and alloy are then ground with about No. 180 carborundum on a flat, hard surface until the desired sharp edge is obtained.

To remove the Wood's metal from the tube and the small capillary opening it is only necessary to put the tip end into a test tube immersed in boiling water and allow the alloy to melt. The latter is then ready for another tube.

The effective radius of the glass tip is generally determined by getting the average weight of drops of water given at a definite temperature. Hence it is quite possible by a proper selection of a capillary tube with suitable size of wall and comparatively circular cross section to omit the previous grinding of the lateral surface. This gives a tip with a sharp edge and the glazed wall makes creeping impossible. Such tips can certainly be substituted for the more expensive ones where only a fair degree of accuracy is wanted and where a considerable outlay of money or waste of time would be involved in getting a proper assortment of sizes.

The method of grinding just outlined is especially useful when it becomes necessary to regrind a much-needed tip whose face has become slightly chipped.

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ACTION OF AROMATIC ALCOHOLS ON AROMATIC COMPOUNDS IN THE PRESENCE OF ALUMINUM CHLORIDE. II.

SECONDARY ALCOHOLS.

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The first article of this series[1] dealt with the condensation of a primary aromatic alcohol, benzyl alcohol, with benzene, using anhydrous aluminum chloride as a dehydrating agent.

In the present paper experiments are described in which some secondary alcohols were allowed to react with benzene under the influence of the same dehydrating agent. Three alcohols were studied. Two of these, methylphenylcarbinol and ethylphenylcarbinol, may be regarded as mixed aromatic aliphatic alcohols. The third, diphenylcarbinol or benzhydrol, is a true secondary aromatic alcohol. A comparative study of these three compounds should, therefore, give us some idea as to the relative effects of aryl and alkyl groups upon the reaction at hand.

It has been shown in the first article that the principal product of the reaction between benzyl alcohol and benzene in the presence of aluminum chloride is diphenylmethane.

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[1] THIS JOURNAL, 38, 2527 (1916).

$$C_6H_5CH_2OH + C_6H_6 \xrightarrow{AlCl_3} C_6H_5CH_2C_6H_5 + H_2O.$$

If equimolecular amounts of the reacting substances are used, the yield of diphenylmethane is not large (about 30%) and the yields of secondary products (*p*- and *o*-dibenzylbenzene, anthracene and tar) are quite large. If, however, an excess (5 mols) of benzene is used the yield of diphenylmethane is greatly increased, while the yields of secondary products are correspondingly decreased.

A rather large number of experiments was made with methylphenyl carbinol, benzene and aluminum chloride, in which the relative amounts of the reacting substances were varied over a wide range. In each case there was formed a considerable amount of 1,1-diphenylethane, as represented by the following equation:

$$C_6H_5CHOHCH_3 + C_6H_6 \xrightarrow{AlCl_3} (C_6H_5)_2CHCH_3 + H_2O$$

If equimolecular amounts of the reagents were used and the aluminum chloride was added in such quantities that the temperature was kept between 25° and 35° the yield of 1,1-diphenylethane was small (about 20%) and secondary products were formed in large amounts. These last consisted of ethylbenzene, diphenylmethane, anthracene and a tarry residue from which we were unable to isolate fractions of constant boiling point.

Since aluminum chloride has the property of eliminating phenyl groups from substituted methane derivatives,[1] we believe that we are justified in the assumption that the ethyl benzene was formed as a result of the elimination of a phenyl group from 1,1-diphenylethane under the influence of aluminum chloride.

The yield of diphenylmethane was small and its separation from 1,1-diphenylethane was very difficult. We were able, however, after more than 25 distillations, to obtain a small amount of the compound which was identified by its boiling point and oxidation to benzophenone. It was probably formed by the elimination of the methyl group of 1,1-diphenylethane, under the influence of aluminum chloride.

Anthracene is a product of the reaction between diphenylmethane and aluminum chloride. Its formation in this reaction was probably preceded by the formation of diphenylmethane. Methylphenylcarbinol or 1,1-diphenylethane would be expected to yield a homolog of anthracene and not anthracene itself.[2]

An experiment in which one molecular equivalent of methylphenylcarbinol was allowed to react with 5 molecular equivalents of benzene and 0.5 molecular equivalent of aluminum chloride, and in which the temperature was kept below 40°, gave a larger yield of 1,1-diphenylethane

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[1] Silva, *Bull. soc. chim.*, [2] 41, 448 (1884); Auger, *Ibid.*, [2] 47, 49 (1887); Meyer and Jacobson, "Lehrbuch der Organischen Chemie," 3, 113; etc.

