acid, mannonic acid to gluconic acid and galactonic acid to talonic acid, in yields comparable with those obtained by the use of pyridine and quinoline.

2. The process described furnishes perhaps the most convenient method for obtaining mannonic and talonic lactones.

3. A possible mechanism has been suggested for the formation of isomeric hexonic acids in the alkaline oxidation of hexoses.

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The Polymerization of Some Unsaturated Hydrocarbons. The Catalytic Action of Aluminum Chloride[1]

BY W. H. HUNTER AND R. V. YOHE

The action of aluminum chloride on unsaturated hydrocarbons has not been studied very extensively. However, as a result of a study of the action of this reagent with ethylene, Stanley[2] concluded that any explanation of the reaction must take into account the formation of an aluminum chloride–hydrocarbon complex which he has shown to lead to the formation of olefinic compounds. An earlier study with ethylene, propylene, isobutylene, *n*-octene and diamylene led Szayna[3] to somewhat similar conclusions. Aside from these investigations, the action of aluminum chloride on unsaturated hydrocarbons has received very little attention. Since aluminum chloride forms complexes so readily with hydrocarbons and certain other substances, it was decided to study the action of some of these complexes as polymerizing agents. The unsaturated hydrocarbons used in this study were acetylene, ethylene and isobutylene.

Preparation and Purification of Materials

Acetylene.—Tank acetylene was purified by passing it through saturated bisulfite solution, concentrated sulfuric acid, concentrated alkali, granular calcium chloride and anhydrone.

Ethylene.—Anesthesia ethylene was used without further purification.

Isobutylene.—Isobutylene was prepared by the dehydration of tertiary butyl alcohol with aluminum oxide at 400°, and also by treating tertiary butyl chloride with alcoholic potassium hydroxide. The isobutylene was washed with water, then passed over soda lime, solid sodium hydroxide, calcium chloride and anhydrone, and was finally condensed in small cylinders.

Aluminum Chloride.—Mallinckrodt anhydrous resublimed C. P. aluminum chloride was used without further purification except in the cases when it was sublimed into adsorption chambers.

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(1) The work described in this paper constituted part of a thesis submitted to the graduate Faculty of the University of Minnesota by R. V. Yohe, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1931. This paper was prepared by the junior author after the death of Dr. Hunter.—L. I. SMITH. (Original manuscript received June 27, 1932.)

(2) Stanley, *J. Am. Concrete Inst.*, **49**, 349–541 (1930).

(3) Szayna, *Przemysl Chem.*, **12**, 637–47 (1928).

Ethyl Ether.—Commercial ether was washed three times with saturated potassium permanganate solution, once with water and dried successively over calcium chloride and phosphorus pentoxide. It was finally distilled from phosphorus pentoxide and kept over sodium.

Dimethylaniline.—Commercial dimethylaniline was acetylated, distilled, frozen out and finally vacuum distilled; m. p. 2.0°, b. p. 59.5–63° at 5 mm.

Trimethylamine.—A solution of pure trimethylamine hydrochloride was dropped on solid sodium hydroxide. The escaping gas was passed over soda lime, anhydrous barium oxide, metallic sodium and finally condensed with liquid air.

The Preparation of Complexes not Containing Hydrocarbons

Ether–Aluminum Chloride Complex.—This complex was prepared by the method of Frankforter and Daniels.[4]

Anal. Calcd. for $Al_2Cl_6 \cdot 2(C_2H_5)_2O$: Al, 13.01. Found: Al, 13.57, 13.18, 13.01, 13.00, 13.19.

Aluminum Chloride–Dimethylaniline Complex (1 : 1).—This was made by treating a quantity of aluminum chloride with a slight excess of dimethylaniline in carbon bisulfide solution. The solution turned dark green. Upon shaking, this green color disappeared and the solid aluminum chloride changed to orange or a dark red in color. When about half an equivalent of dimethylaniline had been added, a red oil, insoluble in carbon bisulfide, appeared. At the equivalent point the solution was a very dark red. Further addition of dimethylaniline caused the solution to become dark green.

When the green solution was cooled, a dark green precipitate appeared. Repeated extractions of this precipitate with boiling carbon bisulfide gave a compound which crystallized in large colorless plates. These crystals were fairly soluble in boiling carbon bisulfide but were quite insoluble in the cold. They were very hygroscopic, turned green in air and were decomposed by water to give dimethylaniline.

Anal. Calcd. for $Al_2Cl_6 \cdot 2C_6H_5N(CH_3)_2$: Al, 10.60; N, 5.52. Found: Al, 10.53, 10.68, 10.83, 10.77, 10.51, 10.61; N, 5.44, 5.50, 5.27, 5.50, 5.30.

Aluminum Chloride Dimethylaniline (2 : 1).—The red oil mentioned above was separated from the carbon bisulfide and unchanged aluminum chloride, extracted ten times with ten times its volume of boiling carbon bisulfide (to remove 1:1 complex), and then heated for fifteen minutes at 75° under vacuum.

