

Summary

1. The enol-acetates of ethyl acetoacetate and benzoylacetone were prepared and reduced with hydrogen and platinum-oxide platinum black in glacial acetic acid. Two mole equivalents of hydrogen were absorbed and there resulted ethyl butyrate and butyrophenone, respectively.

2. The enol-acetates of 1-phenylpentadione-1,3 and 1-phenylhexadione-1,3 were also reduced in a similar manner. A mixture of phenylbutylcarbinol and its acetate was obtained in the first case and phenylamylcarbinol and its acetate in the second.

3. Butyrophenone and valerophenone when reduced catalytically with platinum-oxide platinum black in glacial acetic acid yielded similar mixtures.

4. Ethyl β -aminocrotonate upon catalytic reduction with platinum-oxide platinum black and hydrogen in glacial acetic acid gave ethyl β -acetamidobutyrate. This latter substance upon partial hydrolysis and decomposition by heating gave ethyl crotonate.

5. A similar experiment with ethyl β -amino- α -butylcrotonate gave ethyl β -acetamido- α -butylbutyrate. This product was completely hydrolyzed and the β -amino- α -butylbutyric acid distilled. α -Butylcrotonic acid resulted.

6. These procedures were developed for determining the constitution of the enol-acetates and vinylamine products formed from 1,3-dicarbonyl compounds.

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THE ACTION OF ALIPHATIC OXIDES ON AROMATIC COMPOUNDS. THE PREPARATION OF SUBSTITUTED DIBENZYLs

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Because of the occurrence of the dibenzyl residue in many of the isoquinoline alkaloids, such as narcotine,¹ hydrastine,² berberine,³ corydaline,⁴ papavarine,⁵ laudanosine,⁶ morphine⁷ and probably emetine, research was undertaken with the intent of finding a general method for the syn-

¹ Perkin and Robinson, *J. Chem. Soc.*, **99**, 776 (1911).

² Freund, *Ber.*, **20**, 2403 (1889).

³ Pictet and Gams, *Compt. rend.*, **153**, 386 (1911).

⁴ Dobbie and Lauder, *J. Chem. Soc.*, **83**, 605 (1903).

⁵ Pictet and Gams, *Compt. rend.*, **149**, 210 (1909).

⁶ Pictet and Finkelstein, *ibid.*, **148**, 295 (1909).

⁷ Faltis, *Arch. Pharm.*, **255**, 85 (1917).

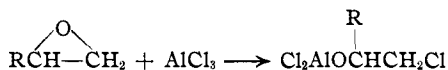
thesis of such alkaloid types starting with substituted dibenzyls. It was therefore necessary to investigate the various methods used for the preparation of the dibenzyls; a survey of the literature revealed that there was no simple, general method applicable to the preparation of multisubstituted dibenzyls. A very promising method was one reported by Silva,⁸ in which ethylene and propylene chloride were treated with benzene in the presence of aluminum chloride to yield dibenzyl and α -methyl dibenzyl. Another, somewhat similar and more interesting, method which also appeared promising was indicated by Schaarschmidt, Hermann and Szenzo.⁹ These authors bubbled a solution of hydrogen chloride in ethylene oxide into a mixture of aluminum chloride and benzene, and obtained dibenzyl. This method was the one chosen for study. It is apparent that, if this reaction is a general one, it is only necessary to prepare substituted benzenes in order to obtain corresponding substituted dibenzyls.

The experimental method of these authors was investigated, but due to the relatively complicated apparatus and procedure necessary, it was found desirable to modify and simplify the mode of procedure. The use of hydrogen chloride was eliminated, and an excess of benzene was used rather than an excess of ethylene oxide. The reaction was then carried out as is an ordinary Friedel-Crafts reaction, the ethylene oxide being added to a mixture of benzene and aluminum chloride. By the use of this simpler method the yields were improved.

The previous workers indicated that β -phenylethyl alcohol, rose oil, was obtained in small yields (1%). The authors also noticed the formation of this product, but in slightly increased yields.

This reaction was then applied to ethylene oxide and bromobenzene with the object of determining whether this reaction was a general one for aromatic compounds. Excellent yields of the corresponding dibenzyl were obtained. To see whether the reaction was also a general one for oxides, propylene oxide was condensed with both benzene and bromobenzene. In both cases satisfactory yields of the corresponding substituted methyl dibenzyls were obtained. In the cases of the bromobenzene condensations, the small quantities of the substituted phenylethyl alcohols which probably formed were ignored.

The course of the reaction may be represented according to the following scheme. Aluminum chloride probably adds to the oxide, as represented



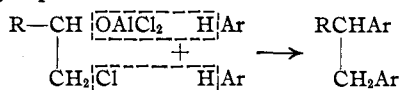
This addition product then condenses either with one molecule of the aromatic compound with the ultimate formation of a β -phenylethyl alcohol

⁸ Silva, *Jahresbericht über die Fortschritte der Chemie*, 606 (1879).

⁹ Schaarschmidt, Hermann and Szenzo, *Ber.*, **58**, 1914 (1925).



or with two molecules of the aromatic compound with the formation of a dibenzyl. The major portion of the reactants reacts in this manner.



