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Synthesis of 4′-Vinylbenzo-15-crown-5 from Benzo-15-crown-5

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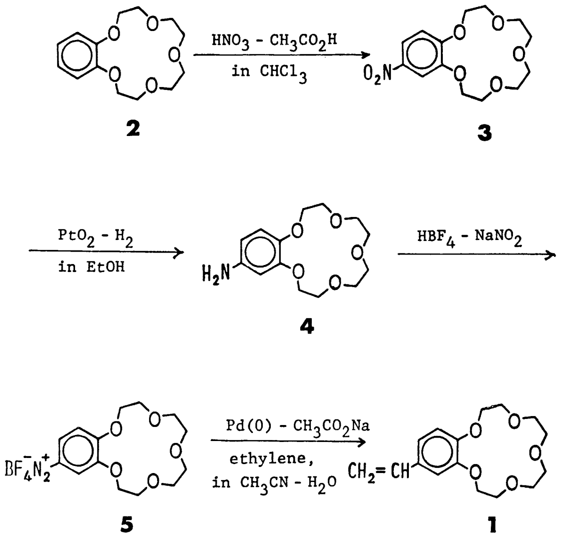
Synopsis. 4′-Vinylbenzo-15-crown-5 was conveniently synthesized in 30% yield by the reaction of diazotized 4′-aminobenzo-15-crown-5 with ethylene (6—10 kg/cm^2) in the presence of zerovalent palladium at room temperature.

Vinylbenzocrown ethers are useful monomers for the preparation of the polymers attached with crown ethers.[1)] 4′-Vinylbenzocrown ethers have been synthesized using 4-acetyl- or 4-formylcatechol as a starting material.[1,2)]

We recently reported a novel catalytic arylation of olefins with arenediazonium salts in the presence of zerovalent palladium.[3)] In view of the higher reactivity of ethylene with arylpalladium reagents, the reaction can be expected to be a convenient method to replace an amino group in primary aromatic amines with a vinyl group. It is interesting to apply this method to the vinylation of benzocrowns, since nitrobenzocrowns and thus aminobenzocrowns are readily available from the parent crown ethers.[4)]

4′-Vinylmonobenzo-15-crown-5 (**1**) was synthesized using monobenzo-15-crown-5 as a starting material in the overall yield of 20—25% (Scheme 1). 4′-Aminobenzo-15-crown-5 (**4**) which is labile to air oxidation, and its diazonium salt (**5**) were used without isolation for the subsequent reactions.



Scheme 1.

Experimental

4′-Nitrobenzo-15-crown-5 (3). This compound was prepared in 70—80% yields according to the procedure described by Smid *et al.*[4)] with some modifications. Thus, the reaction mixture was neutralized with aq NaOH and the crude product was recrystd from methanol.

4′-Aminobenzo-15-crown-5 (4) and the Diazonium Salt (5). In a glass autoclave, 7.79 g of **3** in 200 ml ethanol was hydrogenated to **4** at 30—40 °C for 8 h in the presence of 0.1 g of platinum oxide under hydrogen pressure of 8—10 kg/cm^2. After the reaction, the catalyst was filtered off under nitrogen and the ethanol was evaporated under reduced pressure. To the residue were added 30 ml of 42% HBF_4 and 140 ml of water to give a suspension of the less soluble salts. The mixture was cooled to 0 °C in an ice bath and then 1.7 g of $NaNO_2$ in 20 ml water was added dropwise at 0—5 °C under efficient stirring. The diazonium salt was soluble in water.

4′-Vinylbenzo-15-crown-5 (1). The diazotized soln was placed in a glass autoclave (500 ml), and then 100 ml of acetonitrile, 10.3 g of sodium acetate and 3.0 g of bis(dibenzylideneacetone)palladium(0) were added to the soln. After ethylene was introduced to a pressure of 6—10 kg/cm^2, the soln was stirred at room temp for 2 days. The reaction mixture was extracted with ether, and the extract was washed with satd aq $NaHCO_3$ soln followed by satd aq NaCl soln, and dried over anhyd $MgSO_4$ with the addition of 4-*t*-butylcatechol as an inhibitor. The mixture was filtered, and the filtrate was evaporated under reduced pressure. The residue was extracted several times with hot hexane, and after removal of a small amount of less soluble dibenzylideneacetone, concentration of the hexane soln gave **1** as white crystals. Yield 30% from **3**, mp 40—45 °C. Recrystallization from hexane gave pure **1**, mp 43.5—44.2 °C, which did not exhibit any depression of the mp on admixture with the authentic specimen prepared *via* 4′-acetylbenzo-15-crown-5.[1)] NMR ($CDCl_3$) $\delta=4.0$ (16H, m, $-CH_2-$), 5.3 (2H, m, vinyl $=CH_2$), 6.6 (1H, m, vinyl $-CH-$), 6.9 (3H, m, aromatic H).

References

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4) R. Ungaro, B. El Haj, and J. Smid, *J. Am. Chem. Soc.*, **98**, 5198 (1976).