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Facile Synthesis of a Monomer 4'-Vinyldibenzo-14-Crown-4

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The rather expensive crown ether and cryptand ligands have been used to incorporate into the backbone of an insoluble polymeric network[1,2] or to attach as pendant moieties to the polymer chain[3] in order to retrieve them easily for alkali and alkaline-earth metal ion separation or catalytic purposes. To prepare a crown ether containing copolymer with vinylbenzo group, the vinyl derivatives of crown ether should be synthesized beforehand. The pioneeringly synthetic report of 4'-vinyldibenzo-18-crown-6 involved an eight-step procedure.[4] The final product was obtained with a total yield of 3.4% by reducing the acetonyl derivative of dibenzo-18-crown-6 with $NaBH_4$ and then dehydrating the resulting hydroxyethyl group with p-TsA. We have reported the synthesis of

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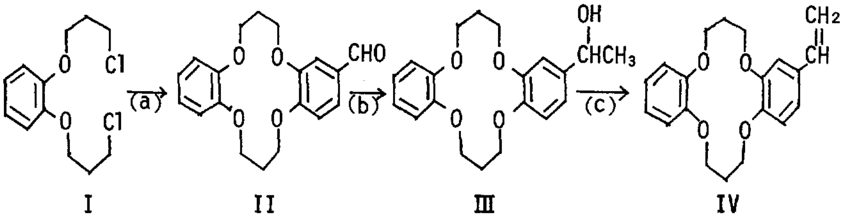
dibenzo-14-crown-4 and their derivatives which can form 1:1 stable complex with lithium ion[5-7] and found that the p-TsA as dehydrating agent did not effect the IV from Ⅲ.

Now, we wish to report that the new monomer of vinyldibenzo crown ether, IV, could be conveniently synthesized with high yield through the below reaction scheme.



Reagents: (a) 4-formylcatechol, NaOH, n-butanol, reflux 22 hrs; (b) CH_3MgI, dryether/benzene, NH_4Cl; (c) Pretreated Al_2O_3, toluene, reflux 10 hrs.

The starting material, o-bis((3-chloropropyl)oxy)benzene (I), has been synthesized in our laboratory.[5,6] Catechol was converted to o-bis((3-hydroxypropyl)oxy)benzene (yield 60%), then followed by chlorination with thionyl chloride (yield 90%). The first-step reaction of the reaction scheme with 39% yield was the combination of I with 4-formylcatechol in n-butanol in the presence of lithium perchlorate as template. The resultant aldehyde (II) was reacted with CH_3MgI to give Ⅲ, and this secondary alcohol was then dehydrated with alumina coated with sulfuric acid as catalyst to give 4'-vinyldibenzo-14-crown-4 (IV) with a total yield about 18%.

The alumina-supported sulfuric acid could readily be prepared by soaking the alumina with sulfuric acid and then evaporating to dryness. The dehydration was carried out simply by vigorous stirring of this pretreated alumina catalyst with the solution of alcohol at reflux. The product was isolated by removal of the solid reagents by filtration and then evaporation of the solvent. The effect of the different reaction conditions on the dehydration of III is shown in Table.

Table: Effect of the Different Reaction Conditions on the Dehydration of III.

Solvent	Catalyst added	Reflux time hr	NMR yield of IV %[c]
dioxane	pretreated Al_2O_3[a]	20	nil
benzene	pretreated Al_2O_3[a]	20	32 (25)[d]
benzene	p-TsA[b]	18	nil
toluene	pretreated Al_2O_3[a]	10	93 (88)[d]

a. 0.77 g pretreated Al_2O_3/1 mmol of III.

b. 0.017 g p-TsA/1 mmol of III.

c. Based on the peak of OH at $\delta = 1.6$ and those of $CH=CH_2$ at $\delta = 5.00$ and 5.42.

d. Isolated yield see experiment.

The pretreated alumina has been proved to be an effective and convenient dehydrating agent and the reaction solvent played an important role in this dehydration process. We found that only few solvents are suitable for this dehydration process. Toluene was better than dioxane and benzene as shown in Table. Dioxane with two oxygen atoms could be favorably adsorbed by alumina and prevented the alcohol derivative from being accessible to sulfuric acid coated on alumina. The reflux temperature of toluene was higher than that of benzene and favored the dehydration of III.

Experimental

Preparation of the supported sulfuric acid on Al_2O_3 — 10 g of active, neutral aluminium oxide 90 (E. Merck, 70-230 mesh), chromatography grade, was added in one portion to a magnetically stirred solution (pH = 1) of 98% sulfuric acid (0.45 g, 4.6 mmol) in 10 ml of water at room temperature. The mixture was stirred for 15 min and then dried in a rotatory evaporator. The resulting white powder was heated at 120°C for 16 hours till a constant weight. The concentration of the catalyst is 0.46 mmol H_2SO_4 on 1 g of alumina. This pretreated catalyst can be stored in a desiccator for months without losing its activity.

