modifications. The aldehyde, purified through the semicarbazone, m. p. 206–208°, boiled at 113° (12 mm.).

2-Methylcinnamyl Alcohol.—Reduction of the above aldehyde was carried out with aluminum isopropylate. The unsaturated alcohol boiled at 124–124.3° (8 mm.), n^{25}_D 1.5697, d^{25}_4 1.034, MR calcd. 45.84, found 46.94. On cooling it solidified, m. p. 19–21°. *Anal.* Calcd. for $C_{10}H_{12}O$: C, 81.1; H, 8.1. Found: C, 80.9; H, 8.1. The dibromide crystallized from Skelly Solve A as needles, m. p. 86.0–87.0°. *Anal.* Calcd. for $C_{10}H_{12}OBr_2$: Br, 51.9. Found: Br, 51.8. The phenylurethan crystallized from Skelly Solve B, m. p. 78.5–79.3°. *Anal.* Calcd. for $C_{17}H_{17}O_2N$: N, 5.6. Found: N, 5.5.

1-Phenylmethallyl Alcohol.—This isomeric alcohol was prepared from α-methylacrolein and phenylmagnesium bromide in the usual way, b. p. 99.8–100.0° (8 mm.), n^{25}_D 1.5361, d^{25}_4 1.010, MR calcd. 45.84, found 45.70. *Anal.* Calcd. for $C_{10}H_{12}O$: C, 81.1; H, 8.1. Found: C, 81.2; H, 8.3.

The dibromide was an oil. The phenylurethan crystallized from Skelly Solve B, m. p. 79.5–79.9° (mixed m. p. with the phenylurethan of its isomer above (m. p. 78.5–79.3°) was 57–65°). *Anal.* Calcd. for $C_{17}H_{17}O_2N$: N, 5.6. Found: N, 5.6.

Action of Hydrobromic Acid on 1-Phenylmethallyl Alcohol.—Fifteen grams of the alcohol was treated with 30 ml. of constant boiling hydrobromic acid for one hour, with frequent shaking. The alcohol layer became olive-green. The upper layer was separated, washed with cold sodium bicarbonate, dried over sodium sulfate and distilled, b. p. 165–165.5° (30–26 mm.), 10.3 g. The bromide was now boiled with dilute aqueous sodium hydroxide for four hours, and then worked up as usual. The unsaturated alcohol was distilled, b. p. 147–150° (33 mm.), and converted to the phenylurethan, m. p. 78.0–78.5° (mixed m. p. with the phenylurethan of 2-methylcinnamyl alcohol (m. p. 78.5–79.3°) 78.5–79.0°).

Reduction of 2-Bromocholestanone.—One-half gram of the bromo-ketone, m. p. 169–170°, prepared according to the directions of Butenandt and Wolff[15] was treated with 55 ml. of a 0.2 molal aluminum isopropylate solution. The ketone did not appear to dissolve even after four and one-half hours boiling. The product, recovered in the usual way, was a gum, which gave only a faint opalescence with boiling alcoholic silver nitrate. It was not investigated further.

Summary

1. Reduction of α-bromopropiophenone yielded the bromohydrin and halogen-free products, one of which was methylbenzylcarbinol.

2. The bromohydrin with methylamine gave *dl*-pseudo-ephedrine and *dl*-pseudo-isoephedrine. No *dl*-ephedrine was isolated.

3. Reduction of α-bromoisobutyrophenone at 80–85° yielded principally bromine-free compounds.

4. Reduction of α-bromoisobutyrophenone at 33° *in vacuo* yielded 2-methylcinnamyl bromide, the result of a loss of hydrogen bromide, reduction and replacement by halogen accompanied by an allylic rearrangement.

5. Reduction of 2-bromocholestanone occurred with complete removal of bromine.

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Intermediate Complexes in the Friedel and Crafts Reaction

BY JAMES F. NORRIS AND JOHN EDWARD WOOD, III[1]

In a former paper[2] a number of complexes were described which contained aluminum halides, aromatic hydrocarbons and hydrogen halides. The complexes differed in stability when submitted to diminished pressure. When the one having the composition $Al_2Br_6 \cdot 2C_6H_3(C_2H_5)_3 \cdot HBr$ was held at 0.002 mm. pressure until constant weight was obtained, one-half of the hydrocarbon was lost. We accordingly attempted to prepare directly a complex which contained its components in molecular ratio of $1Al_2Br_6$ to 1 *s*-$C_6H_3(C_2H_5)_3$. When a mixture of these compounds in the above ratio was treated with hydrogen bromide, a compound was formed which was shown by analysis to have the composition represented by the formula $Al_2Br_6 \cdot s\text{-}C_6H_3(C_2H_5)_3 \cdot HBr$. A compound of similar composition containing aluminum bromide, mesitylene and hydrogen bromide also was prepared.

