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# I. Furfural and some of its derivatives; II. The relative reactivities of some organometallic compounds of group II elements

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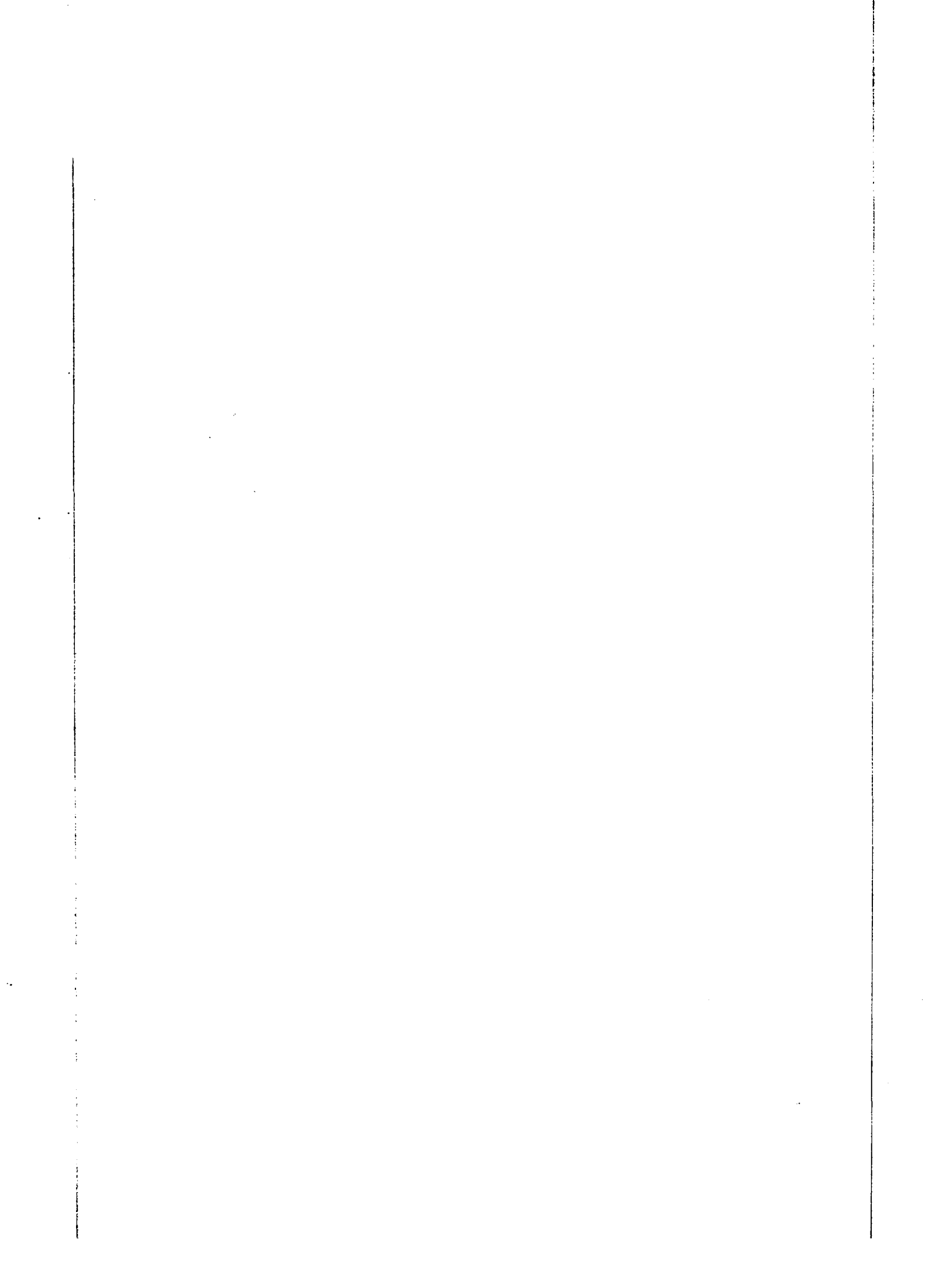
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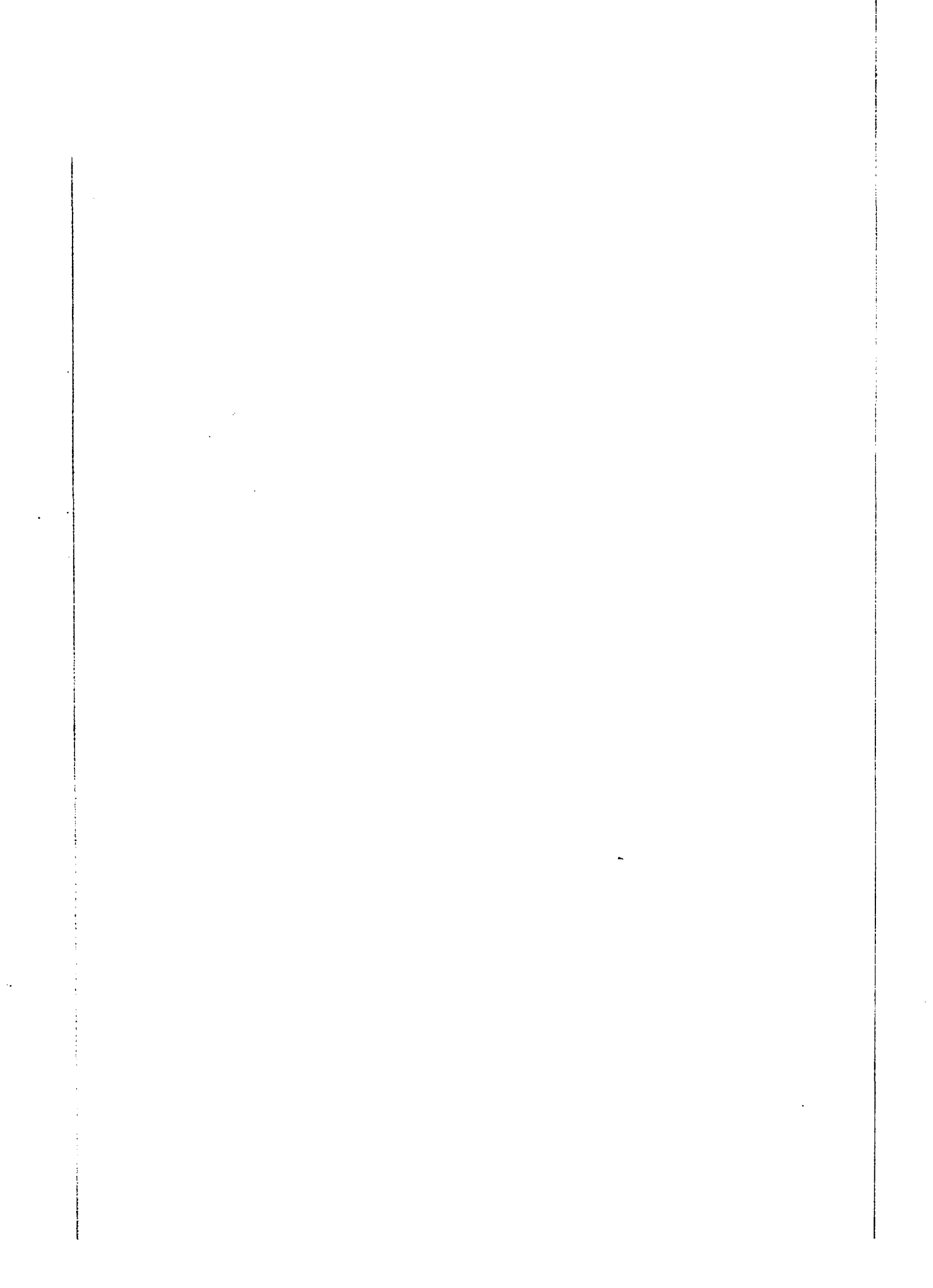
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I. PERFLUORAL AND SOME OF ITS DERIVATIVES.

II. THE RELATIVE REACTIVITIES OF SOME  
ORGANOMETALLIC COMPOUNDS OF  
GROUP II ELEMENTS.

By

Robert E. Brown

A Thesis submitted to the Graduate Faculty  
for the Degree of

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Major subject Organic Chemistry

Approved

Signature was redacted for privacy.

In charge of Major work.

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Head of Major Department.

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Dean of Graduate College.

Iowa State College  
1930

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PARTS I and III

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## PART I

### FURFURAL AND SOME OF ITS DERIVATIVES

#### INTRODUCTION

In recent years many waste products have excited much interest because they often present serious problems of disposal, and because they are often potential sources of income. Very frequently an aggravating waste has been turned into profitable products. A familiar example of this kind of waste is furnished by the petroleum industry whose once troublesome gasoline is now an object of research, of production, and a source of great revenue. More recently "Celotex", an insulating fiber board, was developed from sugar cane stalks, and corn stalks are now being used for the same purpose.

It has been known for many years that furfural could be obtained from many natural materials such as bran, oat hulls, corn cobs, certain woods, etc., but not until the last few years has this aldehyde been prepared in large quantities. Furfural is now being made, as a commercial product, from oat hulls; a by-product of certain cereal manufacture.

At the present time furfural is used chiefly in the manufacture of moulding resins and compounds and as a solvent. It is probable that furfural may be of considerable importance

as a synthetic reagent for the production of organic compounds.

Because the chemistry of furfural had not been too extensively studied it seemed advisable to attempt the better preparation of those derivatives of furfural which are now of some commercial or scientific importance. The study of the synthesis of furylacrylic acid by the Perkin condensation<sup>1</sup> resulted in an improvement in the method of preparation and in the yield of the acid. Ethyl  $\beta$ -furylacrylate was also the subject of a series of studies<sup>2</sup> which resulted in a great improvement in the yield of the ester. From this ester, furylacrylic acid, or its sodium salt, can easily be produced.

Furfural can be reduced by catalytic methods to tetrahydrofurfuryl alcohol. This alcohol was made the basis of a series of studies, the first being some attempts to split the ring, the second being the preparation of the halides of the alcohol. Although the tetrahydrofurfuryl chloride, bromide, and iodide were prepared no Grignard reagent could be obtained by treating them with magnesium in the usual manner.

