

dissolved in methyl alcohol and the solution saturated with hydrochloric acid. The only solid ester obtained in each case was found to be the same as that obtained from the cyclopropane ester. The yield of pure product was 92.5%.

Summary.

1. We have described two general methods for making cyclopropane derivatives that contain both ketonic and carboxyl groups.
2. We have studied the behavior of one of these cyclopropane derivatives towards bases, hydrobromic acid, reducing agents and on heating.
3. The facts presented show that cyclopropane derivatives of this type can enter into a great variety of reactions owing to the peculiar combination of groups possible in a three-ring compound.
4. By using different reagents, it was possible to open the ring at three different points.
5. The facts justify the conclusion that there is no fundamental difference between corresponding derivatives of ethylene and cyclopropane, and that if the peculiarities of the former are due to the presence of a conjugated system, those of the latter prove that a cyclopropane ring and a carbonyl group in the proper position form a conjugated system.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF OHIO STATE UNIVERSITY.]

THE ACTION OF ANHYDROUS ALUMINIUM CHLORIDE UPON UNSATURATED ORGANIC COMPOUNDS. II.

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In a preliminary article¹ the authors described the results of a study of the action of anhydrous aluminium chloride upon some simple unsaturated organic compounds, particularly hydrocarbons. The object of that investigation was to throw light upon the function of such catalysts as anhydrous aluminium chloride or ferric chloride in the process of cracking petroleum. The views suggested at that time appear to have been confirmed by further work which we now report.

Some of the compounds obtained are well crystallized. Others appear more or less granular to the naked eye, but when examined microscopically the crystalline structure is well shown. Without doubt all the compounds to be described are definitely crystalline. Clear cut melting points are not obtained from these compounds since dissociation or decomposition occurs before fusion. Consequently no melting points appear in the description of the products obtained. These compounds are in general unstable and decompose easily. Aluminium chloride itself volatilizes at about 180°, and this tends to promote decomposition.

¹ THIS JOURNAL, 38, 1382 (1916).

The Action of Anhydrous Aluminium Chloride upon Unsaturated Hydrocarbons.

In all cases the absorption of unsaturated products in the gaseous form by dry aluminium chloride is a very slow process—in most cases not being noticeable even within several hours. Upon the application of heat, invariably tars were produced. Organic liquids like amylene, phenyl ethylene, oleic acid and furfuraldehyde, upon treatment with aluminium chloride evolve much heat with the immediate formation of tars. In solution much more favorable results were obtained as will be shown in the following account.

The Action of Aluminium Chloride with Acetylene (C_2H_2).—Acetylene was prepared from calcium carbide, dried over soda lime, and purified from phosphine by means of bleaching powder. The dry gas was led into a solution of aluminium chloride in absolute ethyl alcohol until saturation was complete. More acetylene was passed in from time to time during the following two or three weeks while the solution was concentrated in an atmosphere of acetylene in a desiccator protected from moisture. A granular, light yellow, very hygroscopic product was secured, for which analysis indicated the formula $AlCl_3 \cdot C_2H_2 \cdot 2(C_2H_5OH)$.

Calculated: Al, 10.77; Cl, 42.28; C, 28.61; H, 5.60.

Found: Al, 10.60, 10.68; Cl, 42.32, 42.20; C, 28.22, 28.29; H, 6.21.

Average found: Al, 10.64; Cl, 42.46; C, 28.30; H, 6.21.

As with all the analytical values reported in this paper, these last results are the average for a number of closely agreeing analyses. This product decomposed with extreme ease on standing, losing its organic content very rapidly. This rate of decomposition was measured rather unsatisfactorily by the precipitation of acetylene as cuprous acetylide. In the earlier paper a different compound, $AlCl_3 \cdot 2C_2H_2 \cdot 2H_2O$, was reported.

