

A STUDY OF THE PREPARATION OF ALPHA-DIKETONES

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A Thesis

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By

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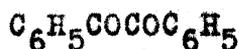
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INTRODUCTION

Since the ordinary methods for the preparation of α -diketones are rather long and rarely yield a high percentage of product, the attempt was made to perfect some short, simple, direct method whereby the straight and mixed α -diketones could be prepared.

Brigel (1), many years ago, saw a possibility of condensing two molecules of acid halide by means of metallic sodium, to give an α -diketone and sodium chloride, bromide or iodide. He attempted to do this and found dry ether to be very essential to the reaction. On account of the limited knowledge of his time he was mistaken in the identity of his product. He obtained a white, almost colorless, compound, crystallizing in needles and melting at 156° C. (2). He called this compound benzil, thinking it to have the structure:



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1. Brigel -- Ann. ~~Chem.~~ Pharm. 135, 172 (1865)
 2. B. 24, 1264

(1841)

but when Klinger (1) checked his results he found Brigel's so-called benzil to be isobenzil, a compound having the structure:-



which is a polymericide of benzil since when saponified with caustic potash it is resolved into benzoic acid and benzoin (2). Klinger, in determining the structure of isobenzil found the ordinary benzil and benzoin formed in relatively considerable quantity (3).

Klinger and Shinitz (4) then conducted an investigation of the compounds dibutyryl and di-valeryl according to the methods of Bruhl (5), Freund (6) and Munchmeyer (7). They found them to be doubled up in the same manner as isobenzil and during their investigation they isolated very little of the ordinary corresponding a-diketones.

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1. Klinger -- B. 16, 994; B. 24, 1271 ⁽¹⁸⁸³⁾ ⁽¹⁸⁹¹⁾
 2. B. 16, 994 ⁽¹⁸⁸³⁾
 3. B. 16, 994 ⁽¹⁸⁸³⁾
 4. Klinger and Shinitz -- B. 24, 1271 ⁽¹⁸⁹¹⁾
 5. Bruhl -- B. 12, 153 ⁽¹⁸⁷⁹⁾
 6. Freund -- Ann. Chem. Pharm. 118 (1861), 33
 7. Munchmeyer -- B. 19, 153; B. 14, 1846; B. 24, 1276 ⁽¹⁸⁸⁶⁾ ⁽¹⁸⁸¹⁾ ⁽¹⁸⁹¹⁾

Victor Meyer's (1) work on the α -diketones was correlated with that of Klinger and Standke (2).

Yields of diketone obtained by all of these investigators were poor and the products obtained were very difficult to analyze since they would not be distilled and on account of their affinity for ether, were crystallized only with the greatest difficulty.

Dean and Berchet (3) investigated the action of metallic sodium on organic halides in liquid ammonia. Benzoyl chloride reacts immediately with the liquid ammonia to give benzamide.

On account of the scarcity and high cost of metallic sodium, it was thought that zinc dust might be substituted for it. V. Yavorski (4) following the methods of Klinger (5), substituted zinc in the form of dust for metallic sodium. He employed diethyl ether as a solvent. His product, a thick yellow oil which could not be distilled or crystallized, he designated as benzil.

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1. Myer, V. -- B. 21, 809 (1888) An Merk
 2. Klinger and Standke -- B. 24, 1264 (1891)
 3. Dean and Berchet -- J. A. C. S. 52, 2823 (1930)
 4. Yavorski -- B. 42, 435 (1909)
 5. Klinger -- B. 16, 994 (1883)

James F. Norris and D. R. Franklin (1) investigated the action of zinc on benzoyl chloride on account of its analogy to triphenylchloromethane. They could not isolate benzil. Zincke (2) obtained the same result. Ethyl acetate was employed instead of ether as the solvent and this accounts for some of the reaction products obtained.

M. D. V. Tistchenko (3) obtained remarkable results by forming a Grignard reagent from some acid halide, dissolving magnesium in the ethereal solution of the halide, and then adding a quantitative amount of the acid halide whose carbon chain was desired on one end of the molecule, splitting out magnesium halide and drawing the two nuclei together to give the corresponding α -diketone. He formed and isolated the organo-magnesium compound. By addition of a free halogen or an acid halide he obtained in a fair yield some α -diketones.

The organo-magnesium compound was obtained by forming a Grignard (4) reagent from an alkyl halide

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1. Norris & Franklin -- Am. Chem. Jour. 28, 141 (1903)
 2. Zincke -- Bull. Soc. Chimie, 19, 516
 3. Tistchenko, M.D.V. -- Bull. Soc. Chimie, 37, 623-37 (1925)
 4. J. Russ. Phys. Chem. Soc. 46, 1319-32 (1914)

and then passing in dry carbon monoxide. By adding the free halogen or an acid halide to this the α -diketones were obtained.

