THE APPLICATION OF MECHANICAL ACTIVATION TO ORGANIC REACTIONS

I. THE INTERACTION OF ALUMINUM AND CARBON TETRACHLORIDE

II. THE PREPARATION OF ORGANOMAGNESIUM COMPOUNDS IN HYDROCARBON MEDIUMS

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CONTENTS

CONTENTS

CONTENTS

THE APPLICATION OF MECHANICAL ACTIVATION TO ORGANIC REACTIONS.

PREFACE

A. INTRODUCTION

In studying the mechanism of action of cutting fluids in the cutting of metals, M. C. Shaw (1) found that an appreciable amount of chemical reaction takes place between the cutting fluid and the metal being cut. This was first noted when aluminum was cut using carbon tetrachloride as a cutting fluid at very low cutting speeds, in which case a white vapor was given off at the point of contact of tool and work, and the freshly-cut aluminum surface was coated with a white granular deposit, identified as aluminum chloride. Similar reactions were noted in other cases, and Shaw postulated that the excellence of a cutting fluid depends upon its reaction in some degree with the metal being cut.

As an outgrowth of this work, Shaw recognized the possibilities inherent in the application of the general principles of metal cutting to chemical synthesis, and prepared phenylmagnesium bromide by cutting magnesium

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1. M. C. Shaw, Doctorate Dissertation, University of Cincinnati, 1942; U. S. Patent No. 2,416,717, March 4, 1947; British Patent No. 571,539, August 29, 1945.

into an ether solution of bromobenzene. He also obtained chemical reactions by cutting aluminum into chloroform, carbon tetrachloride, methyl chloroform, tetrachloroethane, and pentachloroethane, and evidence of some reaction when aluminum was cut into butyl mercaptan.

Shaw's work was primarily concerned with the action of chemical substances as cutting fluids, and a comparatively small amount of work was done with chemical synthesis. During the past six years, however, research on the action of metals cut into liquid reactants has been pursued actively, and today mechanical activation is an established process.

Although careful experiments have proved, as logic dictates, that freshly-cut chips of metal are more active chemically than chips which have been exposed to the atmosphere, particularly in such reactions as the preparation of organomagnesium compounds, no attempt at promoting reaction by cutting the metal in the presence of the liquid reactant has been reported, though Kilpatrick and co-workers (2) found that the formation of ethylmagnesium bromide was induced by rotating a cylinder of magnesium against a glass shoe in the presence of an ethereal solution of ethyl bromide, and ball milling is accepted practice.

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2. Kilpatrick and Simmons, J. Org. Chem., 2, 459 (1937); Gzemski and Kilpatrick, ibid., 5, 264 (1940).

It has been shown in previous experiments (3) that the action of mechanical activation is not always purely, nor even primarily, due to the presence of the fresh, uncontaminated chip surface. Rather, as was first mentioned by Shaw, it is believed that the advantages of mechanical activation are due in great part to the mechanics of cutting, with the attendant very high localized temperatures and pressures, limited only by the melting point and the hardness of the metal being cut, and to the increase in free energy due to the plastic deformation of the crystal lattice of the metal. There has been, however, no quantitative evaluation of the various contributions of metal cutting to the facilitation of chemical reactions; although such evaluation would unquestionably be of great value, the mechanical difficulties involved have thus far prevented the accurate measurement of such elusive factors as the temperature and pressure produced at the tool face during the cutting of a metal in the presence of a reactant, and of the difference in free energy of unstrained metal from that of a metal the instant it is cut. In the present work, mechanical activation is used as a tool for facilitating chemical reactions, and no attempt has been made to determine the influence of the variogs mechanical variables.

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3. B. F. Cameron, Master's Thesis, University of Cincinnati, 1944; M. E. Merchant, private communications.

The present dissertation is divided into two distinct parts, which are entirely unrelated except for the use of mechanical activation in each of them.

The first section of this dissertation is devoted to a study of the products formed in the reaction of aluminum with carbon tetrachloride, while the second section is concerned with the preparation of organomagnesium halides in hydrocarbon mediums, in the absence of any ethers, tertiary amines, or other substances which might facilitate the reaction by the formation of complexes, or by other means.

B. DESCRIPTION OF APPARATUS

A great deal of work has been done on the design, construction, and modification of apparatus for use in mechanical activation. Two machines have been used in the present work, both of which present many advantages over Shaw's original model, though the basic principle remains the same.

The first portion of this work, that dealing with the reaction of aluminum with carbon tetrachloride, was carried out largely in the machine illustrated photographically in Figure 1. Basically, the machine consists of the following elements: A shaft is mounted on sealed ball bearings, carrying on one end a cutter, and being driven at the other end by an H-gear, allowing continuous variation in cutting speeds. The shaft extends through a mechanical seal into the reaction chamber, which is machined from a solid block of stainless steel. The chamber block has openings leading to a reservoir for the liquid reactants, to a reflux condenser, and to a valve for removing the liquid after reaction. The front of the reaction chamber is closed by a plate of Pyrex glass, which allows observation of the course of the reaction, and which is removable to allow access to the shaft and cutter, and to provide for the removal of chips and solid products. A stainless steel electrode is cemented through this glass

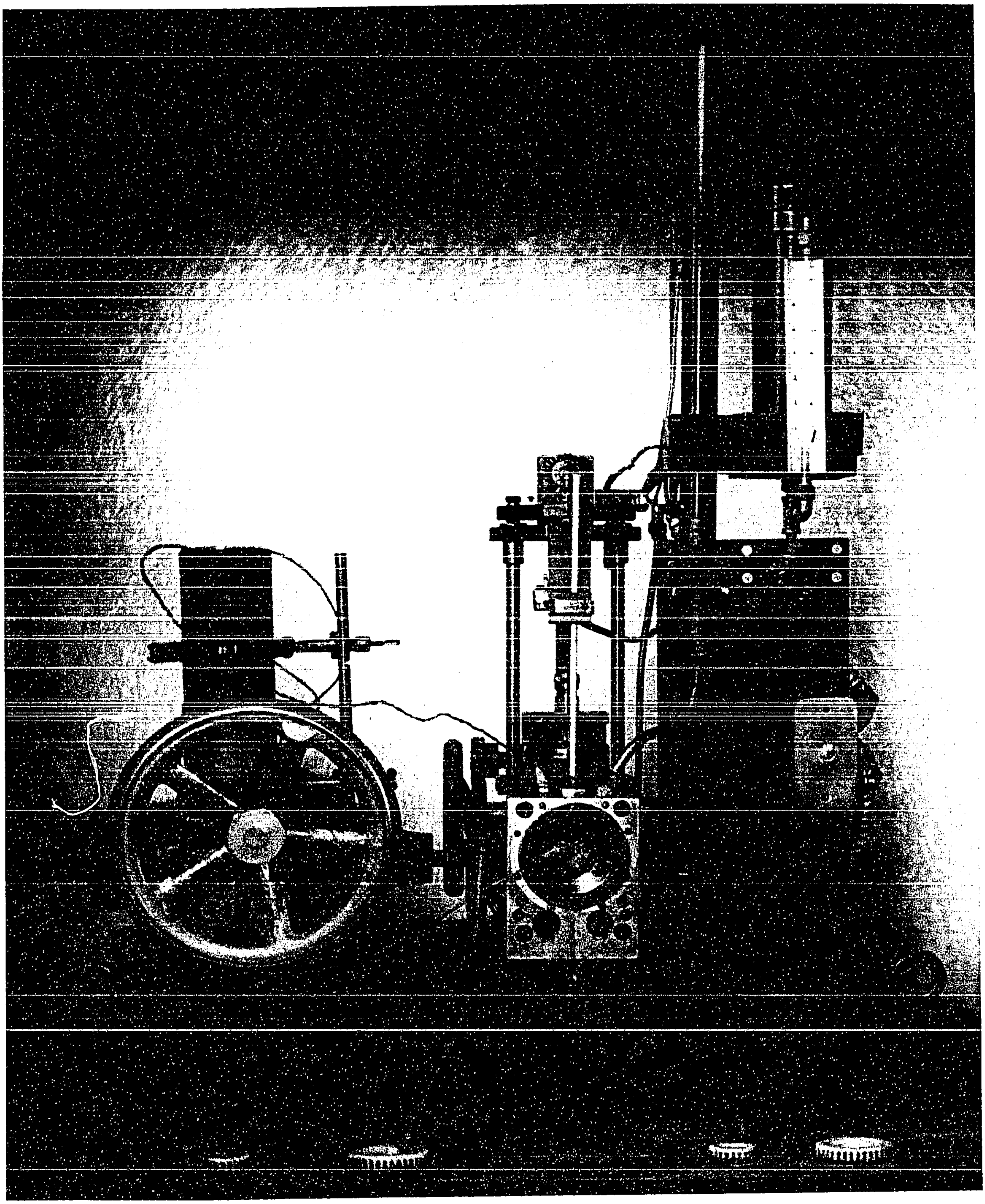

Figure 1

plate to allow measurement of electrical conductivity as the reaction progresses.

The material to be cut is fed into the top of the reaction chamber in the form of a one-quarter inch diameter rod by means of a lead screw, which is driven, through an appropriate gear reduction train, by a separate H-gear, allowing continuous variation in the rate at which the metal is fed into the cutter, independent of the speed of the cutting spindle.

The spindle itself, and all fittings within the reaction chamber, are of stainless steel; connections leading to the reservoir and condenser, and the inner tube of the condenser, are of tinned copper tubing. All valves, with the exception of the stainless steel exit valve, are tinned brass, while the interior of the reservoir is of tinned steel.

An inert gas, usually dry nitrogen, is introduced between two seals around the spindle which carries the cutter. The pressure behind the seal is maintained at a value several pounds per square inch higher than the pressure within the chamber by a pressure differential switch placed at the top of the reflux condenser; this switch in turn operates a solenoid valve which relieves pressure from the chamber, so that any leakage is of an inert gas into the chamber. This decreases the tendency of the liquid to be forced out around the shaft, and furnishes an inert atmosphere for the reaction, as well as allowing control of pressure for carrying out reactions up to 100 pounds per square inch.

A thermocouple well extends into the chamber, allowing remote reading of the temperature of the reaction mixture. All switches and valves are also located on a remote control panel, minimizing any danger from explosion. Provisions are made for heating the reaction chamber with cartridge-type heaters, and for cooling by circulating water or other cooling medium through a jacket milled into the chamber block.

The second part of this work, being the portion concerned with the preparation of organomagnesium compounds in hydrocarbon mediums, as well as a small part of the work on the reaction of aluminum with carbon tetrachloride, utilized a new and vastly improved mechanical activation apparatus, designed and constructed at the Cincinnati Milling Machine Company. This apparatus is shown in the photograph in Figure 2, and its essential elements are shown diagrammatically in Figure 3. In this second apparatus, the spindle carrying the cutter is mounted vertically, and is coupled directly to the shaft of a high speed one-half horsepower Dumore motor, thus obviating the necessity for a liquid seal around the shaft. The cutter is multiple-toothed, having 13 cutting edges machined from

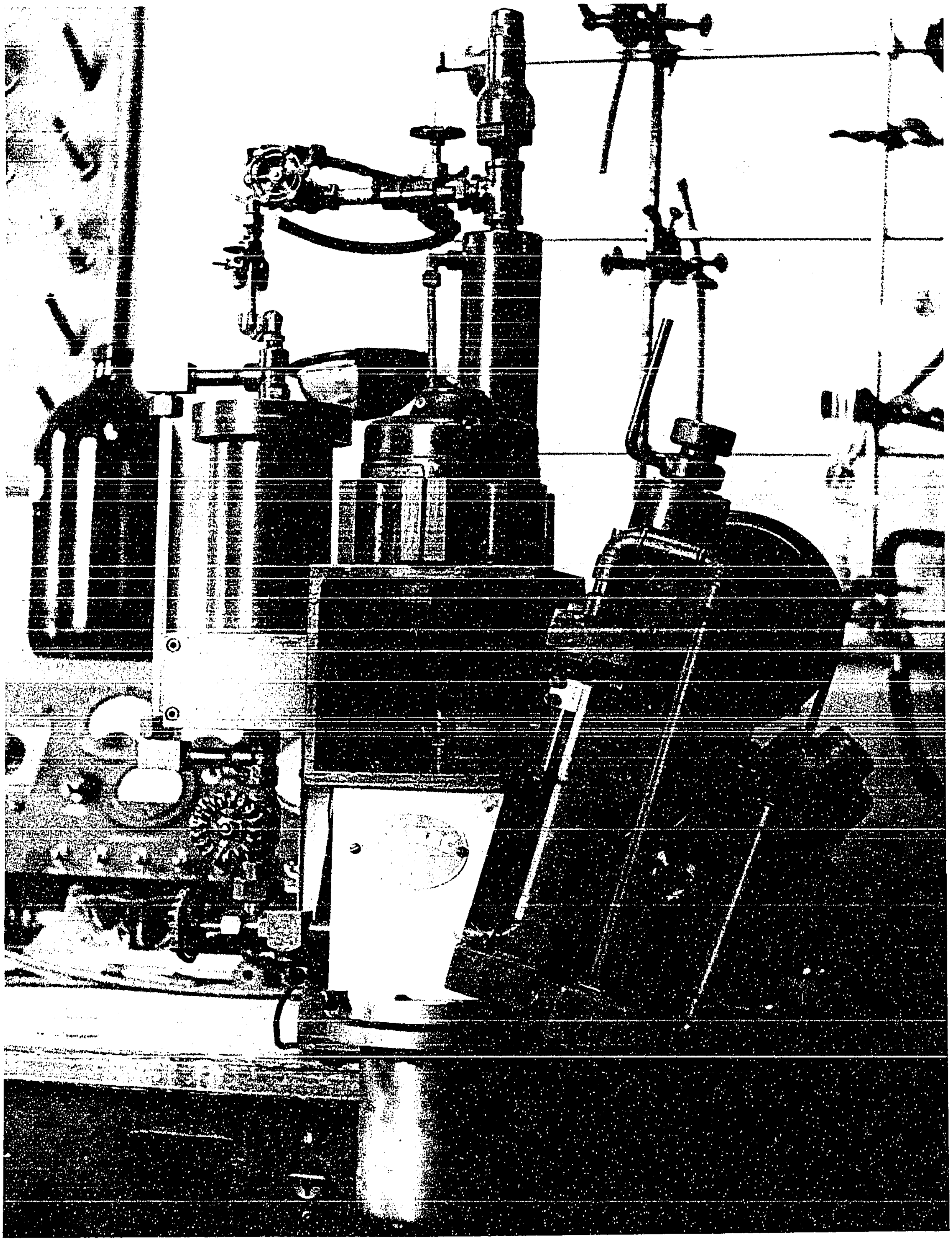

Figure 2

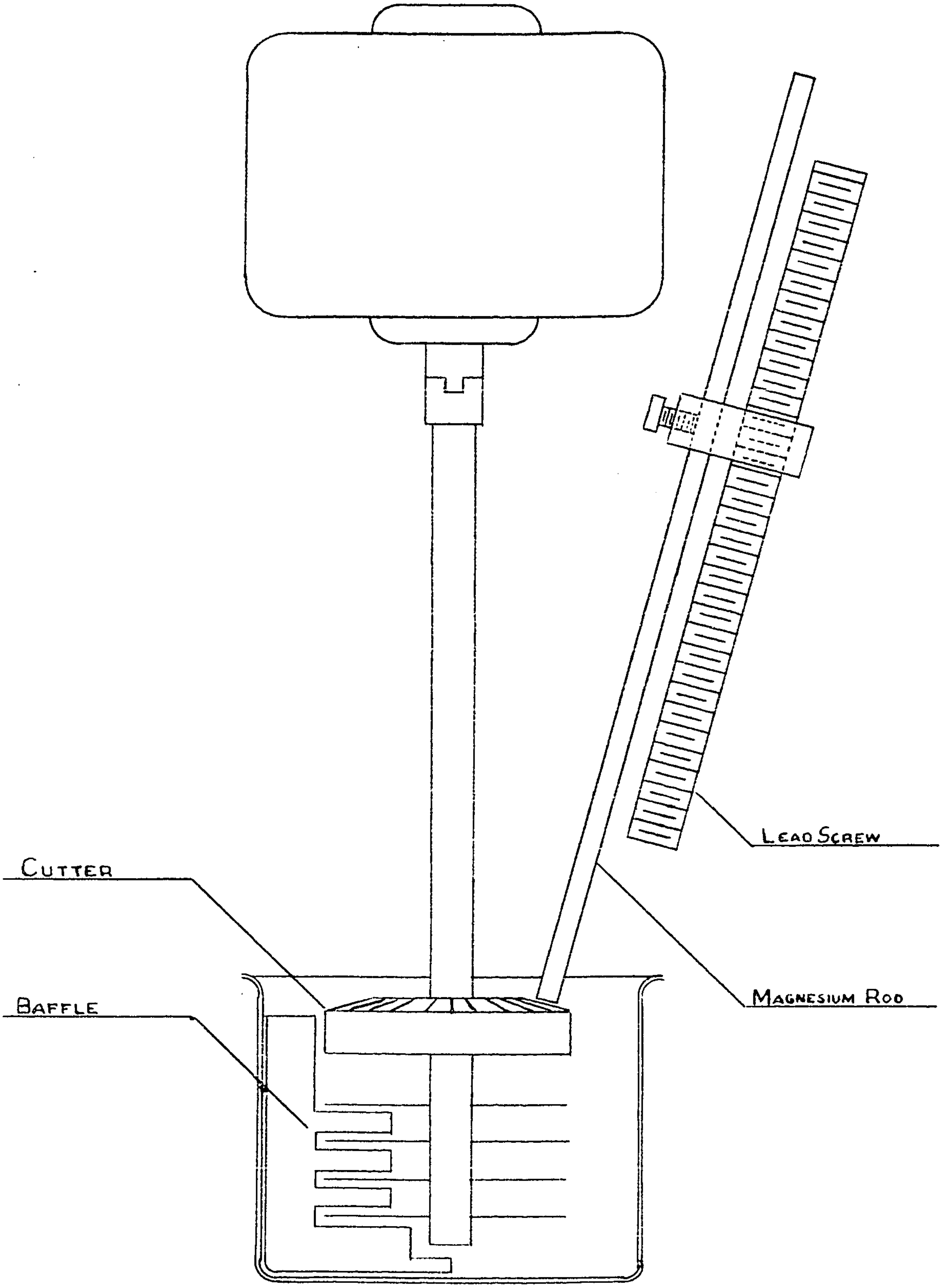

Figure 3

a single piece of high-speed steel. Below the cutter on the spindle are four knife-edged vanes which rotate between stationary baffles, serving to break up chips of metal which have been cut, and to furnish vigorous agitation to the reaction mixture. The cutter spindle is sealed above the surface of the reaction mixture by a face-type mechanical seal, consisting of a stationary ring of carbon attached to a bellows, which bears against a ring of carballoy attached to a shoulder on the spindle.

The metal being cut, again in the form of a one-quarter inch diameter rod, is fed into the cutter at an angle of fifteen degrees from the vertical by a lead screw, which in turn is driven by a small high-speed motor operating through a gear reduction mechanism and a pulley system which allows several feed rates at each motor speed. The amount of rod to be cut is controlled by two limit switches which cut off the feed motor at the two extremes of travel, thus allowing close reproducability of the amount of metal present. The speeds of both the spindle and feed motors are controlled by means of variable transformers.

The reaction chamber is in the form of a wide-mouthed vessel attached from the bottom to the block carrying the spindle and feed mechanism, thus allowing the reaction products to be removed in the chamber without the necessity of draining and exposing the material unduly to the atmosphere. In the present work two chambers were used, one being of Pyrex glass with a capacity of 300 cc., the other of stainless steel with a capacity of one liter.

A reservoir is connected to the chamber for the addition of liquid reactants, but it was not used in the course of these experiments. Also connected to the chamber is a reflux condenser, open at the top to the atmosphere through a relief valve or a bubbling tube, and an inlet for a gas, which may be either nitrogen for an inert atmosphere, or a reactant gas.

A thermocouple well extends into the chamber to allow measurement of the temperature of the reaction mixture, and an electrode, made from a miniature spark plug, is fitted into the chamber to allow measurement of the electrical conductivity of the reaction mixture.

The apparatus is constructed of stainless steel wherever metal may come into contact with the reaction mixture, but other materials may contact the mixture as noted: The cutter is of high speed steel, and the baffle is held together by silver solder. The spark plug electrode contains brass, porcelain, and coated steel, while the seal mechanism, which may at times come into contact with the reactants, contains tungsten carbide, carbon, Sauereisen cement, and Phosphor bronze.

None of these materials should in any way affect the reactions being studied.

In addition to the mechanical activation apparatus, other pieces of specialized equipment were used in performing these experiments. These will be described at appropriate places in the experimental section below.

I. THE INTERACTION OF ALUMINUM AND CARBON TETRACHLORIDE

A. INTRODUCTION

As was mentioned in the preface, the interaction of a metal with a cutting fluid was first noticed by Shaw when he was cutting aluminum in the presence of carbon tetrachloride. Since the action of carbon tetrachloride as a cutting fluid for cutting aluminum is extremely good, Shaw reasoned that the reaction which he noted might well be responsible for its excellence, and built the first mechanical activation apparatus to study the reaction which took place with larger quantities of material.

The products which Shaw obtained from the reaction of aluminum with carbon tetrachloride exhibited many interesting properties, apparently entering into or catalyzing a wide variety of reactions. It was with the idea of identifying or characterizing the reactive agent in the reaction product that the present investigation was undertaken.

B. HISTORICAL BACKGROUND

Shaw (1) performed a large number of experiments in which he cut aluminum into carbon tetrachloride, as well as a number in which he refluxed carbon tetrachloride with previously cut aluminum chips. In all cases a vigorous reaction was observed, accompanied by the appearance of a red color which rapidly changed to brown and black. The appearance of the red color was taken as an indication of the start of reaction; when cutting, the time until the appearance of the color averaged about 25 seconds, while 8-9 minutes were required when refluxing.

Shaw noted that, in most cases, aluminum chips remaining after reaction were coated with a red substance. When these chips, freed of excess carbon tetrachloride under nitrogen, were heated under vacuum, aluminum chloride and hexachloroethane sublimed, leaving a carbonaceous residue. The ratio of aluminum chloride to hexachloroethane obtained varied considerably, but there was usually a large excess of aluminum chloride, examples being 61 to 1 and 14 to 1.

Shaw found that these red-coated chips were extremely active. Although the presence of neither anhydrous aluminum chloride nor hexachloroethane seemed to have any effect on the time required for the reaction between carbon tetrachloride and aluminum to start, the introduction of a few of the red-coated chips caused the mixture to turn red instantly, and reaction to proceed rapidly. These chips also reacted with a number of other substances, with results as summarized below:

Reaction with benzene: Two layers were obtained, the lower one being red, turning to black, the upper layer being yellow. In one experiment the upper layer gave a good yield of chloroform, but this could not be repeated. The lower layer reacted with water to give a light brown precipitate, the black color disappearing. Part of the precipitate was soluble in alcohol to give a deep yellow solution.

Reaction with toluene: Similar to that with benzene. Distillation of the top layer gave only toluene; the bottom layer reacted with water to give a brown solution.

Reaction with acetone: A white, powdery precipitate was obtained, with a yellow solution.

Reaction with diethyl ether: Same as with acetone, through the precipitate had a different appearance.

Reaction with alcohol: Chips dissolved completely, reaction continuing for three or four hours, with the evolution of a gas, thought to be hydrogen. The solid remaining after evaporation of the alcohol had the odor of apples, was very slightly soluble in ether, and very soluble in alcohol. Attempts to recrystallize the solid were unsuccessful.

Reaction with ethyl acetate: Reaction gave a brownish-yellow solution.

Reaction with water: A violent reaction took place, with the emission of a white smoke and the production of a strong odor of phosgene and hydrogen chloride. Hexachloroethane was formed when carbon tetrachloride was present.

Reaction with pyridine: Two layers were formed, the bottom one being brown, the top one purple.

The only material with which Shaw reported no reaction on the addition of a portion of the red-coated chips was chloroform.

These experiments lead Shaw to suspect the existence of an active material other than the anhydrous aluminum chloride formed in the reaction; this active ingredient he postulated to be the red chip material, and it was with the idea of identifying and evaluating any such active agent that the present investigation was undertaken.

Although the formation of organoaluminum halides from the reaction of metallic aluminum with organic monohalides is well known, the only instance of the formation of an organoaluminum compound from poly-halogenated hydrocarbons was reported by Faillebin (4) and Thomas (5),

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4. Faillebin, Compt. rend. 174, 112-4 (1922)
5. V. Thomas, ibid., 174, 464-5 (1922)

who obtained reaction between aluminum and methylene iodide and bromide in diethyl ether solution. He formulated his reaction as follows:

$$3\ CH_2X_2 + 4\ Al = 3\ CH_2{=}AlX + AlX_3.$$

As a side reaction in ether solution, and as the primary reaction in the absence of ether, Faillebin obtained ethylene, by the mechanism:

$$6\ CH_2X_2 + 4\ Al = 3\ C_2H_4 + 4\ AlX_3.$$

With methylene bromide, even in ether solution, the second reaction predominated.

The reaction of aluminum with carbon tetrachloride to produce hexachloroethane was first reported by Hoffman and Seiler (6) in 1905. By heating 100 grams of carbon tetrachloride with an undisclosed amount of aluminum at 70°, they obtained 42 grams of hexachloroethane, recovering 35 grams of "starting material," presumably carbon tetrachloride. Apparently the yield of 65 percent hexachloroethane which they report was based on aluminum, with carbon tetrachloride in excess.

