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The Condensation of Alcohols, Ethers, and Esters with Aromatic Hydrocarbons in the Presence of Aluminum Chloride

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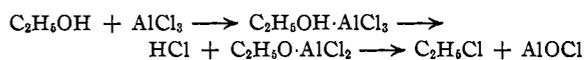
This paper gives the results of experiments undertaken to discover the possibility of the extension of the use of aluminum chloride to bring about condensation between aromatic hydrocarbons and various classes of compounds which had been studied in the past inadequately, or not at all. Important results were obtained with aliphatic alcohols, esters, diethyl ether, and amides. In most cases a detailed study of each reaction was not made because the object of the research was to break the ground for subsequent work. One paper based on the results, in which the preparation of mesitylene from methyl alcohol and *s*-triethylbenzene from ethyl alcohol, has been published.²

Since the work was completed, several papers by other investigators have appeared, but our results in most cases have led to the discovery of facts and the development of excellent synthetic methods which have not been described.

In the condensation of anhydrides with aromatic hydrocarbons by means of aluminum chloride, a bond between oxygen and an acyl group is broken. It was of interest to determine whether or not the bond between oxygen and an alkyl group in an ether would break in a similar way; if this took place the hydrocarbon would be alkylated. In the case of esters experiments were made to find out if the bonds to the acyl and alkyl groups both broke and, if so, which would yield first. These considerations led to the study of alcohols, since it has been shown that acids can be condensed with aromatic hydrocarbons.

An attempt was made to learn something in regard to the mechanism of the reactions. In the case of certain alcohols an addition product was formed at room temperature, ROH·AlCl₃, which on heating yielded the alkyl chloride. In this way methyl alcohol and ethyl alcohol gave nearly the theoretical yields of the corresponding chlorides. Isopropyl alcohol gave 70% of isopropyl chloride. Owing to the relatively low price of

commercial aluminum chloride, the reactions furnish excellent methods for the preparation of these compounds for experimental work. A determination of the hydrogen chloride evolved when the addition product of ethyl alcohol and aluminum chloride was heated leads to the view that the reaction takes place in the following steps



In these reactions 1 mole of alcohol and 1 of aluminum chloride are consumed. If benzene and more than 1 mole of the chloride is used, condensation of the ethyl chloride with the hydrocarbon yields ethyl derivatives of benzene. The compounds formed are determined largely by the molecular ratio of the aluminum chloride to the hydrocarbon.³

Unsuccessful attempts have been reported to condense primary aliphatic alcohols with hydrocarbons.⁴ In the experiments described not enough aluminum chloride was used.

In our experiments when ethyl alcohol, benzene and aluminum chloride (AlCl₃) were used in the molecular ratio 1:6:2, the yield of ethylbenzene was 50% of the theoretical. When methyl alcohol was used the yield of toluene was 21%. Subsequent work showed that a higher temperature is required for methyl than for ethyl alcohol. The yield probably could be increased. A yield of 53% of mesitylene was obtained from methyl alcohol. When isopropyl alcohol was used ethylbenzene was formed, in addition to isopropylbenzene and diisopropylbenzene. With *t*-butyl alcohol the yield of *t*-butylbenzene was 84%. When the reactants were heated for several hours no *t*-butylbenzene was obtained; the product consisted of toluene, ethylbenzene and isopropylbenzene. With *m*-xylene and the alcohol the yield of *sym-t*-butylxylene was 89%.

When an ester is condensed with benzene, 1 mole of aluminum chloride is required to produce the alkyl chloride for alkylation. If an excess of the chloride is used, alkyl benzenes are formed.

(1) From the thesis presented by Bernard M. Sturgis in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1936.

(2) Norris and Ingraham, *THIS JOURNAL*, **60**, 1421 (1938).

(3) Norris and Rubinstein, *ibid.*, **61**, 1163 (1939).

(4) Houston and Sager, *ibid.*, **48**, 1955 (1926).

In the presence of two molecules of the chloride the reaction, when carried out at the proper temperature, yields ketones as the result of the introduction of an acyl group. A recent German patent covers the preparation of ketones in this way.⁵

Work that was completed in this Laboratory before the patent was published is not entirely in accord with the patent. This will be discussed in a later paper.

