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Iowa State College

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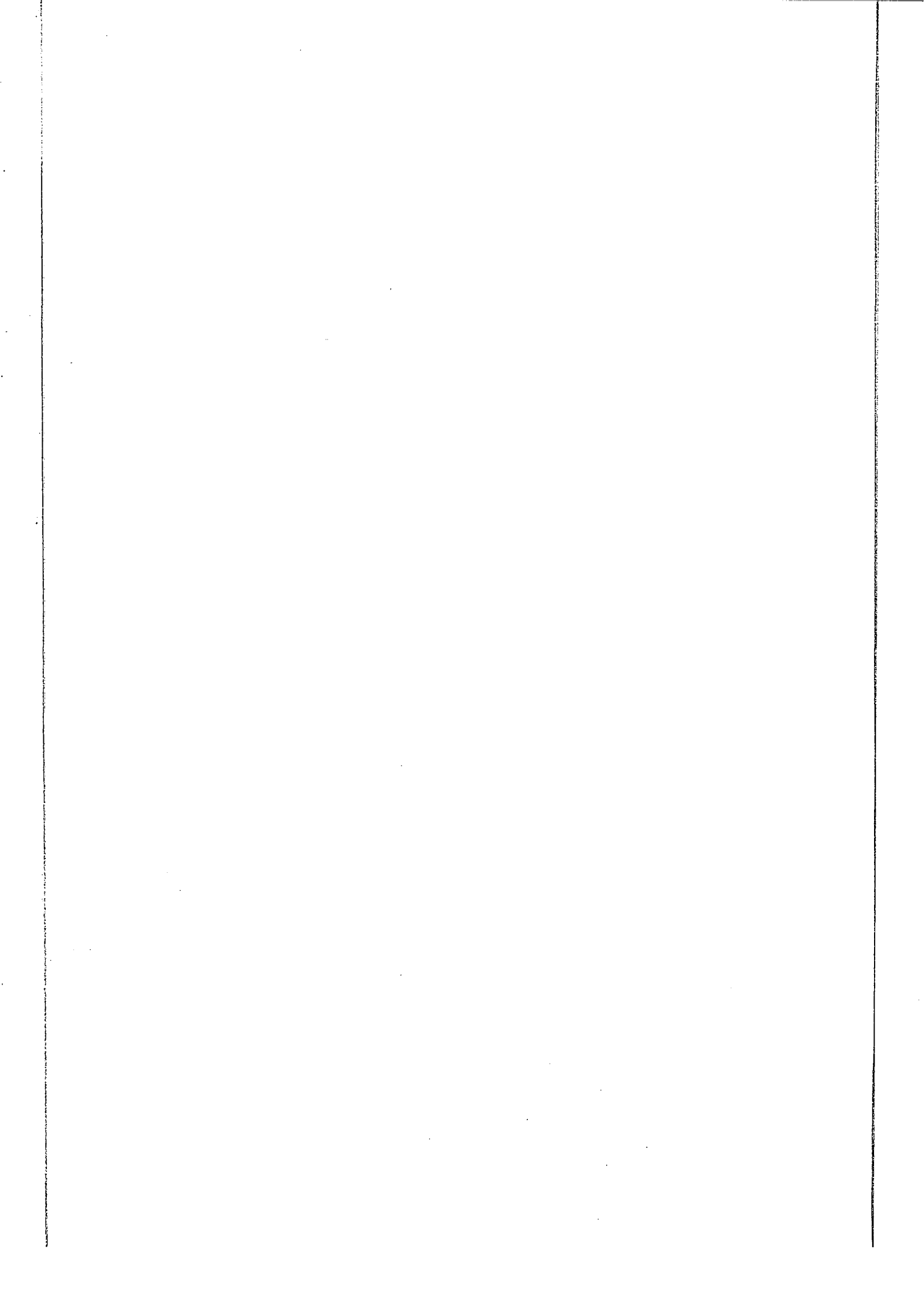
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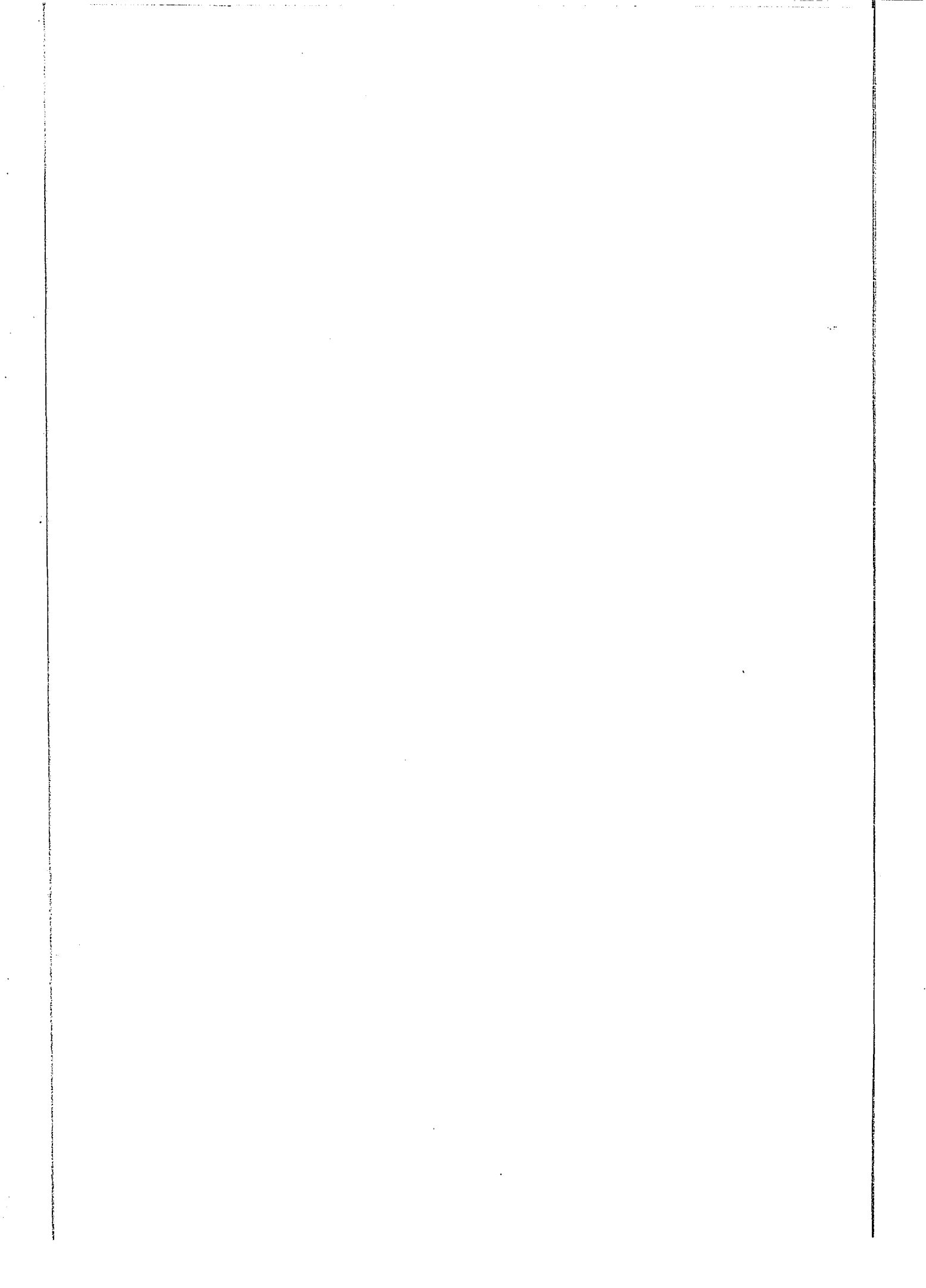
A. STUDIES ON THE CAPTURE OF FREE ORGANIC RADICALS.

B. NEW REACTIONS OF OXALIC ACID AND SOME OF ITS
DERIVATIVES.

BY

Robert E. Fothergill

A Thesis submitted to the Graduate Faculty
for the Degree of

DOCTOR OF PHILOSOPHY

Major subject   Organic Chemistry

Approved

In charge of Major work

Head of Major Department

Dean of Graduate College

Iowa State College

1929

UMI Number: DP14442

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ACKNOWLEDGMENT

Part A

The author wishes to express his appreciation to Dr. Henry Gilman for the suggestion of this problem, and for the generous advice and encouragement given during the progress of this work.

Part B

The author wishes to express his appreciation to Dr. Henry Gilman and Dr. O. R. Sweeney for the suggestion of this problem, and for the generous advice and encouragement given during the progress of this work.
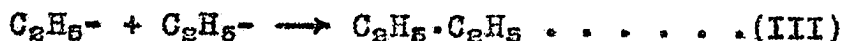
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A. STUDIES ON THE CAPTURE OF FREE ORGANIC RADICALS

INTRODUCTION

The formation of free radicals prior to or during the preparation of organomagnesium halides has been proposed by several investigators on the basis of various independent investigations. Gomberg and Bachmann (1) postulated the formation of free radicals to account for the effect of iodine in the activation of magnesium for the preparation of the Grignard reagent. Gilman and Fothergill (2) obtained evidence of disproportionation, which is a characteristic of free radicals, in the preparation of some alkylmagnesium halides. Gilman and Kirby (3) have attributed the formation of di-p-tolyl during the preparation of benzylmagnesium chloride to the rearrangement of benzyl radicals to p-tolyl (4) radicals and the ensuing coupling of these radicals to di-p-tolyl.

The following reactions illustrate this preliminary formation of free radicals.

$$C_2H_5Br + Mg \longrightarrow C_2H_5\cdot + \cdot MgBr \quad \ldots \ldots \quad (I)$$

$$C_2H_5\cdot + \cdot MgBr \longrightarrow C_2H_5MgBr \quad \ldots \ldots \quad (II)$$

$$C_2H_5\cdot + C_2H_5\cdot \longrightarrow C_2H_5\cdot C_2H_5 \quad \ldots \ldots \quad (III)$$

(1) Gomberg and Bachmann, J. Am. Chem. Soc., 49, 236-257 (1927).
(2) Gilman and Fothergill, ibid., 50, 3334-3341 (1928).
(3) Gilman and Kirby, ibid., 51, 1571-1576 (1929).
(4) There was probably formed a very small quantity of o-tolyl radicals together with the p-tolyl radicals. (See Ref.3).

$$2C_2H_5- \longrightarrow C_2H_6 + CH_2=CH_2 \quad \cdots \cdots \cdots \quad (IV)$$

$$C_6H_5CH_2Cl + Mg \longrightarrow C_6H_5CH_2- + -MgCl \quad \cdots \cdots \quad (V)$$

$$C_6H_5CH_2- \longrightarrow \underline{p}-CH_3C_6H_4- \quad \cdots \cdots \cdots \quad (VI)$$

$$2\underline{p}-CH_3C_6H_4- \longrightarrow \underline{p}-CH_3C_6H_4 \cdot C_6H_4CH_3-\underline{p} \quad \cdots \quad (VII)$$
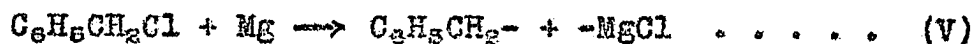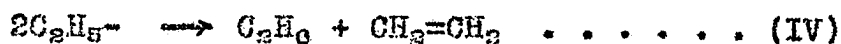
The free radicals first formed may react in other possible ways (2) than those indicated above, but the chief reaction is with the magnesious halide to give the corresponding Grignard reagent in yields of about 95% (5).