V. Egovova (1) passed carbon monoxide into the magnesium derivative of trimethylchloromethane and by oxidation of the product with potassium permanganate obtained oxidized pinacone, a diketone.

Gilliland and Blanchard (2) studied the action of carbon monoxide on Grignard reagents and only obtained results in the cold when using nickel carbonyl as a catalyst. When using phenyl magnesium bromide as the grignard and forcing in carbon monoxide with small amounts of nickel carbonyl they obtained the following products: Triphenyl methane, triphenyl vinyl alcohol, pentaphenyl ethyl, and tetraphenyl ethylene. Contrary to what is expected, no benzoin derivatives were formed.

Through the agency of chromic chloride Job and Cassal (3) caused carbon monoxide to react with phenyl magnesium bromide in the ratio of one mol of carbon monoxide to one mol of phenyl magnesium

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1. Egovova, V. -- J. Russ. Phys. Chem. Soc., 46, 1319-32 (1914)
 2. Gilliland and Blanchard -- J. A. C. S. 48, 410
 3. Job and Cassal -- Compt. rend. 183, 58-60 (1926)

bromide. Hydrolysis of the resulting compound with dil acid yields benzopinacol, di-phenyl ketone, di-phenyl methyl alcohol, diphenyl, diphenylacetaphenon and BzH. No carbon monoxide was absorbed without the chromic chloride being present.

By heating phenyl magnesium bromide at 75° to 80° and a short time at 110° Fischer and Stappens (1) found carbon monoxide absorbed in the ratio of one to one. From 79 grams of phenyl bromide there were isolated 36.5 grams of benzoin, 4 grams of benzene, 2 grams of diphenyl and 3.5 grams of benzil, eighty percent of the products being isolated. Para methyl phenyl magnesium chloride at 150° and 100 atmospheres absorbs carbon monoxide giving para taluais and para taluil, fifty-five percent of the reaction products being isolated. Alpha $C_{10}H_7MgBr$ absorbs carbon monoxide, giving at 160° and 180 atmospheres sixty-eight percent alpha naphthil; naphthain could not be isolated. Triphenyl methyl magnesium chloride or triphenyl methyl did not react with carbon monoxide. Ethyl magnesium bromide and carbon monoxide at 110° give 2-pentene. Butyl magnesium chloride and carbon mon-

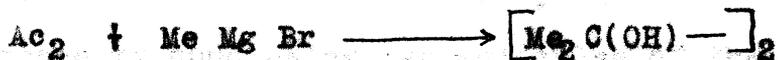
1. Fischer and Stappens -- Ann. 500, 253-70 (1933)

oxide give sixty-five percent of 4-nonene and some butyl alcohol. Iso amyl magnesium bromide gives seventy percent of 2: 8: dimethyl: 4: nonene B. P. 57 - 63° at 13 mm., $d_{\frac{20}{4}} 0.743$, $n_{\frac{20}{D}} 1.4211$ and a compound B. P. 90 - 110° at 13 mm. Phenyl methyl magnesium chloride gives sixty percent of 1:3 di-phenyl propene B. P. 174-5° at 16 mm. Cyclo hexyl magnesium bromide and carbon monoxide at 80° to 100° gives twenty-five percent cyclo hexylmethylenecyclohexane B. P. 111-2° at 12 mm., and forty-four percent of a mixture of dodecalydnabenzoin and dodecahydrazobenzil, the latter boiling at 165-7° at 15 mm., and melting at 38°. B- $C_{10}H_{17}$ Mg Br. yields a ketone and an unsaturated hydrocarbon that were not characterized. No reaction occurs with the magnesium derivatives of pyrnyl bromide, P- $Me_2C_6H_4Mg$. dibromoethane or with phenyl zinc bromide or diethyl aluminum. Alcoholates are accelerators of the reaction. Ethyl magnesium bromide and ethyl magnesium plus C_2H_5O Mg Br are reported as electrolytes.

Under certain conditions α -diketones when treated with grignards give tertiary alcohols (1)

1. Atti. Accad. Lincei. 8, 309-14 (1928)

This reaction has been applied to alpha and beta diketones by Pace (1).

