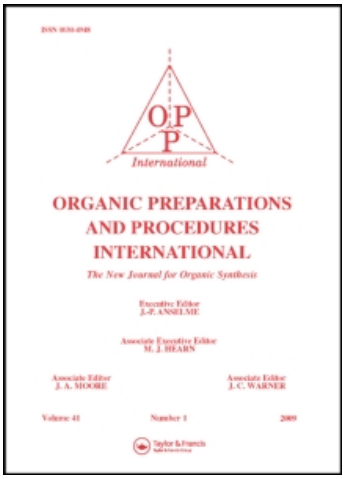

Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

SYNTHESIS OF 4'-VINYLBENZOCROWN ETHERS

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To cite this Article Smid, J. , Haj, B. El , Majewicz, T. , Nonni, A. and Sinta, R.(1976) 'SYNTHESIS OF 4'-VINYLBENZOCROWN ETHERS', Organic Preparations and Procedures International, 8: 4, 193 — 196
To link to this Article: DOI: 10.1080/00304947609355620
URL: http://dx.doi.org/10.1080/00304947609355620

ORGANIC PREPARATIONS AND PROCEDURES INT. 8(4), 193-196 (1976)

SYNTHESIS OF 4'-VINYLBENZOCROWN ETHERS

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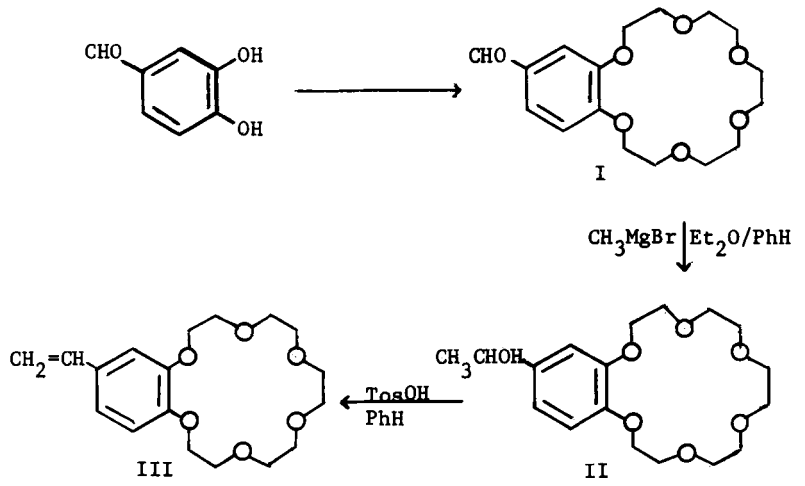
A previously reported synthesis of 4'-vinylbenzo-15-crown-5 and of 4'-vinylbenzo-18-crown-6 involved a five-step procedure.[1] Catechol was converted to 3,4-dihydroxyacetophenone by a Fries rearrangement via catechol diacetate. 3,4-Dihydroxyacetophenone was then coupled with a dichloro derivative to produce the desired crown ring and the acetyl group was reduced to the secondary alcohol which finally yielded the 4'-vinylbenzocrown ether on dehydration.

We now report a substantial improvement of this synthesis. It only requires three steps and avoids the somewhat cumbersome and often low yield Fries rearrangement. The starting material is the commercially



available 3,4-dihydroxybenzaldehyde which is converted to 4'-formylbenzo-crown ether. This aldehyde is then reacted with methylmagnesium bromide, and the resulting secondary alcohol dehydrated to yield the vinylbenzo-ether. One advantage of the use of the crown aldehydes as an intermediate lies in its easy conversion to other crown derivatives, some of which can react to form polymerizable monomers. For example, the 4'-CH_2OH derivative, obtained in high yield by reducing the aldehyde, can easily be coupled with acryloyl or methacryloyl chloride to produce the crown esters of acrylic and methacrylic acid, respectively.