The author is grateful to the Miner Laboratories of Chicago for supplies of furfural and of tetrahydrofurfuryl alcohol.

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1. Gilman, Brown, Wright and Hewlett, Iowa State College Journal of Science, 4, 355 (1930).
  2. Gilman, Brown and Jones, Iowa State College Journal of Science, 2, 317 (1928).

EXPERIMENTAL PART

PREPARATION OF FURYLACRYLIC ACID

A mixture of 288 g. (3.0 moles) of redistilled furfural, 432 g. (5.27 moles) of fused sodium acetate, and 432 g. (4.23 moles) of acetic anhydride was placed in a two liter round bottom flask which was fitted with a reflux condenser bearing a calcium chloride tube. The flask was heated in an oil bath at 150°. At the end of two hours heating most of the sodium acetate had dissolved and the reaction mixture had become dark brown in color. At the end of six hours heating there was little change in the color of the mixture but a large amount of solid had separated out. At the end of eight hours heating there were some evidences of decomposition, so the oil bath was removed. After cooling the reaction product was extracted with 5% sodium carbonate solution. The extract was filtered to remove a large, black residue and the filtrate was acidified with hydrochloric acid which caused the precipitation of the voluminous, light brown furylacrylic acid. The acid was filtered off by suction and washed twice with cold water to remove furfural and chlorides. The acid was then crystallized from hot water, filtered, washed once with cold water, and dried over calcium chloride. The yield of fury-

lacrylic acid was 191 g. or 46% of the theoretical yield based on the furfural used.

PREPARATION OF FURACRYLOYL CHLORIDE

To 34.5 g. (0.25 mole) of furylacrylic acid were added, with cooling, 34.2 g. (0.287+ mole, i.e. 15% excess) of thionyl chloride. The mixture remained solid and there was no evidence of reaction. 50 cc. of dry ether were now added and most of the mixture dissolved in the ether. There was still no apparent reaction so the solution was carefully warmed to about 30°. A brisk evolution of gas soon started and the mixture became very cold. Gentle warming was continued until no further reaction took place. The mixture was allowed to stand over night at room temperature and the ether and excess of thionyl chloride were distilled off with a water pump. Furacryloyl chloride was then distilled off at 78°-80° / 5 mm. pressure. The distillate was a light yellow oil with a rather sharp odor. The acid chloride crystallized to a light yellow, crystalline solid which melted at about 50°. The yield was 29 g., 74.1%.

PREPARATION OF THE ANILIDE OF FURYLACRYLIC ACID

To a solution of 15.6 g. (0.1 mole) of furacryloyl chloride in 60 cc. of dry ether was slowly added a solution of 18.3 g. (0.2 mole) of aniline in 150 cc. of dry ether. The addition of the aniline solution gave rise to a vigorous exothermic reaction. As soon as the aniline solution was added a light brown precipitate appeared and this precipitate increased in volume as more aniline solution was allowed to react with the acid chloride solution. After all of the aniline had been added the mixture was allowed to stand for two hours at room temperature. The reaction mixture was then poured into 200 cc. of water, the ether was distilled off and the residue was filtered off, washed three times with small amounts of water, and finally recrystallized from hot 95% ethyl alcohol. The recrystallized product was filtered, washed three times with water, and then dried over calcium chloride. The product was a solid of a light pink color, m.p. 135°. The yield was 15 g., or 70.4% of the theoretical.

Anal. Calcd. for  $C_{12}H_{11}O_2N$ , N6.58. Found: N 6.43.

PREPARATION OF THE P-PHENETIDE OF FURYLACRYLIC ACID

A solution of 27.5 g. (0.2 mole) of p-phenetidine in 150 cc. of dry ether was slowly added to a solution of 15.6 g. (0.1 mole) of furacryloyl chloride in 75 cc. of dry ether. A vigorous reaction started as soon as the first solution was added and a light yellow precipitate appeared. After all of the solution of p-phenetidine had been added the reaction mixture was allowed to stand over night. It was then poured into 200 cc. of water and the ether was distilled off. The yellow precipitate was filtered off and it was washed twice with small amounts of warm water. This product was recrystallized from 95% ethyl alcohol. The yield was 21 g. or 82% of the theoretical, m. p. 166°.

Anal. Calcd. for  $C_{15}H_{15}O_3N$ , N 5.45. Found: N 5.34.

ATTEMPTED SPLITTING OF TETRAHYDROFURFURYL ALCOHOL  
BY HYDROGEN CHLORIDE

One-fourth mole, 25.5 g., of tetrahydrofurfuryl alcohol was placed in a 100 cc. side arm Erlenmeyer flask and dry hydrogen chloride gas was passed into the flask in a slow

stream. The alcohol became warm and its temperature soon reached about  $70^{\circ}$ . Almost as soon as the gas was passed into the flask the alcohol began to turn dark, and, as more and more gas was introduced and as the temperature rose, the contents of the flask became almost black. Hydrogen chloride was passed into the alcohol until no further absorption of the gas appeared to take place. This took about 1.5 hours. The flask was stoppered, the side tube was protected by a calcium chloride drying tube, and the mixture was allowed to stand for three hours at room temperature. Hydrogen chloride gas was again passed into the flask as before, but no further change took place.

The reaction mixture was then subjected to fractional distillation at reduced pressure. Twelve grams of a colorless distillate, boiling at  $71.5^{\circ}$  to  $72^{\circ}/12$  mm. pressure were obtained. This distillate was soluble in water and it gave the Beilstein test for halogen, but after distillation at atmospheric pressure, boiling point  $175^{\circ}$  to  $174^{\circ}$ , it showed only a very faint Beilstein test. These distillates consisted of the unchanged tetrahydrofurfuryl alcohol. There remained a large amount of black, tarry, undistillable material in the distilling flask. X

Because the reaction of tetrahydrofurfuryl alcohol and hydrogen chloride was so vigorous and gave rise to so great decomposition it was decided to modify the reaction by

the use of an inert diluent and a lower temperature. A second treatment of the alcohol with hydrogen chloride was carried out in the following manner. One-half mole, 51 g., of tetrahydrofurfuryl alcohol was mixed with 50 cc. of pure dry benzene in <sup>a</sup> 250 cc. Erlenmeyer flask provided with a two hole rubber stopper carrying an inlet tube for hydrogen chloride and an outlet tube protected by a calcium chloride drying tube. After the flask had been well cooled in an ice bath, dry hydrogen chloride was slowly passed into the alcohol-benzene solution. The solution turned a greenish black color soon after the gas was introduced and this color deepened considerably as more gas passed in. After the solution was saturated it was allowed to stand for 24 hours at room temperature. The solution was then divided into two equal portions of which one was immediately distilled at reduced pressure. This aliquot yielded 18 g. of tetrahydrofurfuryl alcohol and considerable black, tarry residue.

The second aliquot was gently refluxed for an hour and a half while a slow stream of dry hydrogen chloride gas was passed into the flask. The solution was cooled to room temperature and it was again saturated with hydrogen chloride, allowed to stand 3 hours at room temperature, and then fractionally distilled at reduced pressure. 16.5 g. of tetrahydrofurfuryl alcohol, boiling at 71.5 - 72° / 12 mm. pressure were recovered. There was also obtained a distillate of 5 g. boiling



at 72 - 105° / 12 mm. This distillate became reddish in color on exposure to air. It was also soluble in water and it contained only traces of halogen. This small fraction could not be successfully separated by fractionation so an attempt was made to prepare it in larger amount.

One-half mole, 51 g., of tetrahydrofurfuryl alcohol in 50 cc. of benzene was cooled in an ice bath and it was then saturated with dry hydrogen chloride gas. The solution became dark as before. After saturation with hydrogen chloride the solution was gently refluxed for six hours without the addition of more hydrogen chloride and for a further period of seven hours hydrogen chloride was slowly passed into the refluxing mixture. The solution, which was now black in color, was cooled and distilled at reduced pressure. After the benzene had been distilled off the fraction consisting of tetrahydrofurfuryl alcohol was collected. This fraction was 36 g. There was also a fraction, boiling at 72 - 106° / 12 mm., of 9.5 g. The latter fraction was combined with the previous similar one and the combined fractions were carefully distilled from a modified Claisen flask with a good fractionating column. At 12 mm. pressure a fraction of 7.5 g. of a colorless distillate boiling at 71 - 72° was collected. This was tetrahydrofurfuryl alcohol. About 5 g. of a distillate were collected between 72° and 105°. This distillate was soluble in water and it contained no halogen. In attempting to distil the latter fraction

at atmospheric pressure it decomposed rapidly at temperatures above 140°, and no distillate could be obtained.

ATTEMPTED SPLITTING OF TETRAHYDROFURFURYL ALCOHOL  
BY HYDROGEN BROMIDE

An attempt was now made to split the ring of tetrahydrofurfuryl alcohol by means of hydrogen bromide. One-half mole, 51 g., of tetrahydrofurfuryl alcohol in 50 cc. of benzene was cooled in ice and then saturated with dry hydrogen bromide. As in the previous cases of the treatment of the alcohol with a hydrogen halide the solution soon turned dark. After standing for 24 hours at room temperature in a closed flask the solution was gently refluxed for three hours while a slow stream of hydrogen bromide was passed into the flask. The mixture was fractionally distilled at 12 mm. pressure. A considerable fraction was obtained boiling between 65° and 72°. This fraction contained much halogen and it was only partly miscible with water. Therefore it was well shaken with water and the insoluble layer was separated and dried with calcium chloride. On distillation at atmospheric pressure it boiled at 160 - 161°. This distillate was analyzed by the Carius method and it was found to be tetrahydrofurfuryl bromide<sup>3</sup>.

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3. Dox and Jones, J. Am. Chem. Soc., 50, 2033 (1928).

The yield of bromide amounted to 17 g., or 20.6% of the theoretical yield.

As in the cases of the treatment of tetrahydrofurfuryl alcohol with hydrogen chloride there was here, also, no evidence of scission of the ring.

#### PREPARATION OF TETRAHYDROFURFURYL CHLORIDE

It has previously been shown that the action of hydrogen chloride on tetrahydrofurfuryl alcohol did not produce tetrahydrofurfuryl chloride. The chloride was therefore made by the action of thionyl chloride on the alcohol<sup>4</sup>.

