a crystal of the substance added, the thiourethane separates in thin prismatic plates. It melts at 37° apparently undecomposed.

Calc. for $C_{10}H_{13}ONS$: C, 61.52%; H, 6.66%; N, 7.18%; S. 16.43%.
Found: C, 61.37; H. 6.84; N, 7.31; S, 16.42.

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

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The condensation of aromatic alcohols with aromatic compounds to form derivatives of di- or triphenylmethane is commonly brought about by the following dehydrating agents: sulfuric acid,[1] phosphorus pentoxide,[2] zinc chloride,[3] dilute or concentrated hydrochloric acid,[4] sulfuric and acetic acids,[5] absolute alcohol,[6] stannic chloride,[7] and acetic acid.[8]

Aluminum chloride has been used as a dehydrating agent in organic chemistry by Merz and Weith,[9] Sholl and Seer,[10] Wass,[11] Graebe,[12] Jaubert,[13] Frankforter and Kritchevsky,[14] Frankforter and Kokatnur,[15] and others.[16]

We do not find, however, a record of the dehydrating action of aluminum chloride on aromatic alcohols and aromatic compounds. This preliminary

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[1] Myer and Wurster, *Ber.*, **6**, 964 (1873); Becker, *Ibid.*, **15**, 2091 (1882); Noelting, *Ibid.*, **24**, 3127, 3136 (1891); Gatterman and Koppert, *Ibid.*, **26**, 2811 (1893); Bistrzycki and Flateau, *Ibid.*, **28**, 989 (1895); Fritsch, *Ibid.*, **29**, 2300 (1896); Bistrzycki and Simonis, *Ibid.*, **31**, 2812 (1898), etc.

[2] Hemilian, *Ber.*, **7**, 1203 (1874); Michael and Jeanpretre, *Ibid.*, **25**, 1615 (1892), etc.

[3] Fischer and Roser, *Ber.*, **13**, 674 (1879); *Ann.*, **206**, 113, 155 (1880); Liebmann, *Ber.*, **15**, 152 (1882); Kippenberg, *Ibid.*, **30**, 1140 (1897), etc.

[4] Suais, *Bull.*, [3] **17**, 517 (1897); D. R. P. 27032; Noelting, *Ber.*, **24**, 3127 (1891); Noelting, *Ibid.*, **24**, 553 (1891), etc.

[5] Paterno and Fileti, *Gazz.*, **5**, 381 (1875); Mohlau and Klöpfer, *Ber.*, **32**, 2147, 2149 (1899).

[6] Möhlau and Klöpfer, *Ber.*, **32**, 2150, 2153 (1899).

[7] Bistrzycki, *Ibid.*, **37**, 659 (1904).

[8] Khotinski and Potzewitch, *Ibid.*, **42**, 3104 (1909).

[9] *Ber.*, **14**, 189 (1881).

[10] *Ann.*, **394**, 119 (1912).

[11] *Ber.*, **15**, 1128 (1882).

[12] *Chem. Ztg.*, **25**, 268 (1901); *Ber.*, **34**, 1778 (1901).

[13] *Compt. rend.*, **132**, 841 (1901).

[14] THIS JOURNAL, **36**, 1511 (1914); **37**, 385 (1915).

[15] *Ibid.*, **36**, 1529 (1914).

[16] *Ber.*, **40**, 1694 (1907); D. R. P. 136,015, etc.

paper is the first of a series of articles which we hope to publish on this field.

When benzyl alcohol was mixed with a little more than the molecular equivalent of benzene, and the mixture treated with anhydrous aluminum chloride, a rather vigorous reaction took place. Heat and hydrochloric acid were evolved, and the mass became dark colored and pasty. After decomposing with ice water, and extracting with ether five compounds were isolated by fractional distillation.

The product formed in the largest amount (30% theory) boiled, after redistillation at 262–264°. It was identified further by analysis and oxidation to benzophenone, as diphenylmethane.