A critical test for the prior formation of free radicals is to capture some of them before they combine with magnesious halide to give the RMgX compound, or couple, or disproportion-ate. The investigations by Taylor (6) and co-workers on the mechanism of some reactions suggested a possible means of cap-turing the free radicals formed during the preparation of the Grignard reagent. They first proposed (6a) the following chain type of reactions to account for the reduction of ethylene.

$$CH_2=CH_2 + H \longrightarrow C_2H_5- \quad \cdots \cdots \cdots \quad (VIII)$$

$$C_2H_5- + H_2 \longrightarrow C_2H_6 + H \quad \cdots \cdots \quad (IX)$$
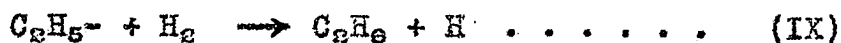
Recently, they (6b) have revised the mechanism of the re-

(5) Gilman, Zoellner and Dickey, _J. Am. Chem. Soc._, 51, 1576-1583 (1929).
(6) a. Taylor, _Proc. Am. Phil. Soc._, 65, 90-98 (1926).
    b. Taylor and Hill, _J. Am. Chem. Soc._, 51, 2922-2936 (1929).

actions between ethylene and hydrogen as follows:

$$H + C_2H_4 + C_2H_4 \longrightarrow C_2H_5- + C_2H_4 + 15,000 \text{ cal. . . . (X)}$$

$$C_2H_5- + H_2 \longrightarrow C_2H_6 + H - 10,000 \text{ cal. . . . . (XI)}$$

However, this revision of the mechanism does not affect the final result of the reaction. In support of these reactions they predicted that "it should be possible to effect the combination of hydrogen and ethylene by liberating into the mixture of these gases the free radical C_2H_5- involved in the second stage of the process". To establish the correctness of this explanation they liberated free ethyl radicals (obtained by the thermal decomposition of mercury diethyl and lead tetraethyl) into a mixture of hydrogen and ethylene at the decomposition temperature of these metal alkyls (200-300°). They "have shown that hydrogen and ethylene readily combine in the presence of decomposing mercury diethyl and lead tetraethyl", and that "more hydrogen and ethylene disappear than would correspond to ethyl groups liberated" (7).

Taylor (6) and co-workers also observed that more complex hydrocarbons than ethane were formed simultaneously in the reaction of hydrogen and ethylene in the presence of decomposing mercury diethyl and lead tetraethyl. They state that "this has

(7) It is interesting to note, in connection with this, that Gilman and Fothergill (Ref.2) observed both ethylene and hydrogen in the gases evolved in the preparation of some alkylmagnesium halides.

been shown to be due to reaction involving ethyl groups and ethylene". They found that ethylene disappeared when heated with decomposing mercury diethyl and that liquid hydrocarbons, boiling above 100°, were recovered from the reaction. They formulated (6a) the addition of ethyl and ethylene as one stage of a chain reaction.

$$C_2H_5^- + C_2H_4 \longrightarrow C_4H_9^- \quad \ldots \ldots \ldots \quad (XII)$$

$$C_4H_9^- + C_2H_4 \longrightarrow C_6H_{15}^-, \text{ etc.} \quad \ldots \quad (XIII)$$
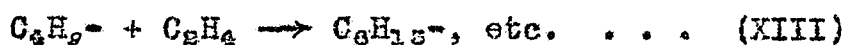
They recently (6b) revised the mechanism of these reactions in the same manner as they did Equations VIII and IX, so that the following equation represents the true reaction more correctly.

$$C_2H_5^- + C_2H_4 + C_2H_4 \longrightarrow C_4H_9^- + C_2H_4 + 15,000 \text{ cal.} (XIV)$$

However, this revision of the mechanism does not alter the product of the reaction.

With the object of capturing any free radicals formed during the preparation of alkylmagnesium halides two series of experiments were performed. In the first series methylmagnesium iodide, ethylmagnesium bromide, and n-propylmagnesium bromide were prepared in the presence of ethylene. If the free methyl, ethyl, and propyl radicals are formed, and if they combine with ethylene under the experimental conditions, then the volume of ethylene should decrease and the quantity of more complex hydro-

carbons should increase. In the second series ethylmagnesium bromide was prepared in the presence of hydrogen with platinum oxide as a catalyst. If free ethyl radicals are formed and if these radicals combine with hydrogen under the conditions of the experiments, larger volumes of ethane should be obtained than are formed under corresponding conditions in the absence of hydrogen.

PREPARATION OF ALKYLMAGNESIUM HALIDES IN THE PRESENCE OF ETHYLENE

Experimental Part

Materials and Apparatus.

The solvent used in these experiments was di-n-butyl ether which had been dried over sodium, filtered, and redistilled. The ether used in some of the experiments was distilled directly from di-n-butyl ether solutions of several Grignard reagents prepared in the early part of the work. Only the middle fractions of these distillations were used.

The alkyl halides and magnesium turnings that were used were the ordinary high grade materials commercially available.

The ethylene was the commercial product which is stored in small cylinders. This ethylene was dried by calcium chloride and phosphorus pentoxide just before being used in the various experiments.

The apparatus was made up of three sections as shown in Figure I. The first section consisted of a large eudiometer (A) (1500 cc. capacity) connected by capillary tubing to two drying tubes, (B) and (C). Tube (B) was filled with calcium chloride and tube (C) was filled with phosphorus pentoxide. The second drying tube was connected to a three-way stopcock, (D), one branch of which was used to remove samples of the ethylene being used during an experiment and the other branch was connected to another three-way stopcock (E). One branch of this second stopcock was connected to a Winkler gas burette
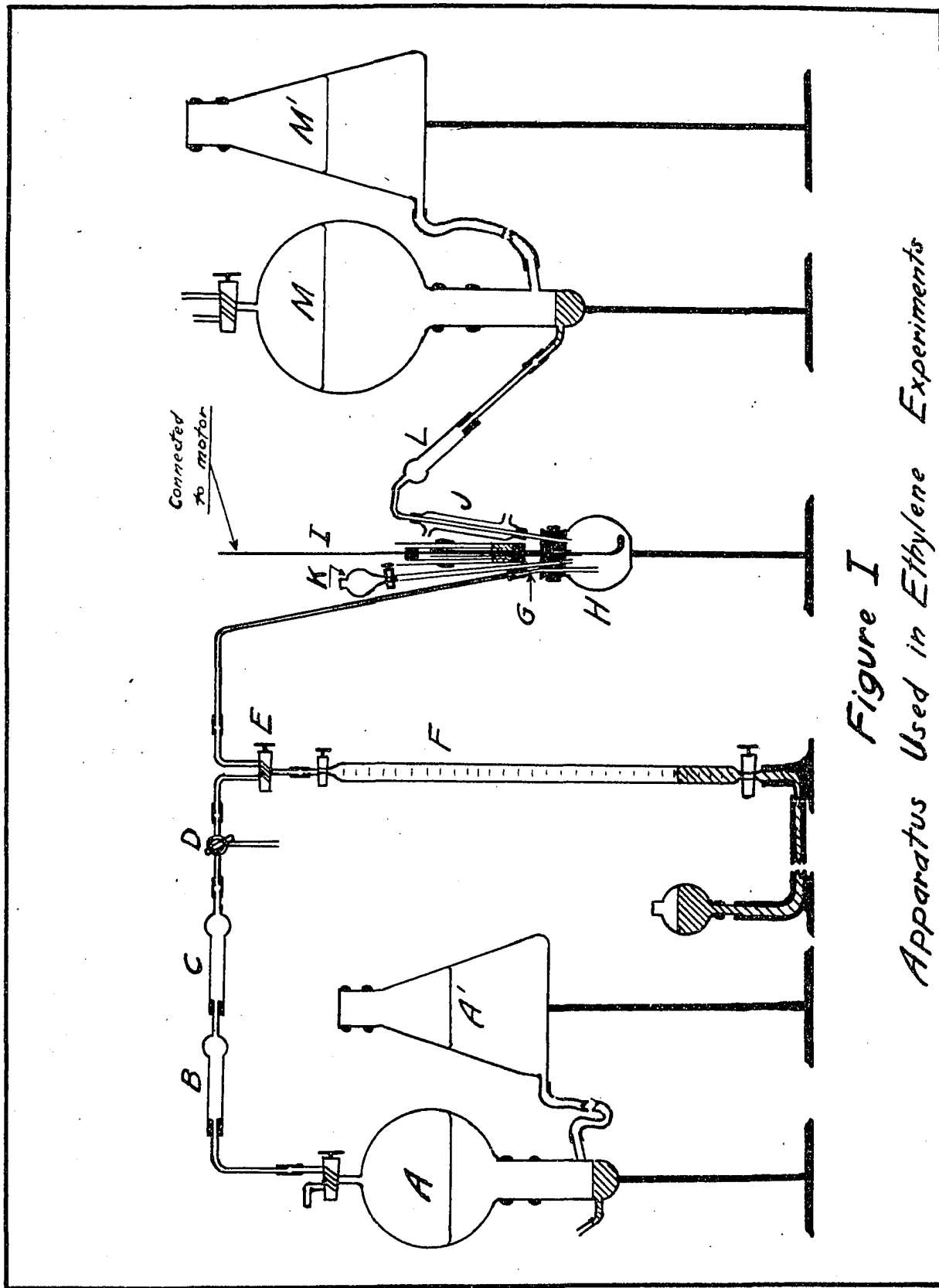
Figure I

Apparatus Used in Ethylene Experiments

(F) containing dry mercury as the confining liquid. The other branch was connected by capillary tubing to the inlet tube (G) of the reaction flask in the second section of the apparatus.

The second section of the apparatus consisted of a reaction flask (H) for the preparation of the Grignard reagent. This was a 150 cc. wide mouthed flask with a tightly fitting rubber stopper fitted with a dropping funnel (K), an inlet tube (G) for the ethylene, a mercury sealed stirrer (I), and a six-inch Liebig condenser (J). A drying tube (L) filled with calcium chloride was sealed to the outlet of this condenser to prevent any water vapor from diffusing back into the reaction flask.

The third section of the apparatus consisted of a large eudiometer (M) (2000 cc. capacity) filled with a saturated sodium chloride solution as the confining liquid, which was used to collect the gases formed during the reaction. This eudiometer was connected by a short piece of rubber tubing to the drying tube sealed to the end of the condenser.

Method of Procedure.

The method of procedure used in all the experiments on the preparation of alkylmagnesium halides in the presence of ethylene is illustrated by the following detailed description of a typical experiment.