Anal. Calcd. for $Al_2Cl_6 \cdot C_6H_5(CH_3)_2$: Al, 13.91; N, 3.60. Found: Al, 13.81, 13.93, 13.99, 13.96; N, 3.49, 3.35, 3.33, 3.53.

Experiments with Acetylene

At room temperature there was very little reaction between acetylene and aluminum chloride. However, at 100° adsorption and reaction were very rapid. There were no liquid products. Analysis of the darkened catalyst indicated the formation of a complex of the approximate composition $AlCl_3 \cdot C_2H_2$. The presence of ether vapor caused an immediate darkening of the catalyst and liquid products resulted. If acetylene was bubbled through ether and then passed over aluminum chloride an extremely exothermic reaction took place and liquid products were formed which were decomposed violently by water to give hydrogen chloride and a dark brown, cuprene-like material. The aluminum content of such liquid products varied between 14.07 and 14.8%. The formula, $Al_2Cl_6 \cdot (C_2H_5)_2O \cdot C_2H_2$ requires 14.7% aluminum.

Since the presence of ether vapor had such a marked effect upon the reaction, it seemed likely that the ethyl ether–aluminum chloride complex would have a similar effect. However, there was no reaction whatever between acetylene and the ether–aluminum chloride complex at room temperature or at 100°. Similarly, the aluminum

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[4] Frankforter and Daniels, THIS JOURNAL, **37**, 2560 (1915).

chloride–dimethylaniline complex failed to catalyze the polymerization of acetylene at room temperature or at 100°. Trimethylamine completely stopped the adsorption of acetylene by aluminum chloride even at 100°.

Experiments with Ethylene

Ethylene was adsorbed slowly by anhydrous aluminum chloride to give a very small amount of a deep red oil. The catalyst, however, gave up most of the adsorbed gas when heated. Neither heat nor ether vapor accelerated the reaction.

There was no reaction between the ether–aluminum chloride complex or the dimethylaniline–aluminum chloride complex and ethylene, either at room temperature or 100°

Experiments with Isobutylene

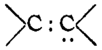
Isobutylene was extremely reactive toward aluminum chloride. Liquid products formed immediately when the hydrocarbon was allowed to come in contact with the aluminum chloride. One of the products was a colorless oil; the other a dark-red viscous oil, insoluble in the colorless product. The colorless liquid had an average molecular weight of 200 and a bromine number of 10–15. The red oil was a complex with an aluminum content averaging 11.5%, which when again treated with isobutylene yielded additional colorless liquid and the aluminum content of the complex dropped to approximately 8.75%. When the treatment of the red oil with isobutylene was carried out at 140° the resulting complex contained about 10.5% aluminum. Treatment of these red viscous complexes with water yielded yellow oils with molecular weights of 260–275.

Isobutylene containing ether vapor reacted vigorously with aluminum chloride to form a red viscous oil with an aluminum content of 11.8–12.3%. The percentage of aluminum decreased to 10.3–10.45% when ether-free isobutylene was passed through this red viscous oil and further treatment even at elevated temperatures failed to alter appreciably the aluminum content of the complex.

The complex of dimethylaniline and aluminum chloride (1:1) failed to react with isobutylene at room temperature; at 140° the color of the complex changed from very pale green to a cherry red, but no layer of hydrocarbons appeared and the composition of the complex remained unchanged. When the 2:1 complex of dimethylaniline and aluminum chloride was treated with isobutylene there was immediate evidence of reaction; a colorless oily layer formed and the composition of the complex changed until it became inactive, at which point it contained 10.48% aluminum and 2.63% nitrogen. The values calculated for the complex $Al_2Cl_6 \cdot C_6H_5N(CH_3)_2 \cdot 2C_4H_8$ are aluminum 10.8% and nitrogen 2.80%.

Discussion

In nearly every case of complex compound formation with aluminum chloride, aluminum functions with a coördination number of 4. Chlorine is not a usual donor for a coördinate bond. However, it should be able to act as such since it has three available pairs of electrons for coördination. It may do so in Al_2Cl_6. Such a coördinate bond should be easily broken giving an "unsaturated" aluminum atom which could take up two electrons from a more active donor.

A possible interpretation of the nature of the complexes formed between aluminum chloride and unsaturated aliphatic compounds is as follows: It has often been suggested that the *activated* olefinic bond may be represented by the following polarized structure:  and it is quite conceivable that a molecule of aluminum chloride could accept the "free" electron pair to give an activated complex in which one of the carbon atoms would momentarily be three covalent. Such a complex should be an excellent catalyst for polymerization, for if such an activated molecule should come in contact with another molecule of an olefin, immediate combination would result, by virtue of the highly unsaturated nature of the carbon atom containing only six electrons in its outer shell.[5] This new complex of higher hydrocarbon content would still be in an activated state, and could therefore react with another molecule of olefin in the same manner as it combined with the first. It can be seen that a long chain of carbon atoms might result from condensation of incoming olefin molecules with those already present in the complex. The length of these chains will depend on the heat of reaction, the ability of the coördinate bond to maintain this combination, and the possibility of ring formation.

