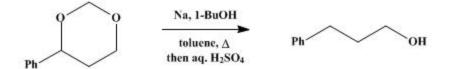
Organic Syntheses, Coll. Vol. 4, p.798 (1963); Vol. 33, p.76 (1953).

3-PHENYL-1-PROPANOL

[<u>1-Propanol, 3-phenyl-</u>]



Submitted by R. L. Shriner and Philip R. Ruby¹. Checked by Richard T. Arnold, W. E. Parham, and Hans Wynberg.

1. Procedure

In a 5-I. round-bottomed flask, equipped with two reflux condensers and a mechanical stirrer (Note 1), are placed 800 g. (925 ml.) of dry toluene and 168 g. (7.3 g. atoms) of sodium. The toluene is heated to boiling, the sodium is melted, and the stirrer is started. The source of external heat is removed, and a solution of 328 g. (2 moles) of 4-phenyl-*m*-dioxane (p. 786) in 311 g. (4.2 moles) of 1-butanol (Note 2) is added through the top of one of the condensers. The vapors should reflux about halfway up the condensers; about 30 to 60 minutes is used for the addition (Note 3). The mixture is cooled to room temperature, and a solution of 100 ml. of concentrated sulfuric acid in 800 ml. of water is added slowly with stirring. After the water layer is separated and discarded, 500 ml. of water is again added to the organic layer. Dilute sulfuric acid (5%) is added with shaking until the water layer is neutral to litmus paper. After the water layer is separated and discarded, the toluene and 1-butanol are removed from the organic layer by distillation. The remaining liquid is fractionated under reduced pressure (Note 4) to give 224–227 g. (82.2–83.4%) of 3-phenyl-1-propanol, b.p. 95–97°/0.4 mm. or 113–115°/3 mm., n_0^{20} 1.5268–1.5269, d_4^{20} 1.004–1.008.

2. Notes

1. The condenser should have a large bore to prevent flooding. A wide-sweep stirrer such as a Hershberg stirrer should be used, and the stirring motor must be capable of operating under heavy loads. The checkers suggest that the minimum size for the stirrer be 8-mm. glass rod.

2. The butanol should be freshly dried and distilled.

3. The addition must be as rapid as possible. An additional 100 to 400 ml. of toluene may have to be added to facilitate stirring.

4. A heated 35-cm. Vigreux column is recommended, but a Claisen flask can be used if care is taken. If a Claisen flask is used, the distillation must not be carried out too rapidly, particularly near the end, at which point some of the residue tends to codistil.

3. Discussion

<u>Ethyl cinnamate</u> has been reduced to <u>3-phenyl-1-propanol</u> with <u>sodium</u> and <u>ethanol</u>, 2,3,4,5 <u>hydrogen</u> and <u>copper chromite</u>, 6 and <u>sodium</u> and <u>ammonia</u>. The alcohol has also been prepared by reduction of the glyceride of cinnamic acid with <u>sodium</u> and <u>amyl alcohol</u>; ⁸ by reduction of <u>cinnamic acid</u> with <u>lithium aluminum hydride</u>; ⁹ by reduction

of <u>cinnamoyl chloride</u> with <u>sodium borohydride</u>; 10 and by reduction of ethyl dihydrocinnamate with sodium and ethanol.^{2,11} Cinnamaldehyde has been reduced to 3-phenyl-1-propanol with hydrogen and palladium.^{12,13} platinum,^{14,15,16} or nickel, ^{17,18,19,20} nickel in alkaline solution (no hydrogen), ²¹ lithium aluminum hydride, ²² electrolysis at a mercury²³ or lead²⁴ electrode, and with an unmentioned catalyst.²⁵ Reduction of cinnamyl alcohol to 3-phenyl-1-propanol has been effected by use of sodium and ethanol,²⁶ sodium amalgam and water,^{27,28} hydrogen and nickel²⁹ or palladium,³⁰ sodium and ammonia, $\frac{31}{2}$ and lithium aluminum hydride. $\frac{32}{2}$ Other syntheses have been brought about by reduction of ethyl a, β-epoxy-β-phenyldihydrocinnamate with sodium and amyl alcohol; 33 by reduction of ethyl benzoylacetate with hydrogen and copper chromite; ³⁴ by reduction of acetonephenyllactic acid with hydrogen and copper chromite; $\frac{35}{25}$ by reaction of ethyl alcohol with sodium benzylate; $\frac{36}{25}$ by reaction of benzylmagnesium chloride with a mixture of ethylene chlorohydrin and ethylmagnesium chloride; ³⁷ by reaction of trimethylene oxide with phenylmagnesium bromide; ³⁸ by condensation of benzylmagnesium chloride with ethylene oxide; $\frac{39}{29}$ and by hydrogenolysis of 1-phenyl-1.3-propanediol over nickel-on-kieselguhr. 40

The reduction of <u>4-phenyl-m-dioxane</u> to give <u>3-phenyl-1-propanol</u>, as described here, is based on the procedure of Beets, $\frac{41}{1}$ who used <u>sodium</u> and <u>diisobutylcarbinol</u>. Other substituted *m*-dioxanes may also be converted to substituted 3-aryl-1-propanols by the same procedure. $\frac{42}{3}$ <u>3-Phenyl-1-propanol</u> also has been obtained in 85% yield by the reduction of <u>4-phenyl-*m*-dioxane</u> over <u>copper chromite</u> catalyst. $\frac{43}{3}$

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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

glyceride of cinnamic acid

ethyl dihydrocinnamate

ethyl a, β-epoxy-β-phenyldihydrocinnamate

acetonephenyllactic acid

ethyl alcohol,

<u>ethanol</u> (64-17-5)

sulfuric acid (7664-93-9)

<u>ammonia</u> (7664-41-7)

hydrogen (1333-74-0)

<u>lead</u> (7439-92-1)

<u>mercury</u> (7439-97-6)

platinum (7440-06-4)

butanol,

<u>1-butanol</u> (71-36-3)

<u>nickel</u> (7440-02-0)

toluene (108-88-3)

sodium (13966-32-0)

palladium (7440-05-3)

Ethylene oxide (75-21-8)

benzylmagnesium chloride (6921-34-2)

Phenylmagnesium bromide (100-58-3)

Ethyl cinnamate (103-36-6)

cinnamic acid (621-82-9)

ethylene chlorohydrin (107-07-3)

<u>cinnamaldehyde</u>

Trimethylene oxide (503-30-0) amyl alcohol (71-41-0) COPPER CHROMITE Ethyl benzoylacetate (94-02-0) cinnamyl alcohol (104-54-1) lithium aluminum hydride (16853-85-3) cinnamoyl chloride 3-Phenyl-1-propanol, 1-Propanol, 3-phenyl- (122-97-4) sodium borohydride (16940-66-2) sodium benzylate ethylmagnesium chloride (2386-64-3) 1-phenyl-1,3-propanediol diisobutylcarbinol (108-82-7) 4-Phenyl-m-dioxane (3141-24-0) Copyright © 1921-2005, Organic Syntheses, Inc. All Rights Reserved