After placing the magnesium turnings (4.86 g. or 0.2 atom) in the reaction flask a stream of dry air was passed through the apparatus for 45 minutes to remove any moisture that might

be present. The inlet tube was then joined to the ethylene supply tube and the outlet of the condenser connected to the eudiometer. The leveling flask of the eudiometer was adjusted until the system was under a vacuum of 1-2 cm. of mercury. About 800 cc. of stock ethylene was placed in the supply eudiometer and the connecting tubes swept out until two analyses of the gas showed no appreciable increase in ethylene content. A solution of 21.9 g. (0.2 mole) of ethyl bromide in 130 cc. of di-n-butyl ether was placed in the dropping funnel and a few cubic centimeters of this solution added to the magnesium turnings. The reaction was started by warming with a flame and the remainder of the ethyl bromide and di-n-butyl ether was added over a period of 35 minutes. As soon as the reaction had started the reaction flask was surrounded by an oil bath which was kept at a temperature of 70-85° while the alkyl halide was being added. During this addition 300 cc. (at 24.5° and 734.9 mm.) of ethylene was measured by means of the gas burette and passed into the reaction flask. Another 100 cc. of ethylene was passed into the reaction flask while the reaction mixture was stirred and the oil bath heated from 70° to 145° during 25 minutes. The solution was then refluxed slowly for 30 minutes to drive out all dissolved gases, then about 100 cc. of dry air was drawn through the apparatus to displace all the evolved gases.

The gas collected in the eudiometer was shaken and allowed to stand a short time to allow it to become homogeneous.

The confining liquid in the eudiometer had been saturated previously with a gas having a composition similar to that being collected. Samples of about 70-90 cc. volume were removed to a 100 cc. gas burette to be measured and then analyzed by standard methods of gas analysis, using Hempel absorption and explosion pipettes. The analyses were made in the following order. The sample of gas was first washed with 30% potassium hydroxide. Unsaturated hydrocarbons were removed by absorption with bromine water followed by 30% potassium hydroxide to remove excess bromine vapor. Oxygen was removed by alkaline pyrogallate. Hydrogen was removed by palladium black at 100°. The saturated hydrocarbons were determined by explosion after mixing the residual gas with oxygen. The total contraction after the explosion was measured and the carbon dioxide formed was absorbed in 30% potassium hydroxide. The method of calculation will be shown later. At least two, and usually three, complete analyses were carried out and the average values used. In order to minimize diffusion losses the gas was measured and analyzed on the same day that the reaction was carried out.

In order to compare the amounts of the various gases formed during the preparation of the alkylmagnesium halides in the presence of ethylene with the amounts formed during the preparation of the same Grignard reagents under ordinary conditions, blank experiments were performed in exactly the same manner except that no ethylene was passed into the reaction flask. These blank experiments were carried out either directly before

or after the corresponding experiments.

Sample Data and Calculations.

The data for the experiment just described in the Method of Procedure are given below, together with the calculations used. All the experiments were calculated in a similar manner.

Analysis of ethylene at start of run:

    36.5 cc. sample
    34.9 cc. absorbed in bromine water   = 95.7% pure.

    39.4 cc. sample
    38.1 cc. absorbed in bromine water   = 96.75% pure.

Analysis of ethylene at end of run:

    45.4 cc. sample
    44.0 cc. absorbed in bromine water   = 96.9% pure.

The average of the last two determinations was used in calculating the amount of ethylene used in the experiment.

Purity of ethylene = 96.825%.

400.0 cc. stock ethylene (at 734.9 mm. and 24.5°C)
  96.825% pure = 343.5 cc. pure ethylene (at 760 mm. and 0°C).

Analyses of the gas collected in the eudiometer.

Analysis I.

    69.7 cc. sample of gas
    69.5 cc. after potassium hydroxide
    37.2 cc. after bromine water followed by
            potassium hydroxide   = 32.3 cc. Ethylene.
                                  = 46.4 % of the gas.

34.2 cc. after pyrogallol.
34.0 cc. after palladium black   = 0.133 cc. Hydrogen (8)
                                 = 0.192%

12.15cc. of the gas residue after absorption with pal-
         ladium black was mixed with oxygen to make
98.7 cc. total volume
83.6 cc. after explosion   = 15.1 cc. Contraction.
71.4 cc. after potassium hydroxide
                                 = 12.2 cc. Carbon dioxide.

The amounts of saturated hydrocarbons present in the gas were calculated by the method described by Dennis (9), using the contraction due to the combustion and the carbon dioxide formed by the combustion.

Let x equal the volume of ethane present.
Let y equal the volume of butane present.
Then
   15.1 cc. = 2-1/2x + 3-1/2y   = Contraction.
   12.2 cc. = 2x   +   4y   = Carbon dioxide.

Solving these two equations simultaneously gives the following amounts of ethane and butane.

Ethane = 5.9 cc. in the sample exploded or 23.7% of the
                 original gas.
Butane = 0.1 cc. in the sample exploded or 0.4% of the
                 original gas.

Analysis II.

87.3 cc. sample of gas
87.0 cc. after KOH
47.2 cc. after bromine water = 39.8 cc. Ethylene.
                              = 45.6%

(8) Since the oxygen in the tube containing the palladium black unites with hydrogen to form water under these conditions, only two-thirds of the decrease in volume is due to the hydrogen present. Of course, when large amounts of hydrogen are present the volume of oxygen held by the tube (0.7 cc.) is simply deducted from the total volume absorbed by the palladium black.
(9) Dennis, L. M. Gas Analysis. The Macmillan Company, New York, p.127-138. 1913.

43.2 cc. after pyrogallol.
43.1 cc. after palladium   = 0.067 cc. Hydrogen.
                                  = 0.0772%

12.45cc. residual gas
97.8 cc. total volume
80.3 cc. after explosion   = 17.5 cc. Contraction.
66.5 cc. after KOH   = 13.8 cc. Carbon dioxide.

Ethane = 6.9 cc. in the sample exploded or 27.35% of
                the original gas.
Butane = 0.0 cc. (The solution of the simultaneous equa-
                tions set up as in the example above
                gave a volume of -0.5 cc. of butane.
                Therefore, the gas was considered as
                containing only ethane. The ethane
                was calculated as one-half the volume
                of carbon dioxide formed).

Analysis III.

76.7 cc. sample of gas
76.3 cc. after KOH
41.4 cc. after bromine water = 34.9 cc. Ethylene.
                              = 45.5%

38.1 cc. after pyrogallol.
38.0 cc. after palladium   = 0.067 cc. Hydrogen.
                              = 0.0873%

12.4 cc. residual gas
91.3 cc. total volume
73.8 cc. after explosion   = 17.5 cc. Contraction.
60.2 cc. after KOH   = 13.6 cc. Carbon dioxide.

Ethane = 6.8 cc. of the sample exploded, or 27.15% of
                the original gas.
Butane = 0.0 cc. (The solution of the simultaneous equa-
                tions set up as before gave a volume
                of -1.0 cc. of butane).

Since Analyses II and III agreed quite closely they were

used to calculate the average composition of the gas.

Average composition of the gas:
    Ethylene 45.55%
    Ethane 27.25%
    Hydrogen 0.082%
    Butane 0.0%

The remainder of the gas that was formed was then measured in the gas burette and the total amount collected was converted to the volume it would occupy under standard conditions. In calculating the results of the experiments in which the gases were collected over a saturated sodium chloride solution, the values for the vapor pressures of saturated sodium chloride solutions at different temperatures were interpolated from the values reported by Speranski (10).

Total volume of gas = 956.1 cc. at 0°C. and 760 mm.

The total volumes of the various gases formed, based on the average composition shown above, are as follows:

Ethylene . . . . 455.0 cc.
Ethane . . . . 260.1 cc.
Hydrogen . . . . 0.79cc.
Butane . . . . 0.0 cc.

The volume of ethylene used was 343.5 cc., therefore there was an increase of 91.5 cc. in the ethylene during the preparation of the ethylmagnesium bromide.

Experiments with Methylmagnesium Iodide.

No.1. This experiment was carried out in the same manner as the one with ethyl bromide described above, except that 28.4 g. (0.2 mole) of methyl iodide was used instead of ethyl-bromide. The amount of ethylene used during the preparation

(10) Speranski, A., Z. physik. Chem., 70, 519-533 (1910).

of the methylmagnesium iodide was 335.0 cc. and the amount recovered was 394.0 cc.; an increase of 59.0 cc. The amounts of other gases formed were: methane, 198.2 cc.; ethane, 24.2 cc.; and hydrogen, 1.90 cc.

No.2. The same amounts of materials were used in this experiment and it was carried out in exactly the same manner as Experiment No.1 except that no ethylene was passed into the reaction flask during the reaction. The amounts of the various gases formed were: methane, 216.0 cc.; ethane, 27.3 cc.; hydrogen, 1.96 cc.; and unsaturated hydrocarbons, 30.6 cc. Gilman and Fothergill (2) showed that the unsaturated gas formed in the preparation of methylmagnesium iodide contained ethylene.

Experiments with Ethylmagnesium Bromide.

No.1. This was the first experiment to be performed in this study. The di-n-butyl ether solution of 21.9 g. (0.2 mole) of ethyl bromide was added to 4.86 g. (0.2 atom) of magnesium turnings during 30 minutes. The solution was stirred at 70° for 1-1/4 hours and the gas evolved was analyzed in the usual manner for ethylene. The solution was next refluxed for one-half hour and the evolved gases collected and analyzed separately. The amount of ethylene (the ethylene used in Experiments No.1 and No.2 was prepared from ethylene bromide and zinc; commercial ethylene from a cylinder was used in all the other experiments) used during the preparation of the ethylmagnesium bromide was 251.2 cc. and the amount recovered was 219.5 cc.

This was a decrease of 31.7 cc. of ethylene. A complete analysis for all the gases was not made in this experiment.

No.2. Except for the following changes this experiment was carried out in the same manner as the first one. The volume of ethylene used was 339.0 cc. The gas evolved was analyzed for all the usual constituents. The volume of ethylene recovered was 312.4 cc. which was 26.6 cc. less than the amount of ethylene used. The amounts of the other gases formed were: ethane, 162.2 cc.; butane, 26.0 cc.; and hydrogen 0.0 cc.

No.3. This experiment was carried out in the manner described in the Method of Procedure. The amount of ethylene used during the preparation of the ethylmagnesium bromide was 339.0 cc. and the volume recovered was 508.0 cc. This was an increase of 169.0 cc. The amounts of the other gases formed were: ethane, 278.0 cc.; butane, 8.45 cc.; and hydrogen, 4.07cc.

No.4. The amounts of materials and method of procedure were the same in this experiment as in Experiment No.3. It was performed to determine the amounts of the different gases formed under similar conditions without passing ethylene into the reaction mixture. The amounts of the various gases formed were: ethylene, 197.0 cc.; ethane, 374.0 cc.; butane, 3.33 cc.; and hydrogen, 2.2 cc.

No.5. This experiment was performed in the same general manner as described in the Method of Procedure. The amount of

ethylene used was 351.0 cc. and the amount recovered was 425.0 cc. This was an increase of 74.0 cc. The amounts of the other gases formed were: ethane, 267.0 cc.; butane, 0.0 cc.; and hydrogen, 0.0 cc.

