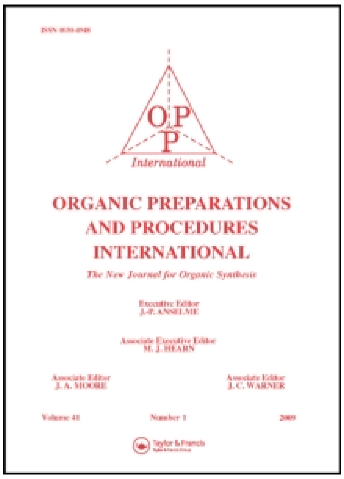

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SYNTHESIS OF 4'-ALKYLDIBENZO CROWN ETHERS

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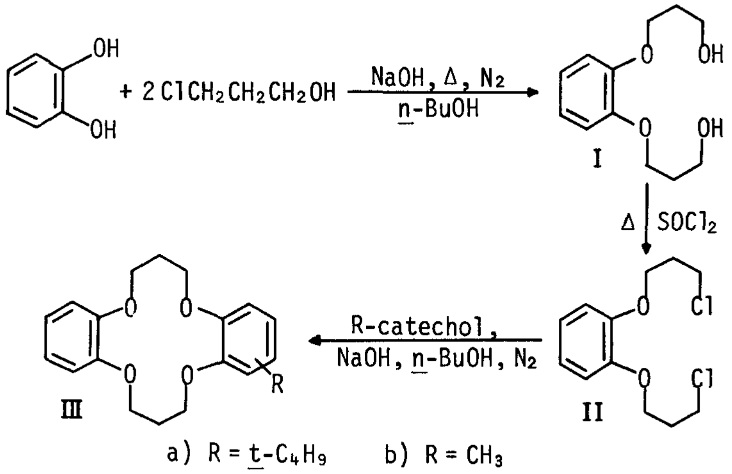
Since Pedersen's[1,2] and Lehn's[3] introduction of synthetic macrocyclic ligands capable of forming stable complexes with the alkali and alkaline earth cations, a large number of crown ethers have been synthesized. However, only a few derivatives of dibenzo-14-crown-4 such as bis-(t-butyl)-dibenzo-14-crown-4,[1,4] 6,13-dihydroxydibenzo-14-crown-4[5] and bis-amino-dibenzo-14-crown-4[6] have been reported. We now describe two new derivatives of dibenzo-14-crown-4 (III). The preparation of these new compounds, 4'-t-butyldibenzo-14-crown-4 (IIIa) and 4'-methyldibenzo-14-crown-4 (IIIb), require only three steps from catechol. Alkylation of catechol gives 1,2-bis(3-hydroxypropoxy)benzene (I), which is then chlorinated with $SOCl_2$; reaction of II with a 4-alkyl catechol yields the 4'-alkyldibenzo crown ether (III). The advantage of 1,2-bis(3-chloropropoxy)benzene lies in its



a) $R = t\text{-}C_4H_9$ b) $R = CH_3$

ease of preparation from 1,2-bis(3-hydroxypropoxy)benzene in high yield (90%) and its usefulness to prepare other crown derivatives, especially for those with two different substituents on two benzo groups.

EXPERIMENTAL

Melting points were measured on a Mel-Temp apparatus. Infrared spectra were recorded using KBr pellets of the compounds (unless otherwise specified) on a JASKA 3A instrument. Proton nmr spectra were recorded in $CDCl_3$ with a Bruker WT 80 DS instrument with TMS as an internal standard. Mass spectra were taken on Varian MAT 112 GC/MS. Elemental analyses were performed by Dr. Hans Hösli using a CHA-1 instrument.

<u>1,2-Bis(3-hydroxypropoxy)benzene (I)</u>.- The procedure used is similar to the method of Smid[7] and Kyba.[8] To a solution of 55 g (0.5 mole) of catechol (Sigma Chemical Company) in 320 ml of *n*-butanol, purged with nitrogen for 0.5 hr, was added 43.02 g of NaOH in 40 ml of H_2O, followed by the dropwise addition of 89 ml of 3-chloro-1-propanol (Tokyo Kasei Kogyo Co., unspecified). After 18 hrs reflux, the mixture was cooled to room temperature and the solvent was then carefully evaporated. The solid residue was dissolved in chloroform and the solution acidified with 0.1 N HCl. Removal of the chloroform left an oily residue which was purified by vacuum distillation to afford 68.23 g (60%) of colorless 1,2-bis(3-hydroxypropoxy)benzene, bp. 160-161°/0.09 mm, which solidified upon standing, mp. 54°.