23.8 g., (0.2 mole) of thionyl chloride was slowly added to 50 cc. of pyridine which had been dried over sodium hydroxide and distilled. The addition was accompanied by the evolution of much heat and the resulting solution was dark brown in color. This solution was slowly added to a solution of 20.4 g., (0.2 mole) of tetrahydrofurfuryl alcohol in 30 cc. of pure, dry pyridine. Considerable heat was evolved as these two solutions were mixed, and when all of the thionyl chloride solution had been added the mixture stood at room temperature for two hours, after which it was gently refluxed for one-half hour. The whole reaction mixture was distilled with a

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4. Kisner, J. Am. Chem. Soc., 52, 3251 (1930).

water pump and the dark colored distillate was poured into about 100 cc. of water. Concentrated hydrochloric acid was added to the solution until the latter no longer fumed on the addition of the acid. The whole mixture, after cooling, was extracted twice with 50 cc. of ether (each time), the combined ether extracts were dried over calcium chloride and distilled. Ten grams of tetrahydrofurfuryl chloride, boiling at 149 - 149.5° were obtained. The chloride is an almost colorless liquid of faint yellow tinge.

Anal. Calcd. for  $C_5H_9OCl$ , Cl 29.53. Found:  
Cl 29.54.

A second preparation of the chloride under somewhat modified conditions was only slightly superior in yield. To 51 g. (0.5 mole) of tetrahydrofurfuryl alcohol in 40 cc. of pure dry pyridine was added a solution of 60.5 g. (0.55 mole) of thionyl chloride in 60 cc. of dry pyridine. The reaction gave off heat and turned dark brown. After two hours refluxing the mixture was distilled and worked up exactly as in the previous run. A yield of 28 g. or 46.5% of the theoretical, was obtained.

PREPARATION OF TETRAHYDROFURFURYL IODIDE

In an attempt to prepare tetrahydrofurfuryl iodide by the action of dry hydrogen iodide on the tetrahydrofurfuryl alcohol no iodide was obtained. The reaction produced a great amount of black decomposition products, and about 50% of the alcohol was recovered. Therefore the preparation of the iodide was attempted by a metathetical reaction of the chloride and sodium iodide.

12 g. (0.1 mole) of tetrahydrofurfuryl chloride were added to a solution of 16 g. (0.2 mole) of dried sodium iodide in 80 cc. of pure acetone in a 150 cc. Erlenmeyer flask. The flask was tightly stoppered and put in a dark place. After several days a small, white precipitate had appeared and the solution was light brown in color. At the end of two weeks the solution had turned to a dark brown and the precipitate had increased considerably in amount. The acetone was then distilled off with a water pump and the residue was treated with 50 cc. of water to dissolve the sodium halides. This mixture was thrice extracted, first with 50 cc. of ether, and twice more with 10cc. portions of ether each time. The combined ether extracts were dried by shaking with calcium chloride in a separatory funnel for about one-half hour. Distillation at 3 mm. pressure produced 6 g. of unchanged chloride, and 4 g.

of an almost colorless liquid at 69 - 70°. This distillate darkened slowly on exposure to air. This 4 g. distillate was the tetrahydrofurfuryl iodide.

Anal. Calcd. for  $C_5H_9OI$ , I 60.09. Found: I 59.54.

THE REACTION OF TETRAHYDROFURFURYL  
CHLORIDE WITH MAGNESIUM

4.8 g. (0.2 atom) of magnesium turnings were placed in a 200 cc., 3-neck, round bottom flask which was fitted with a dropping funnel, a mercury seal stirrer, and a reflux condenser which had a calcium chloride - soda lime tube at its top. About 15 cc. of dry ether were added to the flask and then 2 g. of tetrahydrofurfuryl chloride were added to the flask. After half an hour there was no evidence of reaction and no color test developed by treating the ether solution with Michler's ketone<sup>5</sup>. The contents of the flask were heated to the boiling point for 15 minutes but still no color was obtained. Two grams more of the halide were added and the solution was refluxed for 15 minutes more without any reactions having taken place. Several small crystals of iodine were added to the contents of the flask. The iodine color gradually spread through the solution and the color finally disappeared. A

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<sup>5</sup>. x Gilman and Heck, Rec. trav. chim., 48, 193 (1929).

test of the solution then showed that no Grignard reagent had been formed. Two grams of activated magnesium<sup>6</sup> were now added and the solution was refluxed, with stirring, for three hours but this treatment did not result in the reaction of the halide with the magnesium. Finally 30 cc. of a 20% solution of the halide and 5 g. of activated magnesium were added to the flask and the solution was gently refluxed for ten hours. At the end of this time there was no evidence of reaction. The solution did not give the color test with Michler's ketone.

REACTION OF TETRAHYDROFURFURYL BROMIDE  
WITH MAGNESIUM

Five cc. of a 20% solution of tetrahydrofurfuryl bromide in ether were added to about 0.2 g. of powdered magnesium in a dry test tube. The tube was stoppered, and after an hour, there was no reaction. The tube was warmed until the ether began to boil but still no reaction occurred. A second run, identical with the first one except that the magnesium was replaced with about 0.5 g. of activated magnesium showed no reaction in the cold. On warming the tube a very

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6. Gilman, Peterson and Schultze, Rec. trav. chim., 47, 19 (1928).

vigorous reaction took place but the solution did not produce a color test. This latter run was repeated twice, but in no case was there any evidence of a Grignard reagent.

REACTION OF TETRAHYDROFURFURYL  
IODIDE WITH MAGNESIUM

A gram of tetrahydrofurfuryl iodide in four cc. of dry ether was added to about 0.2 g. of powdered magnesium in a dry test tube. No reaction had taken place after one hour. The solution was gently boiled for ten minutes but no reaction took place. The stoppered test tube showed no evidence of reaction after standing for twelve hours. 0.5 g. of activated magnesium was then used in the place of the powdered magnesium in the above experiment with the same reagents. No reaction took place in the cold, and on warming the mixture a vigorous reaction took place. The ether solution gave no color test. This work was repeated once more with identical results.



PREPARATION OF THE TETRAHYDROFURFURYL ESTER  
OF P-TOLUENESULFONIC ACID

The preparation of the tetrahydrofurfuryl ester of p-toluenesulfonic acid was accomplished by means of the technique of Gilman and Beaber<sup>7</sup> for the preparation of similar esters.

To a solution of 95.3 g. (0.5 mole) of p-toluenesulfonyl chloride in 350 cc. of dry ether in a 500 cc. Erlenmeyer flask were added 51 g., (0.5 mole) of tetrahydrofurfural alcohol. The solution was cooled in an ice-salt bath to zero and finely powdered potassium hydroxide was added in small portions until 56 g., (1.0 mole) had been added. During the addition the temperature of the solution was not allowed to rise above 5°. The flask was well stoppered and it was allowed to stand, with frequent shaking, for two hours in an ice bath. After the reaction had ceased the contents of the flask were creamy-white and somewhat viscous. The mixture was poured into 800 cc. of ice water and it was then well stirred up. The ether layer was separated and the water layer was extracted twice with 100 cc. and 50 cc. of ether, respectively. The combined ether extracts were dried over potassium carbonate and the ether was distilled off on the water bath.

The remaining mass was a light yellow, somewhat viscous

7. Gilman and Beaber, J. Am. Chem. Soc., 47, 518 (1925).

liquid. The last traces of ether were removed by heating the liquid on the water bath at the pressure of a good water pump. This liquid was divided into equal portions and the distillation of each portion was attempted.

The first portion of the ester was placed in a 500 cc. Claisen flask, which was heated by an oil bath, and distillation was attempted at 1 mm. pressure. The temperature of the oil bath was slowly raised and a small amount of distillate boiled over at 120°. While changing the receiver the ester in the Claisen flask decomposed violently. The distillation of the second portion of the ester was attempted under the same conditions except that no attempt was made to change receiver. As before a small amount of distillate appeared at about 120° with the oil bath at about 145°. The temperature of the bath was slowly raised and at about 155° the ester in the flask commenced to darken very slightly. As the temperature of the bath was slowly increased the ester became darker and darker. At 180° it became so dark that the source of heat was removed. In spite of the removal of heat further decomposition took place and suddenly the ester foamed up into a dark brown, almost black, froth which quickly filled the whole distilling apparatus. The pressure on the distilling system, except at the very end, did not exceed 1 mm.

A second amount of the ester was made exactly accord-

ing to the directions given above, but instead of trying to distil the product it was heated in an oil bath at 145 - 150°/ 1 mm. to remove volatile ingredients. The ester was cooled in the flask without releasing the pressure until all danger of decomposition had passed. The product was a light yellow, slightly viscous liquid. The yield of the ester was 119 g., 93% of the theoretical. X

Anal. Calcd. for  $C_{12}H_{14}O_4S$ . S 12.50. Found:  
S 12.09, 12.03.

#### PREPARATION OF TETRAHYDROFURFURYL-PHENYL-METHANE

The reaction of alkyl sulfonates with Grignard reagents has been formulated by Gilman and Beaber<sup>7</sup> thus:



but Gilman and Heck<sup>8</sup> have shown that this reaction gives rise to the alkyl halides, and this reaction might be a source of tetrahydrofurfuryl halides.

To a solution of 0.5 mole of benzylmagnesium chloride in 400 cc. of ether a solution of 102.4 g. (0.4 mole) of tetrahydrofurfuryl p-toluene sulfonate in an equal volume of ether

8. Gilman and Heck, J. Am. Chem. Soc., 50, 2223 (1928). This paper contains leading references to the reactions of alkyl sulfonates and organomagnesium halides.

was slowly added with stirring. A gentle reaction took place when the ester was added to the Grignard reagent and after about half of the ester had been added the mixture in the flask separated into two layers, the lower one a heavy, viscous paste, the upper a mobile ether solution. After the whole of the ester had been added the mixture was stirred as well as could be done for three hours. As much of the mixture as could be poured out of the flask was hydrolyzed by means of ice water; that remaining in the flask was hydrolyzed by adding ice to the flask. These combined portions were extracted well with ether and the ether solutions were dried over anhydrous potassium carbonate. After the ether had been distilled from the solution the remaining oil was distilled at 14 mm. At this pressure 15 g. of a pale yellow liquid distilled at 133°. This was tetrahydrofurfuryl-phenyl-methane. A large, almost black, tarry residue could not be distilled or hydrolyzed by sodium hydroxide. No halide was obtained.