No.6. No ethylene was used in this blank experiment; otherwise it was performed in as nearly a similar manner to Experiment No.5 as possible. The amounts of the different gases formed were: ethylene, 74.1 cc.; ethane, 247.0 cc.; butane, 10.58 cc.; and hydrogen, 0.89 cc.

No.7. This was another experiment carried out in the same manner as Experiments No.3 and No.5, and is the one described in the Method of Procedure above. The amount of ethylene used was 343.5 cc. and the amount recovered was 435.0 cc. This was an increase of 91.5 cc. The volumes of other gases formed were: ethane, 260.1 cc.; butane, 0.0 cc.; and hydrogen, 0.79 cc.

No.8. The amounts of the various gases formed in the blank experiment which was carried out in the same manner as No.7, except that no ethylene was used, were: ethylene 115.3 cc.; ethane, 281.0 cc.; butane, 16.2 cc.; and hydrogen, 1.51 cc.

Experiments with n-Propylmagnesium Bromide.

No.1. This experiment was performed in the same manner as described in the Method of Procedure. The amounts of mag-

nesium and butyl ether used were the usual amounts, and the amount of n-propyl bromide used was 24.6 g. or 0.2 mole. The volume of ethylene used was 340.0 cc. and the volume of unsaturated gas recovered was 432.5 cc. This was an increase of 92.5 cc. The amounts of other gases formed were: propane, 185.5 cc.; hexane, 0.0 cc.; and hydrogen, 0.68 cc. The explosions of the gas residues containing the saturated hydrocarbons actually gave results that indicated a mixture of propane and some hydrocarbon containing fewer carbon atoms, therefore, the hydrocarbon was considered as being only propane.

No.2. No ethylene was passed into the reaction flask of this blank experiment to accompany n-propylmagnesium bromide Experiment No.1. The amounts of the different gases formed were: unsaturated hydrocarbons, 102.7 cc.; propane, 222.0 cc.; hexane, 0.0 cc.; and hydrogen, 1.42 cc. Gilman and Fothergill (2) showed that the unsaturated gas formed in the preparation of n-butylmagnesium bromide contained α-butylene so this unsaturated gas probably contained propylene.

Discussion of Results

The results of these experiments on the preparation of alkylmagnesium halides in the presence of ethylene show that the ethylene probably did not capture the free radicals. The data for these experiments are summarized in the following tables. The first table shows the volumes of ethylene that were added and the volumes that were recovered in the various experiments. The second shows the volumes of other gases formed in the experiments and the corresponding blanks.

Table I.

Ethylene Added and Recovered

RMgX	Exp. No.	(1) C_2H_4 Added cc.	(2) C_2H_4 Recovered cc.	(3) C_2H_4 Decrease cc.	(4) C_2H_4 Increase cc.	(5) C_2H_4 Formed in blank cc.
CH_3MgI	1	335.0	394.0	---	59.0	30.6
C_2H_5MgBr	1	251.2	219.5	31.7[a]	---	---
C_2H_5MgBr	2	339.0	312.4	26.6[a]	---	---
C_2H_5MgBr	3	339.0	508.0	---	169.0	197.0
C_2H_5MgBr	5	351.0	425.0	---	74.0	74.1
C_2H_5MgBr	7	343.5	435.0	---	91.5	115.3
$\underline{n}$-C_3H_7MgBr	1	340.0	432.5	---	92.5	102.7

a. These two experiments were the first ones to be performed and the decrease in ethylene could not be checked in the later work. This disappearance of ethylene was probably due to the diffusion of the ethylene through the confining water in the eudiometer. Water was used for the confining liquid in these two experiments only. In the later experiments a saturated sodium chloride solution was used and precautions were taken to minimize diffusion.

Instead of any decrease in the volume of ethylene (except in the first two experiments with ethylmagnesium bromide which are explained in the footnote to Table I) there was actually an increase. However, the increase in the volume of ethylene in some of the experiments (particularly in the ethylmagnesium bromide Experiments No.3 and No.7 and the n-propylmagnesium bromide Experiment No.1) is appreciably less than the volume of ethylene formed in the corresponding blank experiments. These results would indicate that free radicals had been captured by the ethylene. However, in order to prove conclusively that the free radicals had been captured by the ethylene, the difference between the increase in the ethylene in the experiments and the ethylene formed in the corresponding blanks should be at least equal to, and preferably greater than, the variation in the total amounts of ethylene formed in similar experiments. That is, the difference between any value in column 4 of Table I and the corresponding value in column 5 should be greater than the variation in the values given for similar experiments in column 5. In ethylmagnesium bromide Experiment No.3 for instance, the difference between the increase in ethylene in the experiment and the ethylene formed in the corresponding blank was 28.0 cc. But the amount of ethylene formed in the different blank experiments varied from 74.1 cc. to 197.0 cc., a difference of 112.9 cc. between the highest and the lowest. Therefore, these results are not in close enough agreement to conclude that free radicals have been captured.

The increase in the volume of ethylene in the experiments and the formation of ethylene (or other unsaturated hydrocarbons) in the blanks might be due to the disproportionation (11) of free radicals formed during the preparation, or to a splitting reaction of the di-n-butyl ether by the alkylmagnesium halides at the temperature of the boiling solution. This refluxing of the solution was necessary to expel all the dissolved gas. A preliminary experiment with di-n-butyl ether and ethylene showed that a large amount of ethylene remained in solution unless the ether was refluxed for about twenty minutes.

If the unsaturated hydrocarbons which are formed in the preparation of the alkylmagnesium halides are the result of the disproportionation of free alkyl radicals there is the possibility that free alkyl radicals have already been captured. If ethyl radicals (using the preparation of ethylmagnesium bromide as an example) are formed and then disproportionate, the ethylene which results from the disproportionation could react with ethyl radicals formed later in the preparation to give higher molecular weight saturated hydrocarbons as postulated in the Introduction. If this were the case then the addition of more ethylene possibly did not capture many more free radi-

(11) In this connection it is of interest to note that Gilman and Fothergill (Ref.2) obtained considerable volumes of unsaturated hydrocarbons, together with other gases, during the preparation of several alkylmagnesium halides in both diethyl and di-n-butyl ether. They found from 5.45 cc. (0.12% of ethylbromide used) to 106.5 cc. (4.76% of methyl iodide used) of unsaturated hydrocarbons in the preparation of 0.2 mole quantities of alkylmagnesium halides.

cals, since there were always considerable amounts of unsaturated hydrocarbon found in the blank experiments.

Table II.

Saturated Hydrocarbons and Hydrogen

RMgX	Exp. No.	R·H cc.		R·R cc.		Hydrogen cc.	
		Exp.	Blank	Exp.	Blank	Exp.	Blank
CH_3MgI	1	198.2	216.0	24.2	27.3	1.90	1.96
C_3H_5MgBr	3	278.0	374.0	8.45	3.33	4.07	2.2
C_2H_5MgBr	5	267.0	247.0	0.0	10.58	0.0	0.89
C_2H_5MgBr	7	260.1	281.0	0.0	16.2	0.79	1.51
$n\text{-}C_3H_7MgBr$	1	185.5	222.0	0.0	0.0	0.68	1.42

One other result to be expected if the ethylene had captured the free radicals was an increase in hydrocarbons of higher molecular weight as proposed in the Introduction. The data in Table II show, however, that there was actually a decrease in the amount of higher hydrocarbons (assuming that the amount of all higher hydrocarbons, including non-volatile ones, is proportional to the amount of R·R compound formed). The method of calculating the amounts of the different saturated hydrocarbons from the explosion of the samples of gas is not very accurate. A small error in the volume of water formed (shown by the contraction after the explosion) or in the volume of carbon dioxide formed causes a much larger error in the relative amounts of the different hydrocarbons. However, the analyses were carried out as carefully as possible and in ex-

actly the same manner in order to reduce these inherent errors to a minimum. Of course, any non-volatile hydrocarbons that were formed would be lost because the analysis of the gas formed would not detect them.

The difference in the amounts of R-H hydrocarbons formed in similar experiments was probably due to variations in the amounts of moisture unavoidably present in the apparatus or reagents, since the humidity of the atmosphere was quite high at the time of the year these experiments were performed, or due to different amounts of peroxides present in the different stocks of the di-n-butyl ether that were used (12).

The amount of hydrogen formed was generally greater in the blank experiments than in the experiments where ethylene was added. These differences are very small; however, they indicate that some of the hydrogen formed in the presence of a large amount of ethylene combines with the ethylene as postulated in Equations X and XI in the Introduction. This combination of hydrogen and ethylene indicates that free radicals might have been captured.

(12) Gilman and Wood, J. Am. Chem. Soc., 48, 806-810 (1926), showed that ether peroxide $(C_2H_5OC(H)(CH_3)OOH)$ or some of its decomposition products (its mono-ethyl acetal, ethyl alcohol or acetic acid), having active hydrogens, reacted with RMgX compounds to give the corresponding R-H hydrocarbons. The di-n-butyl ether that was used in these experiments could possibly contain similar impurities having active hydrogen structures.

PREPARATION OF ETHYLMAGNESIUM BROMIDE IN THE PRESENCE OF HYDROGEN

Experimental Part

Materials and Apparatus.

The solvent used for the preparation of ethylmagnesium bromide in the presence of hydrogen was di-n-butyl ether which had been purified by sodium in the same manner as the ether used in the experiments with ethylene.

The ethyl bromide used in Experiments No.1 and No.2 was dried over calcium chloride and then redistilled, while in Experiment No.3 the ethyl bromide was not specially purified.

The magnesium turnings used in all the experiments were the high grade turnings commercially available for the Grignard reaction.

The hydrogen was the ordinary commercial grade and was used directly from the cylinder without further purification.

The catalyst that was used in these experiments was prepared after the directions of Adams and Shriner (13), and in

(13) Adams and Shriner, J. Am. Chem. Soc., 45, 2171-2179 (1923), show that the catalyst must be prepared at a temperature of 490-500°C. in order to have the composition shown by the formula $PtO_2 \cdot H_2O$. If the temperature of fusion is too high or too low a catalyst of different composition is obtained. The following figures, taken from a table given by Adams and Shriner, show the different percentages of water in catalysts prepared at different temperatures:

Temperature °C.	% H_2O
390-400	7.13
490-500	7.37
590-600	9.16
650	8.83
700	8.06

Calc. for $PtO_2 \cdot H_2O$: H_2O, 7.34.

accordance with their directions it should have the composition shown by the formula $PtO_2 \cdot H_2O$.

The same stocks of reagents were used in any experiment together with its corresponding blank, but not in different sets of experiments and blanks.

The experiments were carried out in a reduction apparatus similar to that described by Adams and Vorhees (14).

Method of Procedure.

