of *n*-hexane (or ether) and dichloromethane to give colorless crystalline compound V (Table 2).

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Direct Analysis of Impurities in Solids with Glow Discharge Mass Spectrometry

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A glow discharge mass spectrometric(GDMS) analytical method was developed for direct analysis of impurities in solids. Ions extracted from a glow discharge ion source with a sample as a cathode were analyzed by a quadrupole mass filter. Ion extractions were carried out through differentially-pumped orifices biased to positive and negative potentials. Operating parameters of the glow discharge source such as discharge current, orifice-to-cathode distance, energy analyzer setting and bias voltages have been optimized. The developed GDMS was applied to the analysis of KSS copper-base alloy standards certified by Korea Standards Research Institute(KSRI). In the analysis, the reproducibility and the detection limits were estimated to be about 2.5% RSD, and in the low ppm range, respectively.

Introduction

The glow discharge technique for chemical analysis has some advantages due to its relatively simple way of producing atoms and ions by means of its energetic sputtering and plasma processes[1]. More than 20 years ago, Grimm designed the first practical glow discharge source for optical emisson spectroscopic analysis of metals and alloys[2]. Such sources were modified by many research groups interested in elemental analysis of solid samples[3-10]. In recent years, a direct current (dc) glow discharge ion source for mass spectrometric analysis was developed by Harrison *et al.*[11] GDMS have several analytical advantages that make it increasingly attractive: direct analysis of solids, parts-per-billon detection limits attainable; sensitivities generally uniform for most elements; minimal matrix effects; isotopic information; simple spectra; rapid qualitative and quantitative results; stable ion beam; less complex ion source hastening the demise of the spark source mass spectrometry (SSMS) technique. Glow discharge mass spectrometry is a technique generating increasing interest among elemental analysis groups[12-18]. Excellent reviews of recent development of GDMS have been published[19-21].

The major purpose of our investigations is improving the analytical performance of the glow discharge mass spectrometer system by understanding the basic processes of ion beam generation, extraction, transport, and energy and mass filtering.