IR: 3300-3400, 2800-2950, 1600, 1500, 1200-1275 cm^{-1}. NMR: δ 6.90 (H_4, singlet, Ar-H); 4.20 (H_4, triplet, O-$\underline{CH_2}$-C); 3.90 (H_2, singlet, -$\underline{OH}$); 2.05 (H_4, quintet C-$\underline{CH_2}$-C); 3.85 (H_4, triplet, C-$\underline{CH_2}$OH). MS: m/e 226 (M^+). <u>Anal</u>. Calcd. for $C_{12}H_{18}O_4$: C, 63.72; H, 7.96. Found: C, 63.70; H, 7.92.

<u>1,2-Bis(3-chloropropoxy)benzene (II)</u>.- To a solution of 82.35 g (0.364 mole) of I, in 250 ml of benzene and 57 ml of pyridine heated at reflux (105°) was added dropwise 53 ml of $SOCl_2$. After 18 hrs, the solution was cooled to room temperature and a solution of 40 ml of conc. HCl in 100 ml

of water was added. The benzene layer was washed successively with water, 10% $NaHCO_3$ and water, and then dried over anhydrous magnesium sulfate. Removal of the benzene left a residue which was distilled, yielding 85.8 g (90%) of 1,2-bis(3-chloropropoxy)benzene, bp. 130-132°/0.04 mm, as a pale yellow oily product.

IR: 2800-2950, 1600, 1500, 1200-1275 cm^{-1}. NMR: δ 6.90 (H_4, singlet, Ar-H); 4.05 (H_4, triplet, O-$\underline{CH_2}$-C); 4.72 (H_4, triplet, C-$\underline{CH_2}$-Cl); 2.18 (H_4, quintet, C-$\underline{CH_2}$-C). MS: m/e 263 (M^+).

Anal. Calcd. for $C_{12}H_{16}Cl_2O_2$: C, 54.75; H, 6.08; Cl, 26.99. Found: C, 54.78; H, 6.10; Cl, 26.70.

4'-t-Butyldibenzo-14-crown-4 (IIIa).- To a solution of 3.32 g (0.02 mole) of 4-t-butylcatechol (Tokyo Kasei Kogyo Co.) and 250 ml of n-butanol, at reflux (105°) purged with nitrogen for 0.5 hr, was added a solution of 1.6 g of NaOH in 20 ml of H_2O, followed by the dropwise addition of 5.26 g (0.02 mole) of II in 50 ml of n-butanol. After 22 hrs reflux, the mixture was cooled to room temperature. The solvent was carefully evaporated and the solid residue was dissolved in chloroform. The solution was washed successively with water, 5% NaOH and water, and then dried over anhydrous magnesium sulfate. The solid residue obtained after evaporation of the solvent was washed with methanol to give 2.68 g of crude product, which was recrystallized from n-heptane to give IIIa as a white solid (2.49 g, 30%), mp. 119-120°.

IR: 2800-2950, 1600, 1500, 1200-1275, 1100-1140 cm^{-1}. NMR: δ 6.89 (H_8, singlet, Ar-H); 4.24 (H_8, triplet, O-$\underline{CH_2}$-C); 2.20 (H_4, quintet, C-$\underline{CH_2}$-C); 1.27 (H_9, singlet, C-($\underline{CH_3}$)$_3$). MS: m/e 356 (M^+).

Anal. Calcd. for $C_{22}H_{28}O_4$: C, 74.16; H, 7.86. Found: C, 74.29; H, 7.84.

4'-Methyldibenzo-14-crown-4 (IIIb).- A solution of II (5.26 g, 0.02 mole) in 50 ml of n-butanol was added dropwise to a solution of sodium hydroxide

(1.6 g) and 4-methylcatechol (2.48 g, 0.02 mole) in n-butanol (200 ml) at reflux (105°); reflux was continued for 16 hrs under a nitrogen atmosphere. The resulting mixture was evaporated to dryness and the residue was dissolved in chloroform. The solution washed successively with water, 5% NaOH and water and dried. Removal of the solvent left a residue which was washed with hot methanol to give a blue solid which was crystallized twice from n-heptane to yield IIIb as a white crystalline solid (1.63 g, 26%), mp. 126-127°.

IR: 2920, 2860, 1600, 1520, 1460, 1400, 1240-1260, 1120-1140 cm^{-1}. NMR: δ 6.91 (H_8, singlet, Ar-H); 4.27 (H_8, triplet, O-$\underline{CH_2}$-C); 2.25 (H_4, qunitet, C-$\underline{CH_2}$-C); 1.56 (H_3, singlet, C-$\underline{CH_3}$). MS: m/e 314 (M^+).

Anal. Calcd. for $C_{19}H_{22}O_4$: C, 72.61; H, 7.01. Found: C, 72.62; H, 6.98.

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