[2] Radziewanowski, *Ber.*, 27, 3238 (1894); Anschutz, *Ann.*, 235, 305 (1886).

(about 30%), a small amount of ethylbenzene (about 10%), only a trace of anthracene and a small amount of tarry residue.

The best yields of 1,1-diphenylethane were obtained by keeping the temperature below 10° and using one-half of a molecular equivalent of aluminum chloride to one molecular equivalent of methylphenylcarbinol and 5 of benzene. In these experiments from 8 to 10% of the alcohol was recovered unchanged and the yield of 1,1-diphenylethane was almost 65%. Only about 4 to 5% of the theoretical amount of ethylbenzene was isolated. We were not able to isolate diphenylmethane or anthracene. The amount of residual tar was quite small.

In all of the experiments with ethylphenylcarbinol, benzene and aluminum chloride, an excess (5 mols) of benzene was used, the temperature and amounts of aluminum chloride being varied.

When one molecular equivalent of ethylphenylcarbinol was mixed with benzene in excess and one molecular equivalent of aluminum chloride was added in such quantities that the temperature was between 35° and 40°, 10 to 12 % of the alcohol was recovered unchanged. A yield of 23 to 25% of 1,1-diphenylpropane was obtained.

$$C_2H_5CHOHC_6H_5 + C_6H_6 \xrightarrow{AlCl_3} C_2H_5CH(C_6H_5)_2 + H_2O.$$

Propylbenzene was formed to the extent of about 14% of the theory by the elimination of a phenyl group from the 1,1-diphenylpropane. Diphenylmethane was formed to the extent of about 7% by the elimination of the ethyl group. Anthracene was isolated from the high boiling fraction equal in weight to about 5% of the weight of the ethylphenylcarbinol decomposed.

When the experimental conditions were the same as those just described except that the amount of aluminum chloride was reduced to a little more than 0.5 molecular equivalent and the temperature was kept below 10°, about 15% of the alcohol was recovered unchanged. The yield of 1,1-diphenylpropane was increased to about 40% of the theory. The propylbenzene amounted to about 12% and the diphenylmethane to about 4% of the theory. No evidence of the formation of anthracene was found under these conditions. If the temperature of the reacting mixture was allowed to rise to 40° the yield of 1,1-diphenylpropane was decreased while the yields of propylbenzene, diphenylmethane and tarry residue were correspondingly increased.

The condensation of benzhydrol with benzene under the influence of aluminum chloride takes place more rapidly and completely than does the condensation of either methylphenylcarbinol or ethylphenylcarbinol. One molecular equivalent of benzhydrol, 5 of benzene and one of aluminum chloride react at 35–40° to give a yield of about 40% of triphenylmethane:

$$(C_6H_5)_2CHOH + C_6H_6 \xrightarrow{AlCl_3} (C_6H_5)_3CH + H_2O$$

together with about 15% of the theoretical amount of diphenylmethane. If the aluminum chloride was added in smaller portions while the temperature was kept below 10° by cooling in ice, the yield of triphenylmethane was increased to between 65 and 70% and the amount of diphenylmethane formed was very small (about 1%).[1]

The Friedel and Crafts method for preparing triphenylmethane from chloroform benzene and aluminum chloride[2] is open to the objection that the heating of the reaction mixture brings about the formation of considerable amounts of diphenylmethane and tarry residue. By the use of benzhydrol, benzene and aluminum chloride at low temperatures, there is practically no diphenylmethane formed and the tarry residue is very small. The product is practically pure after one crystallization from alcohol.

From the experimental evidence here presented we may conclude that methyl and ethyl groups interfere to some extent with the condensation of aromatic alcohols with benzene and that the ethyl group has a greater retarding effect than the methyl group. The presence of a second phenyl group in the carbinol molecule on the other hand does not seem to interfere in any way with the condensation. It would rather appear that benzhydrol condenses with benzene more readily than does benzyl alcohol.

Secondary alcohols of the type used in these reactions are very easily prepared from aromatic aldehydes and alkyl or aryl halides by the Grignard synthesis. The method should, therefore, be valuable as a general method for the preparation of derivatives of diphenylmethane and triphenyl methane.

Work in this field is being continued.

Experimental.