The reaction bottle was carefully dried in an electric oven at 115° for at least one hour and cooled by blowing a stream of dry air into it. In this bottle were placed 100 cc. of di-n-butyl ether, 1.2 g. (0.05 atom) of magnesium turnings, and 0.1000 g. of platinum catalyst and the bottle was fastened in the reduction apparatus. The bottle was evacuated, then filled with hydrogen, and this hydrogen allowed to escape into the air to sweep out all air. The bottle was again evacuated and then filled with hydrogen at a pressure of 38-40 lbs. per square inch. It was then shaken until the catalyst had been reduced to a fine black powder. The hydrogen in the bottle was allowed to escape into the air, the stopper quickly removed, 5.45 g. (0.05 mole) of ethyl bromide was added, the stopper replaced, and the bottle replaced in the reduction apparatus. All these operations were performed as quickly as possible to

(14) Adams and Vorhees, J. Am. Chem. Soc., 44, 1397-1407 (1922).

keep the amount of air diffusing into the bottle at a minimum.
The bottle was then shaken for one hour under a pressure of
38-40 lbs. of hydrogen. The reaction bottle warmed up in about
five minutes to a temperature that could be withstood comfort-
ably by the hand. The bottle gradually cooled off during the
remainder of the hour's shaking.

The gas under pressure in the reaction bottle was allowed
to pass through the connecting tubing and valves of the ap-
paratus into a large eudiometer filled with water or saturated
sodium chloride solution as the confining liquid. The gas re-
maining in the bottle above the solution was displaced into
the eudiometer by adding enough dry di-n-butyl ether to fill
the bottle. The solution of ethylmagnesium bromide was quickly
poured into a flask slightly larger than the volume of the solu-
tion. This flask was connected to the eudiometer through a
short reflux condenser and drying tube filled with calcium
chloride. The solution was then refluxed for several minutes
until no more gas was driven out of the solution.

The gas in the eudiometer was allowed to become homogen-
eous, either by shaking the eudiometer or allowing the gas to
stand several hours, before being analyzed. The gas was anal-
yzed by the standard methods of gas analysis already described
in the part of this thesis dealing with the preparation of
alkylmagnesium halides in the presence of ethylene.

In order to correct any errors that might be caused by
moisture or other impurities in the hydrogen or other reagents

used, blank determinations were carried out after each experiment. These blank experiments were carried out in exactly the same manner as the corresponding experiments except that no catalyst was used in them.

Results.

A preliminary experiment was performed to determine if the ethyl bromide would be reduced to ethane under the conditions used in these experiments. However, no reduction could be detected, either by analysis of the gas in the reaction bottle, or by any change in pressure as indicated by the pressure gauge, when 5.45 g. (0.05 mole) of ethyl bromide dissolved in 75 cc. of di-n-butyl ether and 0.1 g. of platinum catalyst were shaken for 4-1/2 hours with hydrogen at a pressure of 40 pounds.

Preparation of Ethylmagnesium Bromide in the Presence of Hydrogen.

No.1. This was the first experiment to be performed in this series and the analysis of the gas was carried out in a slightly different manner. The gas under pressure in the reaction bottle was passed into the eudiometer, containing water which had been saturated with hydrogen, and analyzed in the usual manner. The gas remaining in the bottle was assumed to be of the same composition as the gas collected in the eudiometer. The volume of this gas was found by measuring the total capacity of the bottle and then deducting the volume occupied

by the solution. During the analysis of the gas under pressure the bottle was kept tightly stoppered; then the solution was placed in a flask which was fitted with a condenser and connected to the eudiometer, and the gas dissolved in the solution was then expelled by refluxing. This gas was analyzed in the same manner as the other. The total amounts (from both analyses) of the different gases were: ethane, 155.9 cc.; ethylene, 1.95 cc.; and butane, 16.1 cc.

The blank determination was carried out in exactly the same manner except that no platinum catalyst was used. The water used in the eudiometer in this blank was the water that had been used previously in the experiment. The amounts of the various gases formed under these conditions were: ethane, 100.5 cc.; ethylene, 15.1 cc.; and butane, 32.5 cc.

No. 2. This experiment was carried out in exactly the same manner as Experiment No. 1, except that fresh water was used in the eudiometer instead of water saturated with hydrogen. The volumes of the different gases that were formed were: ethane, 170.4 cc.; ethylene, 0.0 cc.; and butane, 0.0 cc.

The blank experiment was carried out in the same manner except that the catalyst was omitted. The water used in this blank was the water that was used previously in the experiment. However, the method of analyzing the gas was changed slightly. Instead of assuming the gas remaining in the bottle above the solution to have the same composition as the gas that was under pressure in the closed apparatus, it was analyzed separate-

ly. The results of this analysis showed that the assumption was incorrect, and that there were actually 13.8 cc. more ethane and 2.2 cc. more ethylene in the gas above the solution than would have been calculated from the average of the analyses of the first portion of the gas. The total amounts of the different gases that were formed were: ethane, 146.3 cc.; ethylene, 25.4 cc.; and butane, 0.0 cc.

The same peculiarity that was observed in some of the combustions of the saturated hydrocarbons formed in the ethylene experiments was also observed in these two experiments. The simultaneous solution of the equations set up for the contraction from the explosions and the carbon dioxide formed gave negative values for butane (assuming that the gas mixture was composed of ethane and butane). The possibilities of these results being caused by the failure of the palladium black to remove all the hydrogen before the explosion, or by the formation of carbon monoxide in the explosion due to incomplete combustion, were investigated. Tests showed that the amount of palladium black used would remove the hydrogen completely and that the amount of carbon monoxide in the gas sample after explosion (determined by absorption in cuprous chloride solution) was too small to cause the negative values for butane. Therefore, the gas was considered to be only ethane.

No.3. This experiment was performed in the manner described in the Method of Procedure above. The blank, which is described in the next paragraph, was actually carried out first

and the sodium chloride solution used in the eudiometer in the blank was also used in this experiment. The volumes of the different gases formed were: ethane, 142.5 cc.; ethylene, 0.0 cc.; and butane, 17.75 cc.

The blank experiment was carried out in the same manner except that no catalyst was used. The sodium chloride solution used as the confining liquid in the eudiometer was not previously saturated with any gas. The volumes of the different gases that were formed were: ethane, 113.3 cc.; ethylene, 16.5 cc.; and butane, 28.6 cc.

Discussion of Results

The results of the experiments on the preparation of ethylmagnesium bromide in the presence of hydrogen and platinum catalyst show that the hydrogen probably did not capture the free ethyl radicals. In these experiments it was not known whether the hydrogen was atomic or not, although hydrogen in the presence of catalytic nickel, copper, and iron apparently is in the atomic condition (15). However, in accordance with Reaction XI molecular hydrogen combines with ethyl radicals to give ethane and atomic hydrogen. Under the conditions of these experiments no appreciable combination of this type

(15) See pages 91-92 of Ref.6.

to give ethane was observed (16). This absence of reduction
is best shown by the following table.

Table III.

Ethane Formed During the Preparation of Ethylmagnesium Bromide in the Presence of Hydrogen.

	(1)	(2)	(3)	(4)	(5) In-crease in Ethane	(6) De-crease in Ethane	(7) Increase in Ethane if Water had 0.74 Active H[b].
Exp. No.	Total Ethane cc.	Ethane from Catalyst[a] cc.	Net Ethane cc.	Ethane in Blank cc.	cc.	cc.	cc.
1	155.9	54.8	101.1	100.5	0.6	--	35.1
2	170.4	54.8	115.6	146.3	--	30.7	3.8
3	142.5	54.8	87.7	113.3	--	25.6	8.9

a. Since the reduction of the platinum oxide catalyst ($PtO_2 \cdot H_2O$)
   gives three molecules of water the volume of ethane formed
   in the experiment must be corrected for the volume of eth-
   ane which would result from the action of water on ethyl-
   magnesium bromide. There is some question about the amount
   of ethane that would be formed from the water from the re-
   duction of the catalyst under the conditions of these ex-
   periments. The reduction of one molecule of catalyst
   would liberate three molecules of water and these three
   molecules of water would give either three or six molecules
   of ethane depending on whether water has one or two active
   hydrogens. Meisenheimer (17) and Zerewitinoff (18) have
   both reported that both the hydrogens in water react with
   methylmagnesium halide to give methane. These results have
   been confirmed in unpublished work of Mr. R. J. VanderWal
   in This Laboratory. Mr. VanderWal found that water dis-

(16) Unpublished work of Mr. J. A. Leermakers in This Labora-
     tory has shown that similar results are obtained in the
     preparation of n-propylmagnesium bromide in the presence
     of hydrogen and platinum catalyst under similar condi-
     tions.
(17) Meisenheimer, Ber., 61, 708-720 (1928).
(18) Zerewitinoff, Ibid., 40, 2023-2031 (1907); Z. anal. Chem.,
     50, 680-691 (1911).

The discrepancies in the volumes of ethane formed in the different experiments are probably due to the fact that different stocks of reagents were used in the different experiments. A very small difference in the amounts of moisture in the stocks of ether or hydrogen, or a slight difference in the composition of the catalyst (13), or a difference in the amounts of peroxides (12) in the ether, would cause a considerable difference in the volumes of ethane formed in the different experiments. However, the same stocks of reagents were used in any one experiment and its corresponding blank.

solved in pyridine had two active hydrogens when treated with methylmagnesium iodide. However, two experiments on the number of active hydrogens in water suspended in di-n-butyl ether by the Zerewitinoff method gave values of 0.72 and 0.76. Also, Mr. L. L. Heck, in unpublished work in This Laboratory, found that 0.12 mole of water dissolved in diethyl ether was required to react with 0.1 mole of phenylmagnesium bromide in diethyl ether (the phenylmagnesium bromide was considered to be used up when the solution no longer gave a color test for the Grignard reagent (19)). These low values may be due to the formation of a precipitate of magnesium basic halide which occluded some of the water and prevented further reaction. The rapid shaking of the reaction bottle in the hydrogen experiments would probably prevent this interference of any precipitate; consequently the volume of ethane formed from the reduction of 0.1000 g. of catalyst was based on water having two active hydrogens.

b. This column is given to show the increase in the volume of ethane formed in the experiments over the volume formed in the corresponding blanks if the water resulting from the reduction of the catalyst had only 0.74 active hydrogen (the average of the two results obtained by the determination of the number of active hydrogens in water suspended in di-n-butyl ether).

(19) Gilman and Schulze, J. Am. Chem. Soc., 47, 2002-2005 (1925); Bull. soc. chim., 41, 1479-1481 (1927); Gilman and Heck, Rec. trav. chim., 48, 193-197 (1929); Ber., 62, 1379-1384 (1929).

The decrease in the amount of ethane, shown in column six of Table III, might be due to one or both of the following reasons. First, the amount of ethane assumed to have been formed from the water resulting from the reduction of the catalyst may have been too great. Second, the method of determining the amount of ethane in a mixture of ethane and butane by explosion is not very accurate, even though all the explosions were made in as nearly a like manner as possible, and the average values of at least two and usually three explosions were used. To illustrate this, some of the data from one of the experiments are given here.

Total gas collected . . . . . . 830.2 cc.
Ethane, (highest value) . . . . 15.2 %
Ethane, (lowest value) 12.17%
Ethane, difference 3.03%
Ethane, difference in volume . 25.15 cc.

These data were taken from an experiment performed near the end of the work, where the technique could be considered as being representative.