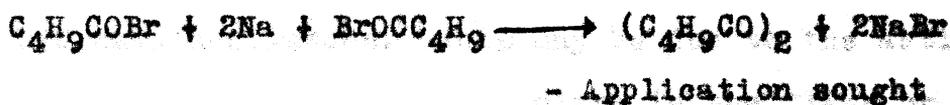
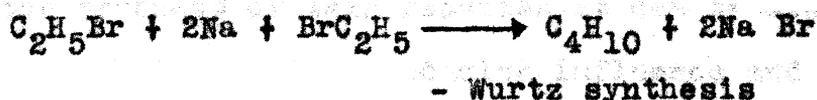


Dehydrogenation (2) occurs when hydrocarbons are heated with metallic catalysts. Radicals formed such as CH_2 may polymerize to benzene, etc. These polymers may, when the conditions are changed, decompose into their respective components in the presence of these same metals. The actions of the alkali metals in this field have been but little investigated. In order to account for some of the products reported in the literature, some such reactions must take place.

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1. Atti. Accad. Lincei, 8, 309-14 (1928)
 2. Cat. in Ind. Chem. - Henderson, p. 115

THEORETICAL DISCUSSION

The Frankland synthesis of paraffine hydrocarbons by condensing two molecules of the brominated alkyl with metallic zinc has been widely extended. Wurtz and Fittig substituted metallic sodium for the zinc and obtained much better results. On account of the analogy between the alkyl halides and the acyl halides a few attempts have been made to apply these syntheses to this type compound.



The only difference in the two compounds at the start is the carbonyl group adjacent to the carbon chain in the acyl halide. Just what influence this group has on the reaction has not been investigated to any great extent and is not very well understood. The activity of the halogens, chlorine, bromine, and iodine is also not in correspondence with their usual activity. The order seems to be reversed so that the chlorine is less

effective than bromine which is less effective than the iodine. No work could be found on the organic fluorides of this nature.

This possibility of condensing two molecules of acid halide by splitting out the halogen by means of some metal to form an α -diketone and an inorganic salt seems very easy at first sight, but on account of the character of the negative oxygen and the carbonyl group the reaction products are not those that would ordinarily be expected. From the products of this reaction it can be seen that the alkali exerts a reducing influence and the reduced diketone is obtained instead of the ordinary α -diketone. This may be due to the action of some small amount of moisture in the flask or reagents which combined with the metallic alkali to form anhydroxide which is a well known reducing agent when used in ethereal solution. However, if the conditions were changed until the proper set-up was found this reaction should go to completion as expected.

In speaking of the general method involved in the completion of this reaction, the best known

authorities recommended that benzoyl chloride and metallic sodium or five percent sodium amalgam be placed in a dry flask equipped with moisture-proof reflux condenser, in two parts of ether in the ratio of 1:1, refluxing at the boiling point of ether on a water bath for from two to three days and then filtering, washing with dry ether and placing in a vacuum under about 10 mm. pressure. This removes the ether without injuring the reaction product by heat. Dissolve the product in absolute alcohol and again place in the vacuum. After the third repetition of this last the compound isobenzil comes down in glittering white crystals. Upon further dissolving in ethyl alcohol and placing in vacuum ordinary benzil comes down according to Klinger (1) in small quantities.

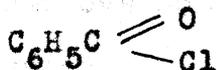
This method gives poor results because the product obtained from the reaction upon being distilled chars and even under reduced pressure yields no benzil. Upon fractional crystallization the difficulty of the affinity of the product for ether is not overcome easily and the product re-

1. B. 24, 1264

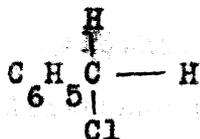
fuses to crystallize. After distilling with steam for several days the product is freed of benzoic acid and is still less willing to crystallize.

In using metallic zinc in the form of dust, the initial reaction is much more severe, when used in place of metallic radium but the reaction products possess the same general characteristics and must therefore be of the same nature.

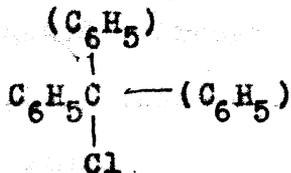
Norris (1) makes the following analogy between benzoyl chloride, phenyl methyl chloride and triphenyl methyl chloride:



The oxygen is negative here



The two hydrogens are positive



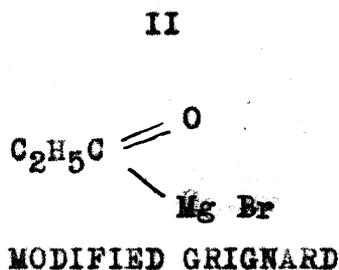
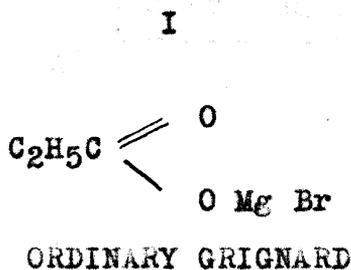
The phenyl groups in brackets are negative in character

By this means he accounts for the difference in activity of the acyl halides and the alkyl halides.