A complex of aluminum chloride with an electronically saturated compound which has given a pair of electrons to aluminum (such as the ether–aluminum chloride complex) should not react with olefins and should not be a catalyst for polymerization. This has experimental support since it was found that this complex is not a catalyst for polymerization of acetylene or ethylene. However, it is a catalyst for the polymerization of isobutylene. This may be due to the fact that since oxonium compounds are not particularly stable, in certain cases an electron pair furnished by the hydrocarbon is more to be preferred by the aluminum chloride than that furnished by the oxygen of the ether. Isobutylene, which shows a greater reactivity, *per se*, than either ethylene or acetylene,[3,6] is apparently able to displace the ether in such a complex.[7] Since nitrogen in tertiary amines

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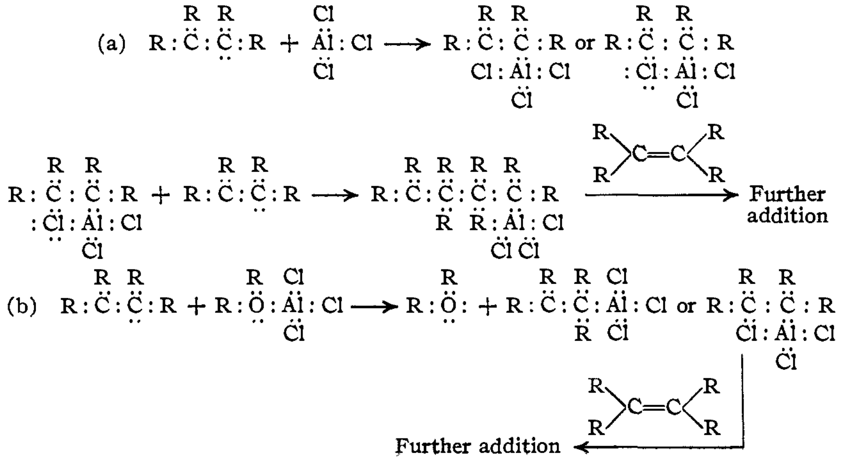
[5] Or we may accept the opinion of Dr. Sidgwick (N. V. Sidgwick, private communication) that it contains six of its own electrons and two electrons which are donated by a chlorine atom.

[6] Lebedev, *Ber.*, **58B**, 1138 (1925).

[7] If we accept Dr. Sidgwick's picture for the olefin–aluminum chloride complex, the combination with a second molecule of olefin involves the breaking of a C–Cl coördinate link and formation of a C–C linkage. The breaking of an Al–O coördinate link and formation of an Al–C link is essentially the same sort of a transformation. The two processes may be represented electronically as follows.



has a strong tendency to coördinate with unsaturated atoms (as in the amine oxides) the 1:1 complex of aluminum chloride and dimethylaniline should be stable in the presence of olefins and should not be a catalyst for the polymerization of the latter, and this was found to be the case. More striking yet, it was found that the introduction of trimethylamine vapor during adsorption runs on acetylene, ethylene and isobutylene stopped adsorption completely. Thus it seems clear that an activated olefin molecule may cause the rupture of a C–Cl coördinate link, or even of an Al–O coördinate link, but is unable to break the much stronger Al═N link.

Summary

1. A study has been made of the reaction of aluminum chloride with acetylene, ethylene and isobutylene.
2. A study has been made of the action upon acetylene, ethylene and isobutylene of some organic complexes of aluminum chloride.
3. A theory of polymerization based on the electronic structures of aluminum chloride and olefins has been advanced.

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The Yields of Some Organolithium Compounds by the Improved Procedure

BY HENRY GILMAN, E. A. ZOELLNER AND W. M. SELBY

Introduction

The valuable and elegant studies by Ziegler and Colonius[1] have pointed the way to the convenient preparation of organolithium compounds. Latterly it was shown that many of these compounds are readily accessible by the simple procedures used for the preparation of Grignard reagents, and in yields closely approximating those noted with organomagnesium compounds.[2] Incidental to other studies, some of which are reported in the following papers, it was necessary to prepare some new organolithium compounds and to determine the limits of applicability of several typical preparations. The results are given in the Experimental Part, and in the discussion of them which follows it will be observed that some organic halides which form Grignard reagents with great ease do not form any significant quantity of organolithium compound by the simplified procedure. On the other hand, some halides which react very sluggishly with magnesium enter into prompt reaction with lithium to give excellent yields of organolithium compounds.

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(1) Ziegler and Colonius, *Ann.*, **479**, 135 (1930).

(2) Gilman, Zoellner and Selby, THIS JOURNAL, **54**, 1957 (1932).