Even if the values for the increases in the volumes of ethane given in column seven of Table III are more nearly correct than the values shown in columns five and six, the average increase is not large enough to show conclusively that ethyl radicals have been captured. The increase should be at least equal to, and preferably greater than, the variation in the total increases in similar experiments. However, too much weight should not be placed on this comparison, because the

different amounts of ethane formed in similar experiments may have been due to different amounts of impurities in the various stocks of reagents that were used, as mentioned before.

Some other conflicting data were obtained in these experiments on the preparation of ethylmagnesium bromide in the presence of hydrogen. These data are summarized in Table IV.

Table IV.

Butane and Ethylene Formed in the
Hydrogen Experiments

Exp.:	Butane, in cc.		:	Ethylene, in cc.	
No.:	Exp.	Blank	:	Exp.	Blank
1 :	16.1	32.5	:	1.95	15.1
2 :	0.0[a]	0.0[a]	:	0.0	25.4
3 :	17.75	28.6	:	0.0	16.5

a. The explanation for the absence of butane is given in the description of Experiment No.2 in the Experimental Part.

From this Table it can be seen that the amounts of butane and ethylene formed in the preparation of the Grignard reagent in the presence of hydrogen were smaller than the amounts formed in the corresponding blanks. This indicates that the free ethyl radicals were captured by the hydrogen before they coupled or disproportionated. If this were true the total amount of ethane in each of the experiments should be larger than the amount in the corresponding blank by twice the decrease in butane plus the decrease in ethylene. This is seen

by a consideration of the following volume relations of the different products. If two ethyl radicals coupled only <u>one</u> volume of butane would be formed, while if two ethyl radicals reacted with hydrogen <u>two</u> volumes of ethane would result. Also, if two ethyl radicals disproportionated <u>one</u> volume of ethane and <u>one</u> volume of ethylene would be formed, while if the two ethyl radicals reacted with hydrogen <u>two</u> volumes of ethane would result. Actually, this was not the case—in two of the experiments there were decreases in the amounts of ethane and in the third experiment there was only a very slight increase. However, this does not necessarily mean that free ethyl radicals were not formed in the preparation of ethylmagnesium bromide. They may have existed momentarily and then reacted further to give non-volatile hydrocarbons according to a series of reactions similar to those postulated by Taylor and Hill (6b).

There is also the possibility that the saturated hydrocarbons formed early in the reaction may have been decomposed by the hydrogen in the presence of platinum catalyst to give methane and a liquid polymer of the composition C_xH_{2x}. Taylor and Hill (6b) have shown that saturated hydrocarbons are decomposed in such a manner both by excited mercury atoms and by atomic hydrogen. This decomposition should not take place to any great extent for they state that "high hydrogen concentration favors mainly ethane formation" and there was certainly a high hydrogen concentration present in these experiments. However, the fact that they had excited mercury atoms present when

they obtained mainly ethane formation must also be considered, for the platinum catalyst present in these experiments may not have had the same influence that excited mercury atoms would have had.

SUMMARY AND CONCLUSIONS

The two series of experiments described in this paper have shown that ethylene and hydrogen have probably failed to capture free alkyl radicals formed during the preparation of some alkylmagnesium halides. These results may be explained by any one or several of the following reasons: there may be no free radicals formed in the preparation of the Grignard reagent; there may be no free radicals formed in the thermal decomposition of organometallic compounds like mercury diethyl and lead tetraethyl; free radicals may be formed in each of these reactions but the free radicals may differ, or the environments may differ (in these experiments magnesious halide is probably present, whereas, in Taylor's (6) experiments the free metal is probably present); or the generally different experimental conditions (solvent, temperature, etc.) make it unwise to correlate the various studies.

However, the general idea of the preliminary formation of free radicals in the preparation of the Grignard reagent is highly attractive in itself, and in addition to this, there is no more satisfactory explanation at the present time for the experimental results on disproportionation (2) and the formation of di-p-tolyl (3). Therefore, it is preferred to believe that free radicals are formed in the preparation of the Grignard reagent and that the ethylene and hydrogen simply have not captured them for any one or several reasons such as the greater facility of their combination with magnesious halide or with

each other or disproportionation; or, because the ethylene and hydrogen were not sufficiently reactive under these experimental conditions.

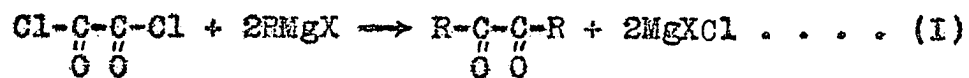## B. NEW REACTIONS OF OXALIC ACID AND SOME OF ITS DERIVATIVES

INTRODUCTION

The general nature of the research work that has been carried on in the Department of Chemical Engineering at Iowa State College, under the direction of Dr. O. R. Sweeney, has been the development of various methods of utilizing agricultural wastes, such as corn cobs and stalks. One of the methods that has been developed is the preparation of oxalic acid from corn cobs and stalks by oxidation with nitric acid and by fusion with alkalies. Sweeney and Webber (1) and Gilman, Sweeney and Pickens (2) are the most recent investigators of the optimum conditions for the preparation of oxalic acid from corn wastes.

The object of this study was to attempt to prepare new derivatives of oxalic acid, for which there would be a commercial demand. The well known use of dimethylglyoxime for the quantitative determination of nickel suggested the investigation of the oximes of a whole series of aromatic α-diketones for their usefulness in the separation of metals.

There is no good general method for the preparation of such a series of α-diketones known at the present time. Therefore, the reaction of oxalyl chloride (a derivative of oxalic

(1)a. Sweeney and Webber, Unpublished Thesis. Library, Iowa State College, Ames, Iowa. 1925.
   b. Sweeney and Webber, Unpublished Thesis. Library, Iowa State College, Ames, Iowa. 1929.
(2)   Gilman, Sweeney and Pickens, Unpublished work done in This Laboratory.

ac'd) with the Grignard reagent was investigated, to see if
α-diketones could be produced. The formation of α-diketones
by this method is illustrated by the following equation.

$$Cl-\underset{O}{\overset{||}{C}}-\underset{O}{\overset{||}{C}}-Cl + 2RMgX \longrightarrow R-\underset{O}{\overset{||}{C}}-\underset{O}{\overset{||}{C}}-R + 2MgXCl \quad . \quad . \quad . \quad . \quad (I)$$

HISTORICAL

The reaction between acid halides (RCX) in general and $\overset{O}{}$ organomagnesium halides to give good yields of ketones has been limited to only a few Grignard reagents. These have been pyrryl-magnesium iodide (3), β-indolylmagnesium iodide(4), and α-naphthylmagnesium bromide (5). Earlier investigators of the reaction between oxalyl halides and the Grignard reagent have obtained α-diketones only in the case of pyrryl- and indolyl-magnesium halides. Hess and Weltzien (6) obtained only tetra-phenylacetenyl glycol (($C_6H_5C\equiv C)_2C-C(C\equiv CC_6H_5)_2$) from oxalyl $\overset{}{OH}\ \overset{}{OH}$ chloride and phenylacetenylmagnesium bromide. Gauerke and Marvel (7) obt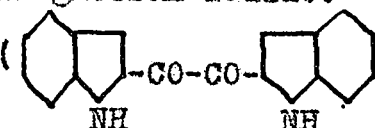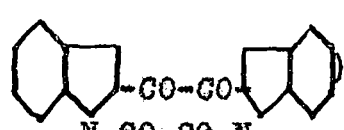ained mainly dicyclohexyl ketone, which they ac-counted for as the result of some sort of decomposition, and a small amount of tetracyclohexyl glycol (($C_6H_{11})_2C - C(C_6H_{11})_2$). $\overset{}{OH}\ \overset{}{OH}$ Oddo and Sanna (8) reported the formation of N,N'-diindoyl

( ) and N,β-bisdiindoyl ( )

from oxalyl chloride and indolylmagnesium iodide; and $\beta,\beta^\perp$-di-methyl ketoyl ( ) from oxalyl chloride and
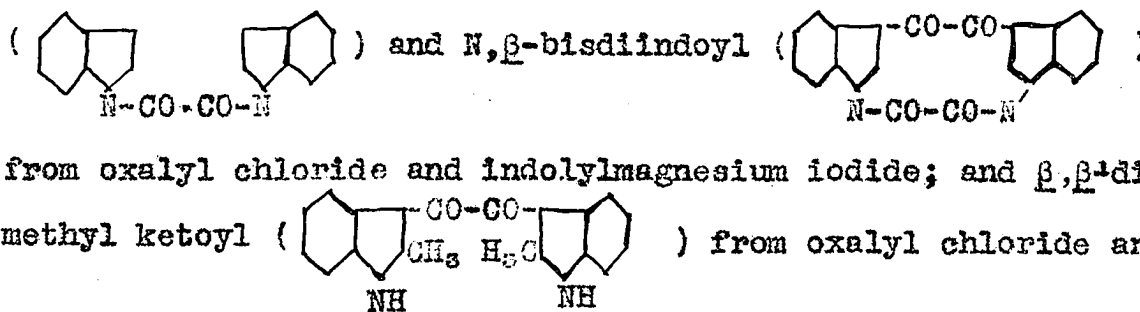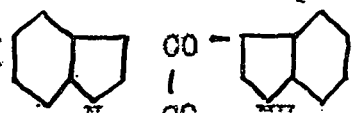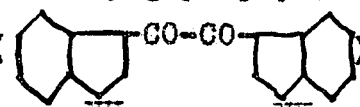
(3)a. Oddo, Ber., 43, 1012-1021 (1910).
 b. Hess and Wissing, ibid., 47, 1416-1428 (1914).
(4) Oddo and Sessa, Gazz. chim. ital., 41, I, 234-248 (1911); C.A., 5, 2638 (1911).
(5)a. Acree, Ber., 37, 625-628 (1904).
 b. Schoepfle, J. Am. Chem. Soc., 44, 188-194 (1922).
(6) Hess and Weltzien, Ber., 54, 2511-2521 (1921).
(7) Gauerke and Marvel, J. Am. Chem. Soc., 50, 1178-1182 (1928).
(8) Oddo and Sanna, Gazz. chim. ital., 51, II, 337-342 (1921); C.A., 16, 1423-1424 (1922).

methylketolylmagnesium iodide. Sanna (9) found the same products as Oddo and Sanna, together with three more, in the reaction of oxalyl chloride with indolylmagnesium iodide. The three new products were: $\underline{a},\underline{a}'$-diindoyl ([structure] -CO-CO- [structure] NH NH), N,$\underline{a}$-bis-diindoyl ([structure] -CO-CO- [structure] N-CO-CO-N), and an unidentified compound melting at 163°. However, Majima and Shigematsu (10) in a repetition of the work of Oddo and Sanna, and Sanna, were only able to isolate two compounds. These were N-(β-indolylglyoxylyl) indole ([structure] CO N - CO NH) and $\underline{\beta},\underline{\beta}'$-diindoyl ([structure] CO-CO NH NH); not N,N'-diindoyl and $\underline{a},\underline{a}'$-diindoyl, respectively, as the compounds having the corresponding melting points were named by Oddo and Sanna. Oddo (11) found dipyrroyl ([structure] -CO-CO- [structure] NH NH) as a product of the reacti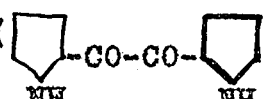on of oxalyl chloride with pyrrylmagnesium iodide. Tistchenko (12) did not obtain tetraketones from the reaction between oxalyl bromide and iso-valeroylmagnesium bromide ($\underline{iso}$-$C_4H_9C(O)MgBr$). He obtained carbon dioxide, ethyl bromide, ethyl iso-valerate, di-iso-valeryl ($\underline{iso}$-C_4H_9CO-COC_4H_9-$\underline{iso}$) and a small amount of iso-valerate of iso-valeroin ($\underline{iso}$-$C_4H_9CH(OOCC_4H_9$-$\underline{iso})COC_4H_9$-$\underline{iso}$).