Although the reaction of carbon tetrachloride has reportedly been used for the commercial production of hexachloroethane, the literature records only one other instance of the use of the reaction for this purpose. In studying the uses to which powdered aluminum might be put in synthetic organic chemistry,

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6. Hoffman and Seiler, Ber. 38, 3038 (1905)

Ray and Dull (7) formed hexachloroethane by refluxing carbon tetrachloride with reduced aluminum. From 15 grams of carbon tetrachloride and seven grams of aluminum a large excess, they obtained 9.3 grams of hexachloroethane after extraction with ether and recrystallization from benzene. It is interesting to note that this represents a yield of 83 per cent, based on carbon tetrachloride which is almost identical with the yield which Hoffman and Seiler (6) obtained, based on carbon tetrachloride less the amount recovered. Ray and Dull noted the appearance of dense white fumes, which condensed to colorless crystals in the neck of the reaction flask, during the course of the reaction.

Other workers have reported the formation of aluminum chloride and hexachloroethane from the reaction of aluminum and carbon tetrachloride. Zappi (8), in an attempt to study the carbon produced by the general reaction

$$CCl_4 + M = MCl_4 + C,$$

reported that ordinary aluminum does not react with carbon tetrachloride in the cold, even after four months. By changing to activated aluminum, he obtained a slow but visible reaction in the cold, producing a resinous

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7. A. C. Ray and S. Dull, J. Ind. Chem. Soc. 5, 107 (1928)
8. E. Zappi, Anales soc. quim. Argentina 2, 217-28 (1914)

substance which formed a brown, cotton-like precipitate. With aluminum powder, which had been extracted with ether to remove grease, Zappi obtained no reaction, even on heating to 280°. By using aluminum wire with a diameter of one millimeter, in proportion with carbon tetrachloride corresponding to the equation

$$3\ CCl_4 + 4\ Al = 4\ AlCl_3 + 3\ C,$$

in sealed tubes heated to 100-120° for six hours, Zappi obtained a black liquid, the walls of the tube being covered with a black substance, in which were noted brilliant white crystals. A large amount of the aluminum present did not react. From the reaction product the only compound identified was hexachloroethane; Zappi assumed the resinous products to be higher chlorides of carbon. A small amount of grayish-black solids, which analysis proved to be carbon, was isolated from the solid.

Although he did not explicitly state the nature of the reaction between aluminum and carbon tetrachloride, Berger (9), in describing his work with smokes during the first World War, for which he was awarded the Grand Prize of the Navy by the French Academy in 1918, said that zinc reacts with carbon tetrachloride (and, presumably, carbon), although if the reaction were carried out in a confined space, hexachloroethane could be detected as a

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9. E. Berger, Compt. rend. <u>171</u>, 29-32 (1920) (70152)

product from the incomplete reaction with zinc. In speaking of the smokes produced by these zinc-carbon tetrachloride mixtures, Berger said, "... aluminum could have been used, the smoke produced being of the same order of volume; for reasons of convenience zinc was preferred."

The remainder of the work on the reaction of aluminum with carbon tetrachloride is confined to studies of the corrosion of metals, including aluminum, by carbon tetrachloride under various conditions. Dubrisay (10), who thought the corrosive action of carbon tetrachloride on metals to be due to the acids formed by the hydrolysis of the carbon tetrachloride in the presence of metals,

$$CCl_4 + H_2O = COCl_2 + 2\ HCl$$

$$CCl_4 + 2\ H_2O = CO_2 + 4\ HCl,$$

found aluminum to be practically unaltered by carbon tetrachloride in the presence of moisture, though copper, zinc, iron, and magnesium were acted on to varying degrees. In this respect, Dubrisay agreed with both Crudes (11) and Sastry (12), who found that carbon tetrachloride in the presence of moisture had almost no

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10. R. Dubrissay, Compt. rend. 204, 1568-70 (1937)
11. P. Crudes, Ind. quim. 13, 265-6 (1916); Chem. Abs. 11, 544 (1917)
12. S. G. Sastry, J. Soc. Chem. Ind. 35 (1916)

effect on aluminum. Rhodes, however, in the course of more accurate work on the corrosion of metals by carbon tetrachloride (13), found that aluminum loses weight slowly in cold, moist carbon tetrachloride, while this loss in weight is much more pronounced at the boiling point of the water-carbon tetrachloride mixture which he used. In the presence of the vapors of refluxing pure carbon tetrachloride, Rhodes found that an aluminum sheet soon became coated with a gray powder, consisting of aluminum chloride, hexachloroethane, and small amounts of some resinous substance and some black substance, while the refluxing liquid contained some hexachloroethane, indicating the principal reaction to be

$$2\ Al + 6\ CCl_4 = 2\ AlCl_3 + C_2Cl_6.$$

Aside from the equation cited by Zappi above, and found by him to be in error, Rhodes alone wrote an equation for the reaction between aluminum and carbon tetrachloride.

In other tests of the corrosion of aluminum by carbon tetrachloride, Formanke (14) found negligible action on aluminum immersed in carbon tetrachloride for eight months, while Popov (15) found no action on aluminum in carbon tetrachloride vapor at a relative humidity of 50-60 per cent.

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13. F. H. Rhodes and J. T. Carty, Ind. and Eng. Chem. 17, 909-11 (1925)

14. J. Formanek, Chem. Obzor 5, 57-9 (1930); Chem. Abs. 24, 4492 (1930)

15. P. V. Popov and N. I. Lebedeva, Trans. Sci. Inst. Fertilizers insectofungicides (U.S.S.R.), No. 135, 102-4 (1939); Chem. Abs. 34, 6210 (1940)

Aside from the studies of the action of moist carbon tetrachloride cited above Ray and Dull (7) alone investigated the reaction of aluminum and carbon tetrachloride in the presence of a third reagent. Ten minutes after starting to reflux 30 grams of carbon tetrachloride and 100 grams of benzene with seven grams of reduced aluminum, they noted a vigorous reaction, with copious evolution of hydrogen chloride, and the formation of a dark brown mass. By hydrolysis of the reaction products with cold dilute hydrochloric acid, followed by extraction and distillation, they obtained 3.7 grams of diphenyl methane and 11.2 grams of triphenyl methane, the only products being reported.

C. DISCUSSION OF RESULTS

1. Description of Reaction

When metallic aluminum is cut into carbon tetrachloride, a vigorous exothermic reaction takes place, beginning usually within a few seconds after cutting starts, although if the reaction chamber is not clean and dry at the start of the reaction, there may be a considerable induction period.

The start of the reaction between aluminum and carbon tetrachloride is usually marked by the appearance of a red color, which rapidly deepens to black. As the reaction proceeds, the temperature rapidly rises, reaching the boiling point of carbon tetrachloride if the cutting process is continued long enough. At a feed rate of about 0.1 inch per minute, aluminum appears to react as rapidly as it is cut. Reaction seems to be complete almost as soon as all of the aluminum has been cut.

In most cases where measurements were made, it was noted that, soon after the start of reaction, the reacting mixture exhibited a small electrical conductivity, which rose to a maximum when all of the aluminum had been cut into the mixture, and then fell fairly rapidly to a value just above zero.

Products of the reaction consist of a deep red, almost black solution in carbon tetrachloride, and a black, finely divided solid. Both the liquid and solid fume in air, giving off a dense white smoke, the evolution of which is made more intense by the addition of water to the reaction mixture. The liquid and solid phases may be separated by vacuum filtration into a black liquid and a black solid, the surface of the latter rapidly becoming white on exposure to the atmosphere.

The dark carbon tetrachloride solution is apparently decolorized by a small amount of any substance having an active hydrogen, such as water, alcohol, acetone, or damp ether. With acetone a white unidentified precipitate is produced, which when ignited, leaves a white ash, and which, on boiling with concentrated nitric acid, yields a solution which contains both aluminum and halogen. The black liquid product, when added to either aliphatic or aromatic hydrocarbons (heptane or benzene) produces a bright red color. Hexachloroethane may be crystallized from the carbon tetrachloride solution by cooling to within a few degrees of the freezing point of carbon tetrachloride. Treatment of the dark solution with activated charcoal gives a clear amber solution. The black liquid gives a weak test for the presence of an organometallic compound by the Gilman (16) color test with Michler's ketone.

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16. H. Gilman and Schulze, J. Am. Chem. Soc. 47, 2002 (1925)

Fractionation of the liquid product under vacuum yields carbon tetrachloride, hexachloroethane, and aluminum chloride, with some indications of the presence of phosgene, A black residue, only a small portion of which is carbon, remains after fractionation.

The black solid reaction product reacts vigorously with water. The hydrolysis is very exothermic, and produces a fairly stable white smoke, as well as a strong odor like that of phosgene. Hexachloroethane may be crystallized from the ether extract of the hydrolysed solid in very small amounts, though there is no definite indication that the hexachloroethane was produced by the hydrolysis. Most of the black solid reaction product is readily soluble in dry diethyl ether without reaction, giving a black solution which displays many of the properties of the solid (vigorous reaction with water to give white smoke, red color with benzene). The ether solution gives a very strongly positive color test for the presence of an organometallic compound with Michler's ketone.

2. Evidence for and against the Presence of Organometallic Compounds

As was previously mentioned, the present investigation was undertaken with the idea of identifying or confirming the presence of any organometallic compounds which might be formed by the action of carbon tetrachloride on aluminum. The reactions which the product undergoes do not necessarily indicate the presence of an organometallic compound, but neither are they typical of the reactions brought about by ordinary anhydrous aluminum chloride. On the other hand, since aluminum chloride is present at all times, it was found almost impossible to obtain conclusive results.

The first real evidence presented for the presence of an organometallic compound lies in the color test with Michler's ketone. An ether solution of commercial anhydrous aluminum chloride gives a very weak color test with Michler's ketone, and one which is typical of the tests obtained with the reaction products here in question except that it is less intense. The test obtained with the carbon tetrachloride solution of reaction products is only slightly more intense than that given by the ether solution of aluminum chloride, but that given by an ether solution of solid reaction products is spectacular. The addition of a small amount of this ether solution to a solution of Michler's ketone in benzene produces a bright orange-red precipitate, which turns to a bluish-gray on the addition of water, though the hydrolysis does not produce a particularly vigorous reaction, while the addition of the iodine solution in glacial acetic acid gives a bright green ether layer, with a deep green precipitate. This evidence, however, cannot be considered to prove the presence of an organometallic compound, since it is entirely possible that aluminum chloride, which is undoubtedly present in a very high state of activity, might lead to a similar reaction with Michler's ketone.

More evidence for the existence of an organometallic compound is presented by the behavior of the electrical conductivity during the course of the reaction, though this behavior also indicates that whatever causes the existence of the electrical conductivity is not stable, and is consumed in the course of the reaction: This will be discussed in more detail later.

The most conclusive evidence for the formation of an organometallic compound is offered by the red coloring matter produced, to which Shaw attributed the primary activity of the reaction product. This red material is negligibly soluble in carbon tetrachloride, as shown by the fact that the darkly colored carbon tetrachloride solution formed in the reaction is immediately decolorized by the action of water or other material containing an active hydrogen. On the other hand, an ether solution of the solid reaction products, which is dark red, retains all of its color on hydrolysis. When, however, the entire reaction product, containing both solid and liquid phases, is hydrolyzed, the carbon tetrachloride solution remains darkly colored. After removal of hexachloroethane from the colored carbon tetrachloride solution so produced, distillation of remaining carbon tetrachloride yields a dark red resin, which is not steam distillable, and which contains chlorine, but no aluminum.

The behavior of the red coloring matter outlined above is difficult of explanation unless it is assumed that an organoaluminum compound of sorts, probably consisting of a polymer containing aluminum, is formed during the reaction. This compound is not soluble in carbon tetrachloride, but is readily soluble in ether, as might be expected of such a substance. Hydrolysis of the organoaluminum complex then removes all aluminum, leaving a polymer which probably contains carbon, chlorine, oxygen, and hydrogen, which is readily soluble in carbon tetrachloride, and only very sparingly soluble in petroleum ether. Although the product of hydrolysis is certainly polymeric, the organoaluminum compound itself may or may not be, and if it is, no evidence has been found to indicate whether the polymeric bonds are carbon-carbon or carbon aluminum. A possible mechanism for the reaction will be discussed in more detail below.

It is to be noted that the extent of formation of any such organoaluminum compound as discussed before is very small, almost negligible. Any large scale formation of an organometallic compounds would be expected to take one or more of the following forms:

$AlCl_2CCl_3$ $AlCl(CCl_3)_2$ $Al(CCl_3)_3$.

The hydrolysis of any of these compounds would almost certainly produce chloroform as the principal product, yet distillation of products of hydrolysis yielded no chloroform or other material boiling at a lower temperature than carbon tetrachloride. Also, reaction of the products with carbon dioxide, either after removal from the reaction chamber, or during the course of the reaction, gave no indication of the presence of trichloroacetic acid.

3. Electrical Conductivity

The electrical conductivity of pure carbon tetrachloride is unmeasurable with apparatus used in the course of these experiments. While the conductivity of a solution of aluminum chloride in carbon tetrachloride is not definitely known, preliminary experiments showed it to be indistinguishable from that of carbon tetrachloride alone.

In most cases in which the electrical conductivity was measured during the reaction of aluminum with carbon tetrachloride, a slight conductivity has been noted soon after visible reaction started, which conductivity rises to a maximum just before all of the aluminum has been cut, and then falls rapidly to zero or slightly above zero. There appears to be little uniformity about the magnitude of the conductivity noted; three different curves for the variation of conductivity with fraction of the time required to cut all of the aluminum are presented as Figure 4. The same weight of aluminum was cut in all cases. Since in most instances the resistance of the solutions was above 2 x 10^6 ohms, the largest value for which conductivity meters could be calibrated with equipment on hand, conductivity is plotted as microamperes of current passing at a potential of 45 volts. The curve with the highest maximum was obtained in an experiment in which reaction did not start until about eleven minutes after cutting was started. When reaction did start, it was with almost explosive violence, leading to the large rise in conductivity depicted. It should be noted that the peak of this curve would be relatively many times higher if conductivity were plotted as reciprocal ohms.

The lowest curve of Figure 4 is one of the curves shown in Figure 5, which were obtained from three runs made under identical conditions, showing that, under such conditions, the variation in conductivity with the fraction of aluminum cut is a fairly definite function.

In the light of present knowledge, there is no definite explanation for the existence of electrical conductivity, nor for its peculiar variation, during

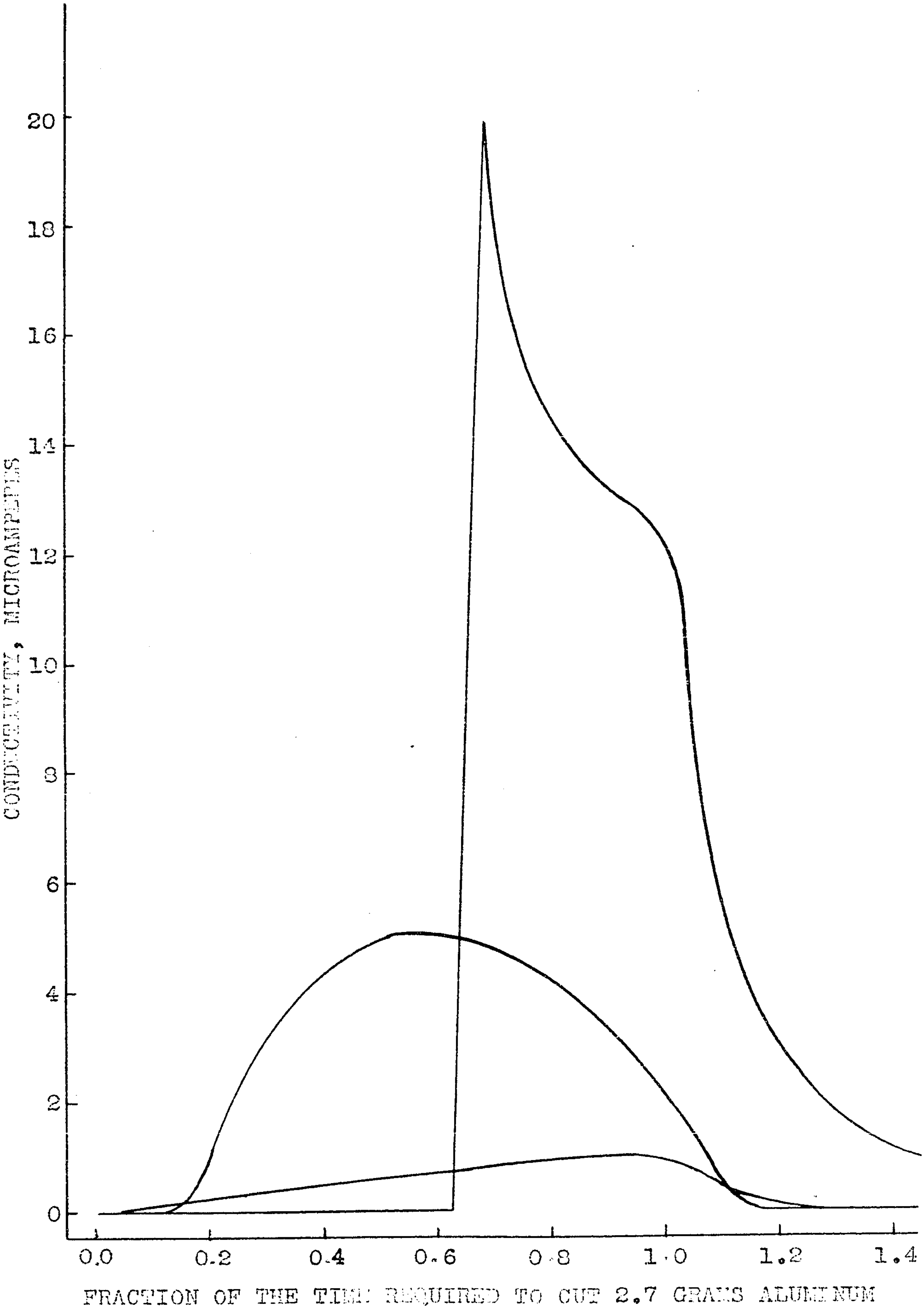
CONDUCTIVITY, MICROAMPERES
0
2
4
6
8
10
12
14
16
18
20
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
FRACTION OF THE TIME REQUIRED TO CUT 2.7 GRAMS ALUMINUM

Figure 4

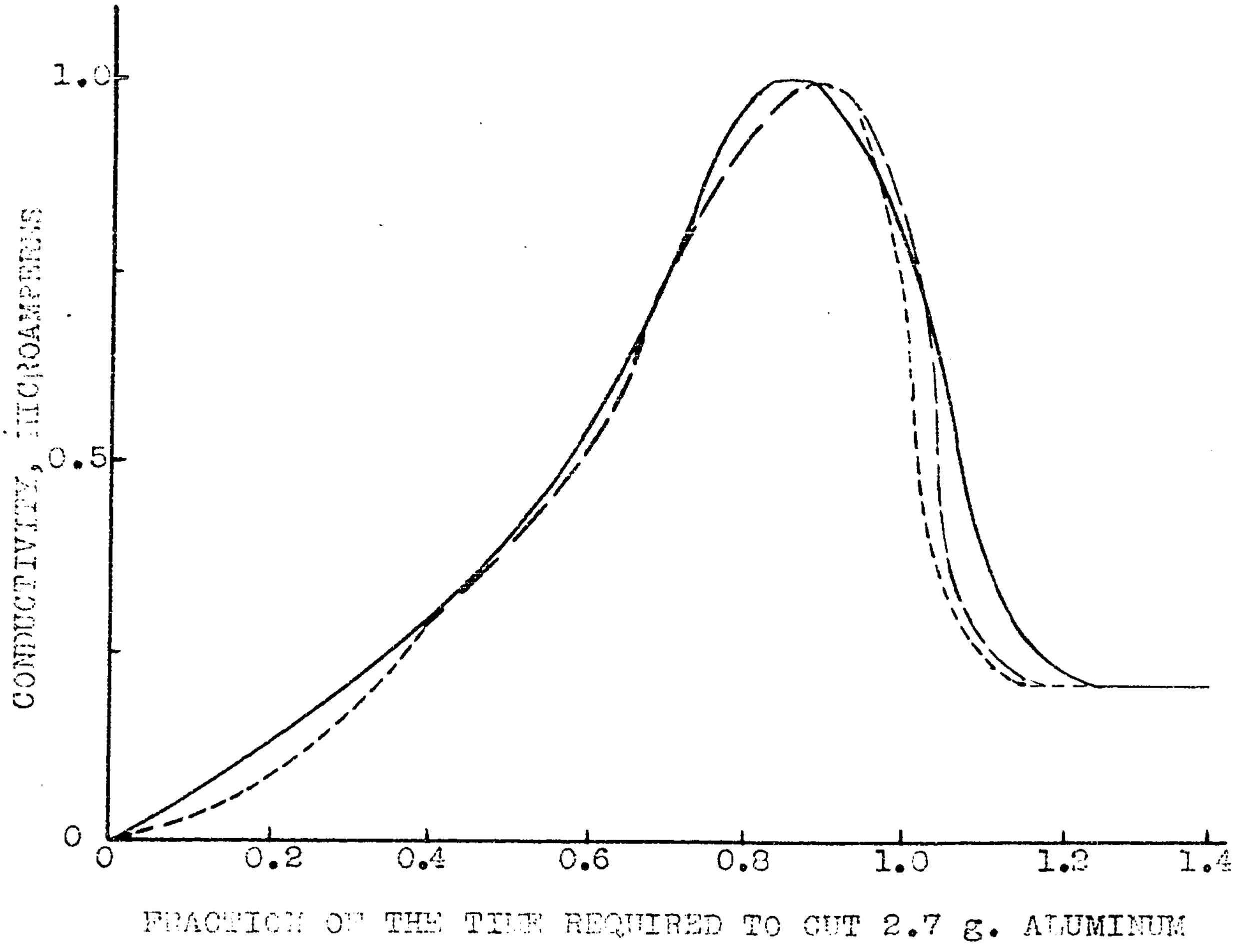
1.0
0.5
0
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
CONDUCTIVITY, MICROAMPERES
FRACTION OF THE TIME REQUIRED TO CUT 2.7 g. ALUMINUM

Figure 5

the reaction of aluminum with carbon tetrachloride. If the reaction between aluminum and carbon tetrachloride be assumed to be a free radical reaction, free radicals existing would be expected to be trichloromethyl radicals, $Cl_3C\cdot$. Such radicals would probably have a very short half-life, and, alone, would be unlikely to show any conductivity in solution. If the conductivity were due to the temporary combination of such radicals with some electron-donor or -acceptor, with the concurrent formation of a negative or positive ion, the conductivity curve might be expected to have a form similar to that of the curves shown. The most logical choice for an electron donor would be an aluminum salt, the action of which might be formulated as follows:

$$Al + 3\ CCl_4 = AlCl_3 + 3\ Cl_3C$$

$$AlCl_3 + Cl_3C\cdot = AlCl_3^{+} + :CCl_3^{-}.$$

Or the free radical mechanism might be formulated as involving the formation of an aluminum subchloride, which would itself act as an electron donor, such a mechanism being tantamount to the formation and ionization of an organoaluminum compound:

$$Al + 2\ CCl_4 = AlCl_2 + 2\ Cl_3C\cdot$$

$$AlCl_2 + Cl_3C\cdot = AlCl_2(CCl_3)$$

$$AlCl_2(CCl_3) = AlCl_2^{+} + :CCl_3^{-}.$$

There are other possible, but less likely, explanations for the behavior of the electrical conductivity. It is conceivable that the rise in temperature which accompanies the rise in conductivity during the course of the reaction between aluminum and carbon tetrachloride might have some effect, but heating the reaction mixture after the completion of reaction, when conductivity had returned to a low value, failed to cause another rise. Another, even less likely, possibility is that the rise and fall in conductivity might be due to the change in the ratio of aluminum chloride to hexachloroethane in solution in the reaction mixture. Since aluminum chloride is only sparingly soluble in carbon tetrachloride, its concentration should become constant soon after the start of the reaction, but the concentration of the very soluble hexachloroethane would increase throughout the reaction. This would be expected to have little or no effect on the electrical conductivity, and an experiment, in which hexachloroethane was added in varying amounts to a saturated carbon tetrachloride solution of commercial anhydrous aluminum chloride showed the conductivity to remain substantially zero at all concentrations.

4. Mechanism of the Reaction

Shaw (1) postulated the mechanism of the reaction between aluminum and carbon tetrachloride as follows:

$$3\ CCl_4 = 3\ Cl\ (\text{radical}) + Cl_3C\cdot$$

$$3\ Cl + Al = AlCl_3$$

$$AlCl_3 + Cl_3C\cdot = AlCl_3\cdot CCl_3$$

$$2\ AlCl_3\cdot CCl_3 = AlCl_3 + CCl_3CCl_3,$$

which is equivalent to the simpler equation presented by Rhodes (13),

$$2\ Al + 6\ CCl_4 = 2\ AlCl_3 + 3\ C_2Cl_6.$$

There appears to be little doubt that the latter is the overall equation of the principle reaction, though the present experiments, and those of Hoffman and Seiler (6), indicate that only about 65 per cent of the aluminum goes to the production of hexachloroethane, presenting the question of the fate of the remaining aluminum.