The earlier attempts to prepare ketones from esters failed because not enough aluminum chloride was used—a fact that was evident after the mechanism of the reaction had been studied. Cryer⁶ reported that phenyl acetate, aspirin and ethyl acetate reacted with benzene and aluminum chloride and formed acetophenone. No experimental details or yields are recorded. Kashtanov⁷ gives no details of experiments in which he obtained from isoamyl benzoate the hydrocarbon C₁₇H₂₀. With ethyl acetate, ethylbenzene and acetophenone were formed. Cox,⁸ in his study of the mechanism of the Fries rearrangement, heated certain phenyl and tolyl esters with aluminum chloride in the presence of diphenyl ether. He obtained, in addition to the products of rearrangement, acyl derivatives of the ether. The significance of the results in regard to the use of esters as acylating agents was not pointed out.

When ethyl acetate, benzene and aluminum chloride (AlCl₃) in the molecular ratios 1:4:2, respectively, were allowed to react at room temperature the product consisted of diethylbenzenes and higher substitution products; no ketones were found. When the molecular ratio was 0.5:3:1.2 and the mixture was heated at 100° for twelve hours, the products formed were ethylbenzene, acetophenone and diethyl acetophenones.

It was evident that the ethyl-oxygen bond broke before the acetyl-oxygen and the procedure could not be used to prepare acetophenone with a satisfactory yield. Since the phenyl-oxygen bond is very difficult to break, the condensation of phenyl acetate with benzene was studied. The reaction was complicated in this case because the phenyl acetate underwent, in part, a Fries rearrangement in the presence of aluminum chloride. The *o*-hydroxy- and *p*-hydroxyacetophenones formed in this way were determined. The highest

yield of acetophenone obtained was 60% of the theoretical. When phenyl acetate was condensed with toluene the yield of methacetophenones was 82%.

o-Nitrophenyl acetate does not undergo the Fries rearrangement and for this reason its condensation with benzene was studied. The yield of acetophenone (82%) could no doubt be increased by further study.

It appeared probable that an intermediate compound was formed when phenyl acetate and aluminum chloride reacted. Perrier⁹ studied the reaction between phenol and aluminum chloride and isolated the compound C₆H₅O·AlCl₂. This compound was prepared and its reactions studied. In one experiment in which acetyl chloride and 19.2 g. of phenol were used, the product consisted of 13.3 g. of *o*-hydroxyacetophenone, 5.1 g. of *p*-hydroxyacetophenone, 4 g. of phenacetin and 1 g. of tar. The compound C₆H₅O·AlCl₂ gave the same products when it reacted with acetic acid.

The use of diethyl carbonate to ethylate benzene has been described recently.¹⁰ In our experiments the products formed in the cold were 24.5% ethylbenzene, 14% *m*-diethylbenzene and 32% *sym*-triethylbenzene based on the utilization of the two ethyl groups in the carbonate. When the reactants were heated, the yields were 53.5% ethylbenzene and 16% *sym*-triethylbenzene.

Cyclohexyl acetate gave small yields of cyclohexylbenzene and higher substitution products.

To determine the effect of chain length on the condensations, methyl palmitate and cetyl acetate were studied. The former was very stable toward aluminum chloride and very little reaction occurred under the conditions used. Cetyl acetate was also relatively stable, but a small yield of cetylbenzene was obtained.

When diethyl ether was condensed with benzene the yield of ethylbenzene was 36% of the theoretical. Subsequent study of the reaction showed that when the proper conditions were used an excellent yield of *sym*-triethylbenzene could be obtained.

Experiments with acetamide and benzamide indicated that neither condensed with benzene in the presence of aluminum chloride. The two amides were dehydrated. The intermediate addition products formed at room temperature underwent decomposition when heated. From acet-

(5) I. G. Farbenind., German Patent 637,384 (1936).

(6) Cryer, *Trans. Roy. Soc. Canada*, 111, 3, 19, 29 (1925).

(7) Kashtanov, *J. Gen. Chem. (U. S. S. R.)*, 2, 515 (1932); *C. A.*, 975 (1935).

(8) Cox, *THIS JOURNAL*, 52, 352 (1930).

(9) Perrier, *Bull. soc. chim.*, [3] 9, 1040 (1893).

(10) Kane and Lowry, *THIS JOURNAL*, 58, 2605 (1936).

amide 60% of the theoretical yield of acetonitrile, and from benzamide 84% of benzonitrile were obtained. When ammonium benzoate was heated with aluminum chloride, the yield of benzonitrile was 50% of the theoretical. The method furnishes a convenient means of preparing these nitriles.