Experimental

The experimental procedure for all the condensations mentioned herein was, in general, the same. To one mole of freshly sublimed powdered aluminum chloride contained in a flask fitted with an efficient reflux condenser, was added six moles of the aromatic compound. To this mixture was then added drop by drop one mole of the oxide. Since the reaction was very vigorous in all cases, it was necessary to cool the reaction vessel with cold water from time to time to prevent too violent a reaction and to prevent loss of the easily volatile oxide. Reaction always took place immediately upon the addition of the oxide. The whole was then refluxed on a steam-bath until the evolution of hydrogen chloride ceased, usually about two hours. In all cases it was observed that the aluminum chloride went into solution with the formation of a dark colored mass. After cooling, the reaction mass was cautiously poured upon crushed ice. The oily layer was separated and the excess aromatic compound removed by distillation on a water-bath, either with or without the aid of a vacuum dependent upon the nature of the compound used. The reaction products were then isolated from the residue by fractional distillation, or by direct recrystallization.

I. Benzene and Ethylene Oxide

Beta-Phenylethyl Alcohol.—After the reaction mass formed by the action of ethylene oxide on benzene in the presence of aluminum chloride was treated with crushed ice, the oily layer which separated was added to powdered, anhydrous calcium chloride. This was allowed to stand for two days, filtered and the residue washed free of adhering mother liquid with anhydrous ether. The calcium chloride addition product was then thrown upon water and the oily layer which separated was removed, dried with anhydrous sodium sulfate and purified by vacuum distillation. A colorless liquid was obtained with an odor resembling that of roses. The yield for one-half molar quantities of oxide was 3 g. (approximately 5%); b. p. 95–100° at 10 mm.; sp. gr. 20°, 1.033; n_D^{21} 1.5200.¹⁰

Dibenzyl.—The oily liquid which was filtered from the calcium chloride addition product was placed in a distillation flask and fractionally distilled. The fraction boiling from 279–285° was collected. On cooling the distillate solidified in the collecting flask. On recrystallizing from alcohol, prisms were obtained which melted at 52°.¹¹ The yield was 59 g. from one-half mole of ethylene oxide, or approximately 65%.

¹⁰ Bouveault and Blanc, *Compt. rend.*, 137, 61 (1898).

¹¹ Cannizzaro and Rossi, *Ann.*, 121, 251 (1862).

II. Bromobenzene and Ethylene Oxide

4,4'-Dibromodibenzyl.—Bromobenzene and ethylene oxide were reacted as was described in the general procedure. After treatment with ice, the excess bromobenzene was removed by distillation *in vacuo*, and the dark colored solid reserved. This solid was recrystallized from alcohol, in which it was difficultly soluble. Very fine white prisms were obtained which melted at 115°. The yield was as high as 70% of the theoretical. No attempt was made to isolate the alcohol, although an odor of roses was discernible.

III. Benzene and Propylene Oxide

1-Phenyl-2-hydroxypropane.—This product was separated from the reaction mixture obtained by condensing propylene oxide with benzene in the presence of aluminum chloride. The oily layer obtained after treatment with ice was fractionally distilled. The portion boiling at 210–214° was retained. The material was then redistilled in a vacuum; the colorless liquid obtained had an odor resembling rose oil; yield, 8%; b. p. 102° at 10 mm.; n_D^{21} 1.5433; sp. gr. 1.023 at 21°.

Methylidibenzyl.—After the alcohol had been removed by distillation, the remainder of the oil (obtained from propylene oxide and benzene) was vacuum distilled. The major portion of the liquid distilled in the neighborhood of 147° at 10 mm. A pleasant odored water-white liquid was obtained. The yield was approximately 46%. Here again the physical constants agree with those reported by earlier investigators; b. p. 147° at 10 mm.; n_D^{20} 1.5700; sp. gr., 0.990 at 21°.

IV. Bromobenzene and Propylene Oxide

***p,p'*-Dibromomethylidibenzyl.**—Propylene oxide and bromobenzene were reacted as was described in the general procedure. After treatment with ice, the excess bromobenzene was removed in a vacuum and the dark colored residue reserved. This residue was recrystallized from alcohol. Colorless plates were obtained in a 32% yield. Since this compound was the first member of the series which had not been previously known, it was necessary to analyze for halogen to establish its identity further; m. p. 95°.

Anal. Calcd. for $C_{15}H_{14}Br_2$: Br, 45.20; Found: Br, 45.41.

Summary

A general method for the preparation of compounds in the dibenzyl series has been described.

It has been shown that aliphatic oxides undergo a condensation with aromatic compounds in the presence of aluminum chloride. This reaction appears to be a general one for aromatic compounds and for oxides of the ethylenic oxide type.

Substituted phenylethyl alcohols are obtained as a by-product in the above reaction.

Further research in this field is being conducted.

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¹² Stelling and Fittig, *Ann.*, 137, 267 (1866).

¹³ Tiffeneau and Fourneau, *Compt. rend.*, 146, 699 (1907).

¹⁴ Klages, *Ber.*, 35, 2648 (1902).