Using purified methyl alcohol as a solvent in place of absolute ethyl alcohol a very similar compound was obtained. This was also extremely hygroscopic and decomposed very easily. It has the formula $AlCl_3 \cdot C_2H_2 \cdot CH_3OH \cdot H_2O$.

Calculated: Al, 12.93; Cl, 50.77; C, 17.18; H, 3.85.

Found: Al, 13.07, 13.12; Cl, 50.69, 50.63; C, 17.02, 16.99; H, 4.20, 4.00.

Average found: Al, 13.09; Cl, 50.66; C, 17.00; H, 4.10.

The Action of Aluminium Chloride with Ethylene (C_2H_4).—The same general procedure as with acetylene was followed. In former work we reported a compound of the formula $AlCl_3 \cdot 3C_2H_4 \cdot H_2O$. Another product was later secured which calculates for either $AlCl_3 \cdot 3C_2H_4 \cdot 2H_2O$ or $AlCl_3 \cdot C_2H_4 \cdot 2C_2H_5OH$.

Calculated: Al, 10.68; Cl, 41.94; C, 28.39; H, 6.36.

Found: Al, 10.70, 10.09; Cl, 42.09, 42.15; C, 26.22; H, 7.00, 7.41.

Average found: Al, 10.40; Cl, 42.12; C, 26.22; H, 7.20.

Using methyl alcohol as solvent a product was obtained which makes us believe the latter of the above two formulas is the correct one. Measurement of liberated ethylene in standard bromine water was unsatisfactory but pointed to the latter formula. This compound has the formula $\text{AlCl}_3 \cdot \text{C}_2\text{H}_4 \cdot \text{CH}_3\text{OH} \cdot \text{H}_2\text{O}$.

Calculated: Al, 12.81; Cl, 50.28; C, 17.02; H, 4.76.

Found: Al, 12.09, 12.91; Cl, 50.50, 51.03; C, 16.99, 16.96; H, 4.98.

Average found: Al, 12.80; Cl, 50.76; C, 16.97; H, 4.98.

The Action of Aluminium Chloride upon γ -Butylene $(\text{CH}_3)_2\text{C}=\text{CH}_2$.

—The reagent, γ -butylene, was prepared from a good quality of isobutyl alcohol by Newth's method.¹ Later the Lermontow method² was used. A considerable amount of trimethyl carbinol was obtained in the formation of this gas. Butlerow³ also mentions the formation of triisobutylene or dodecylene ($\text{C}_{12}\text{H}_{24}$) b. p. 177.5 – 178.5° , but we did not secure this product. It required several months of great patience to secure a granular product suitable for analysis as there was a continual tendency to form a glue-like mass. Methyl alcohol was used for solvent. The product obtained has the formula $\text{AlCl}_3(\text{CH}_3)_2\text{C}=\text{CH}_2 \cdot 2\text{CH}_3\text{OH} \cdot \text{H}_2\text{O}$.

Calculated: Al, 9.94; Cl, 39.01; C, 26.40; H, 7.02.

Found: Al, 9.88, 9.92, 9.90; Cl, 39.20, 38.94; C, 26.18, 25.98; H, 7.40, 7.31.

Average found: Al, 9.90; Cl, 39.07; C, 26.08; H, 7.35.

The Action of Aluminium Chloride upon Amylene $(\text{CH}_3)_2\text{C}=\text{CH} \cdot \text{CH}_3$.

—A good quality of trimethylene $(\text{CH}_3)_2\text{C}=\text{CH} \cdot \text{CH}_3$ (β -iso amylenes) b. p. 36 – 38° was used. Dry, powdered, aluminium chloride reacted at once with the pure liquid giving a series of bright-colored tars, yellow to red to sienna, as the amount of chloride added was increased. These tars, when dissolved in either ethyl or methyl alcohol yielded on fractionation a series of carbinols as verified by the Baumann-Schotten reaction. Trimethyl carbinol was formed in largest amount. On further heating some decylene was obtained as a heavy fluorescent dark oil.