1. Amer. Che. Journal Vol. 23, 141 (1903)

His results indicated that oxygen was absorbed from the air during the reaction to form an anhydrid. The zinc chloride formed exerts the same influence on the reaction that would be exerted in case of aluminum chloride used in Friedel-Krafts synthesis. Since more than the quantitative amount of zinc was used up in the reaction, the results indicated the formation of an organo zinc compound. No benzil was obtained by Norris in any of his experiments even when carried out in an inert atmosphere. He concludes that when the reaction between zinc and benzoyl chloride takes place, the complications involved are such that the products can not be interpreted by the facts so far discovered.

Another theoretical possibility exists whereby a-diketones could be obtained by forming an ordinary grignard reagent of any straight or branch chain, brominated hydrocarbon and then forcing in dry carbon monoxide. This would form an organo magnesium compound similar in nature to the ordinary grignard made by using carbon dioxide, but having one less oxygen atoms. The carbonyl group would go in between the carbon of the hydrocarbon and the magnesium:



Compound II could be varied at will and there should be no polymerization as when condensing acid halides with metallic alkalis.

Only in one instance (1) does the literature give a method of this general type. The resulting α -diketones were produced in the reduced condition in cases of hydrocarbons of lesser carbon atoms. Heat seemed to be all that was necessary for the absorption of the carbon monoxide by the grignard. In all other instances some catalyst such as chromic chloride or nickel carbonyl was necessary in order to force the carbon monoxide into the grignard.

In all cases the manner in which the gaseous carbon monoxide was absorbed was not completely understood. Exactly why it should not be absorbed in the same manner as carbon dioxide is another point about which very little information could be obtained.

The nature of these organo magnesium compounds was so little understood that M. D. V. Tistchenko (2) in 1920 decided to give the problem an exhaustive investigation. Since he concentrates and elaborates on all of the information available at that time and

1. Ann. 500, 253-70 (1933)

2. Bull. Soc. Chimie 37, 623-37 (1925)

discusses the important theories according to the results he obtained, the general ideas and information of his paper will be given in the next paragraphs.

In an absolutely dry apparatus one part acid halide is dissolved in two parts of ether. The apparatus is the same employed in the preparation of a grignard reagent. In the ratio of one mol of magnesium to one mol of acid halide the magnesium in the form of clean dry turnings is added. The acid bromides and iodides immediately give evidences of reaction but the acid chlorides fail to react. The magnesium is dissolved in almost the quantitative amount and in the cases of acetyl bromide, propionyl bromide and the two butyryls, the solution was divided into two parts. The top layer composed of ether and a small amount of dissolved organo magnesium compound; the bottom layer contains the transposed acid bromide and any traces of undissolved magnesium. The two layers are filtered by means of a brominated plug of asbestos. The viscous liquid of the bottom layer retracts its ether very energetically and must be dried at 140° for three hours at the end of which time it comes out as a dry yellow powder corresponding to the formula:



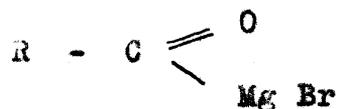
slowly soluble in cold ether giving a viscous

solution while the ordinary magnesium compound:

R - Mg - Br is very slightly soluble.

Upon attempting to synthesize α -diketones a variety of products was obtained. The normal α -diketones were obtained in every case in small quantities and in some cases in yields as high as thirty percent. The constitution of the organo magnesium compounds as products of the reactions between acid bromides and magnesium is proved by the formation of aldehydes from the products of condensation of the last when decomposed by water, by the formation of diisovalenyl after the decomposition of the magnesium derivative of brom diisovalenyl by brom isovalenyl, by formation of ether salts of α -diketones and of acids by the decomposition of brom acyl magnesium compounds by bromine.

By exhaustive treatment Tistchenko proved the presence of the organo magnesium compound that would be necessary in diketone synthesis, namely:



but due to improper conditions failed to obtain the expected diketones in quantitative yields when he reacted them with acid bromides or free bromine.

CONCLUSION

Qualitative evidence of diketone formation is obtained by reaction of acid halides with metallic sodium in ether solution. The reaction seems to go past the diketone and is reduced to secondary alcohol. Some method of control in order to insure proper conditions must be found to guarantee the success of this reaction.

In the attempts at adding carbon monoxide to a Grignard reagent the temperature was thought to be the controlling factor. The conditions of reaction are of primary importance in the successful addition of the gas.

