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I. THE ELECTRONIC INTERPRETATION OF REACTIONS APPLIED TO HALOGEN ORGANIC COMPOUNDS

II. A STUDY OF ANTIKNOCK COMPOUNDS

By

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A Thesis Submitted to the Graduate
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In Charge of Major Work

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THE ELECTRONIC INTERPRETATION OF REACTION APPLIED TO HALOGEN ORGANIC COMPOUNDS

INTRODUCTION

Various formulae for benzene have been suggested since Kekule[1] proposed his well known formula. Fry[2] recently proposed an electronic formula based on Kekule's original model, in which he suggests that the substituents in the benzene ring are alternately positive and negative. Thus, di-ortho and di-para derivatives are of opposite sign, while di-meta substituents are of the same sign.

In writing the preparation of phenylmagnesium bromide electronically we have two possibilities:

$$C_6H_5^+ \, {}^-Br + Mg \longrightarrow C_6H_5^+ \, {}^-Mg^+ \, {}^-Br \qquad (1)$$

$$C_6H_5^+ \, {}^-Br + Mg \longrightarrow C_6H_5^- \, {}^+Mg^+ \, {}^-Br \qquad (2)$$

From a consideration of reactions of organomagnesium derivatives with various reagents, such as, carbon dioxide, sulfur dioxide, and dialkyl sulfates, the second electronic consideration seems the most probable. Thus, we have a reduction of the participating carbon and, according to Fry's formula, this would necessitate a change in sign of the remaining constituents. If this consideration is extended to ortho and para di-bromobenzenes one should secure a di-organomagnesium halide because the second halogen would

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1. Kekule, Ann., 137, 129 (1895).
2. Fry: "The Electronic Conception of Valence and the Constitution of Benzene". Longmans, Green and Co., (1921).

then be of the same sign as the original halogen forming the Grignard reagent. In case there is no shifting in sign after the formation of the first organometallic bromide then both halogens in meta-di-bromobenzene would be of like sign and should react to form a di-Grignard reagent.

Holleman[3], working with 1,2,4- and 1,3,4-chloronitrobromobenzene, showed that negative halogens are replaced, irrespective of the halogen, by heating the above derivatives with .35 normal sodium methylate in a sealed tube at 80° for five hours. Nicolet[4] has recently demonstrated that positive halogens become somewhat labile when heated to high temperatures, but they are distinct in their reactions from negative halogens. Therefore, since negative halogens are known to react in alkyl and aryl derivatives to form organomagnesium halides all negative halogens in poly-halogen aromatic compounds should react to form Grignard reagents.

Since Fry's formula not only explains why an entering group goes ortho, meta, or para, but also many of the reactions of nuclear substituted derivatives, it is of

3. Holleman and Heineken, Rec. trav. chim., 34, 204 (1915).
4. Nicolet, J. Am. Chem. Soc., 43, 2081 (1921).

considerable interest to test his theory as applied to the formation of Grignard reagents of poly-halogen nuclear compounds.

Soon after the introduction of the Grignard reagent into synthetic organic chemistry, Bodroux[5] extended the study to poly-halogen aromatic compounds. On passing carbon dioxide into an ether solution of the Grignard reagent prepared from p-di-bromobenzene and p-chlorobromobenzene, p-bromobenzoic acid and p-chlorobenzoic acid, respectively, were secured as the chief products, and 4,4'-di-bromobenzophenone and 4,4'-di-chlorobenzophenone, respectively, were secured as secondary products. He later extended his study to include p-di-chlorobenzene and m-di-bromobenzene[6]. On treating the respective Grignard reagents with water, carbon dioxide, or iodine, in no case did he secure evidence that more than one halogen reacted to form a Grignard reagent, while p-di-chlorobenzene did not react. On treating the Grignard reagents formed from 1,4-di-bromonaphthalene[7] and 1,4-bromochloronaphthalene with oxygen, 4-bromonaphthol-1 and 4-chloronaphthol-1, respectively, were secured.

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5. Bodroux, Bull. soc. chim., iii, 31, 24 (1904); Compt. rend., 137, 710 (1903).
6. Bodroux, Compt. rend., 136, 1138 (1903).
7. Bodroux, Bull. soc. chim., iii, 31, 33 (1904).

Taboury[8], on treating the Grignard reagents, formed from 1,4-di-bromobenzene, 1,4-bromochlorobenzene, 1,4-di-bromonaphthalene, and 1,4-chlorobromonaphthalene with sulphur and selenium, found evidence that only one halogen had reacted. With chlorobromo derivatives only the bromine entered into the reaction.