A solution of aluminium chloride in absolute ethyl alcohol mixed with amylenes gave a fairly well crystallized product within two weeks. This was recrystallized from methyl alcohol, and has the formula $\text{AlCl}_3 \cdot \text{C}_5\text{H}_{10} \cdot \text{CH}_3\text{OH}$.

Calculated: Al, 11.50; Cl, 45.15; C, 30.56; H, 5.99.

Found: Al, 11.72, 11.62, 11.55; Cl, 45.13, 45.18; C, 30.57, 30.41; H, 6.67, 6.71.

Average found: Al, 11.63; Cl, 45.16; C, 30.49; H, 6.69.

This was the best crystallized product obtained in all our work.

The Action of Aluminium Chloride upon Phenyl Ethylene $(\text{C}_6\text{H}_5\text{CH}=\text{CH}_2)$.—Two products were secured from these reagents. One has the composition $\text{AlCl}_3 \cdot \text{C}_6\text{H}_5\text{CH}=\text{CH}_2$.

¹ *J. Chem. Soc.*, 79, 917 (1901).

² *Ann.*, 196, 117 (1879).

³ *Ber.*, 6, 56 (1873).

Calculated: Al, 11.36; Cl, 44.78; C, 40.41; H, 3.39.

Found: Cl, 11.29, 11.46, 11.60; Cl, 44.71, 44.73; C, 40.00, 39.92; H, 3.67, 3.51.

Average found: Al, 11.45; Cl, 44.72; C, 39.96; H, 3.74.

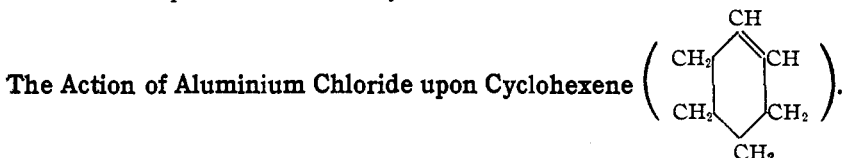
In this compound no water or alcohol of crystallization appears to be necessary for the formation of a crystalline product. This product, however, was well crystallized and relatively stable. A specimen on standing from May, 1916, to Nov., 1916, in a loosely stoppered bottle had lost its crystalline form and was oily. Analysis gave the formula $\text{AlCl}_3 \cdot 2\text{C}_6\text{H}_5 \cdot \text{CH}=\text{CH}_2 \cdot 2\text{H}_2\text{O}$.

Calculated: Al, 7.18; Cl, 28.17; C, 50.84; H, 5.34.

Found: Al, 7.64, 7.93, 7.77; Cl, 28.23, 28.22; C, 50.01; H, 5.96, 5.86.

Average found: Al, 7.78; Cl, 28.22; C, 50.01; H, 5.91.

Both of these products had a very sweet odor.



—No crystalline product suitable for analysis was obtained with cyclohexene.

The Action of Aluminium Chloride upon Unsaturated Acids.

Two series of experiments were carried out to study the products formed between aluminium chloride and unsaturated acids.

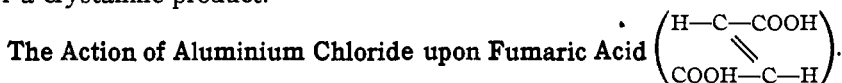
The Action of Aluminium Chloride upon Oleic Acid ($\text{C}_{17}\text{H}_{33}\text{COOH}$). —Highest grade oleic acid was used in this experiment. The addition of the dry chloride to the acid resulted in the immediate formation of heavy tars. On standing these tars became hard like asphalt. Aluminium chloride dissolved in methyl alcohol and mixed with oleic acid in equimolecular amounts gave in about four months a crystalline mass resembling brown sugar. Drying this product was a very difficult matter. The product had the formula $4\text{AlCl}_3 \cdot \text{C}_{17}\text{H}_{33}\text{COOH}$.

