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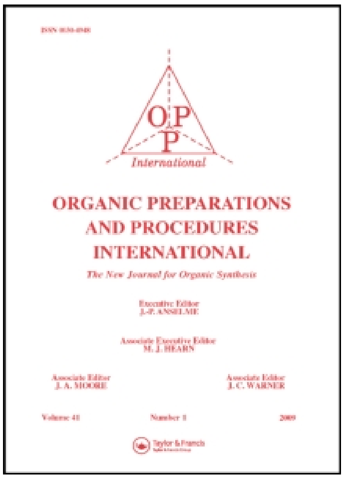

Organic Preparations and Procedures International

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

A ONE-STEP SYNTHESIS OF 1,4-BENZENEDIETHANOL

Peter W. Clark[a]; Eric J. O'reilly[b]
[a] Department of Chemistry, University of Queensland, Brisbane, Australia [b] Department of Chemistry, Queensland Institute of Technology, Brisbane, Australia

To cite this Article Clark, Peter W. and O'reilly, Eric J.(1978) 'A ONE-STEP SYNTHESIS OF 1,4-BENZENEDIETHANOL', Organic Preparations and Procedures International, 10: 4, 173 — 176
To link to this Article: DOI: 10.1080/00304947809355033
URL: http://dx.doi.org/10.1080/00304947809355033

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ORGANIC PREPARATIONS AND PROCEDURES INT. 10(4), 173-176 (1978)

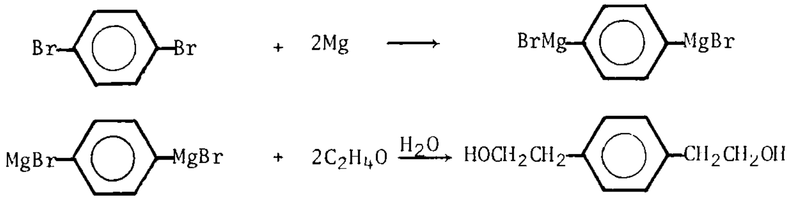
A ONE-STEP SYNTHESIS OF 1,4-BENZENEDIETHANOL

Peter W. Clark* and Eric J. O'Reilly†

*Department of Chemistry
University of Queensland
Brisbane, Australia 4067

†Department of Chemistry
Queensland Institute of Technology
Brisbane, Australia 4000

We have found, as illustrated in the scheme below, a one-step method for the preparation of 1,4-benzenediethanol starting from inexpensive compounds which results in yields of at least 50%.



Although the reaction of Grignard compounds with ethylene oxide is well known,[1] the reaction of di-Grignard aryl compounds has not been investigated. In the preparation above, ethylene oxide reacts smoothly with the di-Grignard of *p*-dibromobenzene[2,3] in THF, and upon subsequent hydrolysis gives 1,4-benzenediethanol in a good yield.

1,4-Benzenediethanol has previously been prepared by a three or four step reaction resulting in a poor overall yield of the product. The general method of preparation of 1,4-benzenediethanol has been the reaction of a *p*-α,α'dihaloxylene with potassium cyanide followed by esterification to the diester and then reduction with either a sodium-alcohol mixture or with lithium aluminum hydride to produce the dialcohol.[4-7] Other multi-step syntheses include the reduction of *p*-diacetonitrilebenzene with Raney nickel followed by the reaction with sodium nitrite,[8] and the reaction of β-acetoxyethylmercuriacetate with β-phenylethylacetate to give *p*-bis-β-acetoxyethylbenzene followed by saponification to yield 1,4-benzenediethanol.[9]

The compound 1,4-benzenediethanol has been used quite extensively in the preparation of polymers. It has been used to prepare polyester elastomers,[10,11] elastic polyisocyanate fibres,[12] linear polyethers used as light and heat stabilisers for polyvinylidenechloride,[13] cross-linked polyurethans[14] and polycarbonates.[6]

EXPERIMENTAL

p-Dibromobenzene was purchased from Koch-Light Laboratories and was used without further purification and the THF was analytical grade purchased from Merck and dried with sodium wire before use. The infrared spectrum was obtained using a Jasco IRA-2 spectrometer, the nmr spectrum obtained using a JEOL MH-100 spectrometer and the mass spectrum taken on an AEI MS 902s instrument. The analysis was carried out by the University of Queensland Micronalytical Service.

1,4-Benzenediethanol.- A solution of 250g (1.06 mol) of *p*-dibromobenzene in 1000 ml of THF was added dropwise to 60g (2.46 g-atoms) of magnesium turnings in 1500 ml of THF in a six litre three neck flask fitted with a dropping funnel, mechanical stirrer and reflux condenser. The reaction was initiated with 1,2-dibromoethane and was carried out under nitrogen. The addition of the *p*-dibromobenzene solution took 3 hrs. and the Grignard solution was then refluxed for a further 16 hrs. The solution was then cooled to room temperature. An additional 500 ml of THF were added and the water condenser was replaced by a Dry-Ice condenser. A solution of 200 ml (4.0 mol) of ethylene oxide in 300 ml of THF was then added dropwise to the di-Grignard solution whereupon the temperature of the solution rose rapidly to about 60°. The addition was controlled so that the temperature remained between 50-60°. When the addition was complete, the solution was refluxed for 6 hrs., then cooled to 0° and the addition product decomposed with ice water followed by dil. hydrochloric acid (ca. 10%) to dissolve the magnesium salts. The organic layer was separated, dried with anhydrous sodium sulphate and the solvent removed at reduced pressure. The by-product of the reaction, β-ethanolbenzene, was removed by vacuum distillation at 80° and 1mm Hg. The product remaining solidified on cooling and was recrystallised twice from boiling benzene to yield 92g (51.5%) of 1,4-benzenediethanol, mp. 85°.

IR (nujol): 3320cm^{-1}(vs), 1908cm^{-1}(vw), 1510cm^{-1}(w), 1119cm^{-1}(w), 1042cm^{-1}(s), 1018cm^{-1}(s), 835cm^{-1}(s), 778cm^{-1}(m), 660cm^{-1}(m,br), 544cm^{-1}(m).

NMR($CDCl_3$): δ ppm 7.18(4H,s, aromatic protons), 3.80(4H,t, J = 7.0 Hz, CH_2-β), 2.81(4H,t, J = 7.0 Hz, CH_2-α), 1.70(2H,s,OH protons) from internal TMS.

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49; MW:166.

Found: C, 72.02; H, 8.50; MW:166 (MS)

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(Received March 20, 1978; in revised form June 5, 1978)