Tschitschibabin[9], working with p-di-bromobenzene, succeeded in getting only one bromine to form a Grignard reagent. Beis[10] likewise secured only a mono-organomagnesium bromide with p-di-bromobenzene and p-chlorobromobenzene.

Baeyer[11], Gomberg and co-workers[12], in the preparation of nuclear halogen derivatives of triaryl carbinol, working with p-chloroiodobenzene, only succeeded in forming a Grignard reagent with the iodide. Gomberg[11], failed to secure tri-iodo-tri-phenyl carbinol by means of the Grignard reagent, while Gomberg[12b] states that in the preparation of ortho di- and tri- chlorotriphenyl carbinol by means of the Grignard reagent, either the reaction did not take place at all, or the yields were too small to warrant further study.

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8. Taboury, ibid., iii 31, 646 (1904); Compt. rend.. 138, 982 (1904).
9. Tschitschibabin, Ber., 37, 186 (1904).
10. Beis, Compt. rend. 137, 575 (1903).
11. Baeyer, Ber., 38, 569 (1905).
12. (a) Gomberg and Cone, Ber., 39, 3275 (1906);
    (b) Gomberg and Van Slyke, J. Am. Chem. Soc., 33, 531 (1911).

In a study on the preparation of carboxylic acids Houben[13] was able to secure a 1.25% yield of terephthalic acid by passing carbon dioxide into the Grignard reagent, obtained from p-di-bromobenzene, for a period of twelve hours. Methyl iodide was used as a catalyst. This work appears to have been overlooked by all later investigators. In a later communication[14], where the same Grignard reagent was treated with carbon disulfide, he states that the second halogen could not be brought into the reaction.

More recently Votocek and Köhler[15] took up a study of the preparation of Grignard reagents with aromatic polyhalides with the intention of ascertaining, first, in what way the formation of Grignard reagents was dependent on the halogens present; second, whether more than one halogen would react. Using iodine as a catalyst, they secured Grignard reagents with ortho-bromoiodobenzene, all three di-iodobenzenes, and 1-iodo-2,4-di-chlorobenzene, while 1-bromo-2,4-di-chlorobenzene and 1,2,4-tri-bromobenzene failed to react. However, except for

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[13] Houben, Ber., <u>38</u>, 3796 (1905).
[14] Houben, Ber., <u>39</u>, 3219 (1906).
[15] Votocek and Köhler, Ber., <u>47</u>, 1219 (1914).

p-di-iodobenzene, they do not state whether they secured a mono- or di-Grignard reagent. From this they concluded that the more negative the halogen the more difficult it is to bring it into the reaction, and by the presence of negative halogens the ability of slightly negative halogens to form Grignard reagents can eventually be reduced to the point of completely preventing the reaction.

On working up the products of the Grignard reagent obtained from p-di-iodobenzene and two moles of magnesium after acid hydrolyses, they secured benzene as the chief product, while bi-phenyl and p-iodobiphenyl were secured in small quantities. Thus, in answer to their second question, they were able to demonstrate for the first time that more than one halogen in polynuclear compounds could readily be brought into reaction with magnesium.

Recently Thomas[16] has taken up a quantitative study of di-iodo derivatives of benzene and thiophene and has secured solution of 78-88% of two equivalents of magnesium.

Lewis and Dufford[17], and Dufford, Calvert and Nightingale[18] in a study of luminescence of Grignard

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[16] Thomas, Compt. rend. 181, 218 (1925).
[17] Lewis and Dufford, J. Am. Chem. Soc., 45, 278 (1923).
[18] Dufford, Calvert and Nightingale, <u>ibid</u>., 45, 2058 (1923); 47, 95 (1925).

reagents have investigated a wide variety of polyhalogen nuclear compounds, but their work is of little value in this connection since some of their results are based on erroneous assumptions, and further, they cannot be sure that the results obtained with chloro derivatives are due to organomagnesium chlorides or to the organomagnesium bromide used as a catalyst.

Because of the inherent difficulties encountered in working up the products obtained from organomagnesium iodides, and as Gilman and McCracken[19] have shown that better yields are secured with the corresponding bromides, it seems important to endeavor to secure a catalyst or experimental condition whereby the second bromine can be brought into the reaction.

Fink[20] has recently endeavored to secure a di-Grignard reagent with p-di-bromobenzene by carrying out the reaction at -10°, at room temperature, by adding a fresh supply of magnesium to p-bromophenylmagnesium bromide, and by adding magnesium activated with Grignard reagents to p-bromophenylmagnesium bromide. However, their experiments were without success.