Calculated: Al, 13.28; Cl, 52.13; C, 26.46; H, 4.19.

Found: Al, 13.24, 13.25, 13.77; Cl, 52.71, 52.40, 52.33; C, 26.20, 26.10; H, 4.32, 4.49.

Average found: Al, 13.42; Cl, 52.47; C, 26.15; H, 4.40.

In this case the effect of the increased number of carbon atoms is noteworthy. Again no water or alcohol of crystallization appears necessary for a crystalline product.



—Two series of experiments were carried out. In one case just double the amount of aluminium chloride was used for the same amount of the acid as in the other in order to determine whether or not the same product

formed when an excess of one of the reagents was present. The product was identical in each case, and has the formula $\text{AlCl}_3 \cdot \text{C}_4\text{H}_4\text{O}_4$.

Calculated: Al, 10.77; Cl, 42.46; C, 19.08; H, 1.60.

Found: (1) Al, 11.41, 11.22, 11.30; Cl, 43.32, 43.29; C, 18.80; H, 1.89.

Average found: (I) Al, 11.31; Cl, 43.31; C, 18.80; H, 1.89.

Found: (2) Al, 11.24, 11.72; Cl, 43.29, 43.30; C, 18.75; H, 1.75; 1.70.

Average found: (II) Al, 11.48; Cl, 43.40; C, 18.75; H, 1.72.

The fumaric acid used was a snow-white product. It sublimed at 200° without decomposition.

The Action of Aluminium Chloride upon Aldehydes.

Two aldehydes were selected for study—one unsaturated, the other not.

The Action of Aluminium Chloride upon Furfuraldehyde $\left(\begin{array}{c} \text{CH}=\text{CH} \\ | \quad \quad \quad \diagup \text{O} \\ \text{CH}=\text{C}-\text{CHO} \end{array} \right)$.

—The dry chloride acting on a sample of furfuraldehyde gave a heavy black tar at once with the evolution of sweet odors. A solution of aluminium chloride in methyl alcohol reacted slowly with the furfuraldehyde forming a well crystallized, shiny, coal-black product in from five to eight days. The formula of the compound is $\text{AlCl}_3 \cdot \text{C}_5\text{H}_4\text{O}_2 \cdot \text{CH}_3\text{OH}$.

Calculated: Al, 10.37; Cl, 40.67; C, 27.53; H, 3.08.

Found: Al, 10.57, 10.48, 10.45; Cl, 40.34, 40.60; C, 27.27, 27.76, 27.40; H, 3.52, 3.60.

Average found: Al, 10.50; Cl, 40.47; C, 27.47; H, 3.56.

The Action of Aluminium Chloride upon Benzaldehyde ($\text{C}_6\text{H}_5\text{CHO}$).

—This is not an unsaturated aldehyde in the same sense as furfuraldehyde is, but its similarity in many reactions led us to try it here. A redistilled, clear sample of benzaldehyde was treated with aluminium chloride dissolved in methyl alcohol. A nice, yellowish white, crystalline product was secured in from eight to ten days, which had the formula $\text{AlCl}_3 \cdot \text{C}_6\text{H}_5\text{CHO} \cdot \text{CH}_3\text{OH}$.

Calculated: Al, 9.97; Cl, 39.17; C, 35.35; H, 3.71.

Found: Al, 9.50, 9.70, 9.30; Cl, 39.18, 39.40; C, 35.00, 34.90, 34.86; H, 4.55, 3.86, 4.07.

Average found: Al, 9.50; Cl, 39.29; C, 34.92; H, 4.12.

The Action of Aluminium Chloride upon Unsaturated Alcohols.

It was deemed advisable to try the action of aluminium chloride upon unsaturated alcohols as they represent another class of unsaturated organic compounds.