Materials.—Methylphenylcarbinol was prepared from benzaldehyde and methyl iodide by the Grignard reaction. It was dried over anhydrous potassium carbonate and purified by fractionation under diminished pressure. It boiled at 100–102° under 18 mm. Ethylphenylcarbinol was prepared in a similar manner from benzaldehyde and ethyl bromide. It distilled at 106–108° under 18 mm. Benzhydrol was prepared from benzaldehyde and phenyl bromide. It was purified by recrystallization from alcohol. It melted at 68°. Commercial benzene was fractionated 3 times with an 8-inch column. Only that portion which came over between 80° and 81° was used. The anhydrous aluminum chloride was a commercial product.

Methylphenylcarbinol, Benzene and Aluminum Chloride, I.—Fifty

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[1] The use of a smaller amount of aluminum chloride did not materially affect the yield of triphenylmethane and the purification was more difficult because of a small amount of unchanged benzhydrol.

[2] *Compt. rend.*, 84, 1451 (1877).

grams of methylphenylcarbinol were added to 40 g. of benzene. This mixture was cooled and constantly stirred by a motor. Aluminum chloride was added in small portions until 25 g. had been added. The temperature remained at 25–35° during the hour required for the addition of the dehydrating agent. The mixture became dark colored and pasty and developed a slight fluorescence. Much hydrochloric acid was given off. After standing 10 days the pasty mass was decomposed with ice water and extracted with ether. The ether extract was dried over calcium chloride. The ether was distilled off and the residue fractionated at atmospheric pressure.

THIRD FRACTIONATION.

125–150°,	2.0 g.
150–225°,	1.5 g.
225–300°,	15.1 g.
300–370°,	3.0 g.
Residues	23.2 g.

The fractions 125–150° from 3 experiments were combined and redistilled. Most of the distillate came over between 135° and 140°. It was oxidized with dilute nitric acid (10%). A good yield of benzoic acid (m. p. 120–121°) was obtained. The distillate was, therefore, ethylbenzene.[1]

The fraction 150–225° was mostly unchanged methylphenylcarbinol.

The fractions 225–300° from 2 experiments were combined and fractionated more than 20 times. One fraction, collected between 255° and 266°, weighed 4.1 g. Most of it came over at 260–263°. It solidified when cooled below 20° and had the odor and appearance of diphenylmethane. On oxidation with potassium dichromate and sulfuric acid it yielded benzophenone. Most of the remainder of the 225–300° fraction came over at 268–270°. When oxidized with chromium trioxide and acetic acid it yielded benzophenone. Analysis for carbon and hydrogen gave the following:

Subst. 0.1558; CO_2, 0.5301; H_2O, 0.1064.

Calc. for $C_{14}H_{14}$: C, 92.25; H, 7.74. Found: C, 92.72; H, 7.64.

It is, therefore, 1,1-diphenylethane.

Fraction 300–375°, on redistillation, partially solidified in the receiver. It was freed from adhering oil by pressing between filter papers, and sublimed. The sublimate melted at 212–215° and was oxidized with chromium trioxide and acetic acid to anthraquinone. This melted after recrystallization from acetic acid at 276–277°. Fraction 300–375° was therefore mostly anthracene.

Methylphenylcarbinol, Benzene and Aluminum Chloride, II.—Fifty g. of methylphenylcarbinol were mixed with 160 g. of benzene. The mixture was stirred and 35 g. of aluminum chloride were added in such portions

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[1] Silva (*Loc. cit.*) obtained ethyl benzene as a by-product of the reaction between CH_3CHCl_2, C_6H_6 and $AlCl_3$.

that the temperature did not rise above 35°. The reaction was quite smooth. Hydrochloric acid was given off and the mixture became dark colored due to the presence of a finely divided precipitate. This settled out slowly. After 5 days the mixture was decomposed with ice and dilute hydrochloric acid. The benzene portion was separated off, and the aqueous portion extracted with ether. The ether was distilled from the extract and the residue was added to the benzene portion. This was dried over calcium chloride and fractionated at atmospheric pressure.

FIFTH FRACTIONATION.

60–100°,	54.0 g.
100–150°,	4.0 g.
150–210°,	0.4 g.
210–300°,	22.6 g.
Residue	14.6 g.