Experimental Details

Preparation of Methyl, Ethyl, and Isopropyl Chlorides from the Corresponding Alcohols and Aluminum Chloride.

—A 250-cc. flask having two necks was used. To one of the latter was attached a dropping funnel, the end of which was close to the bottom of the flask. The other neck was joined to a reflux spiral condenser, connected to a receiver consisting of a spiral and graduated tube which were covered with a mixture of solid carbon dioxide and methanol. In the flask was placed 33.3 g. (0.25 mole) of aluminum chloride. Eight grams of methanol (0.25 mole) was added slowly through the funnel. Heat was generated but only a trace of hydrogen chloride was evolved. The flask was heated on an oil-bath. At 70° the solid product began to melt and hydrogen chloride was given off freely. The bath was kept at 80–90° for two hours; about 3 cc. of liquid condensed in the graduated tube. The temperature was raised to 105–110° when 3 cc. was collected in three hours. Finally, at 140°, the reaction was rapid and in twenty minutes was completed. The methyl chloride was redistilled through a tube containing solid potassium hydroxide to remove hydrogen chloride and was condensed. The chloride boiled at –24–23.5°, most of it coming over at –23.7°, which is the recorded boiling point of methyl chloride. The yield was 13 cc. The theoretical yield is 12.6 g. The time required for the preparation could be reduced by cautiously heating the intermediate compound to 140°.

Ethyl chloride was prepared in a way similar to that just described. At 95–100° the intermediate compound melted. The flask was heated at 110° when only a small amount of product was obtained. At 120° the decomposition was rapid. The final heating was at 150°; after a time the material in the flask frothed. The redistilled chloride boiled at 12–12.5°. The yield was 17 cc. or 97.6% of the theoretical when 0.25 mole portions of the reactants were used.

Isopropyl chloride was made in a similar way. When the reactants were mixed, hydrogen chloride was evolved rapidly and the chloride condensed in the receiver. The reaction was complete at 90–95°. The product in the flask did not melt. The chloride boiled at 35–36°, the recorded boiling point. The yield was 13.7 g., which is 70%.

Attempts to prepare isobutyl chloride and stearyl chloride in a similar manner were unsuccessful.

The Condensation of Alcohols with Benzene.—In testing the mechanism of the reaction, the compound $C_2H_5O \cdot AlCl_2$ was prepared by heating molecular quantities of ethanol and aluminum chloride at 100°. When hydrogen chloride ceased to be evolved, the product was heated with benzene at about 90° for four hours. No ethyl derivatives of benzene were formed.

A mixture of benzene, methanol and aluminum chloride (mole ratio 4:1:1) was heated at 80–90° for eight hours and at 100° for six hours. No methylbenzenes were formed, although hydrogen chloride was evolved.

When 2 moles of aluminum chloride to 1 mole of methanol were used with 6 moles of benzene and the mixture was heated for three hours at 90° and six hours at 90–96°, the amount of toluene formed was 21% of the theoretical yield.

When 2 moles of aluminum chloride, 2.5 moles of toluene and 1 mole of methanol were used and the mixture heated at 100° for three and one-half hours while a stream of dry air was passed through it, the yield of mesitylene was 53% of the theoretical. This reaction has been more fully studied and detailed directions for the preparation have been published.²

A mixture of ethanol (0.5 mole), benzene (3 moles) and aluminum chloride (1 mole) was allowed to stand overnight and heated at 100° for twelve hours. The yield of ethylbenzene was 50% of the theoretical, along with small quantities of other hydrocarbons. From the tar formed, 6 g. of a crystalline solid (m. p. 182–184°) was isolated. It formed a dark red crystalline picrate (m. p. 175°) and a red compound (m. p. 190°) with trinitrobenzene. Its behavior with concentrated sulfuric acid suggested that it was an ether. The same compound was isolated from the reaction product when ethyl ether was condensed with benzene.

Huston and Hsieh¹¹ described the condensation of isopropyl alcohol with benzene during the course of our experiments. It is only necessary to mention here that we found that when the reaction mixture was heated at 90–95° for six hours and then at 100° for six hours, an appreciable quantity of ethylbenzene was formed.