The previous work of Norris and Ingraham indicated that a complex could be formed in which ethyl bromide replaced the hydrogen bromide. We have isolated complexes which have the formulas $Al_2Br_6 \cdot s\text{-}C_6H_3(C_2H_5)_3$, C_2H_5Br and $Al_2Br_6 \cdot s\text{-}C_6H_3(CH_3)_3 \cdot C_2H_5Br$. We were unsuccessful in attempts to prepare complexes of definite composition containing only aluminum halides and

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[1] From the thesis of John Edward Wood, III, presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1939.

[2] Norris and Ingraham, THIS JOURNAL, **62**, 1298 (1940).

hydrocarbons. As far as the work has progressed it appears that a third component is necessary.

The complex which contained ethyl bromide was stable for several days. When it was heated or treated with additional ethyl bromide, hydrogen bromide was eliminated and the hydrocarbon was ethylated. This fact furnishes an explanation of the observation previously reported[3] that when methyl chloride was passed into a mixture of *m*-xylene and aluminum chloride at the temperature of a steam-bath no hydrogen chloride was evolved until about two-thirds of the methyl chloride had been added. It is probable that a ternary complex was first formed and later decomposed with the formation of alkylated benzenes or that the hydrogen chloride formed combined with the hydrocarbon and aluminum chloride to form a ternary complex.

The action of carbon dioxide on several complexes was studied since it has been shown[4] that when a mixture of benzene and aluminum chloride is treated under pressure with carbon dioxide, benzoic acid is formed. When the complex $Al_2Br_6\cdot s\text{-}C_6H_3(C_2H_5)_3\cdot HBr$ was allowed to stand with carbon dioxide at about 60 atmospheres pressure for fifty hours, no reaction took place. Under the same conditions the complex which contained two moles of triethylbenzene gave very small yields of what appeared to be the corresponding acid and ketone. When aluminum bromide and mesitylene without hydrogen bromide were used, 26% of the hydrocarbon was converted into *s*-trimethylbenzoic acid and 47% into the ketone. It was evident that the presence of hydrogen bromide in the complex interfered with the carbonation reaction. It is possible that the intermediate in this case contains aluminum bromide, hydrocarbon and carbon dioxide. If this is the case the hydrogen bromide must be removed before reaction takes place.

In order to gain information which might be of value in the interpretation of the structural relationships of the complexes, the compound having the formula $Al_2Br_6\cdot s\text{-}C_6H_3(C_2H_5)_3\cdot HBr$ was subjected to electrolysis. Wohl and Wertyporoch[5] have reported on the electrolysis of a compound to which they assign the formula $[Al(C_2H_5Br)n(C_6Et_6)_4]^{+++}3(AlBr_4)^-$.

In a preliminary experiment the conductivities were measured of a solution of aluminum bromide in toluene and of a similar solution after hydrogen bromide had been passed into it to form a complex. The conductivity of the latter was over 1000 times as great as that of the simple solution.

The complex $Al_2Br_6\cdot s\text{-}C_6H_3(C_2H_5)_3\cdot HBr$ was electrolyzed in a cell containing a porous cup. When the voltage between the anode and cathode was 18 volts and the current 0.1 ampere, gases were formed at both electrodes. After nine hours the material around the cathode and that around the anode were analyzed. Pure triethylbenzene separated at the cathode only. Analyses of the heavy oils in the two compartments of the cell for hydrocarbon, aluminum and bromine showed that a part of the aluminum bromide had been transferred from the catholyte to the anolyte. The oil from the latter yielded an organic product which consisted of *s*-triethylbenzene and higher boiling substances which contained bromine.

The results indicate that the complex studied is an ionized compound, that the positive ion contains hydrocarbon, and the negative ion aluminum and bromine, that the negative ion is transferred more rapidly than the positive ion, and that the reaction at the anode involves bromination. Whether or not a part of the aluminum bromide is present in the positive ion can be determined only by additional work which is to be done. The simplest formula which could be assigned to the complex with the present knowledge is $[C_6H_3(C_2H_5)_3H]^+Al_2Br_7^-$.