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

The residue was distilled under 30 mm. pressure until the temperature rose to 350°. This distillate was then separated by fractionation at 20 mm. into two portions, which came over between 250° and 265° and between 308° and 316°, respectively. The first of these consisted chiefly of *p*-dibenzylbenzene (8% theory) together with a little *o*-dibenzylbenzene, and an oily impurity. The *p*-dibenzylbenzene was identified by melting point, analysis, bromination and oxidation to *p*-dibenzoylbenzene; the *o*-dibenzylbenzene by its melting point.

The fraction which came over at 308–316° at 20 mm. has the formula, as indicated by analysis and molecular weight determination, $C_{27}H_{24}$. It is probably either tribenzylbenzene, $C_6H_3(CH_2C_6H_5)_3$, or methylene-*bis*-diphenylmethane, $C_6H_5CH_2C_6H_4CH_2C_6H_4CH_2C_6H_5$. A subsequent paper will contain a more complete description of this compound.

The residue from the vacuum distillation was distilled at ordinary pressure and yielded about 20% of the theoretically possible amount of crude anthracene. This was purified by sublimation and oxidized to anthraquinone.

The yields of the products are greatly influenced by the amounts of the reagents used, and the temperature at which the reaction is carried out. In one experiment where the temperature was kept below 35° and a large excess (5.2 mols) of benzene was used, the diphenylmethane almost equaled in weight the benzyl alcohol taken. Conditions which gave large yields of diphenylmethane gave small yields of anthracene.

Schramm[1] and Radziewanowski[2] found that this same rule held when benzylchloride and benzene react in the presence of $AlCl_3$.

Verley[3] (working under reduced pressure) prepared diphenylmethane from chloromethylethyl ether, benzene, and aluminum chloride. Since he obtained evidence of a small amount of benzylethyl ether in the reac-

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[1] *Ber.*, **26**, 1706 (1893).

[2] *Ibid.*, **27**, 3237 (1894).

[3] *Bull.*, [3] **17**, 914 (1897).

tion mixture, he assumed that the reaction takes place in three steps: First, the chloromethylethyl ether reacts with benzene to give benzylethyl ether, $C_6H_5 + ClCH_2OC_2H_5 \xrightarrow{AlCl_3} C_6H_5CH_2OC_2H_5 + HCl$. Second, the ether thus formed reacts with hydrochloric acid to form benzyl chloride and alcohol, $C_6H_5CH_2OC_2H_5 + HCl \longrightarrow C_6H_5CH_2Cl + C_2H_5OH$. Third, the benzyl chloride then reacts with a second molecule of benzene to give diphenylmethane, $C_6H_5CH_2Cl + C_6H_6 \xrightarrow{AlCl_3} C_6H_5CH_2C_6H_5 + HCl$.

In the light of this explanation we thought it of interest to determine the effect of aluminum chloride on a mixture of benzylethyl ether and benzene. The ethyl ether of benzyl alcohol when mixed with $1^2/_3$ mols benzene and treated with $AlCl_3$ reacted much less readily than did benzyl alcohol under the same conditions. The products of the reaction were the same[1] but the yields were much smaller. The reaction mixture yielded, after standing more than a week, about 15% of unchanged benzylethyl ether.

If the hypothesis of Verley is correct and if benzylethyl ether is fairly stable in the presence of benzene and aluminum chloride, one would expect to obtain a considerable amount of benzylethyl ether from the reaction mixture when chloromethylethyl ether is treated with benzene and aluminum chloride. An experiment was made with the conditions comparable to those of the preceding experiment. The reaction was much more vigorous and seemed to be complete at the end of two days. A great deal more anthracene was formed as compared to the diphenylmethane than was the case when either benzyl alcohol or benzylethyl ether was used. We were unable to obtain *any* benzylethyl ether from the reaction mixture.