***t*-Butyl Alcohol.**—To a mixture of the alcohol (0.5 mole) and benzene (3 moles), cooled to 0°, was added, during two hours, 0.6 mole of aluminum chloride. After stirring the mixture at 0° for two hours more, it was allowed to come to room temperature and stand for twenty hours. The fraction obtained, which boiled at 168.5–169.5°, was *t*-butylbenzene. The yield was 84% of the theoretical. In Huston's paper, which appeared subsequent to our work, the yield is reported as 67%.

When the reactants were used in the amounts given above and were heated at 80° for six hours, and then at 95° for two hours, no *t*-butylbenzene was found in the reaction product, which was shown to be a mixture which contained toluene, ethylbenzene, and isopropylbenzene. As far as we are aware the decomposition of alkyl groups in this way has not been observed in Friedel and Crafts condensations.

t-Butyl alcohol was condensed with pure *m*-xylene. The aluminum chloride (0.9 mole) was added to a flask placed in a mixture of ice and salt. A mixture of 1.75 moles of *m*-xylene and 0.3 mole of *t*-butyl alcohol was dropped into the flask with vigorous stirring. The mixture was stirred for five hours while still in the freezing bath and then decomposed. The product was fractionated with a Fenske column. The yield of *t*-butyl-*m*-xylene (b. p. 205.5–206.5°) was 89%. The hydrocarbon was identified by preparing its trinitro derivative (m. p. 108.5–110°). The recorded melting point is 110°.

When two moles of aluminum chloride were used with 1

(11) HUSTON and HSIEH, THIS JOURNAL, 58, 429 (1936).

mole of the alcohol and the mixture stood at room temperature for twelve hours, no *t*-butyl-*m*-xylene was formed; the product contained toluene, isomeric xylenes and a large percentage of tar.

Condensation of Esters with Aromatic Hydrocarbons.—Details in regard to the condensation of ethyl acetate will be given in a subsequent paper. It is advisable to note here the fact that at room temperature alkylation only occurred. When a mixture of 0.5 mole of ethyl acetate, 3 moles of benzene and 1.2 moles of aluminum chloride was heated at 100° for two hours, allowed to stand overnight at room temperature, and heated for twelve hours at 100°, the chief product of the reaction was diethylacetophenone; small proportions of ethylbenzene and acetophenone were formed.

In order to prevent alkylation, phenyl acetate was condensed with benzene. Since the ester undergoes rearrangement in the presence of aluminum chloride to the ortho and para hydroxyacetophenones, it was necessary to devise an analytical method for the separation of these compounds from the reaction product and from each other. The reaction product which contained benzene, acetophenone, phenol, and hydroxyacetophenones was extracted with a 3% solution of potassium hydroxide. The solution was acidified and steam distilled. The residue of *p*-hydroxyacetophenone was extracted and crystallized. The phenol and *o*-hydroxyacetophenone in the distillate were extracted with ether, which was evaporated. The residue was treated with a 30% solution of sodium hydroxide; the sodium salt of the *o*-hydroxyacetophenone separated quantitatively as a solid.

The effects of the molecular proportions of reactants and the temperature were studied. When 0.1 mole of aluminum chloride, 0.1 mole of phenyl acetate, and 0.4 mole of benzene were used and the mixture was refluxed for one hour, no acetophenone was formed. The reaction product consisted of 5.2 g. of $\text{CH}_3\text{COOC}_6\text{H}_5$, 2.2 g. of $\text{C}_6\text{H}_5\text{OH}$, 1.2 g. of *p*- $\text{HOOC}_6\text{H}_4\text{COCH}_3$ and 1 g. of *o*- $\text{HOOC}_6\text{H}_4\text{COCH}_3$.

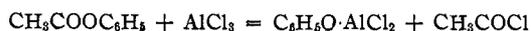
When 0.2 mole of aluminum chloride was used and the conditions were as before, no acetate was recovered. There were obtained 5.2 g. of acetophenone (43%), 4.2 g. of phenol, 2.3 g. of para and 1.4 g. of ortho hydroxyacetophenones. The hydrogen chloride evolved amounted to 0.11 mole (theoretical 0.1 mole).