EXPERIMENTAL

2,3-(4'-formylbenzo)-1,4,7,10,13,16-hexaoxacyclooctadeca-2-ene or 4'-formylbenzo-18-crown-6 (I). — To a mixture of 27.6 g (0.2 mole) of 3,4-dihydroxybenzaldehyde (Aldrich, used without purification) and 1000 ml 1-butanol, purged with nitrogen for 1/2 hr, was added 16.4 g (0.41 mole) of NaOH in 25 ml H_2O. The mixture was heated and 55 g (0.2 mole) of 1,11-dichloro-3,6,9,12-tetraoxatetradecane[2] was added dropwise over a 15 minute period. After refluxing for 24 hrs. the mixture was cooled, acidified with HCl, filtered and the solids washed with methanol. The solvents were then removed carefully by evaporation, the oily residue redissolved in chloroform, and the solution filtered and dried. After removing the chloroform the oily residue was extracted six times with a total of 1000 ml of hot heptane. Evaporation of solvent from the heptane extracts yielded an oily residue which was crystallized from 50 ml ether to yield 22 g (32%) of pure 4'-formylbenzo-18-crown-6 in the form of white needles, mp. 60-62°, NMR ($CDCl_3$), δ 3.6-4.4 (m,20,$-CH_2-$); 7.08 (d,1,H_a,J_{ab} = 9 Hz); 7.50 (s,1,H_c); 7.55 (d,1,H_b); 9.95 (s,1,CHO).

Anal. Calc. for $C_{17}H_{24}O_7$: C, 59.99; H, 7.11
Found: C, 59.70; H, 7.15

2,3-[4'-(1"-Hydroxyethyl)benzo]-1,4,7,10,13,16-hexaoxacyclooctadeca-2-ene or 4'-(1"-hydroxyethyl)benzo-18-crown-6 (II). — The Grignard reagent was prepared by adding a mixture of 17.5 g CH_3I and 50 ml dry ether to 3.0 g Mg in 25 ml dry ether. After the magnesium was dissolved, 14.0 g of I dissolved in 400 ml dry ether/100 ml dry benzene was added dropwise. A white precipitate formed immediately. The reaction mixture was heated to reflux for 1 hr after addition of I was completed, then cooled and a 15% NH_4Cl solution added until two distinct layers appeared. After separation, the aqueous layer was extracted four times with 100 ml $CHCl_3$ and the combined ethereal and chloroform layers, after drying, evaporated to dryness. The oily residue was recrystallized from 500 ml ether to yield 11.0 g (77%) of 4'-(1"-hydroxyethyl)benzo-18-crown-6 as white needles, mp. 58-59°.[3]

2,3-(4'-vinylbenzo)-1,4,7,10,13,16-hexaoxacyclooctadeca-2-ene or 4'-vinylbenzo-18-crown-6 (III). — A trace of p-toluenesulfonic acid monohydrate was added to 8.0 g of II in 350 ml benzene. The mixture was refluxed with removal of water for 14 hrs, then cooled to room temperature and 5 drops of pyridine added. The benzene was evaporated to yield an oil which crystallized upon standing after 15 minutes. The solid product was dissolved in 100 ml $CHCl_3$, extracted four times with 100 ml H_2O, and the $CHCl_3$ layer dried over sodium sulfate. The residue obtained after evaporating the $CHCl_3$ was recrystallized from petroleum ether (1 g of III to 75 ml solvent) to give 6.2 g (80%) of pure 4'-vinylbenzo-18-crown-6, mp. 59-61°.[3]

2,3-(4'-vinylbenzo)-1,4,7,10,13-pentaoxacyclopentadeca-2-ene or 4'-vinylbenzo-15-crown-5 (IV). — This compound was synthesized by the same three step procedure used for III, via 4'-formylbenzo-15-crown-5 prepared from 3,4-dihydroxybenzaldehyde and 1,11-dichloro-3,6,9-trioxaundecane. The crown aldehyde was obtained pure in 31% yield (extraction of the oily residue is often improved by using heptane-ether mixtures), and the 4'-(1"-hydroxyethyl)benzo-15-crown-5 in 84% yield. Dehydration yielded 85% of pure IV after recrystallization from petroleum ether (30-60°).[3]

ACKNOWLEDGMENT. — The financial support of this research by the National Science Foundation (Grant No. 37799) and by the donors of the Petroleum Research Fund administered by the American Chemical Society is gratefully acknowledged.

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(Received June 22, 1976; in revised form August 16, 1976)