In the paper by Norris and Ingraham it was stated that when the complexes which contained aluminum bromide were treated with hydrogen chloride the bromine of the bromide was replaced by chlorine and a complex containing aluminum chloride was formed. It was of interest to find out whether a similar replacement took place when the aluminum halide was combined with other organic molecules. We have shown that similar replacements take place when the complex contains benzene or toluene. When hydrogen bromide was passed into the complex $AlCl_3\cdot C_6H_5NO_2$ the chlorine was replaced by bromine, and the complex so formed was converted into the one containing aluminum chloride when it was heated with hydrogen chloride. A small amount of a by-product was formed. When hydrogen iodide was used some triiodoaniline was isolated.

The complexes containing aluminum halides and nitrobenzene are oxidizing agents. It should be noted the complex $2AlCl_3\cdot C_6H_5NO_2$ must be

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[3] Norris and Rubinstein, THIS JOURNAL, **61**, 1169 (1939).

[4] British Patent 307,223.

[5] Wohl and Wertyporoch, *Ber.*, **64B**, 1357 (1931).

handled with care. Once during its preparation it was heated too hot and an explosion occurred. When it was treated with benzene the mixture ignited. It is possible that under controlled conditions a mixture of aluminum chloride and nitrobenzene might prove to be a valuable oxidizing agent to be used in the absence of water.

In the study of the mechanism of the condensation of acyl chlorides with aromatic hydrocarbons by the Friedel and Crafts reaction, it is usually considered that the halogen in the halogen hydride formed is the halogen present in the acyl halide. To test this view the condensation of acetyl chloride with benzene by means of aluminum bromide and the condensation of acetyl bromide with benzene by means of aluminum chloride were studied. In the two cases both hydrogen chloride and hydrogen bromide were formed. When acetyl chloride and aluminum bromide were used 70 mole per cent. of the mixture of gases evolved was hydrogen bromide. When acetyl bromide and aluminum chloride were used, 77 mole per cent. of hydrogen chloride was obtained. Much the larger part of the halogen liberated as the halide was the halogen which was originally in combination with the aluminum. These facts lead to conclusions which will be tested.

Details of Experiments

The Complex $Al_2Br_6 \cdot s\text{-}C_6H_3(C_2H_5)_3 \cdot HBr$.—Aluminum bromide was distilled under anhydrous conditions into a flask and *s*-triethylbenzene was added. The weights used were 17.811 g. of Al_2Br_6 and 5.564 g. of hydrocarbon (mole ratio 1:1). When the mixture was heated to 100° a solution was obtained from which about one-half of the bromide crystallized out on cooling. Hydrogen bromide was passed into the mixture at room temperature as long as it dissolved. The increase in weight was 2.997 g. equivalent to 1.10 moles of hydrogen bromide. When the product which was an oil was held at 15 to 25 microns pressure for 1.4 hours, the loss in weight was 0.373 g. The hydrogen bromide left in the complex was equivalent to 0.970 mole. The complex was held at the same pressure for an additional eight and one-third hours; the loss in weight was 0.04 mole. A control experiment showed that under the same conditions a saturated solution of aluminum bromide in *s*-triethylbenzene lost 1.1 g. in seven hours. A repetition of the preparation in which 32.3 g. of Al_2Br_6 was used gave closely checking results.

Samples of the complex after evacuation were analyzed in the way described by Norris and Ingraham with the following results: % hydrocarbon, 20.21, 19.45; bromine, 70.4, 70.6; aluminum 7.56, 7.52. Calcd.: 20.85, 72.07, 6.97, respectively.

The Complex $Al_2Br_6 \cdot s\text{-}C_6H_3(CH_3)_3 \cdot HBr$.—The compound was prepared in a way similar to that described above. The product after the removal of excess hydrogen bromide was found to contain 0.95 mole of hydrogen bromide.

The Complex $Al_2Br_6 \cdot s\text{-}C_6H_3(CH_3)_3 \cdot C_2H_5Br$.—A mixture was made at 0° of equal molecular quantities of the components, Al_2Br_6, 23.58 g., mesitylene, 4.98 g., and ethyl bromide, 4.59 g. The mixture was shaken for one hour; at the end of this time a homogeneous red liquid was formed. This oil was held at 12 mm. pressure for three and one-quarter hours; the loss in weight was 0.02 g. The pressure was then reduced to 15–30 microns. At the end of a total of four and one-half hours the loss in weight was 0.03 g. To gain further evidence as to whether the ethyl bromide was chemically combined, the product was shaken with about 10 cc. of petroleum ether and the latter after separation and washing with water was tested for bromine with a copper wire. No halogen was found. A control experiment with a mixture of petroleum ether and ethyl bromide gave a positive test.