These results led us to try the effect of an excess of aluminum chloride on chloromethylethyl ether alone. A vigorous reaction set in and hydrochloric acid was given off. After standing overnight (protected from moisture by $CaCl_2$) the mixture was decomposed with ice water. A volatile oil separated out and the odor of formaldehyde was quite distinct.

While these experiments are not conclusive, they lead us to suggest an alternate explanation for the action of aluminum chloride on a mixture of chloromethylethyl ether and benzene. We suggest that the ether is first decomposed by the aluminum chloride to form formaldehyde,[2] which then reacts with benzene to form diphenylmethane and anthracene. It is quite possible that both reactions occur simultaneously, but the large amount of anthracene formed,[3] and the absence of an appreciable amount of benzylethyl ether both point to the second hypothesis.

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[1] Meyer (*J. prakt. Chem.*, [ii] **82**, 538 (1910)) has shown that P_2O_5 acts on benzylethyl ether and benzene to give diphenylmethane.

[2] Compare with the findings of Waas, *Ber.*, **15**, 1128 (1882).

[3] Frankforter and Kokatnur (*loc. cit.*) have shown that formaldehyde benzene and aluminum chloride yield a large amount of anthracene.

We are unable at the present time to throw much light on the mechanism of the reaction between aromatic alcohols, aromatic compounds and aluminum chloride. We hope to be able to explain it more fully in future papers. Our work, thus far, has shown the formation of an intermediate product which resembles the intermediate product formed in Friedel and Kraft's reaction. A rather large proportion of $AlCl_3$ is necessary for the production of a good yield of diphenylmethane.

It may be that a further study of this reaction will help to give an insight into the mechanism of the reaction between aldehydes, aromatic compounds and aluminum chloride.[1]

Experimental.

Benzyl Alcohol, Benzene and Aluminum Chloride, I.—Fifty-five grams of benzyl alcohol (freshly prepared from benzaldehyde and free from chlorine) were added to 50 g. of benzene. The mixture was cooled and stirred constantly with a motor. Aluminum chloride was added in small portions until a total of 40 g. had been added. The temperature was kept at 30–35° except for a brief period when it rose to 55°. Much hydrochloric acid was evolved and the mixture became dark colored, pasty and fluorescent. It was allowed to stand at room temperature for ten days, and was then decomposed with ice water and extracted with ether. The ether extract was dried over $CaCl_2$. Most of the ether was driven off and the residue was fractionated.

Second Fractionation.

60–130°, 12.5 g. (mostly benzene); 130–240°, 0.7 g.; 240–280°, 25.5 g.

The pressure was reduced to 30 mm. and the distillation continued until nothing more would come over under 350°. The distillate weighed 20 g. This was subjected to fractionation at 20 mm.

Second Fractionation.

245–265°, 10.5 g.; 265–305°, 1.5 g.; 308–316°, 5.27 g.

The residue (15 g.) was distilled at ordinary pressure, until the flask melted and nothing more would come over. 8.5 g. of a yellow oil came over and solidified in the receiver.

The fraction which came over at 240–280° at ordinary pressure had after repeated distillation, a constant boiling point of 262–264°. 20 g. of it yielded 14 g. of benzophenone when oxidized with potassium dichromate, and sulfuric acid.[2] An analysis gave the following:

0.1708 g. subst. gave 0.5802 g. CO_2 and 0.1127 g. H_2O.

Calc. for $C_{13}H_{12}$: C, 92.8%; H, 7.2%. Found: C, 92.58%; H, 7.39%.

The substance is, therefore, diphenylmethane.

The fraction which came over at 245–265° at 20 mm. was redistilled.

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[1] See Dinesmann, *Compt. rend.*, **141**, 201 (1905); and Frankforter and Kritchevsky, THIS JOURNAL, **36**, 1511 (1914); **37**, 385 (1915).

[2] Zincke, *Ann.*, **159**, 377 (1871).