In another experiment in which the reactants were mixed in a flask kept cold by ice water and 0.6 mole of benzene was used to 0.1 mole of the acetate and 0.2 mole of aluminum chloride, the reaction mixture was stirred at room temperature for five hours, stood for twelve hours, and stirred for seven hours. In this case the yield of acetophenone was 60% of the theoretical; no *o*-hydroxyacetophenone was formed; 0.5 g. of the para isomer was isolated.

Methylacetophenones.—Phenyl acetate (0.2 mole) was condensed with toluene (0.8 mole) by means of aluminum chloride (0.4 mole) which was added during the course of an hour to the other reactants and cooled in an ice-bath. After 0.2 mole of the chloride had been added, the liquid first formed solidified. The flask was heated to 35°; the solid melted and the rest of the chloride was added. The mixture stood for thirteen hours; it was then stirred for five hours and heated at 60° for fifteen minutes. The

fractionated reaction product yielded 8 g. at 216–220° and 11.5 g. at 220–225°. *o*-Methylacetophenone boils at 216°, the meta derivative at 218–220°, and the para at 224–225°. Ten grams of a mixture of the fraction 216–220° were oxidized and the phthalic acids formed were separated. No *m*-phthalic acid was found; 6.6 g. of terephthalic acid, 0.6 g. of phthalic acid were isolated. The yield of the methylacetophenones was 82%.

The Mechanism of the Condensation of Phenyl Acetate with Hydrocarbons.—It appeared probable that phenyl acetate reacts with aluminum chloride as follows



The acetyl chloride in the presence of more aluminum chloride would condense with the hydrocarbon present and form a ketone. The chloride might also acylate the compound $\text{C}_6\text{H}_5\text{O}\cdot\text{AlCl}_2$ and the product when decomposed by water yield hydroxyacetophenones.

To test this view, the compound $\text{C}_6\text{H}_5\text{O}\cdot\text{AlCl}_2$ was made by the method of Perrier, by heating phenol with aluminum chloride. A quantitative experiment was made in which resublimed aluminum chloride was used; when 1 mole of phenol and 1 mole of aluminum chloride were taken, 1.02 moles of hydrogen chloride was collected. A sample of the compound when decomposed by water gave the theoretical yield of phenol.

The compound made from 0.2 mole of phenol and 0.2 mole of aluminum chloride was treated with 0.2 mole of acetyl chloride. Heat was generated and the chloride boiled. Suddenly the mixture foamed and turned red. It was heated for ten minutes, during which time much hydrogen chloride was evolved. The product was treated with hot water. From the water solution and the tar formed in the reaction was isolated phenacetin which has been prepared from ortho and para hydroxyacetophenones.¹² The compound was crystallized from alcohol and melted at 264–265° with decomposition. The products of the reaction when 19.2 g. of phenol was used were *o*-hydroxyacetophenone 13.3 g., *p*-hydroxyacetophenone 5.1 g., and phenacetin 4 g.

A mixture of the reactants in the proportions given above was allowed to stand overnight and then stirred for two hours. In this case phenyl acetate (8 g.) was formed. The other products were phenol (9 g.), *o*-hydroxyacetophenone (2 g.), the para isomer (0.5 g.), phenacetin 0.5 g. and tar (3 g.).

The compound $\text{C}_6\text{H}_5\text{O}\cdot\text{AlCl}_2$ reacted with acetic acid very slowly at room temperature in six weeks. The chief product was *p*-hydroxyacetophenone 7.3 g., and some of the *o*-isomer was formed. When twice the amount of aluminum chloride was used and the product was heated for twenty minutes, the products were *o*-hydroxyacetophenone (8 g.), the para isomer (1.2 g.), diphenyl ether (1 g.) and tar (5 g.).

Condensation of *o*-Nitrophenyl Acetate with Benzene.—In order to avoid a Fries rearrangement, the ester of *o*-nitrophenyl acetate was used. In a flask cooled by ice water were placed 0.2 mole of aluminum chloride and 0.2 mole of benzene. The mixture was stirred and a solution of 0.1 mole of the ester in 0.2 mole of benzene was added

(12) Bulow, *Ber.*, **36**, 732 (1903); Rosinski, *J. prakt. Chem.*, [2] **26**, 54 (1882).

during forty-five minutes. The aluminum chloride went into solution but no hydrogen chloride was evolved. The mixture stood for forty hours and was then heated to gentle boiling for three hours. The product was decomposed by ice and shaken with a 5% solution of potassium hydroxide. From the alkaline solution was recovered some *o*-nitrophenol. The benzene solution was distilled through a Vigreux column. There was obtained 9.8 g., 82% of the theoretical yield, of acetophenone, which boiled at 201–202° and melted at 20–20.5°.