Anal. Calcd. for  $C_{12}H_{14}O$ , C 81.81, H 9.16.

Found: C 81.69, H 9.20.

#### PREPARATION OF FURYLACROLEIN<sup>9</sup>

To 2 l. of water at 0° in a 5 l. flask were added 10 g. (0.25 mole) of sodium hydroxide. The water solution was

2. furfural

well stirred with a mechanical stirrer and after the alkali had dissolved the flask was surrounded by an ice bath. To the solution in the flask a solution of 88 g. (2.0 moles) of acetaldehyde in 220 cc. of solution was slowly added from a dropping funnel. After about 20 cc. of the aldehyde solution had been added a yellow crystalline precipitate appeared and it increased in amount during the 3 1/2 hours in which the acetaldehyde solution was added. Stirring was continued for an hour and a half longer and the crystalline product was filtered from the solution. The precipitate was washed five times with small amounts of cold water and then dried over calcium chloride. The dried product was then fractionally distilled under reduced pressure. The furylacrolein boiled at 91°/10 mm. and crystallized to a yellow solid which melted at 52°. The yield was 55 g. or 45% of the theoretical.

Furylacrolein was also prepared by the directions of Ivanoff<sup>10</sup>. 96 g. (1.0 mole) of furfural and 88 g. (2.0 moles) of acetaldehyde were placed in a 5 l. flask. About 500 g. of ice were then added and mechanical stirring was started. 30 g. a 20% solution<sup>?</sup> were then added to the contents of the flask.

The flask was placed in an ice bath and ice was added to the flask from time to time as it was needed. At the end of five hours stirring about 2000 g. of ice had been added

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9. Konig and Hey, Frdl., 13, 110 (1923).

10. Ivanoff, Bull. soc. chim., 35, 1658 (1924).

to the flask. The sodium hydroxide was now neutralized with acetic acid, the solution was extracted with 300 cc. of ether and then with two successive portions of 100 cc. of ether. The combined ether extracts were washed well with water, and dried over calcium chloride. The ether was distilled off and the furylacrolein was distilled at  $76-77^{\circ}/4$  mm. The yield was 50 g. or 41% of the theoretical.

#### REDUCTION OF FURYLACROLEIN

The catalytic reduction of furylacrolein has been carried out by Adams and Bray<sup>11</sup> with the platinum oxide catalyst that was developed by Adams and Shriner<sup>12</sup>. The reduction of furylacrolein gave rise to several products depending on the amount of hydrogen that was added and on the promoter that was used. Using a little ferrous sulfate with the platinum oxide catalyst and adding 4.2-4.4 molecular equivalents of hydrogen the chief product was tetrahydrofurylpropyl alcohol boiling at  $106-107^{\circ}/2$  mm.

The platinum oxide catalyst for this reduction was made strictly in accordance with the directions of Adams and Shriner and the reduction of the aldehyde was carried out after the directions of Adams and Bray. 0.2 g. of platinum oxide and

11. Adams and Bray, J. Am. Chem. Soc., 49, 2101, (1927).

12a). Adams and Shriner, J. Am. Chem. Soc., 45, 2171 (1923).

12b). Hewlett, Doctoral Thesis, Iowa State College, 1930.

and 50 cc. of 95% alcohol were placed in the reduction vessel and reduction to platinum black was effected by means of hydrogen at about 40 lbs. pressure. The reduction vessel was opened and 50 cc. more of 95% alcohol, 0.0055 g. (0.00002 mole) of crystallized ferrous sulfate, and 24.4 g. of furylacrolein were added to it. The vessel was evacuated to the vapor pressure of alcohol and then hydrogen was admitted at 40 lbs. pressure, after the vessel had been shaken for about ten minutes. The catalyst was reactivated once each hour until six reactivations had been made. After that time about one-half of the hydrogen was absorbed so readily that the reaction mixture became warm. The last portions of hydrogen were absorbed only very slowly. The total time for the addition of 4.4 molecular equivalents of hydrogen was about 20 hours. The contents of the reaction vessel were filtered by suction through a small filter and the residue of platinum black was carefully washed with alcohol and recovered. The filtrate, a slightly brownish solution was then distilled. After the alcohol had been distilled off the system was connected to a good oil pump. A colorless distillate, which came over at 106 -107° was collected as the alcohol. This fraction amounted to 12 g. or 46.1% yield. Heptane-diol 1, 4 boiling at 120 -122°/4 mm. was obtained in 10% yield.

All attempts to obtain the 3,5-dinitrobenzoate of tetrahydrofurylpropyl alcohol by the methods of Adams and Bray failed to produce a solid derivative. Molecular equivalents

of the alcohol and of 3,5-dinitrobenzoyl chloride were warmed on a water bath for three hours, but on the addition of water the ester was not obtained. In another attempt the mixture of the alcohol and acid chloride was heated on the water bath for three hours and then allowed to stand over night. This attempt, and another identical one, failed to produce the expected derivative.

The preparation of the alcohol from furylacrolein was again tried exactly as before. The alcohol was obtained in 50% yield but, as before the 5,5-dinitrobenzoate could not be made. No attempt was made to make the acetate of this alcohol because of its less desirable physical properties.

Because tetrahydrofurylpropyl alcohol could not be identified work on it was dropped in order to take up apparently more fruitful research.

#### SUMMARY

Some derivatives of furfural have been made and described. The chloride, bromide and iodide of tetrahydrofurfuryl alcohol have been made and they have been shown to be inactive toward magnesium under a variety of conditions. Tetrahydrofurfuryl-p-toluene sulfonate has been prepared and described and its reaction product with benzylmagnesium chloride has been described. The preparation and reduction of furylacrolein have been described.



PART II

SOME ESTERS OF OXALIC ACID

INTRODUCTION

It has long been known that many natural organic substances such as cellulose, sugar, wood, etc. may be used as sources of oxalic acid. The usual process is to heat the finely divided substance with sodium or potassium hydroxide. The alkali oxalate is dissolved in water, precipitated as the calcium salt from which free oxalic acid solution may be obtained by treatment with sulfuric acid. Oxalic acid crystallizes from water with two molecules of water of crystallization.

The alcohols from which the following esters were prepared are relatively new ones. They were all prepared and donated by the Carbide and Carbon Chemicals Corporation.

The method that was used for the preparation of these esters is one that is very commonly used for the preparation of the esters of oxalic acid. It consists of heating together an excess of the alcohol with anhydrous oxalic acid. The water formed by the reaction can be slowly distilled off at atmospheric pressure if the mixture of the acid and alcohol is not too high boiling, but if a high boiling alcohol is used it is advisable to remove the water formed by the reaction by means of reduced pressure. In all cases the esters

were formed in good yields. None of the esters could be distilled at very low pressures, less than 2 mm. because decomposition and charring set in at higher temperatures.

These esters of oxalic acid are all apparently insoluble in water, but they are slowly hydrolyzed by cold water and rapidly by hot water. The esters all have pleasant odors, and they range in color from almost water-white to light brown.

A list of the alcohols, from which these esters were prepared, with their trade names, chemical names, formulas, boiling points and molecular weights is given in Table I.

Anhydrous oxalic acid was used for these preparations. It was prepared according to the directions of Organic Synthesis<sup>13</sup>.

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13. "Organic Synthesis," John Wiley and Sons, Inc., New York, 1, 67 (1921).

TABLE I

No.	Name	Formula	Boiling Point	Mol. Wt.
1.	"Methyl Cellosolve" Ethylene glycol monomethyl ether	$\begin{array}{l} \text{H}_2\text{C}-\text{OH} \\ \text{H}_2\text{C}-\text{O}-\text{CH}_3 \end{array}$	124.5° C.	76.08
2.	"Cellosolve" Ethylene glycol monoethyl ether	$\begin{array}{l} \text{H}_2\text{C}-\text{OH} \\ \text{H}_2\text{C}-\text{O}-\text{C}_2\text{H}_5 \end{array}$	134.8° C.	90.08
3.	"Butyl Cellosolve" <sup>+</sup> Ethylene glycol monobutyl ether	$\begin{array}{l} \text{H}_2\text{C}-\text{OH} \\ \text{H}_2\text{C}-\text{O}-\text{C}_4\text{H}_9 \end{array}$	170.6° C.	118.11
4.	"Carbitol" Diethylene glycol monoethyl ether	$\begin{array}{l} \text{CH}_2-\text{CH}_2-\text{OH} \\ \text{O} \\ \text{CH}_2-\text{CH}_2-\text{O}-\text{C}_2\text{H}_5 \end{array}$	198.0° C.	134.11
5.	"Butyl Carbitol" <sup>+</sup> Diethylene glycol monobutyl ether	$\begin{array}{l} \text{CH}_2-\text{CH}_2-\text{OH} \\ \text{O} \\ \text{CH}_2-\text{CH}_2-\text{O}-\text{C}_4\text{H}_9 \end{array}$	222.0° C.	162.14
6.	Diethylene glycol	$\begin{array}{l} \text{CH}_2-\text{CH}_2-\text{OH} \\ \text{O} \\ \text{CH}_2-\text{CH}_2-\text{OH} \end{array}$	245.0° C.	106.08

<sup>+</sup> The makers do not state which butyl isomer this compound is.

PREPARATION OF "METHYL CELLOSOLVE" OXALATE

4.5 g., (0.5 mole) of anhydrous oxalic acid and 114 g. (1.5 moles) of "methyl cellosolve" were placed in a 300 cc. Claisen flask. After the flask and its contents had been heated on the water bath for three hours it was gently boiled until the temperature of the distillate rose to 110°. The remainder of the excess alcohol was removed by the aid of a water pump, and an oil pump was attached to the system. No distillate was obtained at 3 mm. pressure when the oil bath surrounding the flask was at 150°. At temperatures above 150° decomposition seemed to take place. When the residue in the flask cooled down it solidified to a white crystalline mass with a slight yellow tinge. A sample of this product was crystallized from ethyl alcohol. It melted at 66 - 67°. The yield was 100 g. or 97%.