There exists another possibility which would account for all of the aluminum cut, and at the same time explain the unusual activity which has been attributed to the anhydrous aluminum chloride. If, instead of aluminum chloride, aluminum subchloride were formed in the reaction between aluminum and carbon tetrachloride,

$$2\ CCl_4 + Al = C_2Cl_6 + AlCl_2,$$

the yields of hexachloroethane, reported as being in the neighborhood of 65 per cent, based on the mechanism by which aluminum chloride is formed, would be increased to about 97 per cent, accounting for all of the aluminum except for the minute amount which apparently goes into the formation of a polymeric organoaluminum compound, In addition, aluminum subchloride would be expected to exhibit activity of the order of that of the reaction products here encountered.

In one experiment, during the hydrolysis of the mixed liquid and solid reaction products, gases evolved ignited and burned with a quiet blue flame. In this case a small amount of unreacted aluminum remained in the reaction product, and it is probable that the flame was due to the ignition of hydrogen produced by the hydrolysis of this aluminum. If aluminum subchloride were formed, however, it would undoubtedly react with water with the formation of hydrogen:

$$AlCl_2 + H_2O = AlCl_2OH + 1/2\ H_2.$$

In later experiments, however, no gases were found to be evolved during the slow hydrolysis of mixed reaction products which contained no aluminum metal, indicating the formation of no aluminum subchloride in these cases.

Friedel and Roux (17) reported the formation of aluminum subchloride when aluminum chloride was heated with aluminum in a sealed tube, but later attempts at repeating the experiment (18) were unsuccessful, and definitely indicated that such formation did not take place. The formation of aluminum subchloride was later reported from the action of metallic aluminum on aqueous

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17. Friedel and Roux, Compt. rend. 100, 1197 (1885)
18. Nilson and Pettersson, Trans. Chem. Soc. 53, 814-26 (1888)

aluminum chloride (19), with the evolution of hydrogen, a case analogous to that mentioned above, in which a flame was noted during the hydrolysis of a reaction product.

In the absence of more conclusive evidence, it does not seem likely that, under ordinary conditions, aluminum subchloride is formed, the more logical conclusion being that the primary reaction is the one formulated above:

$$2\ Al + 6\ CCl_4 = 2\ AlCl_3 + 3\ C_2Cl_6.$$

A logical mechanism for the formation of the apparently polymeric organoaluminum compound is much more difficult to formulate, and can be, at best, merely conjecture. One such mechanism would be,

$$Al + CCl_4 = AlClCCl_3$$

$$Al + CCl_4 + AlClCCl_3 = AlCl(CCl_2)AlCl$$

$$Al + CCl_4 + AlCl(CCl_2)AlCl = AlCl(CCl_2)AlCl(CCl_2)AlCl$$

etc.

The hydrolysis of such a complex would be expected to lead to the formation of methylene chloride, or, if polymerization were to continue, to methyl chloride or methane, and none of these were detected. Also, the polymeric product of hydrolysis, soluble in carbon

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19. C. Formanti and M. G. Lev, Boll. Chim. Farm. *40*, 689 (1901), reported in Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, London, 1924; *V*, 311

tetrachloride, would not be explained. Indeed, to account for the existence of the red resin after hydrolysis, it is again necessary to resort to a free radical mechanism involving the formation of long carbon chains containing chlorine and chloro-aluminum groups. Though the extended formulation of such a mechanism would be meaningless, the first steps would probably involve some such reactions as those below:

$$2\ Al + 2\ CCl_4 = 2\ AlCl_2(Cl_2C\cdot)$$

$$2\ AlCl_2(Cl_2C\cdot) = AlCl_2CCl_2CCl_2AlCl_2.$$

If the polymerization took such a form it would be expected that lower members of the series would also be expected to be present, and that the hydrolysis of these would produce identifiable compounds, such as acetylene tetrachloride, which would be expected from the hydrolysis of the complex shown above. It is entirely possible that such compounds were present in minute amounts.

5. Catalytic Activity of Reaction Product

The subject of the catalytic activity of the products of the reaction of aluminum with carbon tetrachloride has been too scantily investigated to allow any definite conclusions to be drawn.

In the only reaction investigated, being that of a mixture of carbon tetrachloride, benzene, and aluminum, the product was largely resinous, insoluble in any common solvents. Only a minute amount of a white, crystalline solid, which was probably hexaphenyl ethane, was steam distillable from the gummy black mass resulting from the reaction. There was no evidence of the formation of di- or tri-phenyl methane, as reported by Ray and Dull (7) in a similar reaction.

The Friedel-Crafts reaction between carbon tetrachloride and benzene in the presence of anhydrous aluminum chloride has been rather extensively studied. The usual products of the reaction are dichlorodiphenylmethane (20) and triphenylchloromethane (21), the two compounds giving, on steam distillation, benzophenone (22) and triphenylcarbinol (21). The reaction may also be used to form triphenylmethane by decomposing with ether the aluminum chloride complex formed by reacting 3 moles of benzene with 1 mole of carbon tetrachloride (23):

$$3\ C_6H_6 + CCl_4 + AlCl_3 = (C_6H_5)_3CCl.AlCl_3 + 3\ HCl$$

$$(C_6H_5)_3CCl.AlCl_3 + Et_2O = (C_6H_5)_3CH + CH_3CHO + EtCl + AlCl_3.$$

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20. M. Gomberg and R.L. Jickling, J. Am. Chem. Soc., 37, 2575-2591 (1915)

21. M. Gomberg, Ber. 33, 3144-3149 (1900); J. Am. Chem. Soc. 22, 752-757 (1900)

22. C. S. Marvel and W. N. Sperry, "Organic Syntheses," Vol. VIII, pp. 26-29 (1928)

23. J. F. Norris, "Organic Syntheses," Vol. IV, pp 81-83 (1925)

Hexachloroethane, however, with benzene and aluminum chloride, yields only a little chlorobenzene and anthracene, and unchanged hexachloroethane and benzene (24).

It appears, therefore, that the catalytic activity of the product of reaction of aluminum and carbon tetrachloride is very much greater than that of ordinary aluminum chloride, for the reaction between carbon tetrachloride and benzene, at least.

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24. A. Mouneyrat, Bull. soc. chim. (3), 19, 557-559 (1898).

D. EXPERIMENTAL

1. Reaction of Aluminum with Carbon Tetrachloride

Except for one run, all experiments were performed using the mechanical activation apparatus illustrated in Figure 1. In these runs, one-quarter inch rods of 2-S aluminum were cut, using a helical cutter having a pitch of 0.200 inch, and a rake angle of -15°; experimental procedure was essentially as follows:

The chamber of the mechanical activation apparatus was cleaned, and then dried by exposure to an infrared lamp for a period of about 30 minutes. The sight glass was then secured to the chamber black, and the entire system flushed with oil-pumped nitrogen. Carbon tetrachloride was then carefully measured in a graduated cylinder and poured into the reservoir of the apparatus, from which it was forced by nitrogen pressure into the chamber. Conductivity and temperature measurements were recorded at one-minute intervals throughout the course of the run.

When reaction was complete, the contents of the chamber were forced out through the valve at the bottom of the chamber into a flask, which was quickly stoppered to avoid undue exposure to the atmosphere.

All of these runs were made with 2.7 grams, 0.1 gram-atom, of aluminum being cut into 143 grams, 0.93 moles of carbon tetrachloride. Feed rates for the aluminum being cut were usually in the neighborhood of 0.1 inch per minute, varying between the extremes of 0.059 inches per minute to 0.209 inches per minute. In all runs the cutter spindle rotated at 920 revolutions per minute, representing a surface cutting speed of 12.2 feet per minute. Pressure within the chamber varied between four and five pounds per square inch, gauge, while the temperature in most cases rose from room temperature to 50-60 degrees during the course of the reaction. From these experiments there was no evidence that feed rate, pressure, or temperature influenced the course of the reaction in any way.

Reaction times, measured from the start of cutting to the draining of the chamber, were usually in the neighborhood of 30 minutes, though in most cases there appeared to be little reaction after fifteen minutes.

In the one run in which the mechanical activation apparatus illustrated in Figure 2 was used, the procedure followed was varied somewhat, though there appeared to be no difference in the reaction products. In this experiment amounts of reactants were increased ten-fold, 27 grams, 1.0 gram-atom of aluminum being cut into 1,430 grams, 9.3 moles of carbon tetrachloride. The carbon tetrachloride was placed in the stainless-steel chamber, which was then attached to the apparatus. Spindle speed was 8000 revolutions per minute, and during most of the run of the temperature was at the boiling point of carbon tetrachloride. As an example, the treatment of the products of this run is described in detail below.

During reaction approximately 300 cc. of gas were collected, while nothing was collected in two dry ice traps except for a small amount of solid which melted, but did not vaporize, at room temperature, and appeared to be carbon tetrachloride.

When reaction was completed, the reaction mixture was transferred to a three liter, three-necked flask, which was fitted with dropping funnel, stirrer, and reflux condenser. A tube from the top of the condenser led into same gas collection system previously used, except that one dry-ice trap was removed from the system. The flask was cooled by means of an ice bath.

200 cc. of distilled water were added slowly to reaction product in flask, hydrolysis taking place smoothly, with the evolution of no gas, and with no refluxing, except at one point at which water was added too rapidly. After water had been added, 30 cc. of concentrated nitric acid were added to the mixture by means of the dropping funnel, and stirring was continued until most of solid formed during hydrolysis had returned to solution. Ice water in cooling bath was then replaced with warm water, and stirring continued, with no evidence of gas evolution.

Mixture from above was transferred to a separatory funnel, but a stable emulsion formed, preventing separation. Mixture was then filtered, using suction (each filtration and transfer of liquid was followed by washing with CCl_4, the wash solution being added to mixture), to remove solid which was apparently causing emulsification. Because of tarry nature of solid, it was necessary to add 15.5 grams of "Super-Cel" filter aid. Filtrate was then separated, giving a deep reddish-brown carbon tetrachloride solution and a clear greenish water solution. Carbon tetrachloride solution was placed over Drierite to dry after being washed with several small portions of distilled water, the washings being added to water solution.

Super-Cel used in filtration of mixture above was extracted with ether and acetone, successively, extract evaporated, and found to contain approximately 0.1 gram of black tar and red leaflets.

Water solution from above was diluted to 2000 ml. in a volumetric flask at 20°. Two 2 ml. aliquot portions of this solution were diluted and titrated for chlorine with standard silver nitrate solution, followed by back-titration with potassium thiocyanate solution to a ferric ammonium sulfate end point. 21.55 and 21.76 ml. of 0.1000 normal silver nitrate solution were required for the two samples, indicating the presence of 2.166 equivalents of chlorine in the two liters of solution.

Three 10 ml. aliquots from the above solution were treated with 8-hydroxy quinoline for the precipitation of aluminum, as recommended by Kolthoff and Sandell, (25). Precipitates weighing 1.8338, 1.8330, and 1.8296 grams after drying at 130°C. Average weight of precipitate 1.8321 grams. If the precipitate be considered as 11.1 per cent aluminum oxide, this weight represents 38.74 grams of aluminum in the original solution. If the precipitate be considered to be pure aluminum oxinate, the weight represents 21.50 grams of aluminum in the original solution.

Three 3 ml. aliquots of the above solution were treated with 8-hydroxy quinoline by the method recommended by Mellan (26). Precipitates, after drying at 130°C., weighed 0.5437, 0.5404, 0.5403 grams, average 0.5416, representing a weight of 21.16 grams of aluminum in the original solution, the precipitate being considered as pure aluminum oxinate.

Three 10 ml. aliquots of the above solution were treated in the manner outlined by Kolthoff and Sandell (27) for the determination of aluminum as aluminum oxide. Precipitates were dried to constant

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25. I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," New York, 1945; p. 327

26. Mellan, "Organic Reagaats in Inorganic Analysis," Philadelphia, 1941, p. 239

27. Kolthoff and Sandell, op. cit., p. 324

weight at 1000°C. Precipitates of 0.2122, 0.2137, 0.2117 grams, average 0.2125 grams, were obtained. This represents a weight of aluminum of 22.48 grams in the original solution.

Carbon tetrachloride solution from above, which had been dried over Drierite, was transferred to flask for distillation. Including amount used in this transfer, a total of 1000 cc. of carbon tetrachloride had been added to original solution in washing vessels and filters. Total weight of mixture at this point, 2,492 g. Solution fractionated through helices-packed still; carbon tetrachloride began coming off immediately. After 1,879 g. of carbon tetrachloride had been removed, fractionation was interrupted, and the 388.5 grams of still-pot residue were filtered. Crystalline solid, pressed as free as possible of liquid, and air dried for a short time, weighed 186.8 grams.

Black filtrate from above, which weighed 168.5 grams, was chilled to -20°C., and 36.4 grams of additional crystals filtered off. Total weight of crude crystals, presumed to be hexachloroethane, removed to this point, 223.2 grams. Mixed crystals from the two filtration were dissolved in hot petroleum ether, giving orange-red solution. Hot petroleum ether solution was filtered, giving about 0.2 gram of brown solid, of which about half was soluble in diethyl ether.

Filtrate from two filtrations of still-pot residue, above, was fractionated through small Vigreux-type column. Fractions were collected as follows:

Fraction	Volume	Boiling Range	n_D^{26}
1.	9 cc	66.5-67.8°C.	---
2.	21	67.6-70.4	1.4318
3.	13	70.4-75.7	1.4560
4.	6.5	75.7-84.5	1.4570
5.	2.5	81.0-119.7	1.4750

Fraction 2 was refractionated through a small Podbielniak column. 11.1 cc. of pure distillate collected; boiling point, 68.6°C., uncorrected; n_D^{26} 1.4302, $d_4^{27.5}$ 1.308. Fraction was found to contain 75.2 per cent chlorine by combustion of a portion in a Parr bomb, followed by titration of chlorine. No precipitate was formed on treatment with phenyl isocyanate or phenyl hydrazine. Fraction found to be about 18 per cent soluble in water, the water-insoluble portion having a refractive index of n_D^{28} 1.4488. Fraction reacted violently with metallic sodium, with no apparent evolution of hydrogen. Fraction separated into two layers by freezing; layers would not re-combine on warming. $n_D^{29.1}$ for upper layer 1.4030; for lower layer, 1.4476.

Still pot residue following the fractionation of the last portion of the carbon tetrachloride solution, 21.1 grams of a dark brown solid mass, apparently largely crystalline. Mass was boiled with petroleum ether, giving a deep red solution containing some suspended solid material. Filtration of the hot solution yielded 0.3 grams of a brown solid. The petroleum ether filtrate was added to petroleum ether solution containing solids previously removed from solution.

From the petroleum ether solutions, mixed as above, 214.4 grams of hexachloroethane were crystallized (identified by sealed tube melting points of 187.4 - 187.8° and 187.3 - 187.8°C., and mixed melting points with pure hexachloroethane of 186.2 - 186.3° and 186.0 - 186.3°C.). Residual petroleum ether solution was evaporated to dryness in air, the material resulting from the evaporation being a number of apparently dark-red plates plus a deep red oil. These were steam distilled, white crystals being the only material which steam distilled; crystals were identified as hexachloroethane. Residue after steam distillation was a deep red tar which was readily soluble in carbon tetrachloride, very sparingly soluble in petroleum ether, and completely insoluble in alcohol. Evaporation of the carbon tetrachloride solution of the tar left a deep red, tacky tar (about one gram), which became very hard and brittle on cooling to about -20°C. A portion of the tar gave negative tests for aluminum after boiling with concentrated hydrochloric and nitric acid, and after fuzing with sodium. Dilution of a mixture of concentrated hydrochloric and nitric acids, in which a portion of the tar had been boiled, caused the precipitation of a small amount of granular, light brown, apparently resinous solid.

2. Treatment of Reaction Product

Various experiments were performed with the products of the reaction of carbon tetrachloride with aluminum, with results as outlined below:

Hydrolysis: Hydrolysis of liquid reaction product produces a small amount of a white smoke, with disappearance of dark color of solution, but there is no vigorous reaction. Hydrolysis of the solid reaction product, with fairly rapid addition of water and no cooling of reaction vessel, produces a dense white smoke, and the evolution of sufficient heat to cause water to boil. A voluminious white precipitate, which is readily soluble in acid, is produced. Hydrolysis of mixed products, with the slow addition of water to the mixture in a flask fitted with mercury-sealed stirrer, and cooled in an ice bath, produces only a mild reaction, with no gas evolution, and only a very small amount of smoke formation. White precipitate produced is again soluble in acid. Carbon tetrachloride solution after hydrolysis of mixed reaction products remains darkly colored.

Alcoholysis: One drop of 95 per cent ethyl alcohol decolorizes 1 cc. of liquid reaction product, without the formation of a precipitate. Reaction with solid product very similar to hydrolysis.

Reaction with Acetone: One drop of acetone immediately decolorized 10 cc. of liquid reaction product, with the formation of a flocculant white precipitate. Precipitate contains hologen by the Beilstein test, is insoluble in water, dilute hydrochloric acid, and benzene, partially soluble in hot concentrated nitric acid. Original solid does not burn in open flame, but loses some of its mass, leaving a white ash; solid remaining after treatment with hot nitric acid is completely vaporized on heating in open flame, while nitric acid solution gives positive tests for the presence of aluminum and halogen.

Reaction with Diethyl Ether: Liquid reaction product decolorized by either dry or wet ether. Solid reaction product largely dissolves in dry ether, with no apparent reaction; with undried ether, solid dissolves with reaction resembling mild hydrolysis.

Reaction with Dioxane: Reagent decolorizes liquid reaction product with the production of a small amount of a finely divided white precipitate.

Reaction with Benzene: Liquid product produces bright red color with no visible indication of reaction. Solid reacts vigorously, with formation of bright red solution and precipitate.

Reaction with Heptane: Same as with benzene.

Reaction with Methylmagnesium Bromide: Reaction very vigorous, but apparently no different from the reaction of the same reagent with pure carbon tetrachloride.

3. Attempted Preparation of Organic Acids

The products from one reaction were poured over solid carbon dioxide with no detectable reaction. Mixture was hydrolysed, and the organic layer extracted with a saturated solution of sodium carbonate. Sodium carbonate solution was added to water layer from hydrolysis, and the mixture acidified to a methyl orange end point. This acidified mixture was extracted with ether, and the ether extract dried and distilled. No evidence for the presence of an organic acid could be found.

In another experiment, the reaction was carried out as usual, except that a carbon dixoide atmosphere was substituted for a nitrogen atmosphere. There appeared to be no difference in the course of the reaction. Reaction product was treated as above, with the same negative results.

4. Isolation of Hexachloroethane

Although hexachloroethane was isolated from the liquid reaction product from all experiments, and in one case from an ether solution of the solid reaction product, attempts were made at quantitative recovery in only two cases. In these cases excess carbon tetrachloride was removed by distillation, and hexachloroethane crystallized from the remaining solution. Residual hexachloroethane was then removed from remaining carbon tetrachloride solution by further concentration by distillation, followed by crystallization at -20°. Crude hexachloroethane obtained by this procedure was recrystallized from petroleum ether. In one case, from the mixed products of four 0.1 mole runs, 72.5 grams of hexachloroethane were obtained, representing a yield of 51 per cent. In another run, in which one mole of aluminum had been cut, 223.2 grams of hexachloroethane were obtained, a yield of 62.7 per cent.

Identity of hexachloroethane in all cases was checked by sealed-tube melting points, by mixed melting points, and by sublimation temperature.

5. Reaction in the Presence of Benzene

Benzene and carbon tetrachloride were mixed in equimolar amounts, and a portion of the mixture containing 0.47 moles of each was placed in the apparatus. Aluminum was cut as usual. A black color was produced in the chamber as soon as cutting was started, electrical conductivity rising rapidly to full scale deflection, representing almost no electrical resistance in the mixture.

The reaction product from the action of aluminum and carbon tetrachloride was an extremely viscous black mass which did not ignite in an open flame. A small amount of a dark colored oil was separated from a portion of the mass by boiling with acetone and evaporating the solvent; this oil was soluble in petroleum ether only sparingly, and separated from petroleum ether solution only as an oil on cooling to -78°. The oil was very viscous, even at higher temperatures, and had at biting odor resembling that of an ester.

Steam distillation of the bulk of the resinous product yielded a small amount of unreacted carbon tetrachloride, which distilled without residue, and a small amount of a white crystalline material which melted at 141-142°C. The amount of this substance was too small to allow further purification or efforts at identification; it is probably triphenyl methyl or hexaphenylethane (m. 144-145°), or possibly triphenyl carbinol (m. 162.5°).

The reaction between aluminum, carbon tetrachloride and benzene was repeated in a flask by refluxing the same quantities of materials. Reaction began before the mixture reached its boiling point, with very rapid consumption of all the aluminum present, and the formation of the same black resinous product, which appeared to be identical in all respects with that produced in the mechanical activation apparatus. Nitration of this resinous product yielded a brown polymer which was partially soluble in ether and completely soluble in acetone to give a bright red solution. Precipitation of the material from acetone by the addition of water yielded a brown plastic material which became brittle on standing.

E. SUMMARY

1. The nature of the reaction of aluminum with carbon tetrachloride, and of the products of the reaction have been investigated.
2. A mechanism for the reaction, which accounts for the formation of hexachloroethane, aluminum chloride, and a polymeric organoaluminum compound, has been suggested.
4. A possible mechanism has been suggested to account for the electrical conductivity noted during the course of the reaction of aluminum and carbon tetrachloride.
5. The interaction of carbon tetrachloride, benzene, and aluminum indicates that the active agent produced in the reaction of carbon tetrachloride with aluminum is much more active than ordinary anhydrous aluminum chloride.

II. THE PREPARATION OF ORGANOMAGNESIUM COMPOUNDS IN HYDROCARBON MEDIUMS

A. INTRODUCTION

Since the discovery of the Grignard reagent in 1901, there has been a fairly constant, but slackening, stream of papers reporting the studies of solvents other than diethyl ether for the preparation and reaction of organomagnesium compounds. These solvents have largely taken the form of higher ethers, though they have been, by no means, limited to ethers. It is highly probable that many unsuccessful researches have not been published.

From an industrial standpoint, the use of diethyl ether as a solvent has probably been the greatest single deterrent to the more widespread use of the Grignard reagent in synthetic procedures. The high volatility and inflammability of diethyl ether make its use on a large scale extremely dangerous, while the necessary process of rendering the solvent anhydrous and pure is both costly and troublesome. No other solvent yet investigated, however, has been able to compare in affectiveness with diethyl ether, and in cases where the Grignard reagent is used for industrial procedures, it is usually used in ether solutions.

If pure aromatic or aliphatic hydrocarbons could be used for the preparation and reaction of organomagnesium compounds, the industrial potentialities of the compounds would be greatly enhanced. Compared to ether, most of the hydrocarbons are safe to handle; they are easily made anhydrous, and are readily and fairly cheaply available in almost any desired boiling range.

Earlier research, has, however, indicated that hydrocarbons are not suitable for the economical production of organomagnesium compounds, though the work has been incomplete, and much of it is difficult to interpret or reproduce.

In mechanical activation, there is available for the first time a tool which should allow conclusive evaluation of hydrocarbons as mediums for the preparation of organomagnesium compounds. By the use of mechanical activation, it is possible to secure magnesium in a finely divided state, with a surface uncontaminated by oxide or other foreign material, and to secure it reproducibly. In addition, the apparatus used in the present studies furnishes sufficient agitation to keep the surface of the magnesium substantially free of reaction products.

The present investigation was undertaken with the objective of obtaining a definite idea of the utility of hydrocarbons as mediums for the preparation of organomagnesium compounds. This has been successfully accomplished, though the research must be regarded as being primarily exploratory in nature, since wide new fields for further study have been uncovered. It is regretfully admitted that more has been left undone than has been done, but it is hoped that the realization of the breadth of the subject here opened will make apology for omissions unnecessary.

From the wide variety of pure hydrocarbons available, three were chosen for the present study. These were normal heptane, 2,4,4-trimethylpentane (hereinafter referred to as isooctane, for simplicity), and thiophene free benzene, as examples, respectively, of straight- and branched-chain aliphatic, and aromatic hydrocarbons.

Organic halides investigated have been confined to normal aliphatic halides, with emphasis on the bromides, though several chlorides, and one iodide, have been studied.

B. HISTORICAL BACKGROUND

As mentioned earlier, a wide variety of solvents for organomagnesium compounds has been studied. Excellent reviews of the literature on this subject have been made by Gilman (28) and Haubein (29), and no attempt will be made here to cover that portion of the literature which deals with solvents or mediums other than hydrocarbons, or those which are comparable with hydrocarbons in that the medium forms no complex with the organomagnesium compound. The latter field is restricted to the organic halides themselves.

A fairly large number of reactions of organic halides with magnesium has been carried out in the absence of any solvent or medium, other than the halides themselves, though only a few of these preparations have been definitely identified as organomagnesium compounds. Hallwachs and Schafarik (30), over forty years before Grignard's discovery of organomagnesium compounds in ether solution, noted that ethyl iodide attacked magnesium at ordinary temperatures, while the reaction was more rapid at 100°, and vigorous at 150-180°. From this reaction, they got a white mass,

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28. H. Gilman and R. McCracken, Rec. trav. chim. 46, 463-72 (1927)

29. A. E. Haubein, Doctor's Dissertation, Iowa State College, 1942

30. W. Hallwachs and A. Schafarik, Ann. 109, 206 (1858)

plus a gas with the odor of onions. The white mass, on exposure to air, gave a white smoke, which became very dense when the mass was heated. The white reaction product was reported to react with water with explosive violence.