Condensation of Diethyl Ether with Benzene.—Jannasch and Bartels¹³ have reported experiments on this condensation. The chief product was hexaethylbenzene with small quantities of tetra- and pentaethylbenzene. In our experiments attempts were made to obtain ethylbenzene. Diethyl ether (0.5 mole) and benzene (3 moles) were placed in a 500-cc. flask provided with a reflux condenser, a stirrer, and a tube through which aluminum chloride was introduced. One mole of the chloride was added during one hour. One-half of the chloride dissolved as the result of the formation of the molecular compound $(C_2H_5)_2O \cdot AlCl_3$. After standing overnight the flask was heated in an oil-bath (100–110°) for eight hours. Since hydrogen chloride continued to be evolved the flask was allowed to stand again overnight and then heated at 115–121° for six hours. At the end of this time the aluminum chloride had passed into solution. After decomposition with water the product was distilled with steam. The excess benzene was separated by distillation with a Davis column and the residue fractionated with a Podbielniak column. There was obtained 19 g. (134–137°) which was shown to be practically pure ethylbenzene (36% yield based on the utilization of one ethyl group in the ether). Only traces of higher alkylated benzenes were recovered. The ethylbenzene was identified by oxidation to benzoic acid. Subsequent work will be described later.

Preparation of Nitriles from Amides and Aluminum Chloride.—In attempts to condense amides with benzene, it was found that the former were dehydrated. The reaction furnishes a convenient method for the preparation of nitriles.

Acetonitrile.—In a cooled flask provided with a condenser were mixed 0.2 mole of aluminum chloride and 0.2 mole of acetamide. Reaction set in at once with the evolution of heat and hydrogen chloride. After the first vigorous reaction had subsided, the flask was heated at first gently and then strongly. The distillate was redistilled; the yield of acetonitrile, which boiled at 81.5–82°, was 60% of the theoretical. When one-half as much aluminum

chloride was used the yield of nitrile was reduced to about one-half; the excess of amide was converted by the hydrogen chloride evolved into its hydrochloride, which was identified. When the aluminum chloride was doubled no acetonitrile distilled from the mixture. An experiment showed that the molecular compound of acetonitrile and aluminum chloride is relatively stable when heated; it is decomposed into its constituents by water.

Benzonitrile.—When benzamide (0.3 mole) and aluminum chloride (0.3 mole) were heated together, there was no vigorous reaction at the start. When the volatile material was redistilled the benzonitrile boiled at 190–191°; the yield was 84% of that required by theory. When the reactants were refluxed for fifteen minutes and then directly steam distilled, the yield of nitrile was 59%. From the non-volatile residue was extracted the trimer of benzonitrile. Benzonitrile was prepared by distilling ammonium benzoate (0.2 mole) with aluminum chloride (0.4 mole). The yield of the nitrile (b. p. 190.5–191°) was 50%.

Summary

1. The mechanism of the condensation of primary aliphatic alcohols with aromatic hydrocarbons by means of aluminum chloride was studied.
2. The following hydrocarbons were prepared from alcohols: toluene, ethylbenzene, *t*-butylbenzene, and *t*-butyl-*m*-xylene-(1,3,5).
3. Methyl, ethyl, and isopropyl alcohols gave excellent yields of the corresponding chlorides when heated with aluminum chloride.
4. From ethyl acetate, aluminum chloride and benzene, ethylbenzenes, acetophenone, and ethylacetophenones were prepared.
5. Phenyl acetate, benzene, and aluminum chloride gave acetophenone, *p*-hydroxyacetophenone, *o*-hydroxyacetophenone. *o*-Nitrophenyl acetate gave acetophenone only.
6. The compound $C_6H_5O \cdot AlCl_2$ was converted by acetyl chloride or acetic acid into isomeric hydroxyacetophenones.
7. Ethylbenzene was prepared from diethyl ether.
8. Aluminum chloride converted acetamide into acetonitrile. Benzamide and ammonium benzoate gave benzonitrile.

(13) Jannasch and Bartels. *Ber.*, **31**, 1716 (1898); Jannasch, *Chem. Centr.*, **69**, 105 (1898).