Anal. Calcd. for  $C_8H_{14}O_6$ , C 46.50, H 6.85.

Found: C 46.25, H. 6.72.

PREPARATION OF "CELLOSOLVE" OXALATE

45 g. (0.5 mole) of anhydrous oxalic acid and 135 g. (1.5 mole) of "Cellosolve" were placed in a 300 cc. Claisen

flask. This mixture was treated exactly like that in the reaction of "Methyl Cellosolve" and oxalic acid. This ester could not be distilled at 2 mm. at 140°. Above this temperature the liquid darkened somewhat. This ester is a very pale yellow, limpid liquid. The yield was 110 g. or 95%.

Anal. Calcd. for  $C_{12}H_{18}O_4$ . C. 51.28. H 7.75.

Found: C 51.34, H 7.82.

#### PREPARATION OF "BUTYL CELLOSOLVE" OXALATE

45 g., (0.5 mole) of anhydrous oxalic acid and 118 g. (1.25 mole) of "butyl cellosolve" were heated on the water bath for three hours. The mixture was then boiled gently, but after about 20 g. of distillate had come over the contents of the flask seemed to be decomposing somewhat. A sample of gas from the flask was passed into a solution of barium hydroxide and a voluminous white precipitate of barium carbonate appeared. The flask was then cooled and the remaining distillate was removed by a water pump and later by an oil pump. In the latter case the flask was heated by an oil bath at 140°. An unsuccessful attempt was made to distil this ester at 2 mm. pressure but above 150° it darkened somewhat and at higher temperatures decomposition took place. The yield of the ester was 130 g. or 90%. This ester is a slight-

ly yellow liquid of pleasant odor.

Anal. Calcd. for  $C_{11}H_{22}O_8$ . C 57.93, H 9.02.

Found: C 58.08, H 8.94.

#### PREPARATION OF "CARBITOL" OXALATE

45 g. (0.5 mole) of anhydrous oxalic acid and 161 g. (1.2 moles) of "carbitol" were heated together on the water bath for three hours. Distillation was then commenced with a water pump and when no more liquid distilled over at the temperature of the water bath further distillation was affected at 3 mm. by means of an oil pump. The flask was then heated to  $140^{\circ}$  in an oil bath but only a very small amount of distillate could be obtained at that temperature under 2 mm. to 3 mm. pressure. This ester could not be distilled at higher temperatures. When the flask containing the ester was cooled down the ester slowly crystallized to a waxy white solid which melted at  $74^{\circ}$ . The ester is almost odorless.

Anal. Calcd. for  $C_{11}H_{22}O_8$ . C 52.17, H 8.13.

Found: C 52.23, H 8.24.

PREPARATION OF "BUTYL CARBITOL" OXALATE

45 g. (0.5 mole) of anhydrous oxalic acid and 194 g. (1.2 moles) of "butyl carbitol" were heated together in the water bath for three hours. The system was then attached to a water pump and distillation was effected while the flask containing the reactants was heated on the water bath. This process gave rise to very little distillate so an oil pump was substituted for the water pump and the flask was heated in oil bath. Only when the oil bath temperature rose to 150° could no more distillate be obtained, and at higher temperatures the ester would not distil under 2 mm. pressure. The ester is a pale yellow liquid of slight, agreeable odor. The yield was 153 g. or 81%.

Anal. Calcd. for  $C_{18}H_{24}O_8$ , C 57.14, H 9.05.

Found: C 57.01, H 9.14.

PREPARATION OF DIETHYLENE GLYCOL OXALATE

45 g. (0.5 mole) of anhydrous oxalic acid and 58 g. (0.55 mole) of diethylene glycol were heated on the water bath for three hours. Because of the very high boiling point of the alcohol no attempt was made to distil off any portion by means of a water pump. The flask containing the reactants was heated with an oil bath at 120° and a small amount of distil-

late came over under 2 mm. pressure, but the oil bath had to be heated to 160° before no more distillate was obtained. At the latter temperature the ester darkened somewhat and there appeared to be considerable decomposition. The ester is a brownish-yellow, viscous liquid with almost no odor. The yield was 56 g. or 70.8%.

Anal. Calcd. for  $C_6H_8O_6$ , C 45.57, H 3.83.

Found: C 45.91, H 4.05.

#### ATTEMPTED PREPARATION OF ETHYLENE CHLOROXYDRIN

##### OXALATE

45 g. (0.5 mole) of anhydrous oxalic acid and 100.6 g., (1.25 moles) of anhydrous ethylene chlorohydrin were heated on the water bath for three hours. The flask was then heated to boiling and slow distillation was effected at atmospheric pressure. There was no point at which distillation appeared to cease and the mixture in the flask did not at any time produce a water insoluble compound. The above experiment was repeated but in this case distillation at reduced pressure, 30 mm., produced no better results.

##### SUMMARY

The oxalic esters of six new alcohols have been prepared.



PART III

THE RELATIVE REACTIVITIES OF SOME ORGANOMETALLIC  
COMPOUNDS OF THE GROUP II ELEMENTS

INTRODUCTION

Organometallic compounds are those compounds which are characterized by the carbon-metal linkage. The organometallic compounds of the Group II metals fall into three general classes, viz., R - Me - R, R - Me - R', and R - Me - X. (In the last class X is usually halogen). Organometallic compounds have been known for a long time. The now classic researches of Frankland<sup>14</sup> in an attempt to find free radicals ended in his discovery, in 1849, of the zinc dialkyls. These were the first true organometallic compounds with the carbon-metal linkage, exclusive of carbides and acetylides, that were prepared, and their discovery gave rise to much endeavor to prepare other organometallic compounds and to use those compounds in synthetic work. Before 1870, i.e. within twenty years of Frankland's discovery of the organozinc compounds, many new organometallic compounds had been described, and zinc and mercury compounds especially had already been widely used as synthetic reagents. Because of the somewhat unsettled

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14. Frankland, J. Chem. Soc., 2, 297 (1850).

state of many branches of chemistry in the middle of the last century the literature of the organometallic compounds is not as trustworthy as one might wish. Two good examples of unwitting error on the part of researchers are the descriptions of the properties of magnesium dialkyls<sup>15</sup> and of the beryllium dialkyls<sup>16</sup>. Those errors were almost certainly due to the use of impure metals.

The observations of Barbier<sup>17</sup> and their development by Grignard<sup>18</sup> have given organic chemistry organometallic compounds of the very greatest usefulness. The latter compounds, the Grignard reagents, have largely supplanted the other organometallic compounds, particularly the organozincs, in synthetic work.

The metals of Group II of the Periodic System are beryllium, magnesium, calcium, zinc, strontium, cadmium, barium, mercury, and radium in order of increasing atomic weight. Because these metals vary so greatly in their properties one would expect the organometallic of these metals to vary widely in their properties. This is strikingly illustrated by the zinc and mercury dialkyls; the former take fire on exposure to air; the latter are inert towards air.

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15. Cahours, Ann., 114, 240 (1860).  
16. Cahours, Compt. rend., 76, 1383 (1873).  
17. Barbier, Compt. rend., 128, 110 (1899).  
18. Grignard, Compt. rend. 130, 1322 (1900).

Because of our limited knowledge of some of the organometallic compounds of this Group, a comparison of their relative reactivities must be limited to a relatively small number of the organocompounds of each element. In general only the methyl, ethyl, and n-butyl compounds will be compared in the following survey.

### I. ORGANOBERYLLIUM COMPOUNDS

In 1860 Cahours<sup>19</sup> described a compound of beryllium which resulted from the action of ethyl iodide on metallic beryllium. The compound, supposedly beryllium diethyl, was a liquid which reacted vigorously with water. By the action of mercury dialkyls on metallic beryllium Cahours<sup>11</sup> later prepared what were thought to be beryllium diethyl and beryllium dipropyl<sup>20</sup>. He discovered that these two compounds reacted vigorously with water, fumed in air, and could be distilled in an atmosphere of carbon dioxide. In view of later and certainly more accurate work on organoberyllium compounds one must conclude that both of the previously mentioned

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19. Cahours, Ann. chim. phys., 58, 5 (1860).

20. Cahours does not say whether he used the n- or isopropyl mercury compound for this work.

researches were in error, probably because of the use of impure beryllium<sup>21</sup>.

The only other mention of organoberyllium compounds at this early period is by Frankland<sup>22</sup>. It is probable that Lavroff<sup>23</sup> obtained beryllium dimethyl by heating beryllium with mercury dimethyl at 130°. The resulting white, crystalline, volatile compound inflamed with water and gave off a saturated hydrocarbon. The next attempts to prepare organoberyllium compounds were made by Gilman<sup>24</sup> who was unsuccessful in his efforts to make R - Be - X compounds by the action of many RX compounds on beryllium with and without catalysts. In 1926 Durand<sup>25</sup> claimed to have made methylberyllium iodide by the direct action of methyl iodide on beryllium with mercuric chloride as a catalyst. He also reported ethylberyllium iodide by the same method. Durand probably did not have these compounds, because he described methylberyllium iodide as insoluble in ether.

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21. Until very recently pure metallic beryllium has been very rare and extraordinarily expensive.
  22. Frankland, J. Chem. Soc., 13, 177 (1861). See pages 181 and 194. Friend's "Text-Book of Inorganic Chemistry", vol. XI, part 1, 1928, by Goddard and Goddard, Charles Griffin & Company, London, states on page 11 that Frankland obtained beryllium diethyl and dipropyl. Frankland certainly did not say that he made these compounds.
  23. Lavroff, Bull. Soc. Chim., 41, 548 (1884).
  24. Gilman, J. Am. Chem. Soc., 45, 2693 (1923).
  25. Durand, Compt. rend., 182, 1162 (1926).