EXPERIMENTAL

I. Condensation of Acid Halides with Metallic Sodium.

Method

Place in a dry flask one part of benzoyl chloride dissolved in two parts of ether which has been dried over calcium chloride and then distilled from metallic sodium. Add thin clean shavings of metallic sodium, that has been thoroughly washed in dry ether, in the ratio of one mol of sodium to two mols of acid chloride. Equip the flask with a moisture-proof reflux condensor and reflux on a water bath for from twelve to twenty-four hours. The ethereal solution turns slightly yellow and then darkens as the refluxing continues. The ether volume must be kept constant throughout the reaction. The sodium is acted upon by the chlorine and soon the bottom of the flask is covered with crystals of sodium chloride. At the end of the refluxing period the solution has become almost wine colored and the sodium has practically all been acted upon. Filter or carefully decant the solution with repeated ethereal washings of the remains in the flask into

a flask equipped for steam distillation. Here the solution is shaken for fifteen minutes with persistent caustic solution. Heat gently and pass in steam. Steam distill the solution until free of ether and benzoic acid. A dark red viscous material is left in the bottom of the flask. Remove this and after washing with water dissolve in ethyl alcohol. Place in a vacuum dessicator (no calcium chloride) and reduce the pressure down to about ten millimeters. In a little while a yellow amorphous flaky material comes out of solution. Repeatedly evaporate in vacuo, add a mixture of ether and ethyl alcohol each time and each time a new quantity of the yellow material comes down. Finally, after filtering off and saving each portion of the yellow flaky substance, a brown gum remains that refuses to dissolve in alcohol.

Attempt to crystallize the yellow flaky material from alcohol, ether, benzene, carbon bisulfide, carbon tetra chloride, chloroform and petroleum ether. This should be the diketone benzil in the impure state.

This method is the general one employed and was varied both in the metals used and the subsequent treatment of the products.

In order to check the presence of the partially reduced α -diketone alcohol benzoin two analytical methods were employed.

- I. Ordinary Fehlings solution is prepared and added to a small amount of the red gum obtained as a product from the general method. If it reduces the Fehlings solution benzoin is indicated.

- II. Oxidation of Benzoin to Diketones with Iodine (1).
 1. A deep reddish-purple color appears immediately when sodium methylate is added to a methyl alcohol solution of benzoin. When a small amount of iodine is added the color quickly fades to a straw yellow but in a few moments the purple color returns.
 2. Benzoin color test -- The purple color of an alkaline solution of benzoin has long been used as a color test for both benzoin and benzil but it has never been evaluated quantitatively.

Under conditions of the test benzil alone gives no color test, but when added to benzoin the test will give an intense color.

The procedure consists in first adding to a 10 cc. test tube one cc. of sodium methylate solution (4 g. of sodium to 50 cc. of methyl alcohol), next 0.1 cc. of saturated benzil solution, and finally anywhere from 0.02 to one cc. of the methyl alcohol solution of benzoin to be tested (1).

Reagents

Ether used in these experiments was dried in the following manner:

Ordinary commercial diethyl ether U. S. P. was dried over fused calcium chloride for ten days, passed through a fast filter and metallic sodium in the form of small freshly cut lumps or shavings placed in it. This was allowed to stand until no more bubbles arose to the surface. The calcium chloride tube in the cork must be clean and fresh. At the end of this period the ether was distilled into a moisture-proof flask from freshly cut metallic sodium. Aluminum chloride (anhydrous) was dissolved in it to give a clear solution.

Almost always the metallic sodium found

around the laboratory is found to be covered with a crust of sodium hydrate. This will furnish enough moisture to hydrate some of the compounds formed in the experiments. Caustic soda in ether is a well known reducing agent, therefore the sodium used had to be absolutely clean. The following will give the clean metal:

(1) Weigh out 12 g. of metallic sodium in lumps from which all the crust has been removed. Use a common knife and dip into paraffine oil while using. Place sodium in a 300 cc. round bottomed flask and cover with 30 cc. of commercial xylene. Attach an addition tube with sealed joints as a reflux condenser. Stopper the tube and heat the flask gently over a wire gauze until the sodium melts - M. P. 95.6° - B. P. xylene 136° - 141° . Do not boil. Place towel about flask and shake until the sodium appears in globules about the size of bird shot. Let stand until cool. Pour off the xylene and wash twice with dry ether. The sodium should now be used immediately due to its quick oxidation.