2,3,9,10-(4'-formyl)dibenzo-1,4,8,11-tetraoxacyclotetradeca-2,9-diene or 4'-formyldibenzo-14-crown-4 (II) — A solution of I (13.15 g, 50 mmol) in n-butanol (50 ml) was added dropwise by high-dilution method to a solution of 4-formylcatechol (6.9 g, 50 mmol), lithium perchlorate (5.32 g, 50 mmol) and sodium hydroxide (4 g, 100 mmol) in n-butanol (350 ml) at reflux under nitrogen atmosphere with vigorously stirring for 22 hours. After cooling to room temperature, the solvent was removed by means of rotatory evaporator and the solid residue was dissolved in chloroform and washed with 5% aqueous sodium hydroxide to remove the unreacted 4-formylcatechol. Then, the chloroform solution was dried over anhydrous magnesium sulfate, filtered and concentrated to give a brownish solid which was recrystallized from ethanol to give II as white needle crystals (6.40 g, 39%): mp 171-172°C; IR (KBr) ν_{max} 1675, 1600, 1500, 1200-1275 cm^{-1}; ^{1}HNMR ($CDCl_3$) δ 9.80 (1H, s, CHO), 7.18 (7H, m, Ar), 4.20 (8H, t, CH_2-O), 2.30 (4H, quint, CH_2-C); mass spectrum, m/e 328 (M^+).

Anal. Calcd for $C_{19}H_{20}O_5$: C, 69.50; H, 6.14. Found C, 69.51; H, 6.10.

2,3,9,10-[4'-(1"-Hydroxyethyl)dibenzo]-1,4,8,11-tetraoxacyclotetradeca-2,9-diene or 4'(1"-hydroxyethyl)dibenzo-14-crown-4 (III) — In a 500 ml three-necked flask fitted with a mechanical stirrer, a pressure equalized dropping funnel and a reflux condenser protected by P_2O_5 drying tube were placed magnesium turnings (0.3645 g, 15 mmol) and dry ether (20 ml) under positive nitrogen pressure. A solution of methyl iodide (2.13 g, 15 mmol) in dry ether (55 ml) was added slowly at room temperature with stirring. After all the magnesium was reacted, dry benzene (100 ml) was added. Then, a solution of II (1.72 g, 5.2 mmol) in dry benzene (200 ml) was added slowly at room temperature with stirring for a period of 24 hours. The resultant mixture was added

15% aqueous ammonium chloride. The organic layer was separated, dried with anhydrous magnesium sulfate and concentrated. The residue was recrystallized from a cosolvent of benzene-petroleum ether to give III as white crystals (1.5 g, 87.2%): mp 116-117°C; IR (KBr) ν_{max} 3400-3300, 2840-2980, 1600, 1500, 1200-1300 cm^{-1}; ^{1}HNMR ($CDCl_3$) δ 6.90 (7H, m, Ar), 4.65 (1H, q, CH), 4.41 (8H, t, CH_2-O), 2.26 (4H, quint, CH_2-C), 1.6 (1H, broad s, OH), 1.94 (3H, Cl, CH_3); mass spectrum, m/e 344 (M^+).

Anal. Calcd for $C_{20}H_{24}O_5$: C, 69.75; H, 7.02. Found C, 69.64; H, 7.06.

2,3,9,10-(4'-Vinyl)dibenzo-1,4,8,11-tetraoxacyclotetradeca-2,9-diene or 4'-vinyldibenzo-14-crown-4 (IV) — In a 50 ml flask with a reflux condenser protected by $CaCl_2$ drying tube were placed III (0.27 g, 0.78 mmol) and pretreated alumina catalyst (0.6 g, pH ≈ 1) in toluene (20 ml) at reflux for 10 hours. After cooling to room temperature, the mixture was filtered, dried with anhydrous magnesium sulfate, and filtered again and concentrated to give a slight yellow solid (0.25 g) which then was purified through a neutral alumina column with n-hexane-ethylacetate (10:1) as eluent to give white crystals (0.22 g, 88%): mp 138-139°C; IR (KBr) ν_{max} 3070, 2950, 2870, 1630, 1600, 1400, 1340, 1140, 1260, 1060, 995, 895, 740 cm^{-1}; ^{1}HNMR ($CDCl_3$) δ 2.23 (4H, quint, CH_2-C), 4.13 (8H, t, CH_2-O), 5.00 (1H, dd, J = 10 Hz, J = 2 Hz), 5.42 (1H, dd, J = 17 Hz, J = 2 Hz), 6.33 (1H, d, J = 10 Hz), 6.70 (7H, m, Ar); mass spectrum, m/e 326 (M^+).

Anal. Calcd for $C_{20}H_{22}O_4$: C, 73.60; H, 6.80. Found, C, 73.59; H, 6.59.

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