(9) Sanna, Gazz. chim. ital., 52, II, 165-170 (1922); C.A., 17, 1639 (1923).
(10) Majima and Shigematsu, Ber., 57, 1449-1453 (1924).
(11) Oddo, Gazz. chim. ital., 41, I, 248-255 (1911); C.A., 5, 2638 (1911).
(12) Tistchenko, D. V., Bull. soc. chim., 37, 623-657 (1925).

However, Gilman, Fothergill and Parker (13), in a few preliminary experiments, secured fair yields of benzophenone from benzoyl chloride and phenylmagnesium bromide. Therefore, it was thought that the application of the same general experimental procedure to the reaction of oxalyl chloride with arylmagnesium halides would give considerable yields of aromatic α-diketones.

(13) Gilman, Fothergill and Parker, Rec. trav. chim., 48, 748-751 (1929).

EXPERIMENTAL PART

Preparation of Oxalyl Chloride.

Ordinary hydrated oxalic acid was dehydrated by the method of Clarke, Hultman and Davis (14) with a 95% yield. This anhydrous oxalic acid was treated with phosphorus pentachloride, after the method of Staudinger (15), and the reaction mixture was carefully fractionated. The oxalyl chloride boiling at 63-64° was used in these studies. The yield of oxalyl chloride, based on the anhydrous oxalic acid used, was 48%.

Oxalyl Chloride and Phenylmagnesium Bromide.

Experiment No.1. The oxalyl chloride (12.7 g. or 0.1 mole) was dissolved in 150 cc. of anhydrous ether in a 500 cc. three-necked flask provided with a dropping funnel, reflux condenser and mechanical stirrer. To this solution was added 0.2 mole of phenylmagnesium bromide (100 cc. of a stock solution) with stirring. The reaction flask was cooled by means of a mixture of ice and salt. The time required for the addition of the Grignard reagent was 1-1/4 hours and during this addition a yellow precipitate formed. After stirring the reaction mixture another 15 minutes the solution was tested for excess RMgX by

(14) Clarke, Hultman and Davis, J. Am. Chem. Soc., 43, 366-370 (1921).
(15) Staudinger, Ber., 41, 3558-3566 (1908).

the color test of Gilman and co-workers (16). A blue color was obtained when the solution was added to the Michler's ketone before hydrolysis. This color was shown to be due to oxalyl chloride and not RMgX; for in a test experiment the same color was obtained when oxalyl chloride was added to a benzene solution of Michler's ketone. The color persisted even after the addition of a considerable amount of iodine and acetic acid. Therefore, this color test for the Grignard reagent cannot be used in the presence of oxalyl chloride.

The reaction mixture was hydrolyzed with 10% hydrochloric acid and steam distilled. The steam distillate was extracted with ether and the water layer washed twice with more ether. The combined ether layer and washings were dried over anhydrous sodium sulfate and then fractionally distilled. The only fraction isolated was 1.5 g. (9.6%) of a material boiling from 235° to 285°, which was crude diphenyl.

The residue, not volatile with steam, was dissolved in ether and the ether solution dried over sodium sulfate. The evaporation of the solvent left only a yellow waxy solid which proved difficult to crystallize. Ethyl alcohol, methyl alcohol, chloroform, ethyl acetate, ether, glacial acetic acid, and petroleum ether (max. b.p. 80°) were tried as crystallizing media, but only the petroleum ether was satisfactory (in the

(16) Gilman and Schulze, J. Am. Chem. Soc., 47, 2002-2005 (1925); Bull. soc. chim., 41, 1479-1481 (1927); Gilman and Heck, Rec. trav. chim., 48, 193-197 (1929); Ber., 62, 1379-1384 (1929).

later experiments ligroin (b.p. 80-150°) was found to be better than petroleum ether). By extracting the solid with several portions of boiling petroleum ether and allowing these solutions to stand several hours in the ice-box 3.70 g. (19.3%)(17) of phenylbenzoin, m.p. 82-84° (recrystallized from alcohol, m.p. 86-87°), was obtained. This phenylbenzoin was identified by splitting it with alcoholic potassium hydroxide to give benzoic acid and benzohydrol, after the method of Acree (18). The mixed melting point determinations of benzoic acid and benzohydrol with authentic specimens showed no depressions. No other products were isolated.

Experiment No.2. This experiment was a duplicate of Experiment No.1. From the steam distillate there was obtained only 0.4 g. (2.6%) of crude diphenyl, b.p. 240-260°. The residue, not volatile with steam, was extracted for eight hours with 200 cc. of petroleum ether in a Soxhlet extractor. At the end of this time all the solid had been dissolved out of the paper thimble, and 3.75 g. (19.2%) of phenylbenzoin m.p. 83-84°, precipitated on the sides of the flask containing the petroleum ether. By concentrating the petroleum ether solution another 1.05 g. (5.47%) of phenylbenzoin, m.p. 80°, was obtained. The total yield was 4.75 g. or 24.7%. No other products were isolated.

(17) All percentages given in Part B of this thesis are based on the phenylmagnesium bromide used.
(18) Acree, Am. Chem. J., 29, 588-609 (1903).

Experiment No.3. Recently (19) it has been found that
lead and mercury alkyls slowed down the rate of reaction of the
Grignard reagent with ketones and with nitriles. With this in
mind, 1 g. of lead tetraethyl was added to the oxalyl chloride
solution used in this experiment to determine whether it would
slow down the reactivity of the carbonyl groups in oxalyl chlor-
ide to such an extent that benzil would be formed instead of
phenylbenzoin. The reaction was carried out in the same manner
as in the previous experiments, using the same amounts of
oxalyl chloride and phenylmagnesium bromide. The lead tetra-
ethyl was decomposed at the end of the reaction by adding
1-1.5 cc. of bromine in 30 cc. of chloroform. The reaction
mixture was hydrolyzed and steam distilled in the usual manner.
A careful search for chlorobenzene in the steam distillate was
made, but none was found. The residue, not volatile with
steam, was dissolved in ether, dried, and then the ether re-
moved by slow evaporation but no crystals formed. By extract-
ing the solid with several portions of petroleum ether, in the
same manner as in Experiment No.1, there was obtained 3.3 g.
(17.2%) of phenylbenzoin, m.p. 83-84°. No other products were
isolated.

Experiment No.4. Cooling the reaction mixture by means of
a mixture of solid carbon dioxide and ether was resorted to in
this experiment to see if benzil would be formed. Otherwise,

(19) Unpublished work of Mr. R. E. Brown and Miss E. L. St.John
done in This Laboratory.

the reaction was carried out in the same manner, and with the
same amounts of materials, as in Experiment No.1. However,
the method of working up the reaction products was changed.
The clear ether solution was decanted from the yellow precipi-
tate in the reaction mixture and each part hydrolyzed with
dilute hydrochloric acid and worked up separately. Steam dis-
tillation was not used in this experiment, nor in any of the
following experiments.

The solution part of the reaction mixture, after hydrol-
ysis, was separated into the ether and water layers. The water
layer was washed with two portions of ether and these washings
combined with the ether layer. The ether layer was dried over
sodium sulfate and then the solvent was removed by distilla-
tion, followed by a stream of dry air. An oil containing
needle shaped crystals was left in the flask. In an attempt to
separate any diphenyl from these crystals, the oil was extract-
ed with 75 cc. of petroleum ether, and the insoluble part re-
crystallized from ether. In this manner about 0.2 g. of
crystals, in a thick oil, were obtained; after pressing on a
porous plate they melted at 102.5°. The mixed melting point of
these crystals with an authentic specimen of benzil (m.p. 95°)
was 97-100°. These crystals when recrystallized from alcohol
melted at 102.5°. It was thought that this compound might be
a double compound of benzil and phenylbenzoin (20), so a mix-

(20) Klinger, (Ber., 19, 1862-1876 (1886)) obtained a similar
compound, benzilbenzoin, m.p. 134-135°, by the action
of sunlight on an ether solution of benzil.

ture of equal parts of known benzil and phenylbenzoin was dissolved in ether and allowed to crystallize. Good crystals formed; however, they had a wide melting range — from 83° to 92°. This showed the 102.5° compound not to be the double compound benzil-phenylbenzoin.

Ether was added to the precipitate from the reaction mixture after hydrolysis and the ether and water layers separated in the usual manner. The evaporation of the ether left a waxy solid, which after several crystallizations from ligroin (b.p. 80-150°) gave 5.1 g. (26.5%) of phenylbenzoin, melting at 83-84°.

Experiment No.5. An excess of oxalyl chloride was used in this experiment to see if benzil would be formed. The ether solution of 0.1 mole of phenylmagnesium bromide was added during 30 minutes to the ether solution (150 cc.) of 12.7 g. (0.1 mole) of oxalyl chloride. The reaction flask was cooled by a mixture of ice and salt. The light yellow precipitate which formed was filtered out of the reaction mixture. The precipitate and solution were hydrolyzed and worked up separately in the same manner as in Experiment No.4.

The residue after the removal of the ether from the solution part of the reaction mixture was a thick oil containing about 0.2 g. of crystals. Some of these crystals were removed and dried on a porous plate. They melted at 101-102°. This was probably the same compound that was obtained in Experiment No.4, but a mixed melting point determination was not made.

The residue after the removal of the ether from the precipitate of the reaction mixture was a waxy solid. This solid was extracted for five hours with 100 cc. of hot petroleum ether. When the petroleum ether extract was allowed to stand, two crops of crystals were obtained; the first was 1.05 g. of phenylbenzoin, m.p. 82-83°, and the second was 0.5 g. of phenylbenzoin, m.p. 81-82°. The total yield was 1.55 g. or 16.2%.

Experiment No.6. This experiment was carried out in the same manner, and the same amounts of materials were used, as in Experiment No.5, except that the reaction flask was cooled by a mixture of solid carbon dioxide and ether instead of an ice-salt mixture.

The solution part of the reaction mixture yielded about 0.2-0.3 g. of the same crystals melting at 101.5°. This was probably the same compound that was obtained in Experiments No.4 and No.5, but a mixed melting point was not taken.

The waxy solid left after the evaporation of the ether from the precipitate of the reaction mixture was recrystallized from ligroin (80-150°). A total yield of 2.70 g. (28.1%) of phenylbenzoin, m.p. 83-84°, was obtained by several crystallizations.