Data

1. 200 g. of 50% sodium amalgam were placed in a one-liter flask equipped with a very long moisture-proof reflux condenser. 100 g. (82.6 cc.) of benzoyl chloride was dissolved in 200 cc. of dry ether and poured down the reflux. A line was drawn at the level of the liquid in the flask. Ether was added from time to time to keep this level the same throughout the experiment. The contents were refluxed for three days. Upon addition of the ether benzoyl chloride mixture the solution did not react violently. The contents of the flask gradually took on a yellow color as the refluxing was continued. After the second day the contents was about the color of dark red wine and the sodium chloride had fallen out of solution and had covered the bottom of the flask. The temperature was never above that of boiling ether. At the end of the refluxing period the dark brownish red solution was separated from the mercury and sodium chloride and washed out with dry ether; The washing added to the original and the whole divided into three equal parts.

The first part was washed in a separatory funnel with a persistent solution of sodium hydroxide. This converted any free benzoyl chloride to benzoic

acid. The solutions were then separated and the ethereal solution was steam distilled until free from benzoic acid. The heavy yellow syrup remaining in the flask is then dissolved in dry ether and placed in a flask with calcium chloride (anhydrous). This cuts the volume down quite a bit. Placed in a vacuum, the ether volatilizes at once and the syrup is all that remains. Alcohol was then added and the solution again placed under a vacuum. Yellow flakes began falling out of the solution and from time to time were removed and dissolved in ether. The end product remaining was insoluble in alcohol and soluble in ether. Both the flakes and the end product would reduce Fehlings solution and give the sodium methylate test for benzoin, but after many attempts could not be crystallized from ether, alcohol, carbon, tetra chloride, chloroform, benzene or carbon disulfide.

The second part was washed with NaHCO_3 and subjected to the same process. The results were the same as for the first part.

Portion number three was washed with distilled water and subjected to the same process. The product was the same as the previous two portions.

2. Since the yellow color developed in experiment one was too intense for the desired product it was thought that the amalgam might possibly exert a polymerizing influence upon the reaction. Consequently, clean sodium metal was substituted for it.

30 g. of Benzoyl chloride, 150 cc. of ether and 5 g. of metallic sodium in the shot form were placed together under a reflux. The reaction was evident at once and was allowed to proceed at room temperature. After there was no sign of reaction in the flask and the sodium seemed to be all dissolved, the yellow brown solution was removed and washed with persistent NaOH solution. Immediately the solution became very dark brown and apparently the same as that observed in experiment one. This was steam distilled until benzoic acid free and subjected to the vacuum treatment. The products were the same as those of experiment one.

3. Believing that the polymerization was caused by the formation of NaOH from the moisture's action on the metallic sodium, all precautions were taken to have conditions absolutely dry. The ether was redried and the benzoyl chloride tested for moisture. The steam distillations were carried out in persistent

alkali and the deep brown colored product subjected to vacuum treatment. This time no yellow flakes came down at first but soon they all came down at once. The products were found to give the benzoin test with Fehling's solution and with sodium methyate, but could not be crystallized from any of the solvents used in experiment one.

Upon adding the sodium in small quantities in a small experiment the yellow color developed was less intense, but in doing this too much moisture got into the flask and benzoic acid was the product in the main. The small amount of brown syrup was the same as that obtained in experiment one.

4. Believing that alkaline reduction gave an impure benzoin instead of the expected benzil, it was thought that some other metal might give the desired result.

(a) Metallic calcium, benzoyl chloride, and twice its volume of ether were refluxed for two days. The contents of the flask were removed and allowed to stand corked for two weeks. Only a very slight discoloration proved that the reaction if any was very slight.

(b) Metallic copper, benzoyl chloride and dry ether were refluxed for three days and a yellow color developed proving the reaction to take place. This yellow color was caused by the copper chloride formed dissolving in the ether and after two weeks standing the only thing obtained from it was benzoic acid.

(c) Metallic magnesium, benzoyl chloride and ether were refluxed together for four days. Some few crystals of magnesium chloride fell out of solution, but on the whole little evidence of reaction was observed.

(d) 75 cc. of Benzoyl chloride, 3.5 g. of clean metallic potassium, prepared in the same manner as sodium used in previous experiments, and no ether were placed under a reflux. After boiling about fifteen minutes the potassium swelled up and formed a purple crust over itself. White crystals separated on the walls of the flask showing that the chlorine was being removed. The liquid turned dark brown in color. The reaction was continued until all the potassium was used up and the liquid obtained submitted to the general procedure outlined previously. The residue in the flask was potassium chloride. The liquid gave the same products as those obtained

in experiment one. Upon boiling the brown syrup with charcoal some of the color was removed, but upon evaporation of the alcohol solution used the color returned and the product refused to crystallize.