This work was repeated by Cahours (31), who obtained vigorous reaction between magnesium and ethyl bromide at 120-130°, requiring cooling to slow the reaction after it was started. Besides the white solid, Cahours got a liquid; his product ignited on exposure to air, and reacted vigorously with water.

Lohr (32) found no reaction between methyl iodide and magnesium filings or ribbon, or with magnesium amalgam or a copper-magnesium alloy, during three months' exposure. At 160°, he obtained slow reaction with ordinary magnesium, while at 200° the reaction was more rapid, but still incomplete after several hours. At higher temperatures he got an explosion which liberated carbon and iodine. Lohr also found that the addition of ethyl acetate broughtabout a strongly exothermic reaction between magnesium and methyl iodide at room temperature, though the reaction required 40-50 hours to reach completion at 110°. From this reaction he obtained a gas which he asumed to be ethylene. The

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31. A. Cohours, Ann. 114, 240 (1869)
32. Lohr, Ann. 261, 72 (1891)

residue remaining after reaction was distilled in a stream of hydrogen, since earlier experiments had shown the product to be decomposed by carbon dioxide, the distillation yielding only unreacted methyl iodide, even after heating to 330°. The solid remaining after distillation reacted with water with the evolution of a large amount of heat, giving off thick gray clouds having the odor of garlic, which burned with a weakly luminous flame. Lohr repeated this experiment eight to ten times, with the same result. He thought the product to be either CH_3MgI or $(CH_3)_2Mg + MgI_2$. Lohr, in the same way, also reacted ethyl iodide and propyl iodide with magnesium, with similar results.

Spencer and collaborators (33) reacted a series of alkyl and aryl halides with magnesium in the absence of any solvent or catalyst. Their primary purpose apparently lay in the preparation of hydrocarbons by the hydrolysis of reaction products, though in one case Spencer and Stokes ground phenylmagnesium iodide, prepared in the absence of a solvent, together with carbon dioxide and ethyl ether, in a mortar, to obtain about half the theoretical amount of benzoic acid. They reported the yield to be greatly reduced in the absence of ether. Organic halides which were reacted with magnesium, together with conditions of reaction,

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(33) J. F. Spencer and E. M. Stokes, J. Chem. Soc. *93*, 68-72 (1908): Spencer and M. S. Crewdson, *ibid.*, *93*, 1821-96 (1908); Spencer, Ber. *41*, 2303 (1908)

are noted below:

Iodobenzene: heated to boiling, after which reaction continued without further heating. Obtained 44 per cent yield of benzene by hydrolysis.

Bromobenzene: heated to boiling for about 15 minutes before reaction started. Yield of benzene same as above.

Chlorobenzene: heated in sealed tube for six hours at 260°. Hydrolysis gave 60 per cent yield of benzene.

Methyl iodide: sealed tube, seven hours at 280°.

Ethyl bromide: 260°, eight hours.

Ethyl chloride: 260°, six hours.

i-Butyl chloride: 260°, seven hours

i-Amyl chloride: Reaction started after three minutes at boiling point. White micro-crystalline product gave 62 per cent yield of isopentane on hydrolysis.

sec-Octyl iodide: Violent reaction after being heated for a few seconds. Product a white crystalline substance which gave 84 per cent yield of octane on hydrolysis.

Yields of hydrocarbons obtained from the lower aliphatic halides above are not reported here because analytical methods appeared to be in error. In most cases, gases obtained on opening sealed tubes, and after hydrolysis of products, were reported to be mostly hydrogen.

Shoruigin (34) and co-workers found that alpha-chloronaphthalene, when heated with magnesium at 200-220°, reacts very vigorously, with the abundant sublimation of naphthalene, and the formation of naphthylmagnesium chloride in yields of only 10-13 per cent. Apparently the naphthyl radical disproportionated to give naphthalene and dehydrogenated residues. Benzyl chloride gave a resinous mass on being boiled with magnesium, reaction taking place with the evolution of heat and hydrogen chloride. Shoruigin found that n-Butyl, iso-amyl and n-octyl chlorides, heated to their boiling points with magnesium, react quite vigorously, but that any intermediate magnesium derivatives decompose, through disproportionation or coupling, to give only hydrocarbons. The solid part of the reaction product he found to be insoluble in an ether-benzene mixture. From octyl chloride he obtained hexadecane, octane, and octylene, while isoamyl chloride gave decane, isopentane, and amylene, and butyl chloride yielded octane and gaseous products. Treatment of octyl chloride and magnesium during reaction with carbon dioxide gave some pelargonic acid, though treatment with ethylene oxide during reaction did not indicate the presence of any octylmagnesium chloride.

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34. P. P. Shoruigin *et al.*, Ber. 66B, 1426-31 (1933)

An unexpected result was obtained by Shoruigin when toluene was added to isoamyl chloride and butyl chloride during their reactions with magnesium. In the two cases, p-amyltoluene and p-butyltoluene were obtained, though he found that anhydrous magnesium chloride would not bring about a Friedel-Crafts type reaction between isoamyl chloride and toluene.

Gilman and Brown (35) obtained phenylmagnesium chloride from chlorobenzene and magnesium, heated to 150-160° for three hours, in an 85 per cent yield, which was slightly higher than the 70 per cent yield reported by Shoruigin and co-workers (36) at 160-165° for 3-3.5 hours. Shoruigin found that iodine accellerated the reaction without increasing the yield, while dimethylaniline actually slowed the reaction. The solubility of phenylmagnesium chloride which Shoruigin obtained was found to be, in grams of C_6H_5MgCl per 100 cc.; 17 in ether-benzene (1:1), 16 in isoamyl ether, 14.5 in anisole, 14 in phenetole, 3.6 in benzene: the yield of beta-phenylethyl alcohol obtained by the reaction of ethylene chlorohydrin or ethylene oxide with the phenylmagnesium chloride did not appear to be affected by the presence or absence of a solvent during the secondary reaction.

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35. H. Gilman and R. E. Brown, J. Am. Chem. Soc. *52*, 3330-32 (1930)

36. B P. Shoruigin *et al.*, Ber. *64B*, 2584-90 (1931)

In addition to the work noted above, the preparation of phenylmagnesium chloride in the absence of a solvent has been carried out under conditions comparable to those used by Gilman and Shoruigin; this later work is largely in the patent literature(37).

The first reported use of a hydrocarbon as a medium for the preparation of an organomagnesium compound was by Malmgren (38) and Bruhl and Oerdt (39), who reacted bromocamphor with magnesium by long digestion at the boiling point of toluene, though the preparation was unsuccessful in boiling benzene. Tschelinzeff (40), in commenting on their work, attributed the reaction to the high temperatures obtained. In the same paper, Tschelinzeff reported the preparation of organomagnesium iodides from ethyl, propyl, butyl, amyl, isobutyl and isoamyl iodides by digestion in boiling xylene; he thought that organomagnesium bromides could also be

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37. Shoruigin, Trans. VI Mendelieve Cong. Theoret. Applied Chem. 1932, 2, part 1, 973 (1935); Chem. Abs. 30, 4157 (1936); British Patent 398,561 (1933); Swiss Patent, 159,939 (1933); French Patent 738,227 (1932); Russian Patent 36,400 (1934); Russian Patent 36,401 (1934). Britton, U. S. Patent 1,996,746 (1935); U. S. Patent 2,056,822 (1936). Weissenborn, U. S. Patent 2,058,373 (1936). Groves, British Application 474,687 (1937). In addition, the following patents, inventors unknown: French, 807,632 (1937), Chem. Abs. 31, 5816 (1937); German 660,075 (1938), Chem. Abs. 32, 5857(1938); German 697, 420 (1940) Chem. Abs. 35, 6600 (1941).

38. Malmgren, Ber. 36, 2608 (1903)

39. Bruhl and Oerdt, Ber. 36, 668, 4272 (1903); ibid., 37, 746 (1904)

40. W. Tschelinzeff, Ber. 37, 4534-40 (1904)

prepared in boiling xylene, though he did not try to prepare any of them. Though no yields were reported, Tschelinzeff stated that the amounts of useful materials were smaller than when the reaction was carried out in ether.

Pickard and Kenyon (41) failed to obtain any reaction after several hours of boiling methyl iodide, benzene, and magnesium, though reaction did take place after the addition of tribenzyl phosphine oxide.

Hepworth (42) refluxed methyl iodide and benzene with magnesium, and presumably got no reaction, though he does not state his results. Evans and Diepenhorst (43), in the course of studies on the influence of solvent on the chemiluminescence of Grignard reagents, used a large number of organic halides in fifteen ethers, dimethylaniline, and benzene; again it is not stated what, if any, reaction took place in benzene, though results are given for all other solvents, and apparently the benzene solution gave no reaction.

Schlenk (44) has made what appears to be the only quantitative study of organomagnesium compounds prepared in hydrocarbons. Stating that, while the

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41. Pickard and Kenyon, J. Chem. Soc. 89, 262-73 (1906)

42. H. Hepworth, J. Chem. Soc. 119, 1249-56 (1921)

43. W. Evans and E. Diepenhorst, J. Am. Chem. Soc. 48, 715-23 (1926)

44. W. Schlenk, Jr., Ber. 64, 739-43 (1931)

reactivity of the organic halides in benzene is influenced by the halogen, it is much more strikingly influenced by the nature of the hydrocarbon residue, Schlenk shook magnesium ribbon for two months at "summer temperatures" with benzene solutions of the following halides, with yields noted: methyl iodide, zero; ethyl iodide, 11 per cent; propyl iodide, about one per cent; butyl iodide, 95 per cent; heptyl iodide, about three per cent; octyl iodide, 96 per cent (this reaction being substantially complete within six days); ethyl bromide about two per cent; butyl bromide, 38 per cent; butyl chloride, 55 per cent, all of which he identified by subsequent reactions. Schlenk thought the yields of butylmagnesium bromide and chloride to be in error because the product was gray instead of the white solid obtained with the iodides, though he did obtain some of the expected reaction product from the butylmagnesium halides and fluorenone. Schlenk found all of his reaction products to be completely insoluble in benzene.

Aside from the work already mentioned, there have been a number of investigations of the preparation of organomagnesium compounds in the presence of small amounts of substances capable of forming complexes with the organomagnesium compounds formed. Although this work is not directly comparable with the present investigation, it is worthy of brief mention.

Tschelinzeff (40, 45) in a series of papers, investigated the action of tertiary amines in, as he put it, "catalyzing" the formation of organomagnesium compounds. Tingle and Gorsline (46) extended the work to the use of pyridine and quinoline in ligroin solutions, though in these cases the bases were present in excess, rather than in catalytic quantities. Hepworth (42) studied the action of several aliphatic and cyclic sulfides and ethers in benzene solution, while Pickard and Kenyon (41) used tribenzylphosphine oxide in benzene solution. With the exception of Pickard and Kenyon, all of the above workers, as well as Gilman and McCracken (1) also used ether in benzene solution. Gilman and McCracken concluded that, for maximum yield, there must be at least one mole of ether per mole of halide present, and they stated that hydrocarbons definitely have an inhibiting or retarding effect on the formation of organomagnesium compounds.

In some more recent work, Andrianov and Gribanova (47) employed ethyl orthosilicate as a "catalyst" for the preparation of organomagnesium compounds, both in the absence of a solvent, and in hydrocarbons. In this manner, without a solvent, they

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45. W. Tschelinzeff, Ber. 38, 3664 (1905); ibid., 39, 773, 1674, 1682, 1686 (1906); Ibid., 40, 1487 (1907)

46. J. B. Tingle and E. E. Gorsline, Amer. Chem. J. 37, 483 (1907)

47. K. A. Andrianov and Gribanova, J. Gen. Chem. (U.S.S.R.) 8, 552-6 (1938)

obtained the following yields of the organomagnesium compounds: Ethylmagnesium bromide, 96 per cent; isobutylmagnesium chloride, 51 per cent, isoamylmagnesium bromide, 58.5 per cent; n-hexylmagnesium bromide, 35 per cent, and phenylmagnesium bromide, 25 per cent. Later papers (48) reported the use of these compounds in the preparation of silicones.

With the exception of Schlenk's uncertain work, there have been no examples of the preparation of organomagnesium bromides or chlorides in hydrocarbons; also, there have been no reported uses of aliphatic hydrocarbons as mediums for the preparation of organomagnesium compounds.

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48. Andrianov et al., ibid., 8, 969-71, 1255-62 (1908); Chem. Abs. 33, 1266, 4193 (1939)

C. DISCUSSION OF RESULTS

1. General

Preliminary experiments showed that, by means of mechanical activation, organomagnesium compounds could be prepared quite readily from the lower alkyl halides in any of the three hydrocarbons chosen for study. Although yields appeared to be slightly better in isooctane and benzene than they were in heptane, there was no large difference, and heptane was chosen for comparative studies because of its simpler structure, which should decrease any tendency of the organomagnesium compounds to react with the hydrocarbon medium.

It was felt to be outside the scope of this investigation to carry out large-scale developmental work, and little attempt was made to determine optimum conditions for the various reactions studied, though, insofar as possible, the results of previous investigation were applied here in choosing conditions for reaction. These conditions were adhered to wherever possible, so that data are largely comparable, though they do not necessarily represent the best results which might be obtained.

2. Description of Products

Organomagnesium compounds prepared in hydrocarbon mediums, are in general, unstable suspensions of solids in the liquid hydrocarbons, varying in viscosity and in the stability of the suspensions with the nature of the alkyl radical. Ethylmagnesium bromide, for instance, forms a very fluid and unstable suspension, which quickly settles to give a clear supernatent liquid and a light gray solid which occupies less than half of the total volume. Octylmagnesium bromide, however, forms a very viscous suspension, which settles only slowly, and even after centrifuging the gray solid occupies over ninety per cent of the total volume. The higher alkylmagnesium bromides, in fact, approach closely the characteristics of a gel. In all cases, particles of finely divided unreacted magnesium were noted in suspension. In the less viscous products, these settled to the bottom, though in the higher alkylmagnesium halides, they remained dispersed throughout the suspension.

The color of the organomagnesium compounds prepared in hydrocarbons seems to depend largely on the halogen. Butylmagnesium iodide was almost white, in agreement with Schlenk (44), while butylmagnesium chloride was dark gray. In all cases, the organomagnesium bromides were light gray in color, though the shade varied somewhat with alkyl radical, and seemed to depend slightly on reaction conditions.

3. Methods for Determining Yields

The nature of the organomagnesium compounds prepared in hydrocarbon mediums prevented the use of the acid titration (49) customarily employed for the determination of the yield of Grignard reagents, since finely divided magnesium, present in all cases, would react with the acid, leading to high yields. Iodine titration (50), which depends on the reaction

$$RMgX + I_2 = MgXI + RI,$$

has also been shown to give misleading results, even when ether solutions of the Grignard reagent are titrated.

Schlenk (44) and Andrianov (47) both determined their yields by acid titration. The former used magnesium ribbon, and decanted the suspensions obtained from the unreacted ribbon before pipetting an aliquot for titration, but it is quite possible that finely divided magnesium was present in his product. He cautioned against accepting the yields which he found for butylmagnesium bromide and chloride, because he

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49. H. Gilman, *et al.*, J. Am. Chem. Soc. **55**, 1559 (1933)

50. P. Jolibois, Compt. Rend. **155**, 213 (1912)

thought that the solid which he obtained was largely suspended magnesium, though we have shown that these products are gray in color. Andrianov gave no details of the treatment of his products, saying merely that yields were determined by the method of Gilman. If, however, it is conceded that acid titration could be used in these cases, magnesium encountered in the use of mechanical activation is much too finely divided to permit its use.

Wheeler (51) has devised a scheme for the determination of the yield of organomagnesium compounds which depends on their electrical conductivity in ether solution, and the change in this conductivity with the addition of an alcohol. Thus, when an ether solution of an organomagnesium compound is titrated with an alcohol, the electrical conductivity of the mixture falls with the addition of each increment of alcohol until a minimum is reached at the point at which the amount of alcohol added is equivalent to the amount of organomagnesium compound present, after which the conductivity again rises.

In practice, it has been found convenient to use n-butyl alcohol as a titrating agent, and to use for a medium an ether solution containing a small amount of ethylmagnesium bromide to insure the dryness of the

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51. W. R. Wheeler, Private Communication

ether, so that none of the organomagnesium compound being titrated is exhausted by reaction with moisture or other contaminant in the ether. The carefully dried and fractionated butanol is used as a primary standard. By titration of the ether solution before the addition of the unknown sample, a minimum is obtained, and a small amount of alcohol is added beyond this minimum, so that the mixture contains some alcohol when the unknown sample is added. This appears to prevent the further reaction of any organic halide present with unreacted magnesium in the presence of ether.

This conductometric titration with butanol has been found by Wheeler to agree with values obtained by gas analysis of ethylmagnesium bromide, and in the present work yields obtained by this method appear to be accurate for the lower alkylmagnesium halides. There is, however, some doubt as to the accuracy of the yields given by conductometric titration for alkylmagnesium bromides higher than butyl.

Although yields obtained by conductometric methods are recorded for the higher alkylmagnesium bromides, it is believed that more accurate yields are given for these compounds by acid titration corrected for the amount of magnesium present. Metallic magnesium was determined by the evolution of hydrogen on acidification of an aliquot sample of the reaction products.

Yields obtained in this manner were identical with those obtained by conductometric titration of the butylmagnesium halides, but were substantially greater for all higher alkylmagnesium bromides. This method was not applied to alkylmagnesium bromides lower than butyl because of the difficulty and uncertainty involved in the separation of, or correction for, the gaseous hydrocarbons evolved on hydrolysis.

4. Comparative Yields

(a) Alkylmagnesium Bromides

Yields have been determined for organomagnesium compounds prepared in n-heptane for all of the primary, straight-chain alkyl bromides containing from two through ten carbon atoms. All attempts at the preparation of methylmagnesium bromide in n-heptane were unsuccessful, in line with the experience of Schlenk (44), who was unable to prepare methylmagnesium iodide in benzene. Wheeler (52), however, has prepared methylmagnesium chloride in good yield in heptane by the addition of a catalytic amount of ether.

With the exceptions of ethylmagnesium bromide and butylmagnesium bromide, yields given here represent the results of only one run. The yield given for butylmagnesium bromide is the average of the yields obtained for five runs made under comparable conditions. For these five runs, yields ranged from 57.2 to 61.4 per cent, indicating the reproducibility of results. For all of these runs, the temperature of the reaction mixture was maintained substantially between 20-25°, though later experience has shown that slightly higher temperatures during reaction lead to improved yields, and it is probable that the yield reported for butylmagnesium bromide is low in comparison with other yields given.

The yield of ethylmagnesium bromide is the highest obtained in three runs. In two of these runs, and in four unsuccessful attempted preparations, temperature of the reaction mixture was maintained in the neighborhood of 20°. In the third, successful run, however, temperature was maintained in the region of 30°, at which temperature reaction took place rapidly, with a greatly improved yield. Since the conditions for this run are more comparable with those applied for the preparation of higher members of the series, the larger yield is felt to be more representative than the lower ones.

Conditions for the preparation of propylmagnesium bromide are comparable with those for the preparation of ethylmagnesium bromide, the temperature during reaction being maintained near 30°. With amyl bromide, and higher bromides, however, it was found that reaction with magnesium in heptane would not start at temperatures below thirty

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52. W. R. Wheeler, Private Communication

degrees. For the preparation of amyl and all higher alkylmagnesium bromides, therefore, temperatures were maintained largely in the range 45-55°.

With the exception of temperature, all other variables were held fairly constant throughout all runs, though reaction times for the preparation of butylmagnesium bromide were slightly shorter than for other members of the series.

Yields obtained are presented in tabular form below, and are shown graphicly in Figure 6.

Halide	Yield	
	Cond.	Acid
Ethyl bromide	71.5	130 per cent
n-Propyl bromide	64.1	99.5
n-Butyl bromide	59.3	59.4
n-Amyl bromide	50.6	54.0
n-Hexyl bromide	44.6	67.3
n-Heptyl bromide	45.5	58.7
n-Octyl bromide	50.5	63.8
n-Nonyl bromide	32.2	50.5
n-Decyl bromide	31.5	56.7

The yields determined by acid titration recorded in the table above are corrected for unreacted magnesium present for butyl and all higher bromides, though those for ethyl and propylmagnesium bromide are not corrected, and are meaningless.

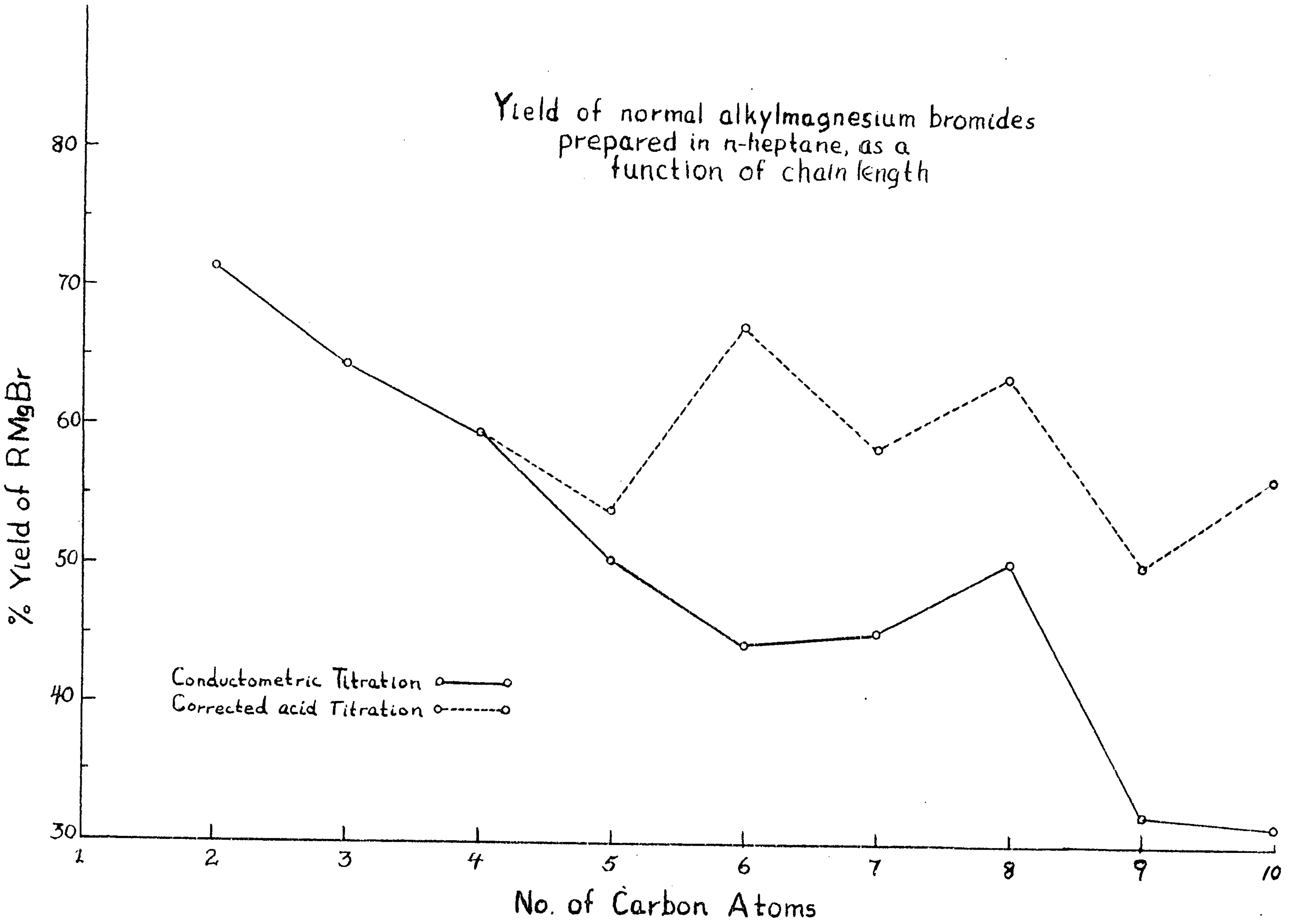
Yield of normal alkylmagnesium bromides
prepared in n-heptane, as a
function of chain length
% Yield of RMgBr
80
70
60
50
40
30
1
2
3
4
5
6
7
8
9
10
No. of Carbon Atoms
Conductometric Titration
Corrected acid Titration

Figure 6

It is to be noted that, for all alkylmagnesium bromides higher than butyl, there is a distinct alternation in yields, the alkyl bromides having an even number of carbon atoms giving higher yields than those with odd-numbered radicals with the exception of propyl bromide. This is substantially in agreement with the experience of previous investigators (53) with the yields of organomagnesium compounds prepared in ether solutions.

As previously stated, it is probable that the yields here given might be greatly improved by modification of reaction conditions. For instance, in all instances recorded above, yields were obtained by cutting magnesium into a hydrocarbon solution containing all of the alkyl halide. Although experience with butylmagnesium bromide indicated an improvement in yield of at least five per cent by the gradual addition of the halide during the cutting of the metal, this procedure was not used for the determination of comparative yields because, in the case of the higher alkyl bromides, it was indicated that reaction was difficult to start with the initial low concentration of halide which would result.