Beryllium dialkyls were first prepared in a high state of purity and in considerable quantities by Gilman and Schultze<sup>26</sup> by the action of anhydrous beryllium chloride on the appropriate Grignard reagent<sup>27</sup>. The pure compounds, beryllium dimethyl, beryllium diethyl and beryllium di-n-butyl react with extreme vigor with water; the dimethyl and diethyl compounds are spontaneously inflammable in air while the di-n-butyl compound is rapidly oxidized by air although it is not spontaneously inflammable in it; these three dialkyls react vigorously with carbon dioxide--beryllium dimethyl inflames in this gas; the color test<sup>28</sup> is readily produced by ether solutions of the beryllium dialkyls; and they readily react with isocyanates to produce the expected derivatives.

In general it can be said that the beryllium dialkyls are very reactive towards water, air, carbon dioxide, isocyanates, and Michler's ketone. Reactions of beryllium dialkyls with ketones, other than Michler's ketone, with acid chlorides, and with esters have not been studied.

The organoberyllium halides have only recently been prepared by Gilman and Schultze<sup>29</sup>. These compounds are readi-

26. Gilman and Schultze, J. Chem. Soc., 1927, 2663.

27. Krause and Wendt, Ber., 56, 466 (1923).

28. Gilman and Heck, Rec. trav. chim., 48, 193 (1929). This article contains also leading references to the color test. See also Gilman and Heck, Ber., 62B, 1379 (1929).

29. Gilman and Schultze, J. Am. Chem. Soc., 49, 2904 (1927).

ly decomposed by water, but they do not fume in air nor do they react at all with carbon dioxide. They react only slowly with Michler's ketone.

The arylberyllium halides are certainly much less active than the corresponding dialkyls. This is remarkable in view of the reactivity of the metallic dialkyls and their corresponding alkylmetallic halides of some of the other metals of Group II.

The mixed beryllium dialkyls of the type R- Be- R' are unknown.

## 2. ORGANOMAGNESIUM COMPOUNDS

The magnesium dialkyls, like the beryllium dialkyls, were first incorrectly reported by Cahours<sup>30</sup>, although it is possible that Hallwochs and Schafarik<sup>31</sup> prepared a very impure sample of magnesium diethyl. Magnesium dialkyls were prepared later in the pure state by Löhr<sup>32</sup>, Fleck<sup>33</sup>, and Gilman and Schultze<sup>34</sup>, and by Gilman and Brown<sup>35</sup>.

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30. Cahours, Ann., 114, 227 (1860).

31. Hallwochs and Schafarik, Ann., 109, 206 (1859).

32. Löhr, Ann., 261, 72 (1891).

33. Fleck, Ann., 276, 129 (1893).

34. Gilman and Schultze, J. Am. Chem. Soc., 49, 2328 (1927).

35. Gilman and Brown, Rec. trav. chim., 49, 724 (1930).

Magnesium dimethyl and diethyl are violently decomposed by water, take fire in air, and in carbon dioxide the compounds may take fire or explode. In ether solution the reactivities of these compounds are not as great as they are in the dry state. Fleck<sup>33</sup> has shown that magnesium dimethyl reacts with acetyl chloride to form trimethyl carbinol, but with magnesium diethyl and the same acid chloride he got trimethyl carbinol instead of the expected methyl-diethyl carbinol. Later work by Gilman and Schultze<sup>34</sup> showed that the latter product is actually obtained from acetyl chloride and magnesium diethyl. Magnesium di-n-butyl has only recently been prepared<sup>35</sup>. This compound, like the dimethyl and diethyl compounds, is a white solid without a melting point. It reacts very vigorously with water and with air. All three of the magnesium dialkyls give the color test with Michler's ketone and all react with  $\alpha$ -naphthyl isocyanate and with it they produce the  $\alpha$ -naphthalides. One very striking property of the magnesium dialkyls is their almost negligible vapor pressure. The dialkyls of beryllium, zinc, cadmium, and mercury are all purified, or obtained from reaction mixtures, by virtue of their very appreciable vapor pressures.

The organomagnesium halides, the Grignard reagents, are so well known and so commonly used that only very brief references will be made to their activity. In general the

Grignard reagents react with oxygen or with air to form alcohols<sup>36</sup> or phenols<sup>37</sup>, with carbon dioxide to form acids<sup>38</sup>, with water to form hydrocarbons<sup>39</sup>, with acid chlorides to form tertiary alcohols and ketones<sup>40</sup>, with  $\alpha$ -naphthyl isocyanates to form  $\alpha$ -naphthalides<sup>41</sup>, and with Michler's ketone to produce the well known color test<sup>28</sup>.

The Grignard reagents appear to be somewhat more reactive than the corresponding magnesium dialkyls<sup>42</sup>. Mixed organomagnesium compounds of the type R - Me - R' are not known.

### 3. ORGANOZINC COMPOUNDS

Organozinc compounds were the first true organo-metallic compounds that were prepared<sup>42</sup>. The organozinc compounds, together with the organomercury compounds, soon assumed a very important place in synthetic organic chemistry because of their activities but the organozinc compounds, as synthetic reagents, have been largely replaced by the more convenient and more active Grignard reagents.

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36. Grignard, Compt. rend., 138, 1048 (1904).  
37. Gilman and Wood, J. Am. Chem. Soc., 48, 806 (1926).  
38. Gilman and Parker, J. Am. Chem. Soc., 46, 2816 (1924).  
39. Spencer, Ber., 41, 2302 (1908).  
40. Gilman, Fothergill and Parker, Rec. trav. chim., 48, 748 (1929).  
41. Gilman and Furry, J. Am. Chem. Soc., 50, 1214 (1928).  
42. (a) Gilman and Brown, J. Am. Chem. Soc., 52, 1181 (1930).  
(b) Bachmann, J. Am. Chem. Soc., 52, 4412 (1930).



The organozinc compounds are best remembered by those who have worked with them by their great affinity for oxygen, and these compounds are not too agreeable to work with because of their astonishing inflammability. The zinc dialkyls are usually prepared by the action of an alkyl halide on metallic zinc<sup>43</sup>, on a zinc-copper couple<sup>44</sup>, or on an alloy of zinc and copper<sup>45</sup>. The first step in the reaction is assumed to be the formation of the alkylzinc iodide which is then decomposed by heat into zinc dialkyl and zinc iodide. The preparation and handling of the zinc dialkyls must be carried out in an inert atmosphere and for this purpose dry carbon dioxide has been most frequently used.

Other than their reactivity with oxygen or air the zinc dialkyls are not as active, chemically, as the beryllium dialkyls, the alkylberyllium halides, the magnesium dialkyls, or the Grignard reagents. Zinc dimethyl ignites spontaneously in air and burns with a greenish-blue flame<sup>46</sup>, but its slow oxidation produces methoxyzinc compounds. Water decomposes zinc dimethyl with great violence<sup>43</sup>. With acid chlorides zinc dimethyl may react in two ways, viz., to form ketones, or to form tertiary alcohols. Pavlov<sup>47</sup> showed, in

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43. Frankland, J. Chem. Soc., 2, 297 (1850).

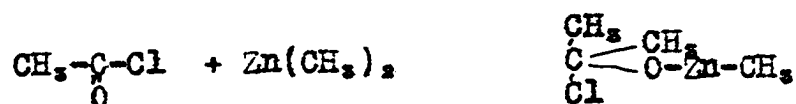
44. Gladstone and Tribe, J. Chem. Soc., 35, 567 (1879).

45. Noller, J. Am. Chem. Soc., 51, 594 (1929).

46. Frankland, Ann., 85, 347 (1853).

47. Pavlov, Ann., 188, 104 (1877).

a very good study on the reactions of zinc dialkyls and acid chlorides, that when two moles of acid chloride and one mole or zinc methyl react ketones are produced in good yield. Using acetyl chloride and zinc dimethyl an 80% yield of acetone was obtained. This reaction takes place at room temperature and in a rather short time. If, however, two moles of zinc dimethyl and one mole of acetyl chloride were allowed to react at room temperature for a period of many days the chief product is trimethyl carbinol. The latter reaction evidently proceeds in two steps, first:



and this product reacts with more zinc dialkyl thus:



On hydrolysis this product produces trimethyl carbinol. Pavlov made use of the two steps of this reaction to make tertiary alcohols with three unlike groups. He added one mole of zinc dimethyl to one mole of butyryl chloride, and, when this reaction had ceased, he then added a mole of zinc diethyl. The whole reaction mixture was allowed to stand two weeks at room temperature. Two layers separated in the reaction flask. Hydrolysis of the mixture produced the expected methylethyl-n-propyl carbinol. Using isobutyryl chloride with the above procedure and reagents the same researcher got methylethyl-

iso-propyl carbinol. Pavlov<sup>48</sup> obtained only methyl-iso-butyl ketone by allowing a reaction mixture of one mole of butyryl chloride and two moles of zinc dimethyl to stand for ten days at room temperature, but the same reactants, on standing thirty days gave him dimethyl-iso-butyl carbinol. Ipat'ev and Grove<sup>49</sup> treated palmityl chloride with zinc dimethyl and got dimethylpentadecyl carbinol in good yield. Freund<sup>50</sup> obtained acetone from the reaction of zinc dimethyl on acetyl chloride. With acetone zinc dimethyl does not produce tertiary alcohols; mesityl oxide and higher condensation products result<sup>47</sup>.

The reactions of zinc diethyl are very similar to those of zinc dimethyl. Zinc diethyl reacts vigorously with water<sup>38</sup> and with air<sup>51</sup>. Frankland thought that the oxidation of zinc diethyl produced zinc oxide, zinc ethylate, and zinc acetate, but Demuth and Meyer<sup>52</sup> showed that the slow oxidation of zinc diethyl by air produced a peroxide which exploded if heated, and which liberated iodine from a solution of potassium iodide even in the absence of air.

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48. Pavlov, Ann., 173, 192 (1874).

49. Ipat'ev and Grove, J. Russ. phys. chem. Soc., 33, 502 (1901). Chem. Zentr., 1901, II 1201.

50. Freund, Ann., 115, 22 (1860); 118, 1(1861).

51. Frankland, Ann., 95, 28 (1855).

52. Demuth and Meyer, Ber., 23, 394 (1890).

Freund<sup>50</sup> made methylethyl ketone by the action of zinc alkyl on acetyl chloride and diethyl ketone from propionyl chloride and the same zinc alkyl. Freund also made ethylphenyl ketone from benzoyl chloride. Nahapetian<sup>53</sup> and Ipat'ev<sup>54</sup> both got triethyl carbinol by the long reaction of zinc diethyl on propionyl chloride. Kalle<sup>55</sup> added an ether solution of zinc ethyl to an ether solution of benzoyl chloride and from this reaction both ethyl phenyl ketone and ethyl benzoate were obtained.