The Complex $Al_2Br_6 \cdot s\text{-}C_6H_3(C_2H_5)_3 \cdot C_2H_5Br$.—A sample of this complex was made in the way described above and the same tests were applied. Petroleum ether did not remove any ethyl bromide. The complex was slowly decomposed under diminished pressure; 41.5 g. of the complex which contained 5.65 g. of ethyl bromide when held at 15–30 microns pressure lost 0.10 g. in one-quarter hour and 0.40 g. in 5.5 hours.

A sample of this complex which weighed 30.6 g. and contained 3.45 g. of ethyl bromide stood at room temperature in a closed tube for seventeen days with no apparent change. At the end of this time 5 cc. of ethyl bromide was added; the complex dissolved at once. In a few minutes hydrogen bromide was evolved freely.

The Reaction of the Complexes with Carbon Dioxide.—In all the experiments the substances in a glass vessel were placed in an autoclave. After the air was displaced by carbon dioxide, the autoclave was connected directly with a cylinder containing liquid carbon dioxide. When 31.9 g. of the complex $Al_2Br_6 \cdot 2s\text{-}C_6H_3(C_2H_5) \cdot HBr$ was kept for fifty hours at 50° in contact with carbon dioxide, carbonation took place to a very small extent. Enough *s*-triethylbenzoic acid was obtained to make its identification possible by the melting point of the acid and its amide. A very small amount of a substance which probably was the corresponding ketone also was isolated.

Experiments with the complex $Al_2Br_6 \cdot 3s\text{-}C_6H_3(CH_3)_3 \cdot HBr$ yielded unsatisfactory results. A small amount of the dimesityl ketone was isolated, but no acid was identified.

The complex $Al_2Br_6 \cdot s\text{-}C_6H_3(CH_3)_3 \cdot HBr$ when treated with carbon dioxide at room temperature for fifty hours gave no ketone and no acid; 96.5% of the mesitylene in the complex was recovered.

The Carbonation of Mesitylene in the Presence of Aluminum Bromide.—A mixture of 51.3 g. of aluminum bromide and 23.1 g. of mesitylene (mole ratio $1AlBr_3$ to 1 hydrocarbon) was treated with carbon dioxide for sixty hours at room temperature. The product was decomposed by water in the way described above, and steam distilled; 6 g. of mesitylene was recovered. The aqueous part of the distillate was returned to the flask from which it had been distilled and the mixture was cooled in an ice-bath. The solid was separated by filtration and digested with 10 g. of sodium hydroxide dissolved in 200 cc. of water. The insoluble residue weighed 11.5 g. The alkaline solution after acidification and cooling gave 8.5 g. of an acid. The material insoluble in alkali was crystallized three times from petroleum ether; it melted at 138.5–139.1°. The recorded melting point of dimesityl ketone is 136–137°. The acid formed was crystallized once from a mixture of alcohol and water and twice from petroleum ether; it melted at 152.0–152.4° (short range standardized thermometer). The recorded melting points of *s*-trimethylbenzoic acid vary from 147 to 155°. A sample of the acid which melted at 152.3° was converted into the amide; this melted at 185–186° (recorded m. p. 187–188°). The neutralization equivalent of the acid was 162.7 (theoretical 164.1). The yield of dimesityl ketone was 44.9% of the theoretical and of *s*-trimethylbenzoic acid 26.9%; 26.3% of the mesitylene used was recovered. When 2 moles of $AlBr_3$ and 1 mole of mesitylene were used the yields were 47.2% ketone, 26.4% acid, and 19.6% hydrocarbon.

Electrolysis of the Complex $Al_2Br_6 \cdot s\text{-}C_6H_3(C_2H_5)_3 \cdot HBr$.—In a preliminary experiment two solutions of aluminum bromide in toluene (mole ratio 1:1) were prepared. One solution was converted into the complex by passing into it hydrogen bromide until no free toluene was present. The conductivities of the solution and of the complex were determined in a conductivity cell of the usual type. The conductance of the simple solution was 1.5×10^{-4} mhos; that of the complex was 0.18 mho.

In another experiment the complex $Al_2Br_6 \cdot s\text{-}C_6H_3(CH_3)_3 \cdot C_2H_5Br$ was placed in a conductivity cell and a potential of 6 volts was applied. The current produced measured 0.05 ampere. For comparison a 0.1 *N* solution of sodium chloride was placed in the cell and a potential of 6 volts was applied; the current measured 0.18 ampere.