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53. See, for example, H. Gilman , Zoellner, and Dickey, J. Am. Chem. Soc. 51, 1576 (1929)

(b) Butylmagnesium Halides

Comparative yields for butylmagnesium halides were determined in isooctane instead of in heptane. Again, temperature of the reaction mixture is the only variable not held constant. Butylmagnesium bromide was prepared at temperatures of around 20-25°, but the reaction between butyl chloride and magnesium in isooctane would not start until a temperature in the neighborhood of 50° was reached, and for the preparation of butylmagnesium chloride the temperature was maintained between 50-60°. On the other hand, reaction between butyl iodide and magnesium was found to be so exothermic that, without varying some other factor, such as feed rate of magnesium, the temperature of the reaction mixture could not be held constant, and during the preparation of butylmagnesium iodide, the temperature rose to 70° for a short time.

For comparative yields, the results of 1.5 mole runs only are considered here; although data are available for the three butyl halides prepared in 0.5 mole runs, the yields obtained in the larger runs are felt to be more representative.

In three 1.5 mole runs, yields of butylmagnesium bromide prepared in isooctane of 63.6, 62.6, and 60.2 per cent were obtained, for an average yield of 62.1

per cent; for two runs, yields for butylmagnesium chloride prepared in isooctane of 62.4 and 65.6 per cent, for an average of 64.0 per cent; a yield of butylmagnesium iodide of 76.0 per cent was obtained in a single run.

It is interesting to note that this order of increasing yield is just the reverse of that obtained by Gilman and Zoellner (53), who found the following yields for butylmagnesium halides prepared in ether:

Butylmagnesium bromide	94.0 per cent
Butylmagnesium chloride	91.2
Butylmagnesium iodide	85.6,

as contrasted to our yields for the same compounds prepared in isooctane of 62.1, 64.0, and 76.0 per cent. Gilman and co-workers (54) found that when the organic halide is added to the magnesium all at once in the preparation of organomagnesium compounds in ether solution, the drop in yield is much greater for the alkyl bromides than for the chlorides, though the drop in yield in the case of the iodides was greater still. In the present work, the halide was, in effect, added all at once; in fact, the addition of magnesium to the halide might be expected to increase the drop in yield, and undoubtedly the yields here reported could, in general, be increased

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54. Gilman, Zoellner and Dickey, J. Am. Chem. Soc. <u>51</u>, 1583 (1929)

by the slow addition of halide, but this factor cannot be considered as the one which causes the reversal of the order of increasing yields of the butylmagnesium halides. As will be brought out later, it appears more likely that the amount of side reaction in hydrocarbons decreases in the same order in which it increases in ether solution.

The order for increasing yields obtained here cannot be regarded as being merely fortuitous, since the agreement between yields obtained in different runs for butylmagnesium bromide and chloride is very close. It is true that the yield for butylmagnesium iodide reported here was from only one run, but in a 0.5 mole run, a yield of butylmagnesium iodide prepared in isooctane of 85.0 per cent was obtained, indicating that the yield of 76 per cent may be low.

(c) Yields in Different Hydrocarbons

Three different organomagnesium compounds, ethylmagnesium bromide, butylmagnesium bromide, and butylmagnesium chloride, were prepared in all of the three hydrocarbons here studied. Yields obtained in the three mediums are tabulated below:

Medium	EtMgBr	BuMgBr	BuMgCl
heptane	43.0	59.3	57.5
isooctane	59.4	62.1	64.0
benzene	65.6	63.3	42.6

Yields here reported for ethylmagnesium bromide are the results of 0.5 mole runs; although higher yields were obtained for this compound in 1.5 mole runs in n-heptane, comparative runs of this size were not made in the different solvents. Yields for both of the butylmagnesium halides are from 1.5 mole runs.

It is noted that, for the alkylmagnesium bromides, yields increase from heptane through isooctane to benzene; though no reason for this phenomenon can be advanced, the trend appears to be definite. As will be brought out later, there was some slight evidence for some interaction between the butylmagnesium halides and isooctane, which might serve to increase the effectiveness of this medium, but this evidence is too meager to allow any conclusions to be drawn.

For butylmagnesium chloride, the same increase in yield is noted in going from heptane to isooctane, but a decided drop in yield is apparent in the compound prepared in benzene. This is readily explained, since a yield of about 12.7 per cent of butyl benzene was obtained in this run. Although there is no evidence that butylmagnesium chloride was consumed in the formation of butyl benzene, the amount of butyl chloride available for the formation of the organomagnesium compound would be reduced.

(d) Amount of Side Reaction

It is well known that the reaction of alkyl halides with magnesium may take any of three courses; the formation of organomagnesium compounds, coupling, or disproportionation:

$$RCH_2CH_2X + Mg = RCH_2CH_2MgX$$

$$2\ RCH_2CH_2X + Mg = (RCH_2CH_2)_2 + MgX_2$$

$$2\ RCH_2CH_2X + Mg = RCH_2CH_3 + RCH{=}CH_2 + MgX_2.$$

The determination of unreacted magnesium made it possible to determine also the approximate extent of the side reactions. Since the amount of magnesium consumed in the preparation of the organomagnesium compounds was known, the difference between that amount and the amount unreacted must represent the amount consumed in coupling and disproportionation reactions. Although data are insufficient to allow any general conclusions to be drawn, it appears that in all cases all of the organic halide was consumed so that the yield of organomagnesium compounds depends directly on the rate of the competing side reactions. From data secured by the distillation of some of the products resulting from the carbonation of butylmagnesium halides, it also appears that disproportionation is much more important than coupling, since in most cases only a very small amount of n-octane was found.

Data obtained for the amount of coupling and disproportionation are presented below, and are plotted in Figures 7 and 8. Because of the lack of data in most cases, no attempt is made to distinguish between coupling and disproportionation; in no case, however, did the amount of n-octane distilled indicate more than three per cent coupling

Halide	Medium	Per cent halide to:		Total RX accounted for
		RMgX	R-R. disp.	
C_2H_5Br	heptane	insufficient	data	
C_3H_7Br	heptane	64.1	36.4	100.5
C_4H_9Br	heptane	59.3	45.2	104.5
C_4H_9Cl	heptane	57.5	56.0	113.5
C_4H_9Cl	isooctane	65.6	33.4	99.0
C_4H_9Cl	benzene	42.6	62.6(a)	105.2
C_4H_9I	isooctane	76.0	24.0	100.0
$C_5H_{11}Br$	heptane	54.0	53.0	107.0
$C_6H_{13}Br$	heptane	67.3	37.8	105.1
$C_7H_{15}Br$	heptane	58.7	56.6	115.3
$C_8H_{17}Br$	heptane	63.8	52.0	115.8
$C_9H_{19}Br$	heptane	50.5	59.4	109.9
$C_{10}H_{21}Br$	heptane	56.7	54.2	110.9

(a) This figure includes butyl chloride consumed in the formation of butyl benzene, a reaction in which magnesium was apparently consumed.

As may be seen, all of the organic halide present is accounted for in every case; the fact that more than 100 per cent is accounted for in most cases is not surprising, since calculations are based on the assumption that all of the magnesium cut was in the reaction mixture, in either reacted or unreacted form.

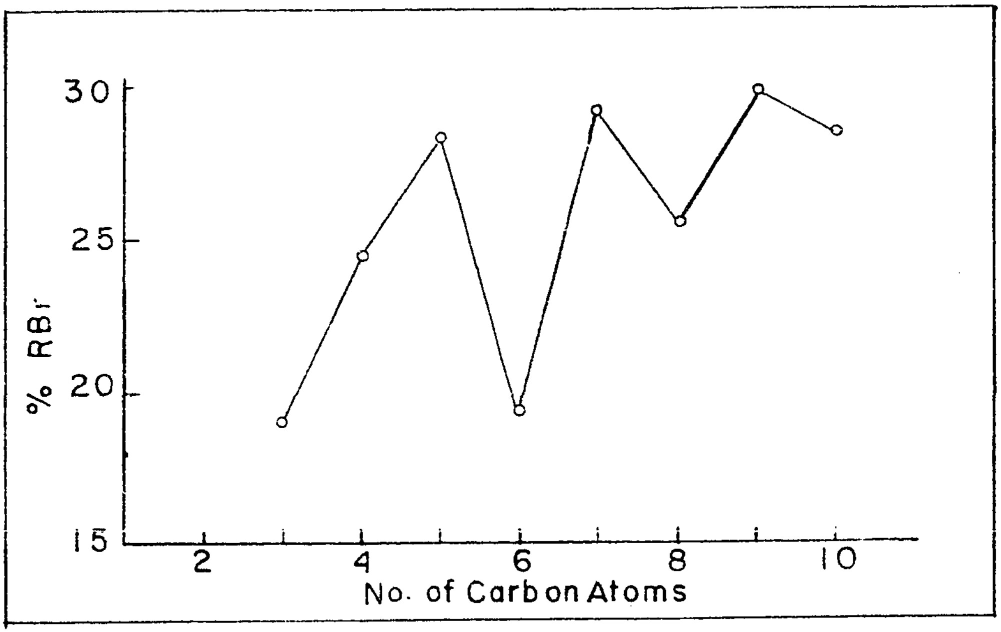

Figure 7

Percent of alkyl bromides entering into coupling or disproportionation reactions during preparation of organomagnesium bromides in n-heptane

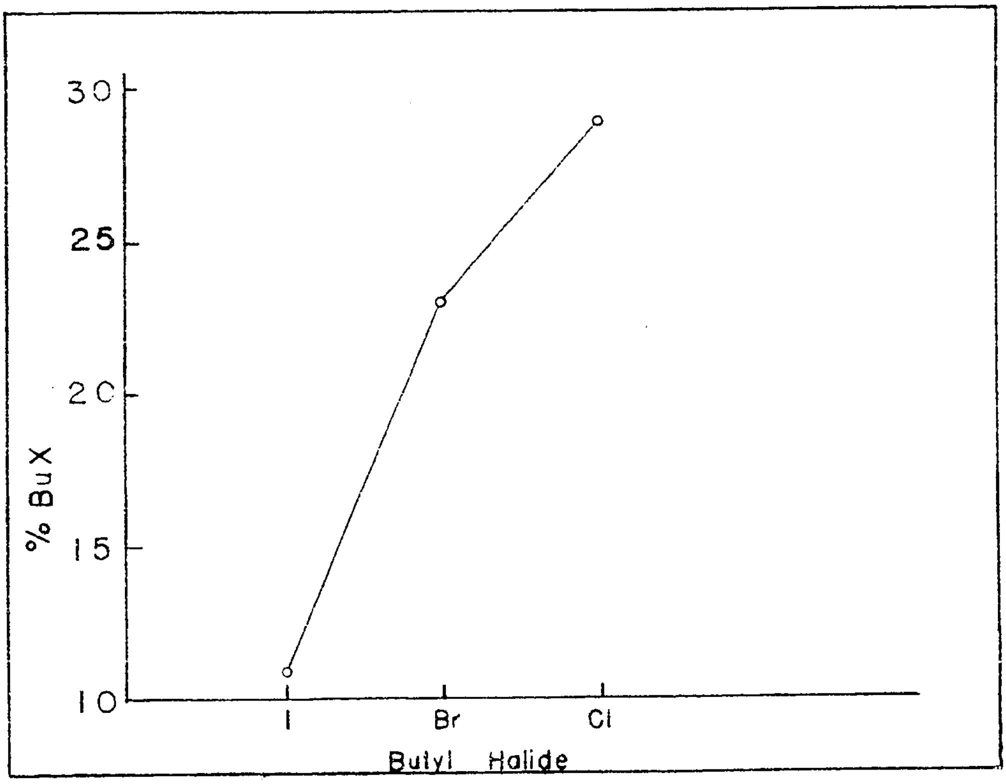

Figure 8

Percent of butyl halide entering into coupling or disproportionation reactions in n-heptane

This assumption was not entirely valid, since it was at no time possible to remove all of the reaction product which adhered to portions of the apparatus. This difficulty increased with higher members of the series, as is reflected by the increase in the amount of organic halide "accounted for" as the number of carbon atoms increases. The surprising fact is that such close agreement with theory is present for some of the lower members of the series, and that all of the organic halide appears to have reacted in every case.

5. Solubility of RMgX in Hydrocarbons

Schlenk (44) found that alkylmagnesium iodides, prepared in benzene, were insoluble in benzene; although there is no definite basis for comparison, since no alkylmagnesium iodides were prepared in benzene in the present work, we have not been able to substantiate his results.

It might be expected that the lower alkylmagnesium halides would be, at best, only sparingly soluble in hydrocarbons, though increasing chain length should increase the solubility. This, in general, has been found to be the case. Although only traces of the lower members of the series of alkylmagnesium bromides were found to be soluble in heptane, some solubility was found for every compound, and this solubility appeared to differ somewhat with the solvent. Solubilities obtained are tabulated below, and are presented in graphical form in Figures 9, 10, and 11.

Halide	Medium	Solubility: milliequivalents of RMgX per 100 cc. of solution
C_2H_5Br	heptane	0.71
C_2H_5Br	benzene	3.85
C_3H_7Br	heptane	0.71
C_4H_9Br	heptane	0.75
C_4H_9Br	isooctane	2.05
C_4H_9Br	benzene	4.29
C_4H_9Cl	heptane	1.91
C_4H_9Cl	isooctane	0.84
C_4H_9Cl	benzene	0.75
C_4H_9I	isooctane	33.5
$C_5H_{11}Br$	heptane	26.1
$C_6H_{13}Br$	heptane	62.5
$C_7H_{15}Br$	heptane	10.2
$C_8H_{17}Br$	heptane	13.5
$C_9H_{19}Br$	heptane	60.1
$C_{10}H_{21}Br$	heptane	17.8

No explanation can be advanced, on the basis of these data alone, for the inordinately high solubilities of hexyl- and nonylmagnesium bromides; it seems possible that there may be a periodicity exhibited here, with a period of three carbon atoms, though the solubility of propylmagnesium bromide in heptane does not conform to any such periodicity, and before making any general statement, it would be necessary to extend the series through members containing twelve and fifteen carbon atoms, at least.

These solubility data are presented for their face value alone. It is not known that true solutions

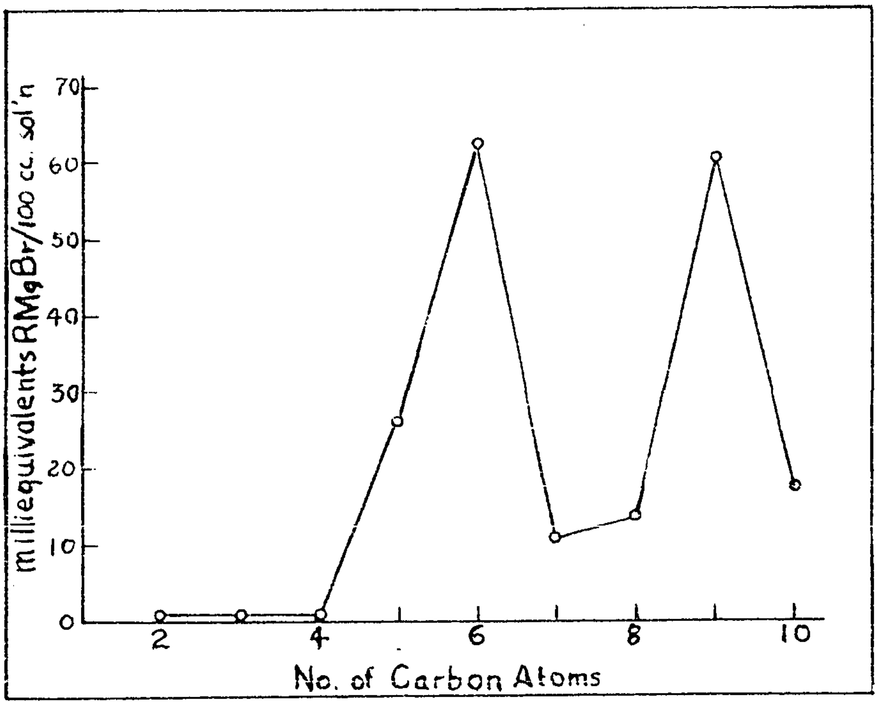

Figure 9

Solubility of n-alkylmagnesium bromides in n-heptane

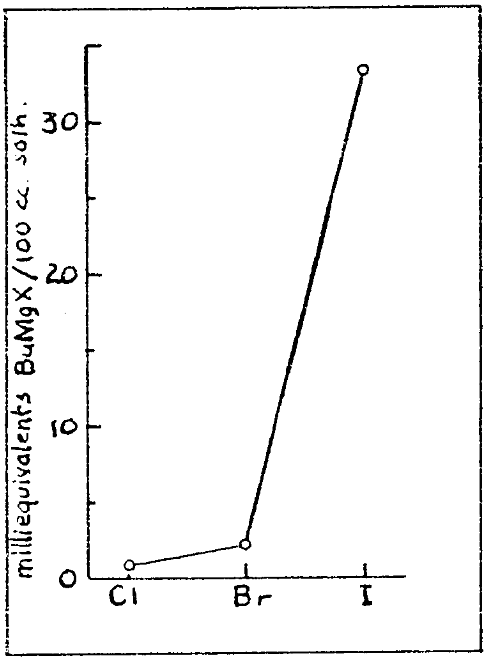

Figure 10

Solubility of butylmagnesium halides in isooctane

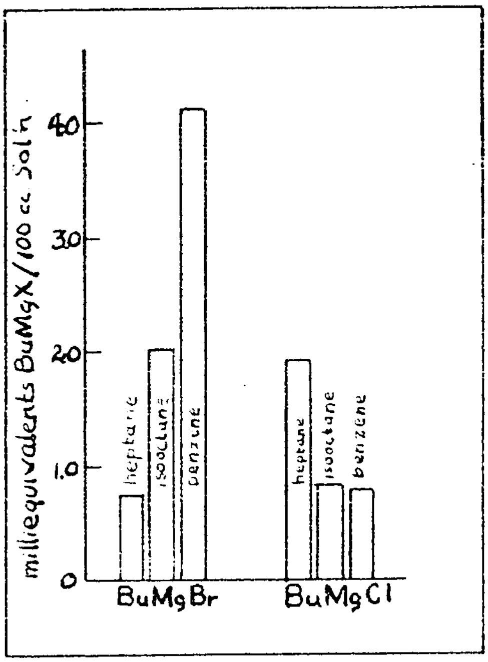

Figure 11

Solubility of butylmagnesium halides in several hydrocarbons exist, nor is it known what form the organomagnesium compounds have in solution. The solutions of butylmagnesium iodide and hexylmagnesium bromide, which exhibit high solubility, are very viscous, presenting evidence that these are not true solutions; the solution of nonylmagnesium bromide, however, is not unusually viscous.

It might be expected that dialkyl magnesium compounds would be more soluble in hydrocarbons than would the corresponding alkylmagnesium halides, and it might well be that the variations in solubility exhibited here are due to differences in the ratio existing between the alkylmagnesium halides and the dialkyl magnesiums. The determination of this ratio was outside the scope of the present investigation, and in the absence of data on the ratio, any statement can be merely speculative. Schlenk (44) found that the solid reaction product resulting from the preparation of alkylmagnesium iodides in benzene was richer in dialkylmagnesium than in the alkylmagnesium iodides, but his method for determining the ratio is open to severe criticism, and, in any case, could not be applied here.

6. Relative Viscosities

It was noted that, in general, the viscosities of the suspensions of alkylmagnesium bromides in hydrocarbons increased with increasing size of the alkyl radical. Since the viscosity of the reaction mixture might conceivably have an effect on the yield of organomagnesium compounds, the relative viscosities of the various suspensions were determined roughly. The data so obtained do not appear to be directly related to the yields obtained, though they do exhibit an alternation which is, qualitatively, the same as that shown for the yields of organomagnesium bromides above butyl. The relative viscosities presented in the table below, and plotted in Figure 12, are related to the viscosity of a suspension of finely divided magnesium in n-heptane as zero on an additive scale, or as one on a multiplicative scale.

RMgX	Medium	Relative Viscosity
C_2H_5MgBr	heptane	2.6
C_3H_7MgBr	heptane	6.0
C_4H_9MgBr	heptane	5.0
C_4H_9MgCl	isooctane	4.8
C_4H_9MgI	isooctane	2.0
$C_5H_{11}MgBr$	heptane	4.0
$C_6H_{13}MgBr$	heptane	6.1
$C_7H_{15}MgBr$	heptane	5.0
$C_8H_{17}MgBr$	heptane	7.1
$C_9H_{19}MgBr$	heptane	4.0
$C_{10}H_{21}MgBr$	heptane	4.6

These data were compiled from samples of the original suspensions which had been standing for some time in tightly closed sample bottles. The condition of some of the samples, especially those in which benzene was the medium, did not permit determination of

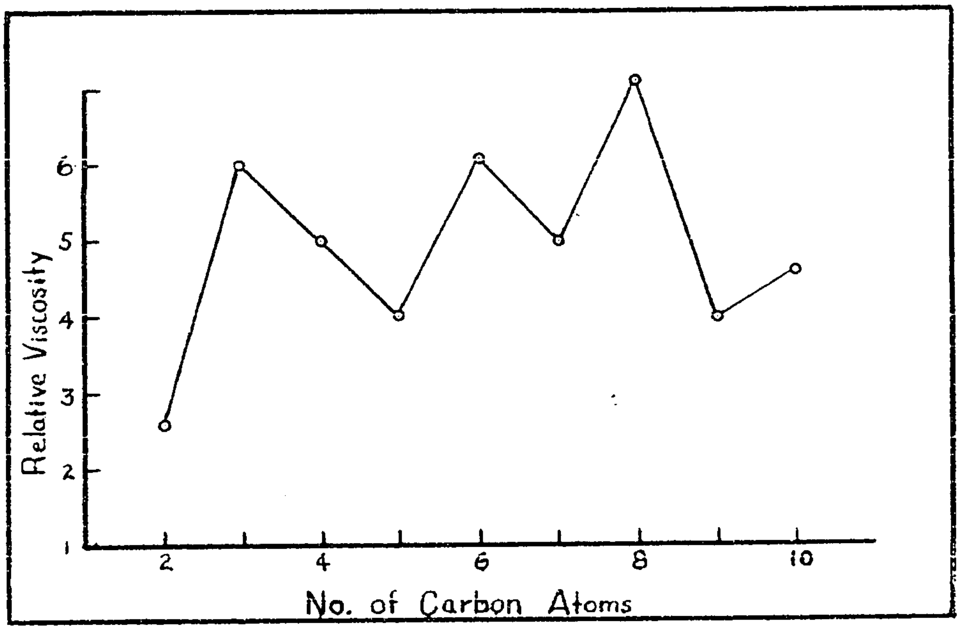

Figure 12

Variation of relative viscosities of alkylmagnesium bromides in n-heptane suspensions viscosity, since it appeared that some of the solvent had been lost by leakage or evaporation.

7. Flask Preparation of Butylmagnesium Chloride

Although the preparation of organomagnesium compounds outside of the mechanical activation apparatus was not considered to be within the scope of this investigation, one preparation of butylmagnesium chloride in heptane in a flask was made. In this preparation, magnesium was cut into heptane, using the standard procedure with the mechanical activation apparatus. This suspension was transferred to a flask, and the mixture was heated to boiling on a water bath. An amount of butyl chloride equivalent to the magnesium present (0.5 mole) was then added, and rather vigorous reaction took place within a short time, the only agitation being furnished by a small glass stirrer. The yield of butylmagnesium chloride obtained in this way was found to be 70.8 per cent, significantly higher than the yield of 57.5 per cent obtained for the preparation of butylmagnesium chloride in heptane in the mechanical activation apparatus. Aside from the difference in apparatus, the primary differences in the two procedures lay in the temperature, which was in the neighborhood of 100° in the flask preparation, and in the fact that all of the magnesium and butyl chloride were present initially in the flask reaction. The reaction product from the flask run was much less viscous, and appeared to be more homogeneous, than that prepared in the mechanical activation apparatus.

8. Reaction with Carbon Dioxide

Although amylmagnesium bromide and octylmagnesium bromide were reacted with carbon dioxide, the carbonation of butylmagnesium halides was rather extensively studied. In all cases, yields of organic acids produced were much lower than the corresponding yields of acids prepared from organomagnesium compounds in diethyl ether, even when comparisons were based on the amount of organomagnesium compound present rather than on the original reactants. The maximum yield of acid obtainable from any of the butylmagnesium halides under conditions employed appeared to be in the neighborhood of 40 per cent, as based on original reactants. In all cases, there were extensive side reactions, dibutyl ketone being the only identifiable product other than valeric acid, though tributyl carbinol, or its dehydration product was probably present also.

The large amount of side reaction found during the preparation of organic acids from organomagnesium compounds appears to be due to an increased reactivity for organomagnesium compounds which are not encumbered by molecularly bound ether. Though this reactivity is objectionable for the preparation of organic acids, where successive reactions are possible, it should prove helpful in reactions which cannot proceed beyond the desired initial stage.

There appeared to be little difference between the yields of acids obtained from butylmagnesium bromide and chloride, though the yield of acid from butylmagnesium iodide was significantly lower than those obtained from the other halides. This low yield appeared to be due more to the greater viscosity of the iodide than to a lower reactivity.