As in the case of zinc dimethyl, tertiary alcohols are not produced by the action of zinc alkyls on ketones. Pavlov<sup>47</sup> found that acetone and zinc diethyl produce mesityl oxide, while Rieth and Beilstein<sup>56</sup> got phorone from the same reactants.

While zinc dialkyls do not react with dry carbon dioxide at room temperature and at atmospheric pressure Schmitt<sup>57</sup> reported zinc propionate and diethyl ketone by the action of zinc diethyl on liquid carbon dioxide under pressure.

Zinc di-n-butyl has only recently been made<sup>45</sup> and its reaction with tertiary halide only has been tried.

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53. Nahapetian, Ann., 162, 44 (1872).  
54. Ipat'ev, J. prakt. Chem., (2) 53, 257 (1896).  
55. Kalle, Ann., 119, 165 (1861).  
56. Rieth and Beilstein, Ann., 126, 145 (1863).  
57. Schmitt, J. prakt. Chem., (2) 42, 568 (1890).

The alkylzinc halides, the zinc analogs of the Grignard reagents, were not carefully studied until rather recently. Like the Grignard reagents, the alkylzinc halides are prepared and used, chiefly in ether, or in ethylacetate solutions. In 1861 Pebal<sup>58</sup> announced a simple method for the preparation of zinc diethyl in which equal parts of ether and of ethyl iodide were allowed to react with zinc. The reaction product was then fractionally distilled in order to separate the zinc diethyl. Later Michael<sup>59</sup> made ethylzinc iodide by the action of ethyl iodide and ether on zinc. He did not attempt to distil the resulting ether solution but used it directly for reactions with acid chlorides. With benzoyl chloride and this ether solution a 30% yield of ethyl phenyl ketone resulted, while with propionyl chloride diethyl ketone was obtained in even better yield. No mention was made that any other products were obtained in those reactions.

Blaise<sup>60</sup> has made the best study of the preparations and reactivities of the organozinc halides. He found that the solution which resulted from the action of the ethereal solution of the alkyl halide and zinc did indeed react with benzoyl chloride but the ketone was of very small amount. Following the directions of Michael the reaction product from

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58. Pebal, Ann., 118, 22 (1861).

59. Michael, Ann. Chem. Jour., 25, 419 (901).

60. Blaise, Bull. soc. chim., (4) 9, I-XXVI (1911).



react with carbon dioxide because they can be handled in an atmosphere of this gas.

In order to prepare more useful solutions of alkylzinc halides Blaise used a mixture of ethyl acetate, together with some inert solvent such as benzene or toluene. With these solutions he obtained ketones from acid chlorides in yields of 75% to 90%. The ethyl acetate solutions of alkylzinc halides fume in air and they are unreactive toward ketones and carbon dioxide. Blaise states that the reactivities of the organozinc halides are not different from those of the zinc dialkyls. Job and Reich<sup>62</sup> say that ether solutions of ethylzinc chloride do not fume in air, but that ethylzinc cyanide is readily attacked by air.

In the ordinary preparation of zinc dialkyls the first step is supposedly the formation of alkylzinc halides, which are white crystalline solids. Those solids from the reaction of methyl iodide<sup>63</sup> and of ethyl iodide<sup>64</sup> with zinc take fire in air and they react vigorously with water. They do not react with carbon dioxide for they are commonly distilled in that atmosphere with the formation of zinc iodide and the zinc dialkyl. Ethylzinc iodide reacts with butyryl chloride to form ethyl-n-propyl ketone, and with benzoyl chloride ethylphenyl ketone is obtained.

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62. Job and Reich, Compt. rend., 174, 1358 (1922).

63. Renshaw and Greenlaw, J. Am. Chem. Soc., 42, 1472 (1920).

Zinc is the first element of Group II of which dialkyls of the type  $R - Zn - R'$  have been made. Job and Reich<sup>61</sup> made methylethylzinc and ethyl-n-butyl-zinc. They found that these compounds are readily converted to the symmetrical ones by distillation at atmospheric pressure. Krause and Fromm<sup>64</sup> prepared ethyl-n-propylzinc, ethyl-iso-propylzinc, n-propyl-iso-butylzinc, and iso-butyl-iso-amylzinc. These compounds slowly reverted to the symmetrical ones on standing. No reactions of the mixed zinc dialkyls have been tried.

#### 4. ORGANOCADMIUM COMPOUNDS

The first attempt to make organocadmium compounds were those of Schuler<sup>65</sup>. His attempts were probably unsuccessful, but three years later Wanklyn<sup>66</sup>, by distilling the product from a reaction between ethyl iodide and metallic cadmium, obtained a liquid which contained cadmium diethyl. This liquid fumed in air giving off first white, then brown fumes, finally bursting into flames. He later discovered that the liquid contained some organozinc compounds. In 1891 Lohr<sup>67</sup> prepared cadmium dimethyl which he found to react vigorously with air and with water.

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64. Krause and Fromm, Ber., 59B, 931 (1926).

65. Schuler, Ann., 87, 55 (1853).

66. Wanklyn, J. Chem. Soc., 9, 193 (1856).

67. Lohr, Ann., 261, 48 (1891).



Krause<sup>68</sup> first made cadmium dialkyls in appreciable amounts and in a high state of purity. He found the cadmium dialkyls to be liquids of very disagreeable and irritating odor. They are readily oxidized by air and under suitable conditions they may take fire in air. Cadmium dimethyl is oxidized to a white film in air, but the other cadmium dialkyls are more rapidly oxidized with the formation of brown fumes. All of the cadmium dialkyls react slowly with water. If they are dropped into water they sink to the bottom of the vessel where their reaction with water produces a loud crackling noise. This reaction is very slow. No other reactions of cadmium dialkyls have been tried.

##### 5. ORGANOMERCURY COMPOUNDS<sup>69</sup>

A very great number of organomercury compounds of the types R-Hg-R, R-Hg-R', and R-Hg-X are known. Chemically all of these types are rather inactive. There is no evidence of their reacting with air, oxygen, water, acid chloride, carbon dioxide, esters or ketones. The vapors of mercury dimethyl are easily ignited by a flame, but spontaneous oxidation does not occur. All of the mercury dialkyls, which are rather volatile, are poisonous. Mercury dimethyl is described as a very deadly poison<sup>69</sup>.

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68. Krause, Ber., 50B, 1815 (1917).

69. "Organic compounds of Mercury" by Frank C. Whitmore, The Chemical Catalog Co. Inc., New York, 1921.

## 6. ORGANOCALCIUM COMPOUNDS

Organocalcium compounds were first prepared by Beckmann<sup>70</sup> by heating an ethereal solution of iodobenzene with metallic calcium. A brown powder, rather soluble in ether, was phenylcalcium iodide, the reaction product. Phenylcalcium iodide reacted with carbon dioxide to give, on hydrolysis, benzoic acid, and with benzaldehyde benzohydrol was produced. The reaction product of an ethereal solution of ethyl iodide and metallic calcium was a white powder, sparingly soluble in ether, decomposing at 40° under vacuum, and giving ethane on treatment with water. The chemiluminescence of ethylcalcium iodide and phenylcalcium iodide was studied by Dufford, Nightingale and Calvert<sup>71</sup>, and Gilman and Pickens<sup>72</sup> used phenylcalcium iodide in a study on the mechanism of the reduction of ozobenzene. Gilman and Schultze<sup>73</sup> showed that phenylcalcium iodide gives the color test with Michler's ketone. In a more accurate study of organocalcium compounds Gilman and Schultze<sup>74</sup> made ethylcalcium iodide, n-butylcalcium iodide and phenylcalcium iodide. Each of these gave the color test that

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70. Beckmann, Ber., 38, 904 (1905).

71. Dufford, Nightingale and Calvert, J. Am. Chem. Soc., 47, 95 (1925).

72. Gilman and Pickens, J. Am. Chem. Soc., 47, 2406 (1925).

73. Gilman and Schultze, J. Am. Chem. Soc., 47, 2002 (1925).

74. Gilman and Schultze, J. Am. Chem. Soc., 48, 2463 (1926).

that is characteristic of active organometallic compounds, but only n-butylcalcium iodide and phenylcalcium iodide produced derivatives with isocyanates. These authors explain the non-reactivity of ethyl-calcium iodide with isocyanates by supposing that this organometallic compound is formed in very poor yields. Phenylcalcium iodide reacts much less readily with benzoyl chloride than is the case with the analogous Grignard reagent.

Calcium dialkyls and compounds of the type R-Ca-R' have not been prepared.

### 7. ORGANOSTRONTIUM COMPOUNDS

The only mention of organostrontium is by Gilman and Peterson<sup>75</sup> in their studies on activated magnesium. No organostrontium compounds were prepared by these authors.

### 8. ORGANOBARIUM COMPOUNDS

The only organobarium compound that has been described in the literature is phenylbarium iodide<sup>76</sup>. It reacts with carbon dioxide,  $\alpha$ -naphthyl isocyanate, and ethyl benzoate, and it gives the color test.

75. Gilman and Peterson, Proc. Iowa. Acad. Sci., 33, 173(1926)

76. Gilman and Schultze, Bull. soc. chim., 41, 1333 (1927).

SUMMARY

The organometallic compounds of the Group II elements cannot be definitely classified as to their relative reactivities. The beryllium dialkyls and the corresponding Grignard reagents appear to have about the same reactivity, but the organoberyllium halides are surprisingly inactive. The magnesium dialkyls are somewhat less reactive than their corresponding Grignard reagents. The organocalcium halides may possibly be more active than the organoberyllium halides, and the same may be true of the organobarium halides. These three classes of compounds must be further investigated before any definite statement can be made as to their relative reactivities. All of the above mentioned organometallic compounds are more active chemically than the organozincs; in the latter group there appears to be no difference between the dialkyls and the alkylzinc halides. The next metal in order of activity of its organometallic compounds is cadmium. Organomercury compounds are the least active of the organometallic compounds of Group II.