The complex $Al_2Br_6 \cdot s\text{-}C_6H_3(C_2H_5)_3 \cdot HBr$ was prepared and placed in a cell consisting of a 100-cc. beaker and a thin-walled alundum cup. Platinum electrodes were used. During the electrolysis a stream of dry nitrogen was passed over the cell. A potential of 18 volts across the electrodes was applied; the current was 0.1 ampere. Bubbling and darkening of the material was observed at both electrodes; no aluminum was deposited. At the end of nineteen hours the material at the cathode was a dark viscous substance and a light colorless oil which was shown to be *s*-triethylbenzene by the melting point of its trinitro derivative. There was no separation of hydrocarbon in the anode compartment of the cell.

The dark viscous material from the anode compartment and that from the cathode compartment were analyzed separately for aluminum, bromine and hydrocarbon. The results were as follows: anode, % Al, 8.29, 8.34; % Br, 74.3, 74.9; % hydrocarbon 14.0, 14.6; mole ratio Al:Br, 1 to 3.0. Cathode, % Al, 6.69, 6.54; % Br, 65.8, 63.5; % hydrocarbon 25.4, 27.6; mole ratio Al:Br, 1:3.3. Seven cc. of the insoluble oil obtained as the result of decomposition of the anolyte with water was distilled through a 2-inch (5 cm.) Podbielniak column; there were obtained 5.5 cc. of a liquid which boiled at 215° (*s*-triethylbenzene) and 1 cc. of a higher boiling fluorescent fraction which was shown to contain bromine.

Halogen Interchange in Complexes.—When hydrogen chloride is passed into a mixture of benzene and aluminum chloride a complex is formed very slowly; when, however, hydrogen bromide is used an oily complex soon begins to separate at room temperature. Hydrogen bromide was passed at room temperature into a mixture of 45 g. of aluminum chloride and 132 g. of benzene which was stirred (mole ratio Al_2Cl_6 to C_6H_6, 1:3). At the end of sixteen hours the heavy oily layer was separated from the benzene and aluminum chloride that had not reacted. The product contained chlorine and bromine in the atomic ratio of approximately 1:1. The treatment with hydrogen bromide was continued until all the aluminum chloride had passed into the lower layer; eleven hours were required. The atomic ratio in the complex was approximately bromine 4 to chlorine 1. Continued treatment with hydrogen bromide did not appreciably alter the ratio.

A similar replacement of chlorine by bromine took place when toluene and aluminum chloride were used. In this case the reaction was more rapid; with benzene twenty-seven hours were required to effect solution of the aluminum chloride, whereas with toluene two hours were sufficient.

The complex having the formula $AlCl_3 \cdot 2C_6H_5NO_2$ was kept at 90–100° and treated with hydrogen bromide for eleven hours. It was then held at diminished pressure for several hours to remove any dissolved hydrogen halides. The product was decomposed by water; it contained about 43% bromine and 2% chlorine; 92% of the chlorine had been replaced by bromine.

The complex $AlCl_3 \cdot C_6H_5NO_2$ was treated with hydrogen bromide for eight hours; at the end of this time 85% of the chlorine had been replaced by bromine. Hydrogen chloride was then passed into the product for eight hours at room temperature. The treatment increased the percentage of chlorine from 6.4 to 24.4%.

In an experiment in which $AlCl_3 \cdot C_6H_5NO_2$ was treated with hydrogen bromide for thirty hours at 90–100°, a small amount of a precipitate appeared in the solution. This was separated and treated with water. The product was shown by its melting point and that of its acetyl derivative to be 2,4-dibromoaniline.

About 39 g. of the complex $AlCl_3 \cdot C_6H_5NO_2$ was made in a tube and treated with hydrogen iodide at dry-ice temperature until 20 g. of the gas condensed. The tube was sealed and stood at room temperature for ten days. It was then heated at 65° for twenty hours. From the product was isolated a small amount of 2,4,6-triiodoaniline.