Gilman (55) found that the best yields of organic acids could be obtained by carbonation at zero degrees, with a rate of flow of carbon dioxide of one-half liter per minute, while stirring at 800 revolutions per minute. When the stirring speed was increased to 1800 revolutions per minute, he found that the rate of flow of carbon dioxide could be increased to one liter per minute. In the present investigation, it was found impossible to keep the temperature of the reaction mixture from rising rapidly if the rate of flow of carbon dioxide were increased above 200 cc. per minute in the initial phases of carbonation; at a stirring speed of 2000 revolutions per minute, with a rate of flow of carbon dioxide of one liter per minute, yields obtained were

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55. Gilman and Parker, J. Am. Chem. Soc. 46, 2816 (1924)

less than half the yields given when the rate of flow was so regulated as to maintain the temperature near zero.

There appeared to be little difference in the effect of the three hydrocarbons studied on the yields of organic acid obtained, though there was some evidence for the formation of an acid other than valeric when isooctane was the medium. On several occasions, the residue from the distillation of valeric acid prepared in isooctane was a solid; from this solid a small amount of a white substance was crystallized. This material had a melting point of 86-87°, and a neutral equivalent of 240. Although the purity of the sample was not assured, and the amount was too small to allow further identification, these properties do not conform to those of any known acid, even approximately.

Because of the apparently high reactivity of the butylmagnesium halides in hydrocarbons, as evidenced by the large amount of side reaction during carbonation, even at temperatures in the neighborhood of zero degrees, an attempt was made to carbonate butylmagnesium bromide with the reaction mixture immersed in an acetone-dry ice bath. There appeared to be little reaction at the low temperature obtained. At -2°, reaction also appeared to be very slow, though at temperatures above 5°, reaction was so rapid as to make control of temperature difficult.

Butylmagnesium chloride, however, seemed to require a higher temperature, and best results were obtained when carbonation was carried out between 10-15°.

The results obtained from the carbonation of butylmagnesium halides, and descriptions of the products of side reactions, are summarized in Table I in the experimental section below.

9. The Formation of Butyl Benzene

Shoruigin (54) reported the formation of p-butyl toluene in the attempted preparation of butylmagnesium chloride in boiling toluene; the corresponding amyl derivative was formed from iso-amyl chloride and magnesium in toluene. Wheeler (56) found that sec-butyl benzene is the only product from the reaction of n-butyl chloride and magnesium in boiling benzene. During the reaction, Wheeler noted the evolution of large amounts of hydrogen chloride.

In view of the results reported above, the formation of butyl benzene during the preparation of butylmagnesium chloride in benzene in the present work is not surprising, though here it was formed, in a yield of 12.7 per cent, concurrently with the formation of

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56. W. R. Wheeler, Private Communication

the organomagnesium compound. There is, however, some evidence found here that may throw some light on the mechanism of formation of the butyl benzene.

Shoruigin (34) attempted the preparation of butyl toluene by the reaction of butyl chloride, toluene, and anhydrous magnesium chloride, and obtained no reaction. He concluded, on the basis of this experiment, that the formation of butyl toluene could not involve a reaction of the Friedel-Crafts type.

In the present work, during the preparation of butylmagnesium chloride in benzene, no evolution of hydrogen chloride was noted; in the course of the reaction, nitrogen was passed through the reacting mixture, and the gas was passed over concentrated aqueous ammonia as it came from the apparatus. At no time was the presence of hydrogen chloride evidenced by the formation of white ammonium chloride. Also, analysis of the magnesium which failed to react during the preparation showed conclusively that magnesium was consumed in whatever reaction was involved in the formation of butyl benzene. From these results, it seems likely that the formation of butyl benzene involves butylene, rather than butyl chloride, the butylene being produced by the dirproportionation reaction which occurs during the reaction of butyl chloride with magnesium.

There is another possible mechanism for the formation of butyl benzene, which would not require the evolution of hydrogen chloride, and which would consume magnesium. Such a mechanism would involve reaction with one of the double bonds of benzene, but there is at present no evidence in support of this theory.

D. EXPERIMENTAL

1. General

All preparations of organomagnesium compounds in hydrocarbon mediums were made in the improved mechanical activation apparatus described previously, and illustrated in Figures 2 and 3. For 0.5 mole runs, the glass chamber, having a volume of slightly over 300 cc., was used, while for the 1.5 mole reactions the stainless steel chamber, having a volume of slightly over one liter, was employed.

Following each run, the mechanical activation apparatus was cleaned by attaching a chamber filled with dilute hydrochloric acid to the apparatus, and running the spindle for a short while, after which the acid was replaced with water and the procedure repeated. In most cases the apparatus was then dried by exposure to an infra-red bulb, though in some cases the spindle, seal mechanism, and lower bearing were removed and cleaned. This was found to be particularly necessary with the higher alkylmagnesium compounds.

2. Chemicals

With the exception of ethyl bromide and butyl chloride, which were distilled before use, all alkyl halides were used as received. Refractive indices of all halides were checked, and these showed the compounds to be substantially pure.

Sources of halides used are listed below:

Methyl bromide:	Matheson Company
Ethyl bromide:	Dow Chemical Company
Propyl bromide:	Columbia Organic Chemicals Co.
Butyl bromide	Eastman Kodak Co. Columbia Organic Chemicals Co.
Butyl iodide:	Eastman Kodak Co.
Amyl bromide:	Dow Chemical Company
Hexyl bromide:	Eastman Kodak Co.
Heptyl bromide:	Columbia Organic Chemicals Co.
Octyl bromide:	Halogen Chemicals Co.
Octyl chloride:	Halogen Chemicals Co.
Nonyl bromide:	Columbia Organic Chemicals Co.
Decyl bromide:	Columbia Organic Chemicals Co.
Dodecyl chloride:	Halogen Chemicals Co.

Heptane and isooctane used as mediums for the preparation of organomagnesium compounds were Phillips Petroleum Company's Pure Grade. Before use they were shaken in a separatory funnel with two portions of concentrated sulfuric acid, after which they were washed with three portions of water, and allowed to dry over Drierite. Sodium wire was pressed into the hydrocarbons so prepared, though there was rarely any gas evolution to indicate the presence of moisture. The hydrocarbons were stored under a nitrogen atmosphere.

Benzene used was Merck's thiophene-free, reagent grade. Treatment of the benzene before use was the same as that for the aliphatic hydrocarbons, with the omission of the sulfuric acid wash.

Carbon dioxide was from Pure Carbonic, and was used directly from the tank, after passing through a drying train consisting of a tube of Drierite followed by a tube of magnesium perchlorate.

3. Procedure for Making Runs

With the exception of the attempted preparation of methylmagnesium bromide, in which methyl bromide was distilled into the reaction mixture during the course of cutting magnesium, and those cases in which the halide was added dropwise to the reaction mixture during the course of cutting magnesium, the procedure used for the preparation of organomagnesium compounds in hydrocarbons was as follows:

In every case, 300 cc. of hydrocarbon were used for each 0.5 mole of alkyl halide. The amount of magnesium cut was exactly equivalent to the amount of halide present. This was easily controlled by measurement of the length of magnesium rod, since the quarter-inch rods had been centerless ground to a constant diameter, and the weight per unit length of rod did not vary significantly, even between different batches of magnesium.

The alkyl halide was weighed into an Erlenmeyer flask to the nearest ten milligrams, and transferred from the flask into a clean, dry reaction chamber. The hydrocarbon was then forced from the storage bottle by nitrogen pressure into a graduated cylinder, the volume of hydrocarbon being measured to the nearest five cubic centimeters. A portion of the hydrocarbon was used to wash any halide remaining in the weighing flask into the reaction mixture, the rest of the hydrocarbon being placed directly into the chamber. The chamber was then attached to the mechanical activation apparatus, and the desired initial temperature attained by means of an external bath. In most cases, the chamber was packed in crushed ice, though when higher temperatures were necessary, they were attained by heating the reaction chamber until the desired temperature was reached. Because of the large amount of heat generated by friction and by the cutting process, it was unnecessary to heat the chamber to maintain a high temperature; instead, a water bath was used, and the temperature was adjusted by varying the depth of the water in the bath. In this manner, any temperatures could be maintained up to the boiling point of the mixture.

During the period while the temperature of the reaction mixture was being adjusted, dry nitrogen was passed into the reaction chamber, though the stream of nitrogen was turned off before starting reaction, and during reaction nitrogen was introduced only when the mixture was being cooled.

After the desired temperature had been reached, cutting was started. For all runs, the Variac controlling the spindle motor was set at 80 volts, while that controlling the feed motor was set at 40 volts, so that the only variation in cutting speed and feed rate between runs would be that due to variation in line voltage. At 80 volts, with no load, the cutter spindle turned at about 5250 revolutions per minute, while under full cutting load it turned at 5000 revolutions per minute. This represents a cutting speed of about 2600 surface feet per minute.

At a Variac setting of 40 volts, and with the lowest pulley ratio, it was found that magnesium was fed at the rate of 0.224 inch per minute, representing a feed per tooth, or apparent chip thickness, of about three micro-inches, at a spindle speed of 5000 revolutions per minute. It must be realized, however, that in all probability only a few of the fifteen teeth on the cutter actually cut metal.

Magnesium was cut into the reaction mixture in increments of 4.36 inches of one-quarter inch rod, each increment representing one-fourth of a gram atom of magnesium. After the cutting of each increment, the feed mechanism was returned to its original position, and another increment cut, until the desired amount of magnesium had been cut.

During the cutting period, temperature of the reaction mixture was recorded at short intervals, together with the amount of magnesium cut. In addition, the electrical conductivity of the reaction mixture was observed, though at no time was any conductivity noted.

After the completion of the cutting process, the spindle was allowed to run for a predetermined length of time, the total time from the start of the cut until the spindle was turned off being recorded as the reaction time. When this length of time had elapsed, the temperature of the reaction mixture, if elevated, was reduced to near room temperature, an atmosphere of nitrogen being maintained in the apparatus during this process. When the mixture had cooled sufficiently, the chamber was removed from the apparatus, and as much as possible of the reaction product adhering to the apparatus was scraped into the chamber with a spatula.

After the chamber was removed, the distance from the top of the chamber to the surface of the reaction product was measured, using a depth gauge. This measurement was later used to determine the total volume of the reaction product, the chamber being filled to the same depth with water, and the volume of water being measured. The chamber was then placed under an air-driven stirrer, and the contents thoroughly agitated, to secure as homogeneous a mixture as possible. From this stirred mixture, samples were pipetted for the determination of yield and solubility, and for retention, the remainder of the mixture being subjected to treatment varying in individual cases.

4. Reaction with Carbon Dioxide

In those cases in which organic acids were prepared by reaction of the organomagnesium compounds with carbon dioxide, the following procedure was used:

After removal of samples, the chamber, containing the remainder of the organomagnesium compound, was attached to an adapter which was fitted with a mechanical stirrer, and two necks for the introduction of reactants. In this manner, the reaction chamber was converted essentially into a three-necked flask. The chamber was then flushed with nitrogen, a slightly positive pressure of nitrogen being maintained to prevent any leakage of air into the apparatus. The chamber was then surrounded by a cooling bath, usually an ice-salt mixture, and the contents were stirred until the desired temperature was attained.

When the temperature of the reaction mixture had fallen sufficiently, usually to zero degrees, the nitrogen atmosphere was replaced by a carbon dioxide atmosphere, the flow of the carbon dioxide being determined by a flow meter, and, in most cases, adjusted so as to prevent any large rises in temperature. Carbonation was deemed complete after a drop in temperature was noted; after this, rate of flow of carbon dioxide was increased, usually to about a liter a minute, the cooling bath was removed, and carbonation was continued for a length of time varying in individual cases.

The mixture resulting from the reaction with carbon dioxide was transferred to a two-liter, stainless steel beaker, which was immersed in an ice bath, and the product was hydrolyzed by the dropwise addition of 11 per cent sulfuric acid, 200 cc. of the acid being used for each one-half mole of original reactants. During hydrolysis, the mixture was well agitated, using a stainless-steel stirrer driven by an air impeller.

Following hydrolysis, the reaction mixture was decanted through a powder funnel, holding a small piece of cotton wool, into a separatory funnel, and the water and hydrocarbon layers separated. The water layer was then extracted with ether (three 75 cc. portions for 0.5 mole runs, four 100 cc. portions for 1.5 mole runs), the ether extracts being added to the hydrocarbon layer. The extracted water solution was then discarded. The organic layer was then placed in a volumetric flask (500 cc. for 0.5 mole runs, 1000 cc. for 1.5 mole runs), and diluted to volume with diethyl ether that had been washed with caustic to remove organic acids. From this solution a 50 cc. aliquot portion was pipetted for the determination of yield of organic acid; the remainder of the ether-hydrocarbon solution was extracted with 6 per cent sodium hydroxide solution to remove organic acids. The extracted organic layer was then washed with two portions of water, and set aside over Drierite to await distillation.

The caustic extract from above, containing only the organic acid produced, was acidified to a methyl orange end point by the dropwise addition of concentrated sulfuric acid to the chilled solution, with stirring. The organic acid was then separated, and the aqueous solution extracted with several portions of ether, the ether extract being added to the separated acid, and the mixture being placed over Drierite to await distillation.

5. Distillation of Carbonation Products

With the exception of the products of carbonation of octylmagnesium bromide, the distillation of which will be described separately, the only products distilled were those resulting from the carbonation of butylmagnesium halides. In all cases, distillations were carried out as follows:

Ether and hydrocarbons were removed from the solutions containing acidic and non-acidic reaction products by distillation through a glass helices packed column, 25 mm. in diameter and 37 cm. in height. There was no reflux return during this distillation, except from condensation in the column. Vapors were lead from the top of the column, through a goose-neck adapter, into a Friedrich condenser. Distillation was continued until no more distillate was coming over; because of the unheated and unjacketed length of the column, none of the higher-boiling products were distilled.

The valeric acid, after removal of ether, was distilled at 16 mm. pressure from a Claisen flask having Vigreux-type indentations in the neck leading to the condenser. A graduated receiver, fitted with stopcocks for removal of product without breaking the vacuum, was used for the collection of the distillate.

After removal of ether and hydrocarbon from the non-acidic reaction product, the residue was, in some cases, distilled through a semi-micro fractionating column to remove n-octane. This column consisted of a vacuum-jacketed tube, 10 mm. in diameter and 50 cm. high, packed with fine Monel wire gauze, bent so as to form a helical vapor path. A total condensation, partial take-off head was used. After removal of octane, the still-pot residue was transferred to the modified Claisen flask previously described, and further distillation was carried out at 16 mm. pressure. In cases where n-octane was not removed, distillation was carried out at 16 mm. immediately after removal of ether and hydrocarbon.

In both vacuum distillations, fractions were usually collected over a five-degree range, though this range was sometimes narrower when definite fractions were being collected.

For all fractions collected, the weight and refractive index, and, in some cases, density, were recorded.

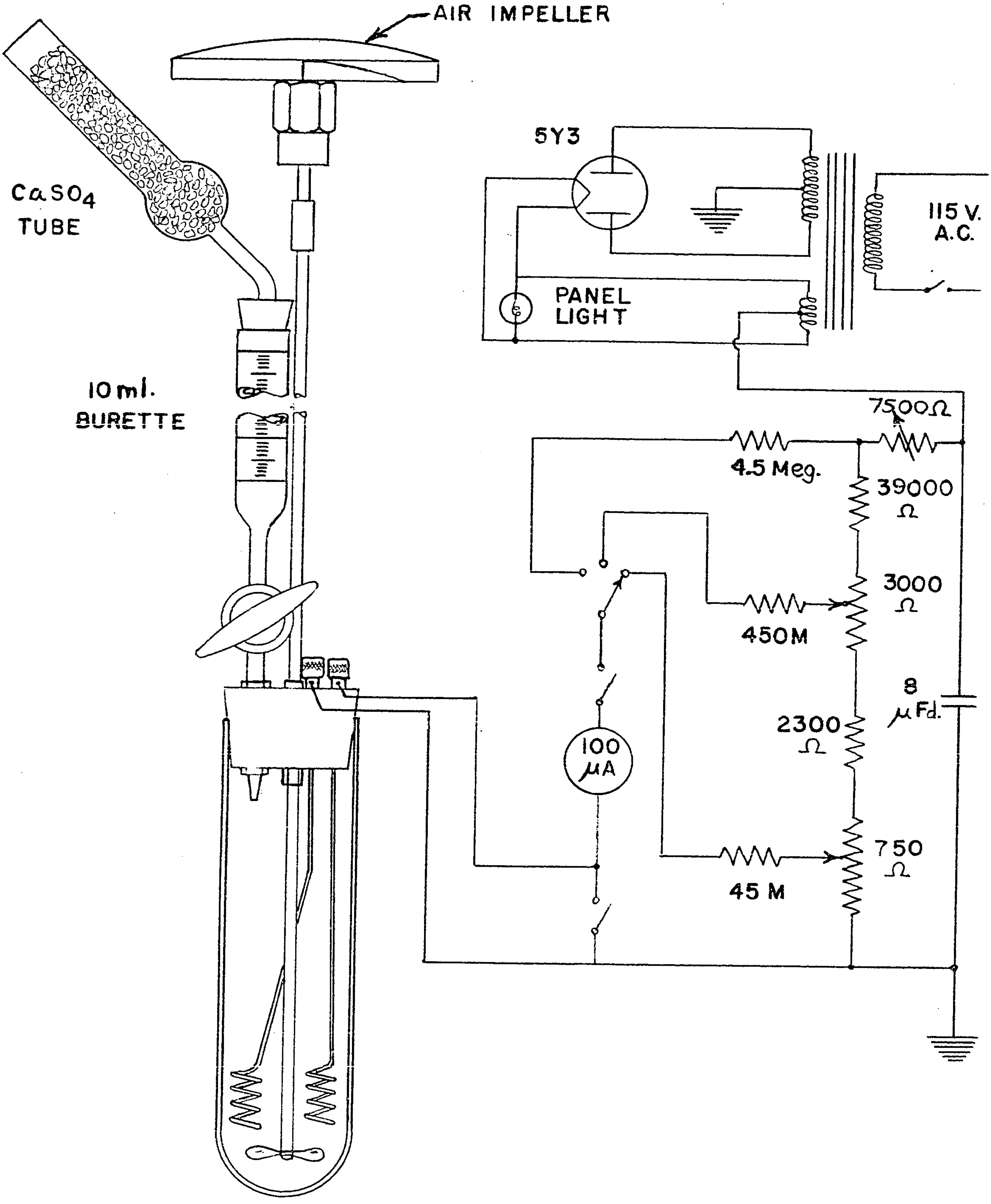
6. Determinations of Yields

(a) Conductometric Titration

The following procedure was used for the conductometric titration for yields of organomagnesium halides in all cases:

Butyl alcohol for titration was carefully fractionated through a glass helices packed column, having a packed, vacuum jacketed, and heated height of 90 cm., and a diameter of 25 mm. A total condensation, partial take-off head was used, the outlet to the atmosphere being protected by a drying tube. In all distillations, 200 cc. of alcohol were collected, at a constant boiling point, before collection of a 100 cc. sample for use in conductometric titration.

The apparatus used for conductometric titration is illustrated in Figure 13. The apparatus consists



APPARATUS FOR CONDUCTOMETRIC TITRATION

FIGURE 13

of a glass cell, fitted with a rubber stopper through which pass a glass stirrer; two electrodes of No. 14 Nichrome wire, having at their ends four-turn helices to increase electrode area; and a tube for the insertion of the tip of a 10 cc. burette. The electrical circuit illustrated is for a simple D. C. ohmeter; in use for conductometric titration, the three-position switch was in the position as indicated on the diagram. In this position, a potential of 4.5 volts is delivered to the electrodes. Readings are made on a 0-100 micro-ammeter by depressing the open switch in the circuit with the meter.

The actual conductometric titration was carried out as is outlined below:

100 cc. of a dilute ether solution of ethylmagnesium bromide (though concentration appeared to be of little importance it was found convenient to use a solution containing an amount of Grignard reagent in 100 cc. equivalent to about 0.5 cc. of n-butyl alcohol) was pipetted into the cell of the apparatus. Then, with rapid stirring, n-butanol was added from the burette in 0.10 cc. increments, the conductivity of the solution, in micro-amperes, being recorded after the addition of each increment. The conductivity decreased after each addition until a minimum was reached, after which it began to rise. Four or five increments of 0.1 cc.

of butyl alcohol were added after this minimum had been passed, after which the stirrer was stopped, and a 25 cc. sample of the organomagnesium halide to be determined was added to the ether solution. The stirrer was again started, and the same procedure was repeated until a minimum in conductivity was again reached and passed. In practice, the reaction could usually be followed visually, since heat of reaction, when organomagnesium compounds were present, caused the ether to boil momentarily after the addition of each increment of alcohol, while no boiling was noted after either of the minima had been passed. Also, in many cases, it was noted that the cloudy suspension, resulting from the addition of organomagnesium compounds in hydrocarbons to the ether solution, cleared abruptly, with coagulation of solids, as the second minimum was reached.

The data obtained in the above titration were plotted, micro-amperes against volume of butyl alcohol, and straight lines drawn through both approaches to the two minima. Using the intersections of these lines at the two minima as stoichemitric points, the volume of butyl alcohol equivalent to the organomagnesium compound in the unknown could be obtained. An example of the curve obtained is presented as Figure 14. It has been found that no significant difference exists in the positions of the minima obtained by plotting conductivity

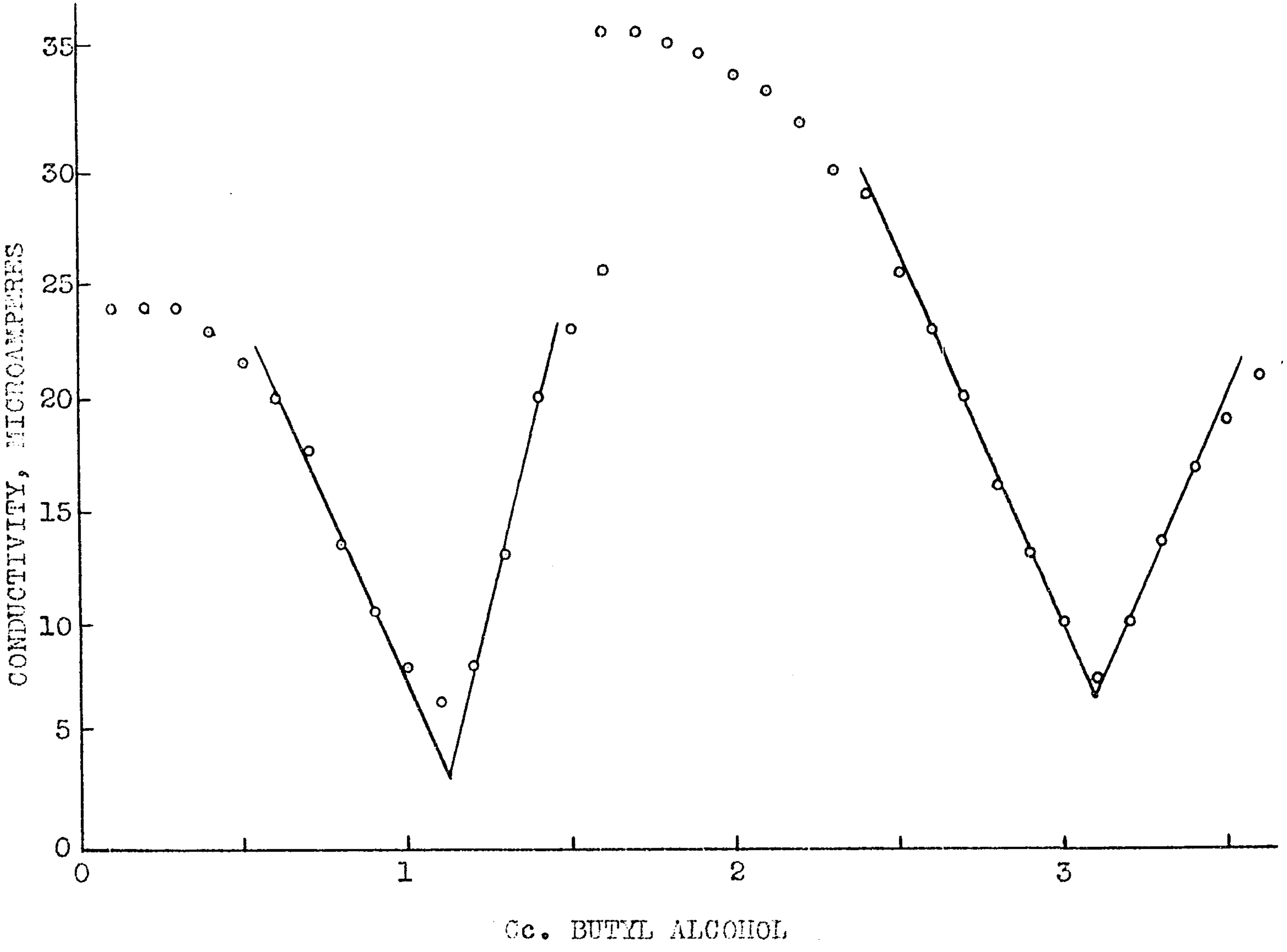

CONDUCTIVITY, MICROAMPERES
35
30
25
20
15
10
5
0
0
1
2
3
Cc. BUTYL ALCOHOL

Figure 14

as reciprocal ohms, and micro-amperes have been used for convenience.