[19] Gilman and McCracken, J. Am. Chem. Soc., 45, 2462 (1923).
[20] Fink, J. Chem. Soc., 123, 3418 (1923).

PROCEDURE

In a recent study of a wide variety of catalysts with compounds that formed Grignard reagents rather sluggishly, Gilman and Peterson[21] obtained several catalysts, copper magnesium alloys, that were exceptionally effective in starting the reaction. It was decided to try these catalysts on aromatic polyhalogen compounds with a view of bringing more than one halogen into the reaction.

One equivalent of magnesium was placed in a three-necked flask fitted with a mercury sealed stirrer and a Hopkin's condenser and then placed in an electric oven and heated to 110° for several hours, when the organic halide was added and heated to its boiling point for two to five minutes. After cooling the flask somewhat, small amounts of ether were added, and in general the reaction started at once, otherwise a couple drops of bromine were added. After the reaction had gone to completion for one equivalent of magnesium, from one half to one equivalent of a 2% or 12.5% copper-magnesium alloy was added.

In several cases high boiling solvents were used, while in other cases the solution was refluxed for 8-12

[21] Gilman and Peterson. Unpublished results.

hours, but in all these experiments more tarry unidentifiable products were secured.

The reaction flask was then packed in an ice-salt mixture and stirred for fifteen to thirty minutes before carbon dioxide was introduced.

The carbon dioxide was passed through two sulphuric acid wash bottles and then a tower filled with soda lime and calcium chloride. It was introduced into the flask with the outlet about one inch above the surface of the liquid until the etheral solution no longer gave a test for Grignard reagent with Michler's ketone. This usually required from one to three hours.

MATERIALS

The magnesium was the ordinary magnesium turnings obtained from the Eastman Kodak Company. All solid compounds were recrystallized from alcohol and dried in a vacuum desiccator over concentrated sulphuric acid for at least a week. The catalysts used were a 2% copper-magnesium alloy, a 2% copper-magnesium alloy activated with iodine by heating them together in a sealed tube for five hours at 180-200°, and a 12.5% copper-magnesium alloy.

EXPERIMENTAL PART

A. The use of various catalysts and conditions in an endeavor to cause both halogens of p-di-bromobenzene to react.

The use of ordinary magnesium:

Carbon dioxide was passed into the Grignard reagent prepared in anhydrous ether from 23.6 g. (.1 mole) p-di-bromobenzene and 5 g. (.2 mole) magnesium turnings for one and one half hours. The reaction product was then hydrolysed with iced hydrochloric acid. After evaporating the ether the insoluble product was filtered, and then extracted with alkali. The alkali insoluble product after recrystallization from alcohol gave 1 g. (.003 mole 5.9%) 4,4'-di-bromobenzophenone, m. p. 170-171°.

The alkaline solution was acidified with hydrochloric acid, digested on the steam bath for an hour in order to coagulate the fine precipitate, cooled, and then filtered. After recrystallizing from alcohol 12.5 g. (62.2%, .062 mole) p-bromobenzoic acid was secured, melting at 251°. It was further identified by conversion into the methyl ester which melted at 74°.

The use of a small amount of 12.5% copper-magnesium alloy:

During the preparation of the Grignard reagent from 23.6 g. (.1 mole) p-di-bromobenzene and 5 g. (.2 mole) magnesium the ether stopped refluxing after about half of the magnesium had gone into solution. Then .5 g. of 12.5% copper-magnesium alloy was added, but, as no apparent reaction took place, the reaction mixture was boiled for three hours. No further reaction had taken place. Then .5 g. of the alloy was activated in a test tube with iodine and added to the reaction product. After no apparent reaction had taken place in fifteen minutes the reaction product was again maintained at a gentle boil for three hours without apparently causing further reaction.

The reaction flask was then immersed in an ice-salt bath and treated with carbon dioxide for one hour. The ether layer was decanted, treated with dilute hydrochloric acid, and dried over calcium chloride. On evaporating the ether about .5 g. of an oily solid was secured which consisted of a halogen containing oil and .2 g. melting at 150-160°. A mixed melting point with some pure 4,4'-di-bromobenzophenone melted at 160-170°.

The residue from the decanted ether was hydrolysed with iced-hydrochloric acid, filtered, washed with cold water, dried for an hour at 110° and then taken up in a large volume of ether. A small amount of solid remained in suspension even after the use of an extra large volume of ether (about 500 cc.). The ether solution was then filtered, and the insoluble product, after being washed with about 100 cc. more ether, weighed .2 g. It did not melt below 300°. About .1 g. was heated with phosphorous pentachloride and then esterified with methyl alcohol, giving a very small amount of white flaky solid which melted at 134-138° except for a very small portion which clung to the side of the melting-point tube and did not melt completely below 200°. A mixed m. p. with some pure dimethyl terephthalate melted at 136-139°.