The Condensation with Benzene of Acetyl Chloride in the Presence of Aluminum Bromide and of Acetyl Bromide in the Presence of Aluminum Chloride.—The two reactions were carried out under the same conditions and equal molecular quantities were used. The molecular ratio was 1 aluminum halide, 1 acyl halide, 5 benzene. The weight of acetyl bromide was 45 g. During the reaction the flask containing the reactant was surrounded by ice and the contents were stirred. The aluminum halide was added slowly to the acyl halide and the benzene was allowed to drop, during one hour, onto the mixture. The evolved gases were collected in water. When the reaction was complete the flask was heated on a steam-bath until the evolution of gas ceased. The mixture of hydrogen halides in the water was analyzed. When acetyl bromide and aluminum chloride were used the mole percentage of hydrogen bromide was 23 and of hydrogen chloride 77; for each mole of hydrogen bromide there was formed 3.3 moles of hydrogen chloride. When acetyl chloride and aluminum bromide were used the mole percentage of hydrogen chloride was 30 and of hydrogen bromide 70; for each mole of hydrogen chloride there was 2.3 moles of hydrogen bromide. The yields of acetophenone in the two cases were nearly the same, 72 and 76%, respectively.

Summary

1. The preparation and some of the properties of the complexes having the following formulas are described: $Al_2Br_6 \cdot s\text{-}C_6H_3(CH_3)_3 \cdot HBr$, $Al_2Br_6 \cdot s\text{-}C_6H_3(C_2H_5)_3 \cdot C_2H_5Br$, $Al_2Br_6 \cdot s\text{-}C_6H_3(CH_3)_3 \cdot C_2H_5Br$.

2. The complex $Al_2Br_6 \cdot s\text{-}C_6H_3(C_2H_5)_3 \cdot HBr$ did not react with CO_2 at 60 atmospheres, but a mixture of Al_2Br_6 and $s\text{-}C_6H_3(CH_3)_3$ under the same conditions gave high yields of the dimesityl ketone and *s*-trimethylbenzoic acid.

3. When a complex which contains aluminum chloride and benzene, toluene, triethylbenzene or nitrobenzene was treated with hydrogen bromide at room temperature an exchange of halogen atoms took place. When the complex which contained aluminum bromide was treated with hydrogen chloride, exchange also took place.

4. When acetyl chloride was condensed with benzene by means of aluminum bromide 77 mole per cent. of the hydrogen halides formed was hydrogen bromide. When acetyl bromide and aluminum chloride were used the mole per cent. of hydrogen chloride was 70.

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The Preparation of Nitriles and Amides. Reactions of Esters with Acids and with Aluminum Chloride. The Use of the Salt NaCl·AlCl$_3$ in the Friedel and Crafts Reaction

BY JAMES F. NORRIS AND ALBERT JOHN KLEMKA[1]

In a former paper[2] the preparation was described of benzonitrile from benzamide or ammonium benzoate by means of aluminum chloride. Since the results were satisfactory, the method has been studied further and applied to the preparation of a number of typical compounds. As a guide in the use of the method the steps involved in the reaction were investigated. The results are indicated as follows

$$C_6H_5CONH_2 + AlCl_3 \xrightarrow{\text{heated}} HCl + C_6H_5CONHAlCl_2 \xrightarrow{\text{higher temperature}} C_6H_5CN + HCl + AlOCl$$

In one experiment a part of the product formed after the first evolution of hydrogen chloride had ceased was decomposed by water; benzamide was recovered. The second part was heated to a higher temperature; more hydrogen chloride was formed and the nitrile distilled.

Eleven nitriles were prepared by this method; the yields were from 63 to 97%. In most cases, the double salt of aluminum chloride and sodium chloride ($NaCl \cdot AlCl_3$) was used. This compound can be prepared easily, is convenient to handle and has the added advantage that it gives higher yields and does not melt during the reaction and cause frothing. The method cannot be applied to amides containing functional groups which react with aluminum chloride; unsatisfactory yields were obtained from amides of dibasic acids.

A simple procedure was devised for a semimicro method to be used in the identification of certain amides by converting them into nitriles and determining the melting point of the latter; about 10 milligrams of the amide is sufficient for the identification.

When ammonium salts of the acids were used the yields were low. It was shown that the first step in the reaction with aluminum chloride was not the formation of an amide.

Since this method of preparing nitriles involved the use of amides, the preparation of the latter directly from acids was studied. Biehringer and Borsum[3] have reported the interaction of an acid and an amide, as the result of which there is an interchange of the hydroxyl and amino groups. The reactions were carried out in sealed tubes at a high temperature and the yields were low.

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[1] From a part of the thesis of Albert John Klemka presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1939.

[2] Norris and Sturgis, THIS JOURNAL, **61**, 1413 (1939).

[3] Biehringer and Borsum, *Ber.*, **39**, 3348 (1906).