Tetrahedron Letters Vol. 21, pp 4197 - 4198 0040-4039/80/1022-4197$02.00/0

ALTERNATIVE, SIMPLE ROUTE TO HYDROXYMETHYL CROWN ETHERS

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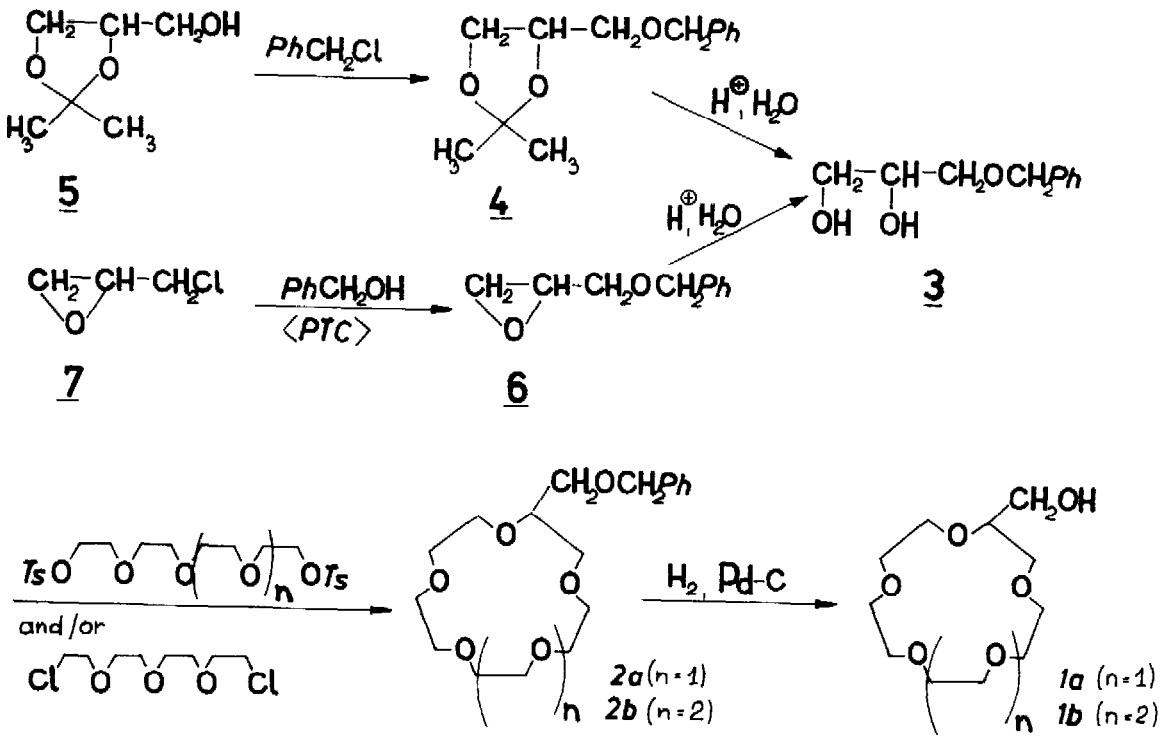
Summary: Components for polymer-supported catalysts, hydroxymethyl-substituted 15-crown-5 and 18-crown-6 were prepared from readily available starting materials on relatively simple way.

The syntheses of macrocyclic polyethers with additional functional groups allowing their immobilization on the polymer backbone, have attracted considerable attention recently[1]. Montanari and Tundo have described the multistep synthesis of hydroxymethyl 18-crown-6 by a route which is rather tedious and expensive[1a]. At the same time this compound was obtained by hydroxylation of acroleine ethyl acetal, coupling with pentaethylene glycol ditosylate and subsequent deacetalization and reduction.[2]

This communication presents an alternative and convenient method for the preparation of hydroxymethyl-substituted crown ethers. The diol component, 3-benzyloxy-1,2-propanediol 3 can be obtained on two different ways. Benzylation of commercially available 1,2-O-isopropylidene glycerol 5 with benzyl chloride followed by hydrolysis of the isopropylidene group gave the diol 3 with 84% total yield[3]. The diol 3 was also prepared by O-alkylation of benzyl alkohol with readily accessible 1-chloro-2,3-epoxypropane 7 under typical PTC conditions /TEBA, 50% NaOH/[4] and subsequent acid catalyzed oxirane ring opening / 0.05 M H_2SO_4 in acetone-water 1:1, reflux, 3h, 54% overall yield/. Reaction of 3 with tetraethylene glycol ditosylate /t-BuOK in THF, reflux, 20h/ gave benzyloxymethyl 15-crown-5, 2a /alumina, methylene chloride-chloroform 1:1, 23%/. When tetraethylene glycol dichloride /NaOH, dioxan, reflux, 24h/ was used instead of the ditosylate, 2a was obtained with significantly higher yield /35%/. The benzyl group was removed by hydrogenolysis on Pd-C catalyst /ethanol/ affording hydroxymethyl 15-crown-5, 1a almost quantitatively[6].

Similarly, coupling of 3 with pentaethylene glycol ditosylate led to formation of benzyl-



oxymethyl 18-crown-6, 2b /alumina, benzene-chloroform 2:1, 25%/ which after hydrogenolysis afforded hydroxymethyl 18-crown-6, 1b.

The method described here is attractive because of its simplicity and the relatively high total yields obtained.

References and Notes:

1. a/ F. Montanari, P. Tundo, Tetrahedron Lett., 1979, 5055 and references cited therein; b/ M. Tomoi, O. Abe, M. Ikeda, K. Kihara, H. Kakiuchi, Tetrahedron Lett., 1978, 3031.
2. S.L. Regen, B. Czech, in preparation.
3. M. Kates, T.H. Chan, N.Z. Stancel, Biochemistry, 2,394/1963/.
4. The yield of 6 was much higher than reported[5] though was not optimized.
5. M.M. Baizer, J.R. Clark, J.Swidinsky, J.Org.Chem., 22,1595/1957/.
6. All new compounds which are colourless, hygroscopic oils were characterized by ^{1}H NMR, IR and mass spectrometry and gave satisfactory analytical results.
7. This work was partly supported by the Polish Academy of Sciences /Project MRI-12/.

(Received in UK 8 August 1980)