Most of it came over between 252–255°. On standing overnight the larger part of it crystallized. It was cooled and filtered at the pump. The crystals were dried between filter papers and recrystallized alternately from alcohol and ether. 5.3 g. of colorless plates melting at 85–86° were obtained. 1 g. of these when oxidized with 2 g. of CrO_3 in acetic acid gave 0.8 g. of *p*-dibenzoyl benzene, melting at 159–160°.[1] Another 1 g. portion was brominated in chloroform solution.[2] A dibromide was obtained which melted, after repeated recrystallization, from petroleum, ether and benzene, at 112.5°. An analysis of the hydrocarbon gave:

0.1826 g. subst. gave 0.6247 g. CO_2 and 0.1142 g. H_2O.

Calc. for $C_{20}H_{18}$: C, 92.97%; H, 7.03%. Found: C, 93.29%; H, 7.01%.

It is, therefore, *p*-dibenzylbenzene, $C_6H_5CH_2C_6H_4CH_2C_6H_5$.

From the combined filtrates of the *p*-dibenzylbenzene, a small amount (0.7 g.) of *o*-dibenzylbenzene melting at 78° was obtained.

The fraction which came over at 308–316° at 20 mm. was redistilled. Most of it came over between 312° and 314°. An analysis and molecular weight determination indicated the formula $C_{27}H_{24}$.

0.2067 g. and 0.1998 g. of subst. gave 0.702 g. and 0.6807 g. CO_2, and 0.1275 g. and 0.1284 g. H_2O.

Calc. for $C_{27}H_{24}$: C, 93.05%; H, 6.95%. Found: C, 92.64%, 92.91%; H, 6.91%, 7.19%.

Calculated molecular weight, 348.2. Found: 342.4 and 354.

The yellow solid which was obtained by heating the residue after the vacuum distillation was freed from oil by means of a porous plate, crystallized from benzene and alcohol and sublimed. The sublimate had the characteristic appearance of anthracene. It melted sharply at 212–213°. 2 g. were oxidized with chromium trioxide and acetic acid. After recrystallization from glacial acetic acid the resulting fine needles melted at the correct temperature for anthraquinone, 276–277°.

Benzyl Alcohol, Benzene and Aluminum Chloride, II.—Fifty grams of benzyl alcohol were added to 200 g. benzene and treated with 35 g. aluminum chloride in small portions. The temperature was easily kept between 30° and 35°. The mixture turned reddish brown and gave off hydrochloric acid. After five days it was poured into ice water. The aqueous portion was separated from the benzene portion and extracted with ether. Most of the ether was driven from the extract and the residue was added to the benzene portion. This was dried over $CaCl_2$ and subjected to fractionation.

Second Fractionation

60–110°, 142 g. (benzene); 110–235°, 4 g.; 235–280°, 46.5 g.

The pressure was reduced to 30 mm. and the distillation continued to 350°. 11.5 g. came over. This was refractionated at 20 mm.

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[1] Zincke, *Ber.*, **9**, 31 (1876).

[2] Thiele and Balhorn. *Ibid.*, **37**, 1467 (1904).

Second Fractionation.

245–265°, 7.5 g.; 265–305°, 1 g.; 308–316°, 2.5 g.

The small amount of residue (2.5 g.) was heated under atmospheric pressure. About 1 g. of crude anthracene was obtained.

These fractions yielded, on purification:

Diphenylmethane	44.5 g.
p-Dibenzyl benzene	4.2 g.
o-Dibenzyl benzene	0.5 g.
Hydrocarbon, $C_{27}H_{24}$	2.0 g.
Anthracene	0.6 g.

Benzylethyl Ether,[1] Benzene and Aluminum Chloride.—Fifty grams of the ether were mixed with an equal weight of benzene and stirred while 40 g. of aluminum chloride were added in small portions. Cooling was omitted. The temperature rose to about 45°. Hydrochloric acid was given off and the mixture became dark colored. The reaction was quite slow, hydrochloric acid being evolved in considerable amount for about a week. After ten days the mass was decomposed with ice water, extracted with ether, dried and distilled.