Experiment No.7. Liquid air was used to cool the reaction mixture in this experiment. The oxalyl chloride (12.7 g. or 0.1 mole) was dissolved in 100 cc. of ether in a 200 cc. three-necked flask. A pentane thermometer graduated to -200° C.

was fitted in the flask so that the temperature of the reaction mixture could be read at any time during the reaction. The flask was first cooled by a mixture of solid carbon dioxide and ether. Then the carbon dioxide-ether bath was replaced by liquid air. At a temperature of -140° the ether solution solidified. The liquid air bath was lowered slightly and 0.2 mole of phenylmagnesium bromide solution added slowly with stirring. The addition required 30 minutes, and during this time the temperature of the mixture was kept at -120 to -130° by the occasional addition of liquid air to the bath. The reaction mixture was stirred for 10 minutes cooled by liquid air and for 15 minutes after the liquid air bath had been removed. The supernatant ether solution was decanted from the yellow precipitate. The solution and the precipitate were hydrolyzed and worked up separately in the usual manner.

The evaporation of the ether from the solution part of the reaction mixture gave the same oil containing about 0.2 g. of crystals melting at 101-102°. Some of these crystals were removed and dried on a porous plate, and tested for benzil by the method given in Mulliken (21). No violet color was formed when an alcohol solution of the compound was boiled with a little solid potassium hydroxide. The same amount of known benzil when treated in the same manner gave a beautiful deep violet color.

The usual waxy solid was obtained from the precipitate of

(21) Mulliken. The identification of pure organic compounds. John Wiley and Sons, New York, Vol.I, p.206. 1904.

the reaction mixture. When this solid was recrystallized from ligroin (80-150°) 2.65 g. (13.8%) of phenylbenzoin was obtained, melting at 84-85°.

Experiment No.8. The only difference between this experiment and Experiment No.7 was that only 0.1 mole of phenylmagnesium bromide was used with 0.1 mole of oxalyl chloride. Liquid air cooling was used, and the reaction product was worked up in the same manner.

After evaporating the ether from the solution part of the reaction mixture there remained an oil containing a few crystals. Some of these crystals were removed, and after pressing on a porous plate started to melt at 97°. The unmelted part started to decompose slowly at 120°. This substance was also tested for benzil by the method of Mulliken (21) but no violet color was obtained.

The evaporation of the ether from the precipitate of the reaction mixture left an oil containing a few needle shaped crystals. Some of these crystals were removed and dried on a porous plate. They melted at 102°. A mixed melting point determination with some of the crystals obtained from the solution part of the reaction mixture of Experiment No.7 showed no depression. The oil all solidified after standing a few days and the fractional crystallization of this solid in ligroin (80-150°) gave only 1.0 g. (10.4%) of phenylbenzoin, m.p. 79-80°.

DISCUSSION OF RESULTS

The results of the various experiments are summarized in Table I.

Table I.

Results of Experiments

Exp. No.	Reactants		Cooling Medium	Products		
	Oxalyl Chloride: Moles	C_6H_5MgBr: Moles		Benzil: g.	Phenylbenzoin g.	(a) %
1	0.1	0.2	ice - salt	0.0	3.70	19.3
2	0.1	0.2	ice - salt	0.0	4.75	24.7
3	0.1	0.2(b)	ice - salt	0.0	3.30	17.2
4	0.1	0.2(c)	CO_2 - ether	0.0	5.10	26.5
5	0.1	0.1	ice - salt	0.0	1.55	16.2
6	0.1	0.1	CO_2 - ether	0.0	2.70	28.1
7	0.1	0.2	liquid air (-130°)	0.0	2.65	13.8
8	0.1	0.1	liquid air (-130°)	0.0	1.00	10.4

a. All percentage yields are based on the amount of phenyl-magnesium bromide used.

b. Lead tetraethyl (1.0 g.) was used as a negative catalyst in this experiment.

c. In this, and all following experiments, the precipitate in the reaction mixture was separated from the solution before hydrolysis and each part worked up separately.

From these results it can be seen that the lowering of the temperature from that of an ice-salt mixture to -130°C. had no effect on the formation of benzil. The decreased yield of
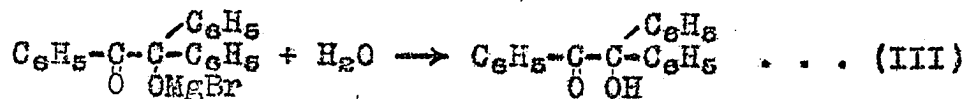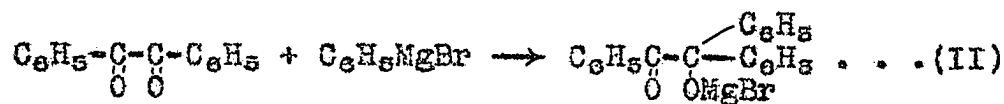
phenylbenzoin in the two liquid air experiments indicates that
the result of the extremely low temperature was a slowing down
of the rates of reaction of the phenylmagnesium bromide with
the chlorine atoms and the carbonyl groups to the same extent.

The only effect of having a 100% excess of oxalyl chlor-
ide was a decrease (compared with the amount formed under sim-
ilar conditions with no excess of oxalyl chloride) in the
amount of phenylbenzoin formed in two experiments, and an in-
crease in one experiment. There was no benzil formed even in
the presence of excess oxalyl chloride. A too critical compar-
ison of the amounts of phenylbenzoin formed in the different
experiments should not be made, since different methods of work-
ing up the reaction products were used in the various experi-
ments; and on account of the limited time available for this
problem the total quantities of phenylbenzoin formed may not
have been completely isolated in all of the experiments.

The absence of any benzil, and the formation of phenyl-
benzoin, in the products of the reaction of oxalyl chloride
with phenylmagnesium bromide can be interpreted as follows.
The rate of reaction of phenylmagnesium bromide with one of
the carbonyl groups of benzil is probably greater than its
rate of reaction with the chlorine atoms in oxalyl chloride.
Some benzil is probably formed during the first part of the re-
action and this then reacts with more Grignard reagent to give
phenyl benzoin (22) in accordance with the following reactions:

(22) Phenylbenzoin has been obtained by Acree (Ber., 37, 2753-

$$C_6H_5-\underset{O}{\underset{\|}{C}}-\underset{O}{\underset{\|}{C}}-C_6H_5 + C_6H_5MgBr \longrightarrow C_6H_5\underset{O}{\underset{\|}{C}}-\underset{OMgBr}{C}\diagdown^{C_6H_5}_{C_6H_5} \quad \ldots (II)$$

$$C_6H_5-\underset{O}{\underset{\|}{C}}-\underset{OMgBr}{C}\diagup^{C_6H_5} + H_2O \longrightarrow C_6H_5-\underset{O}{\underset{\|}{C}}-\underset{OH}{C}\diagup^{C_6H_5} \quad \ldots (III)$$
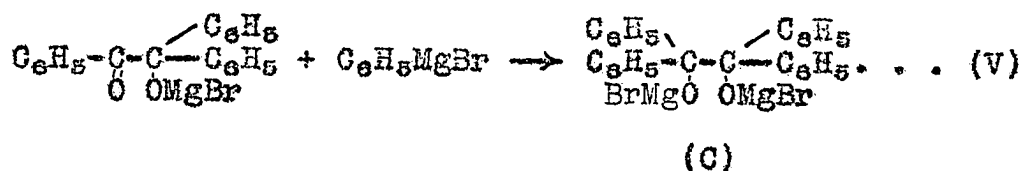
The low yield of phenylbenzoin leaves a large amount of oxalyl chloride and phenylmagnesium bromide unaccounted for. There is the possibility of a chain type of reaction taking place of the type shown by the following equation:

$$C_6H_5-\underset{O}{\underset{\|}{C}}-\underset{OMgBr}{C}\diagup^{C_6H_5} + Cl-\underset{O}{\underset{\|}{C}}-\underset{O}{\underset{\|}{C}}-Cl \longrightarrow C_6H_5-\underset{O}{\underset{\|}{C}}-\underset{O\underset{\|}{C}-\underset{\|}{C}-Cl}{C}\diagup^{C_6H_5} + MgBrCl \quad (IV)$$

(A)   (B)
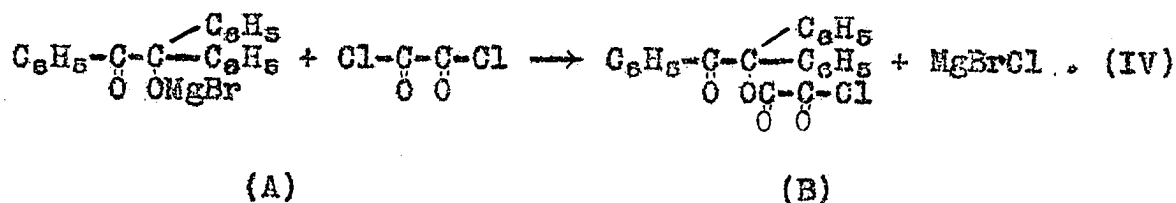
(B) could then react further with phenylmagnesium bromide, intermediate product (A) or some other intermediate product of the same type. Of course, some of the phenylmagnesium bromide could react with intermediate product (A) as follows:

$$C_6H_5-\underset{O}{\underset{\|}{C}}-\underset{OMgBr}{C}\diagup^{C_6H_5} + C_6H_5MgBr \longrightarrow \underset{BrMgO}{\overset{C_6H_5\diagdown}{C}}-\underset{OMgBr}{C}\diagup^{C_6H_5} \quad \ldots (V)$$

(C)

and this intermediate product (C), after hydrolysis, would give benzopinacol; or it could react further with oxalyl chloride to give more complex esters. The existence of such esters

(22 cont.)
    2764 (1904)) in an almost quantitative yield from the reaction of benzil with phenylmagnesium bromide. Acree added the phenylmagnesium bromide (0.048 mole) to an ether solution of 0.038 mole of benzil, cooled by a freezing mixture. At the end of the addition the reaction mixture was refluxed for an hour.

could probably be proved by hydrolyzing the residues in the experiments with dilute alkali and identifying any acids or alcohols that formed.

The difficulty experienced in crystallizing the reaction products seems to be good evidence that some of these other possible products were formed. However, on account of the limited amount of time available for the investigation of this problem, it was not possible to completely separate the residues into their components.

Since there was no benzil isolated in these experiments, the reaction of oxalyl chloride with other arylmagnesium halides was not investigated, for phenylmagnesium bromide is a typical arylmagnesium halide.

It would be interesting to carry out a reaction between oxalyl chloride and an insufficient quantity of phenylmagnesium bromide at the temperature of a refluxing ether solution. Perhaps the activity of the chlorine atoms at this higher temperature would be such that the phenylmagnesium bromide would react with them in preference to the carbonyl groups.

SUMMARY AND CONCLUSIONS

It has been shown that the reaction between oxalyl chloride and arylmagnesium halides is not a suitable method for the preparation of α-diketones. Phenylbenzoin is the only product that has been isolated from the reaction of oxalyl chloride with phenylmagnesium bromide in ether solution at temperatures of an ice and salt mixture, an ether and solid carbon dioxide mixture and at -130°C.