Using the butyl alcohol as a primary standard, and the volume of alcohol found to be equivalent to the organomagnesium halide in the sample titrated, and knowing the volume of the original mixture containing the organomagnesium compound, the yield of organomagnesium halide is easily calculated. For example, using the data obtained from the curve in Figure 14, which was obtained for the yield of butylmagnesium bromide prepared in isooctane in a 0.5 mole run, the yield of organomagnesium compound is found as follows:

1.98 cc. BuOH
Total volume reaction products, 345 cc.

Yield of BuMgBr = 0.0874 x 1.98 x 345
= 59.7 per cent

The factor 0.0874 is arrived at from the density of butyl alcohol, its molecular weight, the size of the run (0.5 mole), and the volume of the aliquot. For 1.5 mole runs, this factor is decreased to 0.0291, while the total volume of the reaction mixture is used just as illustrated. It was found by calculations that the change in density of butyl alcohol with variation of room temperature had no significant effect on the yield obtained, and the density of butyl alcohol at 20°, 0.810, was used for all calculations.

(b) Acid Titration

Although the uncorrected yields obtained by acid titration are, in most cases, meaningless, they were determined in all instances by the following procedure:

A 10 cc. aliquot of the original reaction product was pipetted into a 250 cc. Erlenmeyer flask. This sample was hydrolyzed by the addition of 100 cc. of distilled water, and acidified by the addition of 15 cc. of N/1 hydrochloric acid. After reaction with acid was complete, the mixture was titrated to a methyl orange end point with N/10 sodium hydroxide solution. All standard solutions were obtained from the Fisher Scientific Company, and were checked by titration against each other, and by titration of the base with an acid solution standardized with sodium carbonate.

(c) Correction for Magnesium

The amount of magnesium which failed to react during the preparation of organomagnesium compounds from butyl and higher halides was determined by the measurement of the volume of gas evolved upon acidification of a 10 cc. sample of the original reaction mixture. This measurement was carried out as follows:

The system for measurement of hydrogen consisted of a water-jacketed 250 cc. gas burette, with leveling bulb, connected through a trap immersed in an acetone-dry ice mixture, to a flask fitted with a dropping funnel for the addition of acid.

The 10 cc. sample of reaction product was pipetted into a 125 cc. Erlenmeyer flask, which was then fitted to the above apparatus. Pressure within the gas burette was carefully adjusted to atmospheric, using a U-tube containing water to indicate the pressure. The U-tube was then closed, and 11 per cent sulfuric acid added very slowly to the mixture in the reaction flask, so that hydrocarbon vapors would be condensed in passing through the dry ice trap. A slight negative pressure was maintained in the gas burette throughout the gas evolution.

When hydrolysis was complete, the system was allowed to reach equilibrium, as indicated by no change in the pressure within the burette over a period of one-half hour, and the volume of gas in the burette recorded, together with the atmospheric pressure, the temperature of the burette's water jacket, and the amount of liquid remaining in the reaction flask (the amount of liquid condensed in the cold trap was found to be negligible in comparison with the total volume). Then, correcting for the vapor pressure of water in the burette, assuming the gas to be saturated with water, the amount of magnesium in the sample equivalent to the hydrogen evolved could be calculated by the application of the gas laws. This figure was used to correct for the amount of magnesium in the 10 cc. samples used for acid titrations, and to find the total amount of unreacted magnesium in the original mixture.

(d) Determination of Yield of Organic Acid

Although organic acids were distilled, and the amount distilled recorded, distillation of the small amounts usually present resulted in significant losses, so that the yields of the acid were determined by titration, as follows:

To the 50 cc. aliquot portion pipetted from the ether-hydrocarbon solution of organic acid obtained after hydrolysis, were added 100 cc. of distilled water. This mixture, in a glass-stoppered Erlenmeyer flask, was titrated first to a methyl orange end point, and then to a phenolphthalein end point, with N/1 sodium hydroxide solution. The methyl orange end point appears when all mineral acid present has been neutralized; the volume of caustic required to reach this end point was always small, and usually negligible. The phenolphthalein end point appears when all organic acid has been neutralized, and the volume of base represented by the difference between the two end points should be equivalent to the organic acid present in the aliquot.

Because of the greater solubility of the organic acid in the hydrocarbon-ether layer, it was found necessary to shake the mixture vigorously in the neighborhood of the end point, after the addition of each drop of base. Apparently no error was introduced by the partition of acid, since no end point which persisted through shaking for a few seconds would fade on prolonged shaking or standing.

7. Preparation of Organomagnesium Compounds

Below are outlined the conditions prevailing during, and the results obtained from, the preparation of the various organomagnesium compounds.

(a) Methylmagnesium Bromide

Methyl bromide was condensed by passing the gas from a cylinder into a trap immersed in a dry-ice-acetone bath, and allowed to distil from this trap through the gas inlet tube on the reactor, into heptane solution.

In one run, temperature was maintained in the range of 55-60° during most of the cutting and addition of methyl bromide, though the temperature fell below this value as the concentration of methyl bromide increased.

The spindle was left on until 315 minutes, after cutting of 1.5 gram atoms of magnesium had been completed at 179 minutes. There was no evidence of reaction.

In a second run, no water bath was used to cool the reaction chamber. The temperature rose to 84° during the first twenty minutes of cutting, and then fell steadily until it reached a constant value of 45° on the completion of the addition of the methyl bromide, after the cutting of 1.5 gram atoms of magnesium had been completed at 154 minutes. Spindle allowed to run 249 minutes. There was no indication of any reaction.

(b) Ethylmagnesium bromide in Heptane

In a 1.5 mole run, magnesium was cut into a heptane solution of ethyl bromide, temperature rising from ten to fifteen degrees during the first 20 minutes, and remaining constant at 23-24° until 107 minutes, when five of the six increments of magnesium had been cut. At that time the chamber was removed, and the appearance of the contents indicated there had been no reaction. Ice bath was removed, and temperature allowed to rise, being maintained at 35-37° until the end of the cut at 155 minutes, and until spindle was turned off at 245 minutes. Reaction product was a fluid gray suspension. Conductometric titration required 2.48 cc. of butyl alcohol, for total product volume of 990 cc., indicating a yield of 71.5 per cent. Acid titration indicated the yield to be 130 per cent. Product was carbonated, but acid resulting was lost before the yield could be determined.

In a 1.5 mole run, magnesium was cut into a heptane solution of ethyl bromide during 135 minutes. Temperature rose from 15 to 25° during the first ten minutes, and remained at 22-25° to end of cut, after which it was allowed to rise to 44° at 185 minutes, and cooled to 32° when spindle off at 197 minutes. Quadruplicate conductometric titration of the product indicated yields of 46.0, 44.5, 44.2, and 44.5 per cent. Gas evolved from quadruplicate samples was measured, and analyzed for hydrogen by using an Orsat apparatus. Yield determined by gas evolution, correcting for hydrogen and oxygen present 38.1 ± 1.7 per cent. Yield determined by duplicate acid titrations, correcting for magnesium required to evolve amount of hydrogen found in gas, 96.7 per cent.

In a 0.5 mole run, magnesium was cut into a heptane solution of ethyl bromide during 48 minutes, temperature varying from 34° to 76° during cut, and rising to 90° until spindle turned off at 135 minutes. Reaction was noticed at 10 minutes, temperature 47°. Conductometric titration indicated a yield of 45 per cent. Product discarded.

In a 1.5 mole run, magnesium was cut into a heptane solution of ethyl bromide during 187 minutes, temperature varying from 8-24° during cut, and from 12-24° until spindle turned off at 345 minutes. Gas was evolved steadily throughout the run, 10.36 liters being collected. Gas would not burn, but it decolorized bromine water and dilute potassium permanganate solution. Analysis of the gas failed to indicate the presence of oxygen, or of a hydrocarbon. Products showed no indication of reaction.

In a 1.5 mole run, magnesium was cut into a heptane solution of ethyl bromide. Temperature rose from six degrees to 24° during first seven minutes of cut, and remained at 20-24° until completion of cut at 128 minutes, and at 26-29° until spindle turned off at 244 minutes. There was no indication of any reaction.

In a 1.5 mole run, magnesium was cut into a heptane solution of ethyl bromide, temperature rising from 12° to 21° in the first two minutes of cutting, and remaining at 20-24° to completion of cut at 149 minutes, rising to 29° by the time the spindle was turned off and chamber removed at 210 minutes. There was no indication of any reaction.

(c) Ethylmagnesium Bromide in Isooctane

In a 0.5 mole run, magnesium was cut into an isooctane solution of ethyl bromide during 59 minutes, temperature rising from 22 to 70° during cut, and to 80° when spindle turned off at 125 minutes. Conductometric titration indicated a yield of 59.4 per cent. Product was reacted with benzaldehyde, but it was found later that the aldehyde contained a large percentage of benzoic acid, which was the only product identified from the reaction products.

(d) Ethylmagnesium Bromide in Benzene

In a 0.5 mole run, magnesium was cut into a benzene solution of ethyl bromide during 48 minutes, temperature rising from 23 to 69° during cut, and to 78° by 100 minutes, when spindle turned off. Product a darker gray than similar products in aliphatic hydrocarbons. Conductometric titration indicated a yield of 65.6 per cent. No products were identified after the reaction of the ethylmagnesium bromide formed with benzaldehyde.

(e) Propylmagnesium Bromide in Heptane

In a 1.5 mole run, magnesium was cut into a heptane solution of n-propyl bromide during 131 minutes, temperature rising from 13-28° during first seven minutes of cut, and being maintained from 22-28° for remainder of cutting time. Temperature rose to a maximum of 44° at 215 minutes; spindle off at 230 minutes. Product of a light gray, fluid suspension. Conductometric titration indicated a yield of 64.1 per cent, while acid titration, uncorrected, showed a yield of 99.5 per cent.

(f) Butylmagnesium Halides in Hydrocarbons

The data on the preparation of butylmagnesium halides in hydrocarbons are too extensive to permit their inclusion in their entirety here. The data are summarized in Table I.

(g) Amylmagnesium Bromide in Heptane

In a 1.5 mole run, magnesium was cut into a heptane solution of n-amyl bromide during 137 minutes. Temperature rose from 10-20° during the first three minutes of the cut, and remained at 20-25° through 82 minutes, at which time half of the magnesium had been cut and no reaction was noted. Temperature was increased, and maintained at 50-56° until all the magnesium had been cut, and the spindle was turned off at 215 minutes. The reaction product was a viscous, light gray mass. Conductometric titration indicated a yield of 50.6 per cent, while acid titration, corrected for unreacted

TABLE I. Summary of Data on Bu

Run No.	Moles Halide Medium	Conditions of Run	Yield of BuMgX			Carbonation	
			BuOH	Acid	Acid, Less Mg	Time	Temp.
134	BuI, .5, heptane	10-50°, White viscous product	85 %	75.6		Dry	Ice
135	BuCl, .5, hept	14-48°, No Reaction					
136	BuBr, .5, iso-oct.	17.5-48°, Thick gray Product				Dry	Ice
137	BuBr, .5, iso-oct.	18-70°, "	53.2	74.2		"	"
138	BuBr, .5, C_6H_6	20-71°	49.9	73.2		"	"
C-56-3	BuBr, .5, isooct.	10-50°, 1 hour	63.3	77.5			
C-56-7	"	18-71°, 1.5 hour	58.5	70.0			
C-56-11	"	33-60°, 2.5 hours	59.7	102			
C-56-19	n-BuBr 1.5 mole isooctane	14-33°, 3.5 hours with spindle (85 minutes after end of cut)	63.6	86.5		6 hrs. @ 1 L./min.	salt-ice bath
C-56-43	Ditto	8-31°; cut for 184 min., spindle on until 231 min.	62.6	87.2		5¼ hrs 1 L/min. 1 hr, 8 L/min.	-78° -78 - +50°
C-56-71	Ditto	21-32°, Cut in 163 min., spindle on to 184 min.	60.2	79.2		5 hrs	0-10°
C-56-59	n-BuBr 1.5 mole n-heptane	10-32°, Cut in 143 min., spindle on to 210 min.	60.9	100 +		5 hrs., 1 L./min.	Salt-ice bath
C-56-105	Ditto	9-28°, cut in 186 min., spindle on to 275 min.	57.2	75.4		160 min.	0-8°
C-58-13	Ditto	8-27°, cut in 130 min., spindle on to 183 min. BuBr added dropwise during cut.	65.0	82.3		200 min.	0-12°
C-58-21	Ditto	11-28° for 149 min. of cut. 28-62° until 278 min. with spindle on. Product much lighter gray than usual	61.4	84.4		250 min. 62 min.	0-12° 9-22°
C-58-55	Ditto	6-35° during 130 min of cut. 32-58° during time to 229 min., when spindle off.	59.3	90.6	59.4	160 min. 50 min.	-3 to 7° 5-50°
C-56-93	n-BuBr 1.5 mole Benzene	8.5-30°, cut in 160 min., spindle on to 295 min.	63.3	83.7		100 min. 25 " 95 "	3-8° 3° (1 L/m 3-28°
C-58-105	n-BuI 1.5 mole isooctane	10-42° during 139 min. of cut; 37-61° during time to 222 min., when spindle off.	76.0	100.0	77.0	242 min.	2-14°
	n-BuCl	12-77°; Cut in 154 min.,				60 min	4°

Butylmagnesium Halides

on	Yield RCOOH, Titrated	Distillation										F
		Acidic										
mp.		Gms. Acid	Yield	% of Titrated	Fraction	BP/15mm.	Wt.	n_D^{20}	% of Total Product	n-octane	Yield	
												I_2 prevent
e												No Reacti
e												Leakage of
	25.8											
	22.2											
												No Reactio
												Product
	0											No Reactio
lt- e bath	32 %	36.33 (57.7 % of product)	26.1	81.7	3	30-81.5		1.4104	4.9			Semicarba m. 88-89° residue f About 5 for in pr
					4	81.5-83.5	6.3	1.4260	10.3			
					5	83.5-98.0	4.39	1.4358	7.2			
					6	98-105	3.84	1.4430	6.3			
					7	105-139	3.83	1.4482	6.3			
78° 8 - -50°	24.5	29.38 (46.7 % of prod.)	21.6	88.1	6	34-38 a	1.54	1.4001	2.4	Sample 7	4.8%	(a) Fract.c Solid resi acid, m. 8 240. Abo for in p
					7	38-49 a	3.75	1.3987	6.0			
					8	88-95 a	3.67	1.4208	5.8			
					9	95-102 a	4.91	1.4260	7.8			
					10	93-98	1.33	1.4252	2.1			
					11	98-104	2.26	1.4312	3.6			
					12	104-116	2.30	1.4379	4.1			
					13	116-129.5	2.56	1.4426	4.1			
					14	12.5 120	0.90		1.7			
-10°	37.3	41.26 (60.6 % of prod.)	30.4	81.5	6	29°	0.66	1.3966	1.0	Sample 7	9.4 %	Residue solid. A accounte
					7	29-76	7.34	1.3978	10.8			
					8	76-83.5	6.10	1.4218	9.0			
					9	83.5-87.5	2.78	1.4250	4.1			
					10	87.5-103	3.03	1.4360	4.5			
alt- e ath	35.1	24.47 (59.4 % of prod.)	18.0	51.3	4	23-24	5.15	1.3919	12.5	Sample 5	2.4 %	About 3 for in p
					5	29-54	1.86	1.3961	4.5			
					6	73-76	0.98	1.4080	2.4			
					7	77-79.5	3.63	1.4195	8.8			
					8	79-82	.46	1.4222	3.5			
					9	87-102	0.47	1.4267	1.1			
					10	102-108	1	1.4379	2.4			
- 8°	39.0	47.01 (67.8 % of prod.)	34.5	88.4	8	44-78	2.19	1.4020	3.2	2.63 g b.124-124.5 748 mm n_D^{20} 1.3970	3.5 %	About 6 in produ
					9	79-85	543	1.4208	7.8			
					10	87-88	2.43	1.4229	3.5			
					11	88-93	0.82	1.4259	1.2			
					12	96-112	1.43	1.4322	2.1			
					13	118 +	0.56	1.4400	0.8			
-12°	37.9	45.13 (66.6% of prod.)	33.9	89.4	7	79-84	9.47	1.4207	14.0	0.82 g b.124-.26° 735 mm. n_D^{20} 1.3980	1.1 %	Apparen carbonatio accounted
					8	84-96	2.64	1.4241	3.9			
					9	98-102	0.56	1.4292	0.8			
					10	102-118	1.64	1.4371	2.4			
-12° -22°	8.1	7.90 (37.6% of prod.)	5.85	72.3	6	78-82	2.12	1.4121	10.1	2.33 g. b.122-126° 749 mm. n_D^{20} 1.3971	3.1 %	Carbonat seemed About 23 in produ
					7	84-87	5.03	1.4218	23.9			
					8	93-98	2.18	1.4249	10.4			
					9	98-110	1.48	1.4323	7.0			
to 7° -50°	39.8	48.31 (70.7 % of prod.)	36.7	92.2	6	56-78	1.86	1.4100	1.5	1.86 g. b.123-127° 744 mm. n_D^{20} 1.3980	2.5%	About 58%
					7	82-87	4.65	1.4203	6.8			
					8	88-98	3.68	1.4240	5.4			
					9	103-115	1.85	1.4337	2.7			
-8° 0 ([illegible]) -28°	35.6	43.87 (62.8% of prod.)	32.1	90.0	7	62-76	2.20	1.4192	3.1	3.70 g. 123-124°, 749 mm. n_D^{20} 1.4000	4.9 %	About 6 for (63%
					8	50-77	1.89	1.4197	2.6			
					9	78-85	8.01	1.4338	11.2			
					10	90-93	2.98	1.4255	4.2			
					11	93-117	2.80	1.4292	3.9			
					12	116-126	1.63	1.4418	2.3			
-19°	26.2	17.36 (38.9% of prod.)	13	49.7	6	48-91	2.32	1.4240	5.2	None	0	(b) Fract valeric a Incomple 40% o in proc
					7	91-96(b)	9.03	1.4281	20.2			
					8	98	0.96	1.4313	2.1			
					9	99-102	3.34	1.4340	7.5			
					10	102-107	5.50	1.4380	8.1			
					11	107-109	1.01	1.4400	2.3			
4°		32.10			5	67-73	8.00	1.4660	14.1	1.64g 122-127°,	2.3%	About for in pr
					6	73-80	5.23	1.4579	9.2			

	Distillation							Remarks
d	Fraction	BP/15mm.	Wt.	n_D^{20}	% of Total Product	n-octane	Yield	
								I_2 prevented titration of acid
								No Reaction
								Leakage of chamber lost about ½ product
								No Reaction despite titrated yield
								Product discarded
								No Reaction despite titrated yield
	3	30-81.5		1.4104	4.9			Semicarbazone from fraction 4 m. 88-89°; Same solid obtained from residue from distillation of acid. About 56% of BuBr accounted for in product.
	4	81.5-83.5	6.3	1.4260	10.3			
	5	835-98.0	4.39	1.4358	7.2			
	6	98-105	3.84	1.4430	6.3			
	7	105-139	3.83	1.4482	6.3			
	6	34-38 a	1.54	1.4001	2.4	Sample 7	4.8%	(a) Fractions 6-9 distilled at 22 mm. Solid residue from distillation of acid, m. 86-87°; neutral equivalent 240. About 57% of BuBr accounted for in product.
	7	38-49 a	2.75	1.3987	6.0			
	8	88-95 a	3.57	1.4208	5.8			
	9	95-102 a	4.91	1.4260	7.8			
	10	93-98	1.33	1.4277	3.1			
	11	98-104	2.26	1.4312	3.6			
	12	104-116	2.50	1.4379	4.1			
	13	116-129.5	2.56	1.4484	4.1			
	14	112.5-120	0.90		1.4			
	6	29°	0.66	1.3966	1.0	Sample 7	9.4%	Residue from distillation of acid solid. About 60% of BuBr accounted for in product.
	7	29-76	7.34	1.3978	10.8			
	8	76-83.5	6.10	1.4218	9.0			
	9	83.5-87.5	2.78	1.4250	4.1			
	10	87.5-103	3.03	1.4360	4.5			
	4	23-24	5.15	1.3919	12.5	Sample 5	2.4%	About 32% of BuBr accounted for in product.
	5	29-54	1.86	1.3961	4.5			
	6	73-76	0.98	1.4080	2.4			
	7	77-79.5	3.63	1.4195	8.8			
	8	79-82	1.46	1.4222	3.5			
	9	87-102	0.47	1.4267	1.1			
	10	102-108	1	1.4389	2.4			
	8	44-78	2.19	1.4020	3.2	2.63 g b.124-124.5 748 mm n_D^{20} 1.3970	3.5%	About 62% of BuBr accounted for in product.
	9	79-85	5.43	1.4208	7.8			
	10	87-88	2.43	1.4229	3.5			
	11	88-93	0.82	1.4259	1.2			
	12	96-112	1.43	1.4322	2.1			
	13	118 +	0.56	1.4400	0.8			
	7	79-84	9.47	1.4207	14.0	0.82 g b.124-126° 735 mm. n_D^{20} 1.3980	1.1%	Apparently induction period in carbonation. About 57% of BuBr accounted for in product.
	8	84-96	2.64	1.4241	3.9			
	9	98-102	0.56	1.4292	0.8			
	10	102-118	1.64	1.4371	2.4			
	6	78-82	2.12	1.4121	10.1	2.33 g. b.122-126° 749 mm. n_D^{20} 1.3971	3.1%	Carbonation stopped in middle; seemed to be induction period. About 23% of BuBr accounted for in product.
	7	84-87	5.03	1.4218	23.9			
	8	93-98	2.18	1.4249	10.4			
	9	98-110	1.48	1.4323	7.0			
	6	56-78	1.86	1.4100	1.5	1.86 g. b.123-127° 744 mm. n_D^{20} 1.3980	2.5%	About 58% of BuBr accounted for.
	7	82-88	4.65	1.4203	6.8			
	8	88-98	3.68	1.4240	5.4			
	9	103-115	1.85	1.4337	2.7			
	7	62-76	2.20	1.4192	3.1	3.70 g. 123-124°, 749 mm. n_D^{20} 1.4000	4.9%	About 68% of BuBr accounted for (63% as RMgX)
	8	50-77	1.89	1.4197	2.6			
	9	78-85	8.01	1.4338	11.2			
	10	90-93	2.98	1.4255	4.2			
	11	93-117	2.80	1.4292	3.9			
	12	116-126	1.63	1.4418	2.3			
	6	48-91	2.32	1.4240	5.2	None	0	(b) Fraction 7 probably largely valeric acid present because of incomplete extraction. About 40% of BuI accounted for in product.
	7	91-96(b)	9.03	1.4281	20.2			
	8	98	0.96	1.4313	2.1			
	9	99-102	3.34	1.4340	7.5			
	10	102-107	5.50	1.4380	8.1			
	11	107-109	1.01	1.4400	2.3			
	5	67-73	8.00	1.4660	14.1	1.64g		About 53% of BuCl accounted
	6	73-80	5.23	1.4579	9.2			

C-56-43	Ditto	spindle on until 251 min.	62.6	87.2		1 hr., 8 L/min.	-78 - +50°
C-56-71	Ditto	21-32°, Cut in 163 min., spindle on to 184 min.	60.2	79.2		5 hrs	0-10°
C-56-59	n-BuBr 1.5 mole n-heptane	10-32°, Cut in 143 min., spindle on to 210 min.	60.9	100 +		5 hrs., 1 L./min.	Salt-ice bath
C-56-105	Ditto	9-28°, cut in 186 min., spindle on to 275 min.	57.2	75.4		160 min.	0-8°
C-58-13	Ditto	8-27°, cut in 130 min., spindle on to 183 min. BuBr added dropwise during cut.	65.0	82.3		200 min.	0-12°
C-58-21	Ditto	11-28° for 149 min. of cut. 28-62° until 278 min. with spindle on. Product much lighter gray than usual	61.4	84.4		250 min 62 min.	0-12° 9-22°
C-58-55	Ditto	6-35° during 130 min of cut. 32-58° during time to 229 min., when spindle off.	59.3	90.6	59.4	160 min. 50 min.	-3 to 7° 5-50°
C-56-93	n-BuBr 1.5 mole Benzene	8.5-30°, cut in 160 min., spindle on to 295 min.	63.3	83.7		100 min. 25 " 95 "	3-8° 3° ([illegible]) 3-28°
C-58-105	n-Bu I 1.5 mole isooctane	10-42° during 139 min. of cut; 37-61° during time to 222 min., when spindle off.	76.0	100.0	77.0	242 min.	2-19°
C-58-71	n-BuCl 1.5 mole Benzene	12-77°; Cut in 154 min., spindle on to 220 min. Gas formation at start of reaction at 146 min.	42.6	107.5	60.7	60 min 210 min.	4° 4-26°
C-58-29	n-BuCl 1.5 mole isooctane	6-58° during 138 min. of cut, 55-64° to 210 min., when spindle off.	62.4	86.3		280 min.	4-38°
C-58-89	Ditto	28-65°, cut in 122 min., spindle off at 227 min. Gas evolution at start of reaction at 105-112 min.	65.6	84.6	49	431 min.	2-42°
C-56-117	BuCl, .5, isooct.	20-62°, cut in 46.8 min., spindle off at 160 min.	56.5	79.6		180 min.	0-20°
C-58-123	BuCl, 1.5, hept.	22-84°, cut in 126 min., spindle off at 240 min., gas at 90 min.	57.5	83.0	54.6	260 min.	0-32°