Second Fractionation.

60–110°, 18 g. (benzene); 110–220°, 7.5 g.; 220–280°, 9 g.; 240–350° (30 mm.), 6 g.

The residue distilled at atmospheric pressure yielded 4 g. of crude anthracene.

Most of the fraction from 110° to 220° boiled at 178–182°. It was identified as unchanged benzylethyl ether. The fraction from 220° to 280° was crude diphenylmethane. The fraction from 240° to 350° (30 mm.) yielded 2 g. of *p*-dibenzyl benzene, 0.3 g. *o*-dibenzyl benzene, and about 1 g. of the hydrocarbon $C_{27}H_{24}$.

Chloromethylethyl Ether, Benzene and Aluminum Chloride.—Thirty-five grams of freshly prepared chloromethylethyl ether were dissolved in 75 g. of benzene, and treated with 35 g. of aluminum chloride. The reaction was quite violent. Although the aluminum chloride was added very slowly and the mixture well cooled, the temperature rose to 43°. Hydrochloric acid was evolved rapidly. The mixture turned red, then reddish brown and became rather pasty. After three days it was decomposed with ice water and extracted with ether. A small amount (2 g.) of a yellow precipitate remained undissolved and was filtered off. This was not investigated. The ether extract was dried over $CaCl_2$ and distilled.

Second Fractionation.

60–120°, 12 g. (benzene); 120–220°, 0.5 g.; 220–280°, 9.8 g.; 235–350° (30 mm.), 2.5 g.

Twelve grams crude anthracene were obtained from the residue.

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[1] This ether was freshly prepared from benzyl chloride and sodium ethylate. It gave a faint cloudiness when tested for chlorine.

The thermometer rose rapidly from 120° to 220°. No evidence of benzylethyl ether was found. The fraction from 220° to 280° was identified as diphenylmethane. No investigation was made for the oil which came over between 235° and 350° at 30 mm.

Chloromethylethyl Ether and Aluminum Chloride.—Fourteen grams of chloromethylethyl ether were placed in a flask fitted with a calcium chloride tube and treated with an excess (22 g.) of aluminum chloride in small amounts. A vigorous reaction set in, heat was evolved, and hydrochloric acid was given off rapidly. After standing overnight, all reaction seemed to have ceased. The flask contained a reddish brown syrup and some unchanged aluminum chloride. The whole was poured into ice water. A small amount of volatile oil came to the surface. The aqueous solution smelled strongly of formaldehyde. A portion was just neutralized with NaOH and filtered. A piece of filter paper, moistened with ammoniacal silver nitrate solution, was turned black when held over the warmed filtrate.

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THE MOLECULAR WEIGHT OF SOME ALCOHOLATES OF CHLORAL AND BUTYLCHLORAL IN BENZENE SOLUTION.

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The partial dissociation of chloralethylalcoholate into its constituents when dissolved in organic solvents, first investigated by Beckman,[1] was more extensively examined by Willcox and Brunel in a recent article,[2] in connection with an investigation of the replacement of one alcohol by another in such alcoholates. It has now been found that other alcoholates of chloral and butylchloral are likewise, as would be expected, somewhat dissociated in solution.

An examination of Table II, p. 1827, in the above paper by the authors, and of the reactions on which it is based, make evident certain conclusions as to the relative tendency to dissociation which these alcoholates of various alcohols should exhibit. It is there concluded that as we pass downward in the table, in the list of alcohols there studied, the affinity of the alkyl groups for the hydroxyl becomes relatively greater than their affinity for the chloral and butylchloral radicals. The tendency of the alcohols to form alcoholates with the aldehydes, involving separation of the alkyl group from the hydroxyl, should, therefore, decrease in this order, so that the degree of dissociation of the alcoholates should increase as we pass downward in the list of alcohols it this table. The following experiments show

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[1] *Z. physik. Chem.*, **2**, 724 (1888).

[2] THIS JOURNAL, **38**, 1821 (1916).