(e) 30 cc. of Benzoyl chloride, 60 cc. of ether, and 8 g. of zinc dust and a pinch of Cu_2Cl_2 were placed in a flask under a reflux. The reaction took place spontaneously and was so violent that it had to be cooled with water. Refluxing was continued for three days. Once a yellow solid condensed on the walls of the reflux but was soon dissolved by the ether. The contents were filtered after removal and submitted to the general procedure. No benzil could be crystallized from them.

Attempts were made to isolate the yellow solid condensing on the walls of the reflux but this could not be duplicated.

(f) 35.12 g. of benzoil chloride, 100 cc. of ether, 15.3 g. of zinc dust and 20 g. of acetyl chloride were added in order as given. Upon addition of the acetyl chloride the reaction was violent and exploded. Nothing recovered.

(g) 30 cc. of benzoyl chloride, 30 cc. of ether and 8 g. of zinc dust with a pinch of Cu_2Cl_2 were allowed to react under a reflux and warmed for ten minutes after the initial reaction. The contents were placed in distillation apparatus and distilled under a pressure of 6 mm. of mercury. After the ether had boiled off, a mixture of substances came over at $51^\circ / 6$ mm. which had a bad odor and remained colorless. This liquid did not crystallize. No evidence of ketone odor was found and the remainder of the contents charred without distilling.

5. Since the products of the reactions were never those to be expected experiments were run to determine the conductivity of both reagents and products.

(a) Benzoyl chloride will not carry the electric current, therefore it does not have the properties of an electrolyte.

(b) Benzoyl chloride dissolved in ether will not carry the electric current.

(c) Add a drop or two of NaOH to (b) and the current is carried.

(d) The brown syrup from experiment one dissolved in ether will not carry the electric current, proving it to have non-electrolytic properties and free from inorganic sodium salts.