50°	24.5	of prod.)	21.6	88.1	10	93-98	1.33	1.4297	3.1	7	4.8%	acid, m. 86- 240. About for in prod
					11	98-104	2.26	1.4312	3.6			
					12	104-116	2.50	1.4379	4.1			
					13	116-129.5	2.56	1.4426	4.1			
					14	112.5 120	0.70		1.4			
	37.3	41.26 (60.6% of prod.)	30.4	81.5	6	29°	0.66	1.3966	1.0	Sample 7	9.4%	Residue fro solid. Abo accounted f
					7	29-76	7.34	1.3978	10.8			
					8	76-83.5	6.10	1.4218	9.0			
					9	83.5-87.5	2.78	1.4250	4.1			
					10	87.5-103	3.03	1.4360	4.5			
	35.1	24.47 (59.4% of prod.)	18.0	51.3	4	23-24	5.15	1.3919	12.5	Sample 5	2.4%	About 32% for in prod
					5	29-54	1.86	1.3961	4.5			
					6	73-76	0.98	1.4080	2.4			
					7	77-79.5	7.63	1.4195	8.8			
					8	79-82	1.46	1.4222	3.5			
					9	87-102	0.47	1.4267	1.1			
					10	102-108	1	1.4379	2.4			
	39.0	47.01 (67.8% of prod.)	34.5	88.4	8	44-78	2.19	1.4020	3.2	2.63 g b.124-124.5 748 mm n_D^{20} 1.3970	3.5%	About 62% in product.
					9	79-85	5.43	1.4208	7.8			
					10	87-88	2.43	1.4229	3.5			
					11	88-93	0.82	1.4259	1.2			
					12	96-112	1.43	1.4322	2.1			
					13	118 +	0.56	1.4400	0.8			
	37.9	45.13 (66.6% of prod.)	33.9	89.4	7	79-84	9.47	1.4207	14.0	0.82 g b.124-126° 735 mm. n_D^{20} 1.3980	1.1%	Apparently carbonation. accounted for
					8	84-96	2.64	1.4241	3.9			
					9	98-102	0.56	1.4292	0.8			
					10	102-118	1.64	1.4371	2.4			
	8.1	7.90 (37.6% of prod.)	5.85	72.3	6	78-82	2.12	1.4121	10.1	2.33 g. b.122-126° 749 mm. n_D^{20} 1.3971	3.1%	Carbonation seemed to b About 23% in product.
					7	84-87	5.03	1.4218	23.9			
					8	93-98	2.18	1.4249	10.4			
					9	98-110	1.48	1.4323	7.0			
	39.8	48.31 (70.7% of prod.)	36.7	92.2	6	56-78	1.86	1.4100	1.5	1.86 g. b.123-127° 744 mm. n_D^{20} 1.3980	2.5%	About 58% of
					7	82-87	4.65	1.4203	6.8			
					8	88-98	3.68	1.4240	5.4			
					9	103-115	1.85	1.4337	2.7			
	35.6	43.87 (62.8% of prod.)	32.1	90.0	7	62-76	2.20	1.4192	3.1	3.70 g. 123-124°, 749 mm. n_D^{20} 1.4000	4.9%	About 68% for (63% as
					8	50-77	1.89	1.4197	2.6			
					9	78-85	8.01	1.4338	11.2			
					10	90-93	2.98	1.4255	4.2			
					11	93-117	2.80	1.4292	3.9			
					12	116-126	1.63	1.4418	2.3			
	26.2	17.36 (38.9% of prod.)	13	49.7	6	48-91	2.32	1.4240	5.2	None	0	(b) Fraction 7 valeric acid pr incomplete e 40% of Bu in product.
					7	91-96(6)	9.03	1.4281	20.2			
					8	98	0.96	1.4313	2.1			
					9	99-102	3.34	1.4340	7.5			
					10	102-107	5.50	1.4380	8.1			
					11	107-109	1.51	1.4400	2.3			
	26.1	32.10 (56.7% of prod.)	24.7	95	5	67-73	8.00	1.4660	14.1	1.64 g 122-127°, n_D^{20} 1.3992	2.3%	About 53% for in produc
					6	73-80	5.23	1.4579	9.2			
					7	8[illegible]-116	3.97	1.4389	7.0			
					8	116-125	0.44	1.4315	0.8			
					9	125-30	0.90	1.4482	1.6			
					10	132-143	2.07	1.4521	3.6			
	19.6	22.90 (60% of prod.)	17.3	88.5	5	68-82	1.10	1.4172	2.9	None	0	11.18 g. of m 741.2 mm., n_D^{20} 1. Residue from solid. About for in produ
					6	82-86	3.30	1.4217	8.7			
					7	87-91	3.98	1.4236	10.4			
					8	95-116	3.56	1.4299	7.3			
					9	116-122	1.42	1.4405	3.7			
	31.2	38.60 (56.5% of prod.)	28.6	91.5	6	81-86	5.59	1.4237	8.2	None	0	2.23 g. mate n_D^{20} 1.3919. accounted for
					7	88-99	5.62	1.4241	8.2			
					8	102-118	1.90	1.4299	2.8			
					9	122-130	3.11	1.4419	4.6			
					10	130-137	3.67	1.4552	5.4			
	44.0											
	32.2											

.1	10	93-98	1.33	1.4387	2.1	6	4.8%	acid, m. 86-87°; neutral equivalent 240. About 57 % of BuBr accounted for in product.
	11	98-104	2.25	1.4312	3.6			
	12	104-116	2.60	1.4379	4.1			
	13	116-129.5	2.56	1.4486	4.1			
	14	112.5 120	0.70		1.7			
.5	6	29°	0.66	1.3966	1.0	Sample 7	9.4 %	Residue from distillation of acid solid. About 60 % of BuBr accounted for in product.
	7	29-76	7.34	1.3978	10.8			
	8	76-83.5	6.10	1.4218	9.0			
	9	83.5-87.5	2.78	1.4250	4.1			
	10	87.5-103	3.03	1.4360	4.5			
3	4	23-24	5.15	1.3919	12.5	Sample 5	2.4 %	About 32 % of BuBr accounted for in product.
	5	29-54	1.86	1.3961	4.5			
	6	73-76	0.98	1.4080	2.4			
	7	77-79.5	3.63	1.4195	8.8			
	8	79-82	.46	1.4222	3.5			
	9	87-102	0.47	1.4267	1.1			
	10	102-108	1	1.4389	2.4			
.4	8	44-78	2.19	1.4020	3.2	2.63 g b.124-124.5 748 mm n_D^{20} 1.3970	3.5 %	About 62 % of BuBr accounted for in product.
	9	79-85	5.43	1.4208	7.8			
	10	87-88	2.43	1.4229	3.5			
	11	88-93	0.82	1.4259	1.2			
	12	96-112	1.43	1.4322	2.1			
	13	118 +	0.56	1.4400	0.8			
4	7	79-84	9.47	1.4207	14.0	0.82 g b.124-126° 735 mm. n_D^{20} 1.3980	1.1 %	Apparently induction period in carbonation. About 57 % of BuBr accounted for in product.
	8	84-96	2.64	1.4241	3.9			
	9	98-102	0.56	1.4292	0.8			
	10	102-118	1.64	1.4371	2.4			
3	6	78-82	2.12	1.4121	10.1	2.33 g. b.122-126° 749 mm. n_D^{20} 1.3971	3.1 %	Carbonation stopped in middle; seemed to be induction period. About 23 % of BuBr accounted for in product.
	7	84-87	5.03	1.4218	23.9			
	8	93-98	2.18	1.4249	10.4			
	9	98-110	1.48	1.4323	7.0			
2	6	56-78	1.86	1.4100	1.5	1.86 g. b.123-127° 744 mm. n_D^{20} 1.3980	2.5 %	About 58 % of BuBr accounted for.
	7	82-87	4.65	1.4203	6.8			
	8	88-98	3.68	1.4240	5.4			
	9	103-115	1.85	1.4337	2.7			
.0	7	62-76	2.20	1.4192	3.1	3.70 g. 123-124°, 749 mm. n_D^{20} 1.4000	4.9 %	About 68 % of BuBr accounted for (63 % as RMgX)
	8	50-77	1.89	1.4197	2.6			
	9	78-85	8.01	1.4338	11.2			
	10	90-93	2.98	1.4255	4.2			
	11	93-117	2.80	1.4292	3.9			
	12	116-126	1.63	1.4418	2.3			
7	6	48-91	2.32	1.4240	5.2	None	0	(b) Fraction 7 probably largely valeric acid present because of incomplete extraction. About 40 % of BuI accounted for in product.
	7	91-96 (b)	9.03	1.4281	20.2			
	8	98	0.96	1.4313	2.1			
	9	99-102	3.34	1.4340	7.5			
	10	102-107	5.50	1.4380	8.1			
	11	107-109	1.01	1.4400	2.3			
	5	67-73	8.00	1.4660	14.1	1.64 g 122-127°, n_D^{20} 1.3992	2.3 %	About 53 % of BuCl accounted for in product (41 % as BuMgCl)
	6	73-80	5.23	1.4579	9.2			
	7	83-116	3.77	1.4389	7.0			
	8	116-125	0.44	1.4315	0.8			
	9	125-130	0.90	1.4492	1.6			
	10	132-143	2.07	1.4521	3.6			
5	5	68-82	1.10	1.4172	2.9	None	0	11.18 g. of material, b. 93.5-94°, 741.2 mm., n_D^{20} 1.3920, $n_D^{22.2}$ 1.3909. Residue from distillation of acid solid. About 36 % of BuBr accounted for in product.
	6	82-86	3.30	1.4227	8.7			
	7	87-91	3.98	1.4236	10.4			
	8	95-116	3.56	1.4299	7.3			
	9	116-122	1.42	1.4405	3.7			
	6	81-86	5.59	1.4237	8.2	None	0	2.23 g. material b.104-105°/737 mm., n_D^{20} 1.3919. 58.4 % of BuCl accounted for in product.
	7	88-99	5.62	1.4241	8.2			
	8	102-118	1.90	1.4299	2.8			
	9	122-130	3.11	1.4419	4.6			
	10	130-137	3.67	1.4552	5.4			

magnesium, showed a yield of 54 per cent. Material was reacted with carbon dioxide for 60 minutes, at a rate of flow of CO_2 of 100-150 cc. per minute, at a temperature of 2-8°, then for 60 minutes, at a temperature of 10-15°, at the same rate of flow. Rate of flow then increased to 800 cc. per minute, and carbonation continued for 75 minutes, at temperatures of 4-62°, heat being applied to attain the higher temperatures. Titration of the organic acid present indicated a yield of 14.4 per cent, based on the original reactants.

(h) Hexylmagnesium Bromide in Heptane

In a 1.27 mole run, magnesium was cut into a heptane solution of n-hexyl bromide in 108 minutes, temperature ranging from 10-14° during the first 41 minutes of cutting, and from 25-42° during the remainder of the cut. Temperature rose to 43-48° during the time to 240 minutes, when the spindle was turned off. Reaction product was a very viscous suspension. Conductometric titration showed a yield of hexylmagnesium bromide of 44.6 per cent, while acid titration, corrected for unreacted magnesium, indicated a yield of 67.3 per cent.

(i) Heptylmagnesium Bromide in Heptane

In a 1.39 mole run, magnesium was cut into a heptane solution of n-heptyl bromide in 128 minutes, temperature rising from 12-24° during the first 13 minutes, and remaining at 24-25° until 60 minutes, when no reaction was noted. Temperature allowed to rise, and remained at 32-54° until 100 minutes, after which it rose sharply, and remained at 68-75° until end of cut, then at 55° until spindle was turned off at 240 minutes. Conductometric titration showed a yield of 45.5 per cent, while corrected acid titration indicated a yield of 58.7 per cent of heptylmagnesium bromide.

(j) Octylmagnesium Bromide in Heptane

In a 1.5 mole run, magnesium was cut into a solution of n-octyl bromide in 750 cc. of n-heptane in 134 minutes, temperature rising from 12-21° until 73 minutes, when observation showed no reaction. Temperature was allowed to rise, and remained at 40-48° until spindle was turned off at 211 minutes. Product was a viscous gray suspension. Conductometric titration showed a yield of 50.5 per cent, while corrected acid titration indicated the yield to be 63.8 per cent.

Carbonation of the reaction mixture was greatly hampered by the viscosity of the mass, which prevented efficient agitation during reaction with carbon dioxide. Carbonation carried out, at a flow of 125 cc. of carbon dioxide per minute for 90 minutes at a temperature of -2 to 0°. Flow increased to 900 cc. per minute, but temperature had not risen up to 120 minutes, at which time bath was removed. By 145 minutes, at the same rate of flow, temperature had risen to 33°; bath replaced, and carbonation continued at same rate of flow until 293 minutes, by which time temperature had fallen to 9°. Bath was again removed, and rate of flow maintained at 900-1000 cc. per minute until 360 minutes, temperature rising to 32° with the application of heat. Titration of the organic acid formed showed a yield of 10.7 per cent.

On acidification of the caustic extract of organic acid, a solid white substance separated from solution. When the material was re-dissolved in caustic, and again acidified, a solid again separated, the solid turning to an oil on standing. Distillation of the acid gave only pelargonic acid (23.3 grams, 81 per cent of titrated acid), which distilled at 141-144° at 12 mm. When temperature reached 122°, there was a vigorous evolution of gas from the material being distilled, indicating possible loss of carbon dioxide. Residue from distillation was a small amount of solid, from which no material could be identified.

Distillation of the non-acidic portion of the reaction mixture through a Podbielniak Hyper-Cal column.

After removal of ether and heptane, the following fractions were collected:

Cut No.	Final B. P.	Pressure, mm. Hg	Wt.	n_D^{20}
1	34°	48	3.6 g.	1.3879
2	42.5	48	5.0	1.4033
3	42.5	48	3.1	1.4000
4	50	48	5.2	1.3983
5	66	48	7.4	1.3983
6	110	48	14.8	1.4469
7	92	25	5.0	1.4487
8	95	25	9.7	1.4516
9	96.5	25	9.2	1.4516
10	97.5	25	11.9	1.4510
11	97.5	25	4.9	1.4501
12	138	25	5.0	1.4473
13	162	25	2.2	1.4380
14	165	25	8.8	1.4357
15	172	25	4.4	1.4363
16	180	25	3.5	1.4370
17	184	25	3.8	Solid
Residue			11.1	

Samples 2 through 5 appear to be a mixture of n-octane and octene-1, for a total weight of 20.5 grams, while samples 7 through 11 are probably largely n-octyl bromide. This recovery of octyl bromide is surprising, in view of the analysis for unreacted magnesium.

(k) Octylmagnesium Chloride in Heptane

In a 1.37 mole run, magnesium was cut into a solution which contained originally 20 g. of n-octyl chloride in 811 cc. of n-heptane, the remainder of the 204 g. of octyl chloride being added dropwise, so that the halide was completely added when the cut was completed. Temperature ranged from 47°, to which it rose during the first six minutes of cutting, to 53° during the course of the cut, which was completed at 110 minutes. At 145 minutes, observation showed no reaction; temperature of reaction mixture was allowed to rise to 96°, and remain there to 360 minutes, but there was at no time any evidence of reaction. Gas evolution from a portion of the mixture indicated that only 0.99 gram atoms of magnesium remained, through conductometric titration confirmed the fact that there had been no reaction. Gas evolution repeated, with more careful agitation of reaction mixture during pipetting of sample; this indicated the presence of 1.06 gram atom of magnesium.

Reaction mixture was hydrolyzed by the addition of an excess of 11 per cent sulfuric acid, the layers were separated, and the organic layer fractionated through a Podbielniak Hyper-Cal column. Distillation failed to indicate the presence of any fraction boiling in the range between the boiling points of heptane and nonyl chloride.

(1) Nonylmagnesium Bromide in Heptane

In a 1.21 mole run, magnesium was cut into a solution of 250 g. of n-nonyl bromide in 710 cc. of n-heptane during 96 minutes. Temperature rose to 48° during the first 13 minutes of cutting, and varied from 49-64° through the remainder of the cut, and from 64-68° until 240 minutes, when observation showed no reaction had taken place. Temperature was then allowed to rise to the boiling point of the mixture, 104°, until 383 minutes, when observation showed no reaction. The spindle was then allowed to run to 445 minutes, with the temperature at 38-40°. The product was a gray suspension, unusually fluid for a higher member of the series. Conductometric titration showed a yield of 32.2 per cent, while corrected acid titration indicated a yield of 50.5 per cent of nonylmagnesium bromide.

(m) Decylmagnesium Bromide in Heptane

In a 1.30 mole run, magnesium was cut into a solution of 288 grams of n-decyl bromide in 765 cc. of heptane during 114 minutes. Temperature had risen to 40° by four minutes, and was maintained at 52-59° from 18-62 minutes, when three increments of magnesium had been cut, and observation showed no reaction. Temperature was allowed to rise, and ranged from 72-94° to end of cut. At 150 minutes, at a temperature of 102°, a portion of the reaction mixture, which appeared to contain only unreacted magnesium, was blown out the top of the condenser. Spindle was slowed, and the temperature maintained at 70-78° until 377 minutes, when spindle was stopped. Product was a viscous gray suspension; conductometric titration showed a yield of 51.5 per cent, while acid titration, corrected for unreacted magnesium indicated a yield of 56.7 per cent.

8. Solubility Determination

The solubilities of the organomagnesium compounds in the hydrocarbons was determined as follows:

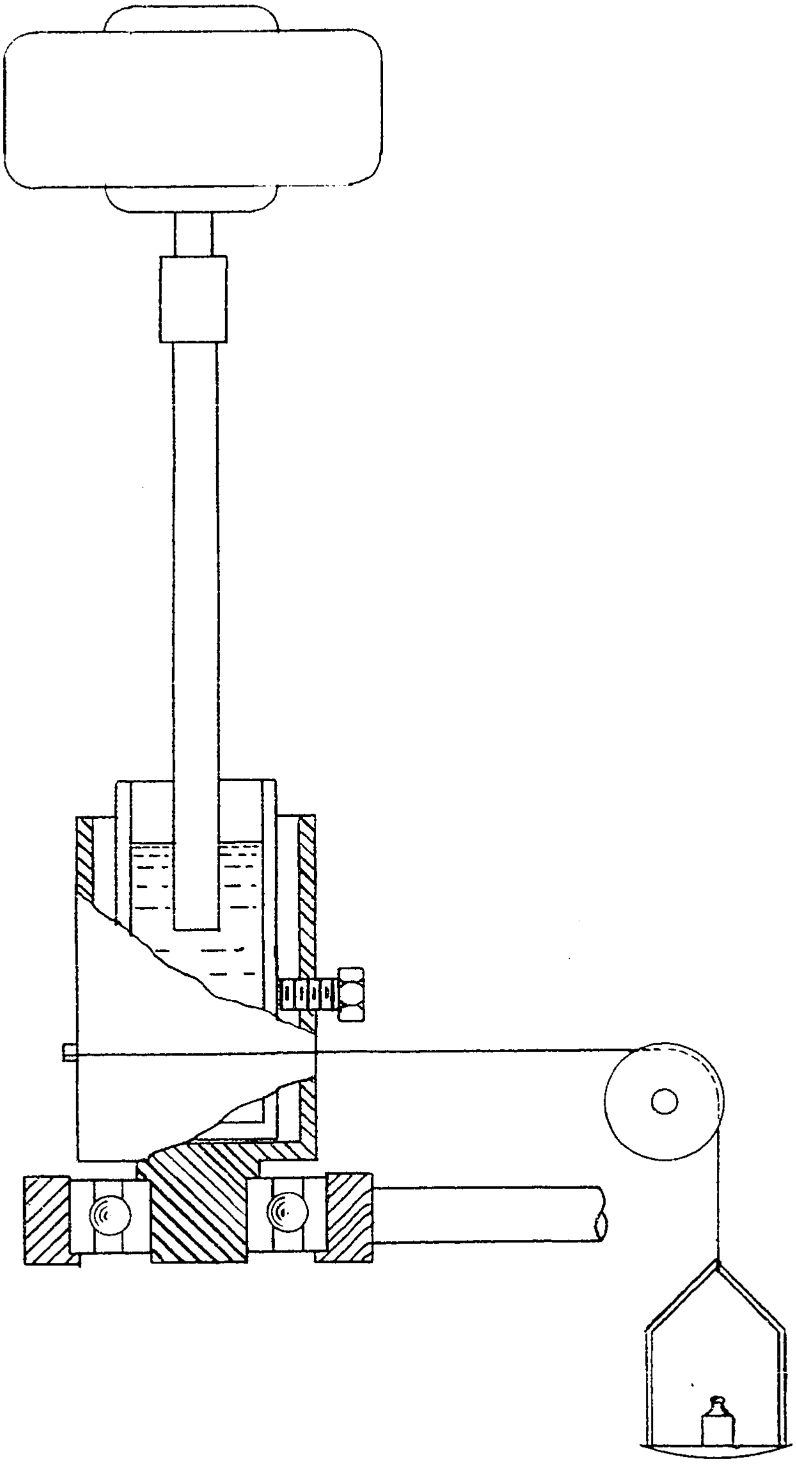
A 25 cc. portion of the mixed reaction products was pipetted, immediately after completion of the run, into a nitrogen-flushed test tube, which was immediately stoppered and paraffined. These tubes were allowed to stand for a minimum of two weeks, with occasional shaking, at room temperature; at the end of this period it was assumed that the solutions had reached equilibrium. The sealed test tubes were then centrifuged, and a 5 cc. portion of the supernatent liquid removed with a nitrogen-flushed pipette. These portions were hydrolyzed by the addition of 50 cc. of water, and then acidified with N/10 hydrochloric acid until methyl orange showed an acid reaction. The acidified solutions were allowed to stand overnight, and then titrated to a methyl orange end point with N/100 sodium hydroxide solution. From the data thus obtained, the amount of organomagnesium compound present in the solution was calculated, and expressed in milliequivalents per 100 cc. of solution. Several of the suspensions of organomagnesium compounds could not be sufficiently separated by centrifuging. In these cases, a portion of the original suspension was pipetted into another test tube containing some of the appropriate hydrocarbon. This test tube was then tumbled at room temperature for five days. Solubilities determined in this way included butylmagnesium chloride in heptane, isooctane, and benzene; amylmagnesium bromide in heptane, and octylmagnesium bromide in heptane. In addition, the samples which were used for the determination of the solubilities of propyl-, hexyl-, heptyl, and decylmagnesium bromides in heptane were pipetted from the supernatent liquid resulting after the total reaction products had been standing under nitrogen for periods of at least two weeks; none of the samples which had been pipetted from the original reaction mixtures could be separated by centrifuging in these cases either.

9. Determination of Relative Viscosity

The relative viscosities of the reaction products were determined roughly, using the apparatus shown in Figure 15. Samples used for viscosity determination were those pipetted from the original reaction mixtures for retention. These samples were shaken vigorously, and the vials containing the samples placed in the cup of the apparatus. The spindle, of three-eighths inch brass, was immersed in the mixture for three-quarters of an inch, and the motor turned on to revolve the spindle at 1750 revolutions per minute.

In practice, instead of using the weights in a pan attached to a thread, as shown in Figure 15, the thread was attached to a lever extending upwards from a point directly above the pan on the beam of a triple-beam balance, thus introducing considerable mechanical advantage, and eliminating the necessity of a pulley.

The weights recorded in each case were the weights required to cause the beam of the balance to fall when the cup of the viscosimiter was turned so as to raise the beam; these weights were determined to the nearest tenth of a gram.



APPARATUS FOR VISCOSITY DETERMINATION

Figure 15

Data obtained are summarized below:

Tare of lever arm, 14.25 g.
Total weight (including tare) necessary to overcome static friction of bearing, 15.0 g.

Weights required to balance torque of cup with:

Suspension of Mg in heptane:	15.0 g.; diff.	0.0
EtMgBr in heptane	17.6	2.6
PrMgBr in heptane	21.0	6.0
BuMgBr in heptane	20.0	5.0
BuMgCl in heptane	16.9	1.9
BuMgCl in isooctane	18.8	3.8
BuMgI in isooctane	17.0	2.0
AmMgBr in heptane	19.0	4.0
$C_6H_{13}MgBr$ in heptane	21.1	6.1
$C_7H_{15}MgBr$ in heptane	20.0	5.0
$C_8H_{17}MgBr$ in heptane	22.1	7.1
$C_9H_{19}MgBr$ in heptane	16.0	11.0
$C_{10}H_{21}MgBr$ in heptane	18.6	3.6

E. SUMMARY

1. The normal alkylmagnesium bromides having from two to ten carbon atoms have been prepared in normal heptane, by means of mechanical activation, without the use of any catalytic substance, and their yields determined.
2. Ethylmagnesium bromide, butylmagnesium bromide, and butylmagnesium chloride have been prepared in normal heptane, 2,2,4-trimethylpentane, and thiophene free benzene, and the effect of the different hydrocarbon mediums on the yields of products has been determined.
3. Valeric acid has been prepared from butylmagnesium bromide and butylmagnesium chloride prepared in normal heptane, 2,2,4-trimethylpentane, and benzene, and from butylmagnesium iodide prepared in 2,2,4-trimethylpentane, and some of the variables involved in the reaction have been studies.
4. The solubilities of all of the organomagnesium compounds mentioned above in the hydrocarbons in which they were prepared have been determined.
5. The relative viscosities of the series of organomagnesium compounds prepared in hydrocarbons have been determined.
6. A possible mechanism for the formation of butyl benzene during the preparation of butylmagnesium chloride in benzene has been suggested.