The Action of Aluminium Chloride upon Allyl Alcohol ($\text{CH}_2=\text{CH} \cdot \text{CH}_2\text{OH}$).—Using methyl alcohol as solvent, a poorly crystallized product appeared in twenty-four days. There was a tendency for a feathery

deposit resembling spun glass to appear along the surface and sides of the crystallizing dish. The product obtained had a very pungent odor. The formula is $\text{AlCl}_3 \cdot \text{C}_3\text{H}_5\text{O} \cdot \text{CH}_3\text{OH}$.

Calculated: Al, 12.12; Cl, 47.58; C, 21.47; H, 4.50.

Found: Al, 12.13, 12.17, 12.12; Cl, 48.62, 48.66; C, 21.00; H, 5.20.

Average found: Al, 12.13; Cl, 48.64; C, 21.00; H, 5.20.

Inability to secure other suitable organic reagents prevented further multiplication of such type reactions.

The Action of Anhydrous Ferric Chlorides upon Unsaturated Compounds.

In order to further study the nature of these additive products, freshly prepared anhydrous ferric chloride was substituted for aluminium chloride in a series of experiments. In all cases tried, the reactions were very similar to those of aluminium chloride but were less vigorous and not so complete.

The Action of Ferric Chloride upon Amylene ($(\text{CH}_3)_2\text{C}=\text{CH} \cdot \text{CH}_3$).

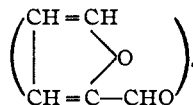
—Using the same general procedure as with aluminium chloride a dark brown compound was obtained, of the formula $\text{FeCl}_3 \cdot \text{C}_5\text{H}_{10} \cdot \text{CH}_3\text{OH}$.

Calculated: Fe, 21.12; Cl, 40.24; C, 27.23; H, 5.34.

Found: Fe, 21.29; 21.34; Cl, 40.34, 40.35; C, 26.98; H, 5.52, 5.68.

Average found: Fe, 21.31; Cl, 40.34; C, 26.98; H, 5.60.

The Action of Ferric Chloride upon Furfuraldehyde



—A product was secured analogous to that obtained with aluminium chloride, and having the formula $\text{FeCl}_3 \cdot \text{C}_5\text{H}_4\text{O}_2 \cdot \text{CH}_3\text{OH}$.

Calculated: Fe, 19.23; Cl, 36.65; C, 24.80; H, 2.77.

Found: Fe, 19.54, 19.37; Cl, 36.75, 36.67; C, 24.43, 24.10; H, 2.70, 2.91.

Average found: Fe, 19.45; Cl, 36.71; C, 24.26; H, 2.80.

The Comparison of Different Anhydrous Chlorides as Catalysts in Condensation.

A few experiments were undertaken to test the relative value of different anhydrous chlorides in condensation reactions.

In the preparation of benzophenone from benzoyl chloride and benzene, aluminium chloride was found to be the most efficient, giving yields of 70–71%. Under the same conditions with reactions carried out simultaneously, ferric chloride gave yields of 60–62%; zinc chloride 28–32% but chromic chloride gave no yield at all. Careful experiment showed pure anhydrous chromic chloride to be practically insoluble in water, dry ethyl ether, benzene, toluene, ligroin, chloroform, carbon tetrachloride, carbon disulfide, acetone, methyl acetate, ethyl acetate, glacial acetic acid, phenol, pyridine, amyl alcohol, amylenes, isobutyl alcohol, succinic acid, and oleic acid. It was slightly soluble in purified methyl

alcohol and in absolute alcohol, and gave a greenish to pink-colored solution with glycerine. Chromic chloride does not appear to be able to act as a condensing agent but resembles more closely some of the rare earth chlorides, *e. g.*, those of lanthanum, neodymium, praseodymium, etc. Cuprous chloride also failed to effect condensation. These results along with the low yields obtained with anhydrous zinc chloride make it appear that some of these anhydrous chlorides are specific in their action. Menschutkin¹ working with the anhydrous chlorides of iron, antimony, arsenic, tin, etc., found similar results. This supports our views that in the catalytic methods for cracking oil, the process is one of far greater complexity than the mere splitting out of water which anhydrous zinc chloride will do so well in many organic syntheses.