It is interesting to note that Pfeiffer<sup>77</sup> and his co-workers have recently presented a paper on the place of beryllium and magnesium in the periodic classification of the elements. They have arrived at the conclusion that these two

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77. Pfeiffer, Fleitmann and Hansen, J.prakt.Chem., 128, 47 (1930).

elements exhibit properties which entitle them to be placed in the class with zinc, cadmium and mercury, i.e. Group IIB, rather than with the alkali earth metals of Group IIA.

At present, because of the lack of information about many organometallic compounds of the Group II elements, it seems best to classify the organometallic compounds of beryllium and magnesium with zinc, cadmium and mercury rather than with calcium, strontium and barium.

THE RELATIVE REACTIVITIES OF METHYLMAGNESIUM

IODIDE AND BERYLLIUM DIMETHYL

The Grignard reagents are among the most reactive of compounds, and in an effort to find out if there is any difference in reactivity between them and beryllium dialkyls a series of reactions with both organometallic compounds was tried with a series of compounds that have been reported as not reacting with Grignard reagents.

Troger and Beck<sup>78</sup> report that both benzenesulfonacetonitrile ( $C_6H_5SO_2CH_2CN$ ) and benzenesulfonacetophenone ( $C_6H_5SO_2CH_2COC_6H_5$ ) do not react either with methylmagnesium iodide or with phenylmagnesium bromide. F. and L. Sachs<sup>79</sup> report that *p*-dimethylaminobenzonitrile ( $p(CH_3)_2NC_6H_4CN$ ) do not react with phenylmagnesium bromide or with ethylmagnesium iodide and Angeli<sup>80</sup> found that *p*-methoxybenzonitrile does not react with Grignard reagents. The latter author states that many *o*- and *p*- substituted benzene compounds have peculiar stability toward decomposition or action of other compounds.

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78. Troger and Beck, J. prakt. Chem., 87, 289 (1913).  
79. F. and L. Sachs, Ber., 37, 3089 (1904).  
80. Angeli, Atti. accad. Lincei., (6) 3, 450 (1926).  
C.A., 20, 2845 (1926).

It is suggested that some other compounds might be used for a differentiation in reactivity between Grignard reagents and beryllium dialkyls. It is possible that the rates of reaction of these two types of organometallic compounds with a compound with which they act slowly, such as n-valeronitrile or benzonitrile, might show some difference. It may be that reactions of the Grignard reagents and of the beryllium dialkyls may be different with compounds such as anisole, phenetol or the halogen substituted toluenes. In view of the small amount of work that has been done on the reactions of these compounds with organometallic compounds it is doubtful if any significant differences could be noted. It is possible, however, that marked differences might be noticed by the use of higher reaction temperatures than are possible with the commonly used ether solutions. Such reactions would probably best be carried out by the use of a reactant with the pure, ether-free organometallic compound in vacuum.

Another line of attack toward the solution of this problem would be the action of the two types of organometallic compounds. This has been done by Kohler<sup>81</sup> with the Grignard reagents.

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81. Kohler, Am. Chem. Jour., 38, 511 (1907), and 31, 642.

It has been shown by Marvel, Hagar and Coffman<sup>82</sup> that lithium n-butyl reacts with many organic halides. With o- and m-bromotoluene and lithium n-butyl the only isolated products were toluene, but with p-bromotoluene a 75% yield of p-butyltoluene was obtained. The o- and p- bromotoluenes, and also benzonitrile, were treated with beryllium dimethyl in order to find out if it were as active as the lithium compounds.

82. Marvel, Hagar and Coffman, J. Am. Chem. Soc., 49, 2323(1927).



EXPERIMENTAL PART

An ethereal solution of beryllium dimethyl was made up in accordance with the directions of Gilman and Schultze<sup>83</sup>. This solution was titrated and aliquots were used for reactions.

REACTION OF BERYLLIUM DIMETHYL WITH p-BROMOTOLUENE

To 10.2 g. (0.06 mole) of p-bromotoluene in 25 cc. of ether was added 0.075 mole of an ethereal solution of beryllium dimethyl. All operations of handling the beryllium dimethyl were carried out in an atmosphere of dry nitrogen. There was no evidence of reaction when the solution of beryllium dimethyl was added to the p-bromotoluene. This reaction mixture then stood for three days at room temperature but no reaction appeared to have taken place at that time. The solution was then carefully hydrolyzed, first with wet ether, then with water and finally with dilute sulfuric acid. The ether layer was separated, washed twice with small amounts of water and then dried over calcium chloride. On distillation, after the ether had been boiled off, a sample of 9 g. of p-bromotoluene, b.p. 184°, was recovered. This

<sup>83</sup>. Gilman and Schultze, Rec. trav. Chim., 48, 1129 (1930). This reagent was made up under the personal direction and with the help of Dr. Schultze.

represents a recovery of 88.2%. A small sample of the distillate showed a strong test for bromine after a sodium fusion. It is evident that no reaction had occurred between beryllium dimethyl and p-bromotoluene. No higher boiling fraction than the one mentioned was obtained and there was no evidence of any material at the boiling point of p-xylene.

REACTION OF BERYLLIUM DIMETHYL WITH o-BROMOTOLUENE

An ethereal solution of 0.075 mole of beryllium dimethyl was added to 10.2 g. (0.06 mole) of o-bromotoluene in 25 cc. of ether. As before all operations were carried out in a nitrogen atmosphere. The flask containing the mixture was well stoppered to exclude air and the mixture stood for three days at room temperature. At the end of this time the reaction mixture was hydrolyzed exactly as in the previous case and the product was worked up in the same manner. On distillation the temperature rose very rapidly, after the ether had been distilled off, to 181° where the remainder of the material boiled. The recovery was 8.5 g. (83.3%). There is, therefore, no reaction between o-bromotoluene and beryllium dimethyl.

REACTION OF BERYLLIUM DIMETHYL WITH BENZONITRILE

An ethereal solution of 0.075 mole of beryllium dimethyl was added to a solution of 6.2 g. (0.06 mole) of benzonitrile in 50 cc. of ether under an atmosphere of nitrogen. There was some heat of reaction at the time of addition and a grey, flocculent precipitate appeared. The solution remained warm for about one-half hour, during which time the precipitate slowly increased in amount. The flask was tightly stoppered and allowed to stand for four days at room temperature. The mixture was then hydrolyzed carefully and worked up exactly as in the two previous cases. The fraction which boiled at  $202^{\circ}$  gave a positive test for acetophenone with sodium nitroprusside. A small portion of the distillate was treated with semicarbazide hydrochloride and sodium acetate. From this reaction acetophenone semicarbazone, m. p.  $197^{\circ}$  was obtained. This compound was not identified by a mixed melting point. The yield of ketone was 4 g. or 38%.

QUANTITATIVE STUDIES WITH METHYLMAGNESIUM IODIDE

The four compounds mentioned above were treated with methylmagnesium iodide using the methods and technique of Gilman and co-workers<sup>84</sup>. An aliquot of methylmagnesium iodide was forced into the calibrated reaction flask F shown in the figure in the article by Gilman and Crawford<sup>84</sup>. In each case one gram of the reactant was added and the mixture in flask F was heated to refluxing for a quarter of an hour. The mixture was then hydrolyzed and the gas was collected and measured exactly according to the directions of Gilman and Crawford. The blank runs were made in exactly the same manner. The collected gases were corrected to the volume from 20 cc. of the Grignard reagent. A summary of the results is given in TABLE II.

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84. Gilman and Crawford, J. Am. Chem. Soc., 45, 554 (1923).  
Gilman and Peterson, J. Am. Chem. Soc., 48, 423 (1926).  
Gilman and Peterson, Rec. trav. chim., 48, 247 (1929).

TABLE II

Compound	Av. corr. vol. of CH <sub>4</sub> from 20 cc. CH <sub>3</sub> MgI	% reaction
Blank	197.5 cc.	---
"	199.0 cc.	---
"	198.0 cc.	---
Benzenesulfonacetophenone <sup>+</sup>	104.6 cc.	47.3
" " "	106.3 cc.	46.4
Benzenesulfonacetonitrile	196.3 cc.	1.0
" " "	196.8 cc.	0.8
p-dimethylaminobenzonitrile	197.0 cc.	0.7
" " "	197.8 cc.	0.2
p-methoxybenzonitrile	196.7 cc.	1.0
" "	197.5 cc.	0.7

+ This compound reacted vigorously with methylmagnesium iodide. The product was not identified.

REACTIONS WITH BERYLLIUM DIMETHYL

These quantitative studies with beryllium dimethyl were carried out exactly like those of Gilman and Schultze. One gram of each of the reactants was added to separate, clean dry test tubes and to each of these test tubes was added 5 cc. of a solution of beryllium dimethyl. The test tubes were then carefully sealed off. All operations were carried out in an atmosphere of nitrogen. The test tubes were allowed to stand for ten months and then hydrolyzed by the method of Gilman and Schultze<sup>83</sup>. The results are given in TABLE III.

The differences in reactivity of benzenesulfonacetophenone with the two organometallic compounds are not as they appear to be. The differences between the gas evolved in blank runs and that in those in which the compound was treated with the organometallic compounds are somewhat greater in the reactions with beryllium dimethyl than in those with the Grignard reagent.

TABLE III

Reactant	cc. of methane evolved	% reaction
Blank	341.4 cc.	---
"	344.0 cc.	---
Benzenesulfonacetophenone <sup>+</sup>	275.1 cc.	19.7
" " "	280.4 cc.	18.2
Benzenesulfonacetonitrile	340.8 cc.	0.6
" " "	338.7 cc.	1.2
p-dimethylaminobenzonitrile	340.4 cc.	0.6
" " "	341.3 cc.	0.5
p-methoxybenzonitrile	338.0 cc.	1.3
" "	339.5 cc.	1.0-

+ This compound reacted vigorously with beryllium dimethyl. The product was not identified.

SUMMARY

From the quantitative studies of beryllium dimethyl and methylmagnesium iodide there appears to be no essential difference in reactivity between the Grignard reagents and the corresponding beryllium dialkyls.

Some suggestions have been made for future work with the problem of reactivity of organometallic compounds.