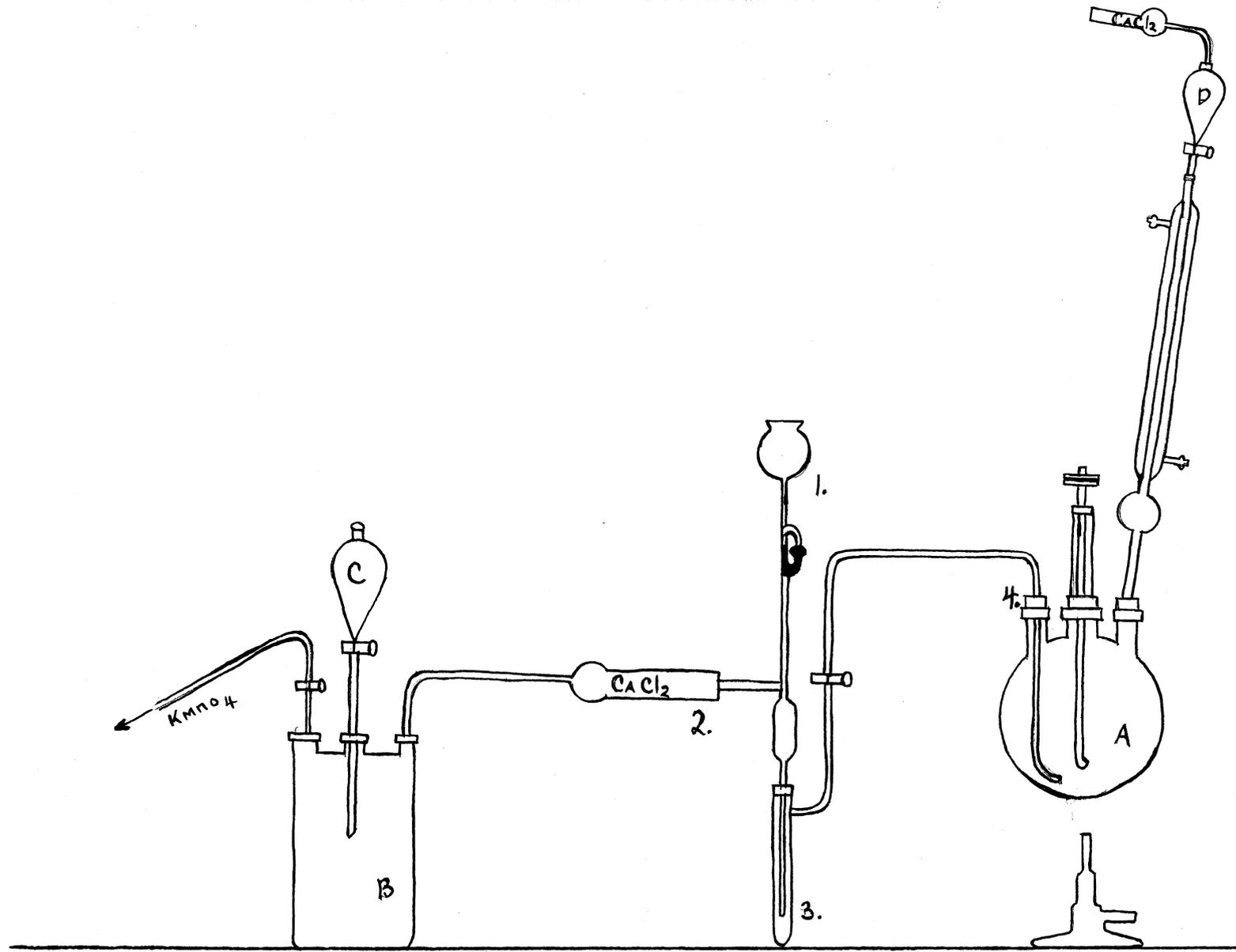


Fig 1.

II. The Addition of Carbon Monoxide to a Grignard Reagent with the Subsequent Removal of the Magnesium Halide.

Method

Set up the apparatus as shown in figure 1, and place in flask A one-third of a mol of an alkyl bromide dissolved in twice its volume of dry ether. By loosening the apparatus at 4, add one-third of mol of clean strips of magnesium about one centimeter long. Add a small amount of iodine dissolved in dry ether down the condenser at D. The magnesium begins to dissolve and the initial reaction must be cooled until it proceeds regularly. At the end of an hour most of the magnesium has been dissolved. Reflux with water bath for an additional hour. While the refluxing is in progress place 150 cc. concentrated H_2SO_4 in flask B and 100 cc. of formic acid in flask C. Add about half of the formic acid to the H_2SO_4 and warm. Open valve between 3 and 4 and the carbon monoxide generated passes into the prepared grignard at the temperature of boiling ether. Stir with the mechanical stirrer intermittently and allow the carbon monoxide to pass in four hours at the temperature of boiling ether. A darkening of the

solution will be observed.

Set up distillation apparatus equipped with dropping funnel and thermometer. By means of drying tubes on the receiver make the apparatus moisture-proof. Place the contents of the flask in the distillation set up and add through the dropping funnel the quantitative amount of the free halogen, iodine, dissolved in ether, or the acid halid whose group is desired. The iodine solution immediately loses its color giving evidence of reaction and the halide will form with the formation of soluble magnesium halide.

Distill according to the principle of fractional distillation and collect the products.

Data

#1. Using n-amyl bromide the Grignard reagent was formed and the carbon monoxide passed in. The product reacted with:

- (a) iodine -- iodine-like odor
- (b) water -- aldehyde odor
- (c) benzoyl chloride-- ketone odor
- (d) methyl bromide -- ketone odor

#2. Again using n-amyl bromide the Grignard reagent was prepared and the carbon monoxide passed in. Ether saturated with iodine was added until a slight pink product color developed. This was distilled. After the ether passed over the boiling point went to about 60° and decomposition took place with a white gas passing through and a charring taking place in the flask. No ketone odor was detected in any of the products.

Since the properties of the products obtained from n-amyl bromide were not in the ordinary handbooks, n-propyl bromide was substituted for it.

#3. One-third mol of n-propyl bromide was used, the Grignard was prepared and carbon monoxide passed in. The product was removed to the distillation apparatus and one-third mol of methyl iodide was added. Reaction took place. The resulting product was distilled. After the ether had distilled off, a white gas that could not be condensed came over and the products in the flask took on a jelly-like appearance. The boiling point of the monoketone expected, methyl propyl ketone, is 102° C. The boiling point never rose above 75° C. No ketone was obtained.

#4. Some of the n-amyl Grignard was subjected to carbon monoxide treatment and methyl iodide was added. The mixture was allowed to stand stoppered for ten days and distilled. No ketone could be isolated.

#5. One-third mol of n-propyl bromide, one-third mol of magnesium and 150 cc. of ether were placed in apparatus and Grignard reagent formed. Carbon monoxide was passed in for eight hours at boiling point of ether. Immediately the contents were transferred to the distillation apparatus and about half of the ether distilled off. The quantitative amount of ethyl bromide was added and the distillation continued. The boiling point of ethyl propyl ketone which was expected was $122-4^{\circ}$ C. The thermometer never rose above 80° C. and decomposition took place. No ketone was isolated. Evidently the carbon monoxide does not go in at this temperature.