Fraction 60–100° was found to consist largely of unchanged benzene. Fraction 100–150° came over mostly between 133° and 140° and was identified by the method already described as ethylbenzene. Fraction 150–210° had the odor of methylphenylcarbinol. Fraction 210–300° was repeatedly fractionated and was found to consist almost entirely of 1,1-diphenylethane. We were able to isolate but a small amount of anthracene from the residue.

Methylphenylcarbinol, Benzene and Aluminum Chloride, III.—The same weights of the alcohol and benzene were used as in the preceding experiment. The mixture was cooled in ice and treated with 33 g. of aluminum chloride. The temperature was kept below 10° except for a short time when it rose to 12°. After 8 days' decomposition, separation, extraction and fractionation were carried out as in the preceding experiment.

SIXTH FRACTIONATION.

60–100°,	110.0 g.
100–150°,	2.3 g.
150–210°,	4.1 g.
210–300°,	41.0 g.
Residue	6.2 g.

As before these fractions were found to consist of benzene, ethylbenzene, methylphenylcarbinol and 1,1-diphenylethane. No anthracene was isolated from the small tarry residue.

Ethylphenylcarbinol, Benzene and Aluminum Chloride, I.—Fifty grams of ethylphenylcarbinol were dissolved in 145 g. of benzene. While the solution was stirred 60 g. of aluminum chloride were added in such portions that the temperature remained between 35° and 40°. The mixture turned brick-red and then a very dark red. The last 20 g. of the chloride were added quite rapidly and caused very little increase in temperature. After standing 5 days at room temperature the mixture was decomposed with ice and dilute hydrochloric acid. The upper (benzene) layer was separated. The aqueous portion was extracted with ether and the residue from the ether extract was added to the benzene portion. After drying over calcium chloride this was fractionated.

TENTH FRACTIONATION.

60–120°,	117.0 g.
120–180°,	5.5 g.
180–225°,	5.6 g.
225–268°,	4.1 g.
268–300°,	16.1 g.
Residue	10.2 g.

The first fraction was unchanged benzene. Practically all of the second fraction (120–180°) came over at 159–162°. Dilute nitric acid oxidized it to benzoic acid. It was therefore, propylbenzene.[1] The third fraction distilled at 210–216°. It was identified by its odor and by oxidation to ethylphenylketone as unchanged ethylphenylcarbinol. The fraction 225–268° was identified as diphenylmethane. The last fraction came over at 273–275° at atmospheric pressure. Under 11 mm. pressure it distilled at 139°.[2] It was oxidized by chromium trioxide and acetic acid to benzophenone.

Subst., 0.1592; CO_2, 0.5361; H_2O, 0.1115.

Calc. for $C_{15}H_{16}$: C, 91.78; H, 8.22. Found: C, 91.83; H, 7.93.

It was therefore 1,1-diphenylpropane. The residue was heated in a distilling flask to 370°. About 4.6 g. of impure anthracene came over. This was purified by sublimation and identified by its melting point and oxidation to anthraquinone.

Ethylphenylcarbinol, Benzene and Aluminum Chloride, II.—Fifty grams of the alcohol and 150 g. of benzene were cooled in ice and treated with 30 g. of aluminum chloride. The dehydrating agent was added in such quantities that the temperature remained below 10° except for a brief period when it rose to 13.5°. After 12 days the mixture was decomposed with ice water and fractionated in the usual manner.

TENTH FRACTIONATION.

60–125°,	114.0 g.
125–180°,	4.6 g.
180–230°,	7.4 g.
230–268°,	2.2 g.
268–290°,	24.2 g.
Residue	8.4 g.

The fractions were identified as benzene, propylbenzene, ethylphenylcarbinol, diphenylmethane and 1,1-diphenylpropane, respectively. We were unable to isolate anthracene from the residue.

Benzhydrol, Benzene and Aluminum Chloride, I.—Twenty-five grams of benzhydrol were dissolved in 53 g. benzene and treated with 18 g. of

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[1] Silva, *Loc. cit.*

[2] Klages, *Ber.*, **37**, 1447 (1904).

aluminum chloride in small portions. The reaction was quite vigorous and hydrochloric acid was given off rapidly. The temperature remained between 30° and 40° except for a brief period when it went to 45°.

After 3 days the dark-colored intermediate compound was decomposed with ice and dilute hydrochloric acid. It formed a semicrystalline yellow oil. The whole was extracted with ether. The extract was dried over calcium chloride and distilled. The temperature rose rapidly from 100° to 240°.

FOURTH FRACTIONATION.

