

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

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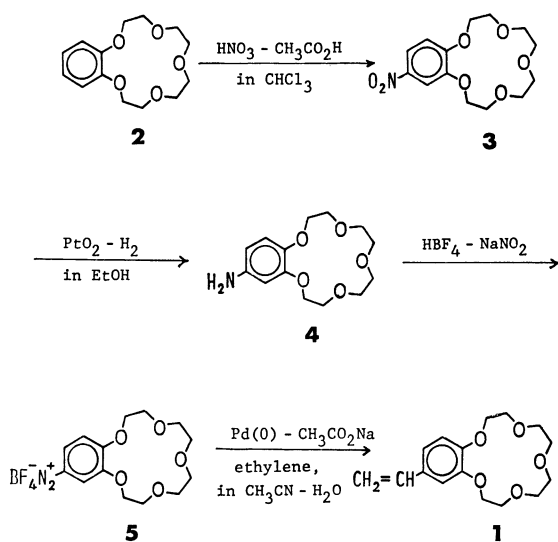
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Synopsis. 4'-Vinylbenzo-15-crown-5 was conveniently synthesized in 30% yield by the reaction of diazotized 4'-aminobenzo-15-crown-5 with ethylene (6–10 kg/cm²) in the presence of zerovalent palladium at room temperature.

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/cm². 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% HBF₄ 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 NaNO₂ 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/cm², 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 NaHCO₃ soln followed by satd aq NaCl soln, and dried over anhyd MgSO₄ 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 (CDCl₃) δ=4.0 (16H, m, -CH₂-), 5.3 (2H, m, vinyl =CH₂), 6.6 (1H, m, vinyl -CH-), 6.9 (3H, m, aromatic H).

References

- 1) S. Kopolow, T. E. Hogen Esch, and J. Smid, *Macromolecules*, **6**, 133 (1973).
- 2) J. Smid, B. El Haj, T. Majewicz, A. Nonni, and R. Sinta, *Org. Prep. Proced. Int.*, **8**, 193 (1976).
- 3) K. Kikukawa and T. Matsuda, *Chem. Lett.*, **1977**, 159.
- 4) R. Ungaro, B. El Haj, and J. Smid, *J. Am. Chem. Soc.*, **98**, 5198 (1976).