Discussion of Results.

All the compounds obtained are difficult to prepare and analyze. Attempts to remove the alcohol of crystallization alone, always resulted in disintegration of the compound. In some compounds the organic content was lost very readily. Schröeter,² has shown that when Grignard reagents are treated with carbon dioxide, corresponding acids are obtained. These compounds with aluminium chloride, which may appear analogous, failed to give the corresponding acids. Combustions had to be made very slowly and over two to three hours to obtain all the carbon content.

The time and patience required to obtain these products must be emphasized. In some cases in which gases were used, saturation with the organic body was required from time to time for months. Duplication of exactly the same conditions and reagents in such work is very difficult, tedious, and painstaking, so that the lack of concordance in the literature in regard to such compounds is only to be expected.

Owing to the higher temperature conditions involved in the process of oil cracking it is not likely that the compounds we have obtained are exactly the ones formed in that process. However it is only reasonable to assume the formation of similar combinations between the metallic chlorides and the unsaturated hydrocarbons and other unsaturated bodies present. In many petroleum oils, appreciably more oxygen is present than is ordinarily considered. In the oil cracking processes then, the oxidation actions must not be overlooked. In general, these tend to convert the aluminium chloride into oxide.

A few experiments were made upon some Mahoning petroleum oils. Aluminium chloride and ferric chloride each reacted at once with these petroleums, and yielded heavy black tars. As the quantity of these oils available for our work was limited, the amounts of tars obtained were insufficient for further investigation. There appears to be little doubt

¹ *J. Russ. Phys. Chem. Soc.*, 41, 1089 (1909); 43, 1329 (1911).

² *Ber.*, 40, 1584 (1907).

however that in the catalytic oil cracking processes, the catalyst combines with certain products in the reaction so that the unsaturated portion of the oil is held back from the distillate.

Summary.

1. Experiments upon the formation of a series of compounds between anhydrous aluminium chloride and some of the simpler unsaturated organic compounds have been described.
2. A number of such compounds are described and their analyses given.
3. The hypothesis that similar products are formed during the cracking of oils has been suggested.

COLUMBUS, OHIO.

[CONTRIBUTION FROM THE HENRY PHIPPS INSTITUTE OF THE UNIVERSITY OF PENNSYLVANIA.]

ON THE ELECTROLYTIC DIAZOTATION OF AN ALIPHATIC COMPOUND.

BY ROBERT B. KRAUSS.

Received April 21, 1917.

Introduction.

In the course of the preparation of a large number of new azo dyes and our study of their relation to the chemotherapy of tuberculosis during recent years, it became desirable to synthesize compounds containing aliphatic side chains linked to benzol and naphthalene rings through the N-N group. Since the literature of the diazo reaction held but little prospect of a method of general application along strictly chemical lines, our attention was turned to the development of the electrolytic method suggested for aromatic derivatives by Löb.¹

Historical.

The diazo reaction was discovered by Peter Griess² in 1862 and carefully studied by him. On adding a concentrated potash solution to diazo benzene chloride, he obtained potassium diazotate. In 1894 Schraube and Schmidt³ observed that diazo benzene chloride and strong caustic heated together to 130–140° gave a salt isomeric with Griess' salt, an iso-diazotate. It did not have the property of forming azo colors directly with an alkaline phenol, but regained this property on making it acid first and then adding it to an alkaline phenol. In the next thirty years countless attempts were made to diazotize aliphatic amino compounds and isolate or couple them. It was found that the amino group was replaced by a hydroxy group and that the intermediate diazo compound was not stable.

¹ *Z. Electrochem.*, 10, 237 (1904).

² *Ann.*, 121, 257 (1862); 137, 39 (1866).

³ *Ber.*, 27, 514 (1894).