240-275°,	3.2 g.
275-325°,	0.8 g.
325-370°,	13.7 g.
Residue (tar)	6.3 g.

The first fraction was identified as diphenylmethane. The third fraction solidified in the receiver. It was recrystallized from alcohol and identified by melting point, oxidation to triphenylcarbinol (m. p. 157-159°) and analysis as triphenylmethane.

Subst. 0.1662; CO_2, 0.5694; H_2O, 0.1004.

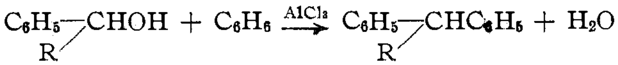
Calc. for $C_{19}H_{16}$: C, 93.39; H, 6.61. Found: C, 93.42; H, 6.74.

Benzhydrol, Benzene and Aluminum Chloride, II.—The condition of the previous experiment was duplicated, with the exception that the solution of benzhydrol was cooled in ice while the chloride was added. The temperature remained at 8° most of the time. It was never above 10°. After 3 days the mixture was decomposed and extracted with ether.

On distillation nothing came over between 120° and 290°. Between 290° and 330°, 1.8 g. of distillate came over which solidified in the receiver. After pressing between filter papers to remove the small amount of adhering oil (odor of diphenylmethane) the solid was recrystallized twice from alcohol. It melted sharply at 92-92.5°, the melting point of triphenylmethane. Between 330° and 370° (mostly 355-362°), 19.6 g. of crude triphenylmethane came over. After one crystallization from alcohol this melted at 91.5-92.5°. About 5 g. of residue remained in the flask.

Summary.

Secondary aromatic alcohols condense with benzene under the dehydrating influence of anhydrous aluminum chloride according to the following general equation:



$$\underset{\textstyle R\diagup}{C_6H_5-}CHOH + C_6H_6 \xrightarrow{AlCl_3} \underset{\textstyle R\diagup}{C_6H_5-}CHC_6H_5 + H_2O$$

When R is the phenyl group the reaction is smoother and a larger yield of the condensation product is obtained than when R is methyl or ethyl. The ethyl group has a greater retarding effect on the reaction than the methyl group.

An excess of aluminum chloride tends to eliminate a phenyl or an alkyl radical from the product especially if the temperature is not kept low.

Since secondary alcohols of the type studied are easily prepared it is believed that the process will be of importance in synthetic organic chemistry.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN.]

ON THE PREPARATION OF FORMAMIDE.[1]

BY ALBERT BRANN.

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In order to carry out a series of experiments on the linear velocity of the crystallization of formamide, it was necessary to use a product that had a definite melting point. Such a product apparently has not heretofore been prepared. Freer and Sherman,[2] who did a great deal of work on the preparation of formamide, determined its freezing point to be —1.0°. Davis and Putnam,[3] in their work on the conductivities of formamide and its solutions, very carefully distilled formamide that gave a minimum conductivity. However, they seem not to have determined the melting point of the formamide used by them, but quoted Walden,[4] who at different times obtained products with melting points varying between 1.5° and 2.1°. English and Turner[5] prepared formamide by fractional distillation that froze between 2.0° and 2.2°, a small sample freezing at the last named temperature. To show that the true melting point of formamide has been found, that it is a very definite thing, and to emphasize a few details regarding the preparation of formamide, are the objects of this paper.

Hoffman[6] discovered the fact that formamide is formed when ammonium formate is decomposed by heat. Freer and Sherman,[2] utilizing this reaction, worked out a very favorable method for its formation. However, the product with a freezing point of —1.0° produced by them was far from pure, probably due to the fact that they failed to distill off all the products of decomposition.

For the sake of clearness, the detailed operations in the preparation of formamide are given here. The operations are not new, but have been carried out and studied to a finality not hitherto accomplished.

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[1] A portion of a thesis to be submitted to the Graduate School of the University of Wisconsin in partial fulfilment of the requirements for the Degree of Doctor of Philosophy.

[2] *Am. Chem. J.*, 20, 223 (1898).

[3] Jones, "Conductivities and Viscosities in Solvents," *Carnegie Inst. Publication* 230.

[4] *Z. phys. Chem.*, 46, 145 (1903); *Ibid.*, 55, 230 (1906); *Ibid.*, 75, 575 (1910).

[5] *Trans. Chem. Soc. J.*, 105, 1656 (1914).

[6] *Ber.*, 15, 980 (1882).