

Friedel Crafts Reactions of Three-Member Heterocycles I.
Reaction of Propylene Oxide with Benzene

Norman Milstein

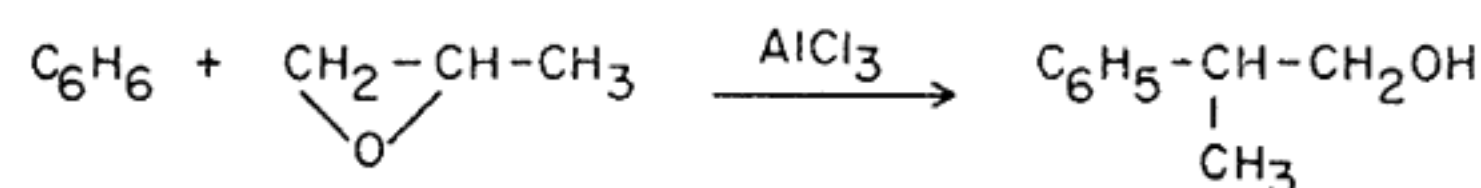
The Friedel Crafts reaction of propylene oxide with benzene has been reinvestigated, and under anhydrous conditions the product is 2-phenylpropanol.

The condensation of propylene oxide with benzene in the presence of anhydrous aluminum chloride has been the subject of controversy over the years. Smith and Natelson obtained 1,2-diphenylpropane in 46% yield, and claimed to have isolated 1-phenyl-2-propanol in 8% yield (1). However, Theimer reported the investigation of the Friedel Crafts reaction of propylene oxide with benzene, and on the basis of the Lucas test, concluded that the reaction gives the primary alcohol (2). Likhterov and Etlis reinvestigated the condensation of propylene oxide with benzene and claimed to have isolated 1-phenyl-2-propanol in 41% yield (3). These workers prepared the 3,5-dinitrobenzoate of their carbinol (m.p. 62.5°) and reported that a mixture of this derivative with the 3,5-dinitrobenzoate of the carbinol prepared from phenylmagnesium bromide and propylene oxide melted without depression. However, they did not report the yield in preparing their reference compound.

In order to rationalize the 1-phenyl-2-propanol claimed by Smith and Natelson and by Likhterov and Etlis, one would have to consider the benzene to function as a nucleophile in which the π electrons attack the aluminum chloride-coordinated propylene oxide ring at the least hindered position.

We now report that the aluminum chloride catalyzed reaction of propylene oxide with benzene under strictly anhydrous conditions gives only 2-phenylpropanol (no 1-phenyl-2-propanol) plus a trace of a high-boiling compound.

Since only 2-phenylpropanol is obtained, it is evident that the aluminum chloride-coordinated propylene oxide opens to give the most stable carbonium ion before it attacks the benzene.



EXPERIMENTAL

N.m.r. spectra were determined on a Varian Model A-60 spectrometer neat using tetramethylsilane as internal standard.

Reaction of Benzene with Propylene Oxide.

To a magnetically stirred, ice water-cooled mixture of 31.5 ml. of benzene and 7.6 g. of anhydrous aluminum chloride (0.057 mole) was added a solution of 3.3 g. of propylene oxide (0.057 mole) in 20 ml. benzene dropwise. The reaction was stirred for one hour at room temperature under dry nitrogen. The reaction mixture was poured into 125 ml. ice water, the benzene layer was separated, and the aqueous layer was extracted with benzene several times. The combined benzene extracts were dried over anhydrous magnesium sulfate, filtered; and the solvent was removed on the rotary evaporator. The residue, which was used directly to avoid possible fractionation, gives an infrared spectrum which is identical to that of authentic 2-phenylpropanol (K and K laboratories) but quite different from that of authentic 1-phenyl-2-propanol (K and K). The yield was 4.9 g. or 64% of theoretical. The isomeric 1-phenyl-2-propanol was shown by gas chromatography to be virtually absent (less than 1%) by adding some authentic material to an aliquot of the product and observing an extra peak. The identity of the K and K 2-phenylpropanol was confirmed by its n.m.r. spectrum which exhibits a singlet at 2.8 τ of relative area 5, a triplet at 5.7 τ of area 1, a complex multiplet centered at 6.5 τ of area 2, a quartet at 7.2 τ of area 1, and a doublet at 8.8 τ of area 3. Upon addition of one drop of concentrated sulfuric acid, the triplet at 5.7 disappears and a broad singlet at 3.6 τ of area 1 appears. The identity of the K and K 1-phenyl-2-propanol was confirmed by chromic acid oxidation to phenylacetone and comparison of its infrared spectrum to that of authentic phenylacetone (Hexagon Laboratories). The n.m.r.

spectrum of the phenylacetone consists of three sharp singlets:

2.8 τ (5 H), 6.5 τ (2 H), and 8.1 τ (3 H).

REFERENCES

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(3) V. R. Likhterov, and V. S. Etlis, *Zh. Obsch. Khim.*, **27**, 2903 (1957).