The ether solution, after being concentrated, yielded 10 g. (.05 mole, 49.8%) of dried p-bromobenzoic acid melting at 250°.

The use of 2% copper-magnesium alloy:

To .1 mole p-bromophenyl magnesium bromide prepared in anhydrous ether from 23.6 g. (.1 mole) p-di-bromobenzene and 2.4 g. (.1 mole) magnesium turnings, 2.5 g. (.1 mole magnesium) 2% copper-magnesium alloy was added.

After about five minutes stirring the ether began to reflux gently and continued refluxing for about five minutes. The reaction product was then maintained at a gentle refluxing of the ether for two hours, and then treated with carbon dioxide.

The ether solution was decanted, treated with dilute hydrochloric acid, dried over calcium chloride and then concentrated, when a pasty solid was secured. After recrystallization from alcohol, .1 g. (.6%, .0003 mole) 4,4'-di-bromobenzophenone melting at 168-170° was obtained.

The residue from the decanted ether was hydrolysed with iced hydrochloric acid and filtered. It was then taken up in ether and allowed to stand in a separatory funnel when a fine white solid settled out. This was then separated and dried. As it gave a Beilstein test for halogen, it was taken up in alkali, reprecipitated with hydrochloric acid, filtered, and washed with ether when .2 g. terephthalic acid (1.2%, .0012 mole) was secured which gave a feeble Beilstein test, and did not melt below 300°. It was then converted into the dimethyl ether which melted at 140-142°.

From the ether solution 13.5 g. (.067 mole, 67.1%) p-bromobenzoic acid was secured.

The use of activated 2% copper-magnesium alloy:

To an ether solution of p-bromophenyl magnesium bromide prepared from 23.6 g. (.1 mole) p-di-bromobenzene and 2.4 g. (.1 mole) magnesium turnings, 2.5 g. (.1 mole magnesium) 2% activated copper-magnesium alloy was added. Soon after the addition of the alloy the ether began to reflux and continued to do so for about ten minutes. The reaction product was then maintained at a gentle boil for two hours before treating it with carbon dioxide.

The decanted ether solution was treated with dilute hydrochloric acid and dried over calcium chloride. On being concentrated it gave a dark pasty solid which on recrystallization from alcohol gave .2 g. (1.2%, .0006 mole) 4,4'-di-bromobenzophenone melting at 164-168°.

The residue from the decanted ether was hydrolysed with iced-hydrochloric acid and filtered. It was then taken up in ether and filtered from the insoluble portion. The insoluble residue was washed with ether, taken up in dilute alkali and reprecipitated with hydrochloric acid. The dried acid did not melt below 300°. The supposed terephthalic acid (.2 g. crude) was first treated with phosphorous pentachloride and then with methyl alcohol.

A very small amount of white flaky solid was secured which partially melted at 135-140° but was not completely melted until 170°. A mixed melting point with di-methyl-terephthalate melted at 130-135°, 125-133°, and 125-130°.

The ether gave 12.5 g. (62.2%, .062 mole) p-bromobenzoic acid melting at 250°.

A second run using the above catalyst:

Since the above supposed terephthalic acid, on being converted into its di-methyl ester, yielded such a poor product a second larger run was made in order that more of this product could be obtained.

To the p-bromophenylmagnesium bromide prepared in 1-l. of ether from 236 g. (1 mole) p-di-bromobenzene and 24.3 g. magnesium, 3 g. of the activated 2% copper-magnesium alloy was added. This caused the ether to start refluxing, and continued for two hours. Most of the alloy appeared to have gone into solution. After standing for several hours another 3 g. alloy was added, but it failed to cause the reaction mixture to warm up. Although stirring was continued for 8 hours, little if any of the last added alloy went into solution.

During the early addition of carbon dioxide it had to be introduced very slowly or the ether would reflux. After carbon dioxide had been introduced for one and one-half hours the reaction product became very thick. It was treated with iced hydrochloric acid and a large volume of ether (2.5-3 l.) when an insoluble product was secured at the interface. This was filtered off, and extracted with alkali, when 4 g. of a tarry insoluble product was left. The alkaline solution was acidified, filtered, and dried over night at 110°. 11.5 g. were thus secured. It was then powdered and again extracted with ether, after which only .8 g. (.005 mole, .5%) terephthalic acid was secured. It did not melt below 300°, and gave a di-methyl ester melting at 135-138°. A mixed melting point with some known ester showed no depression. The ether extract gave 3 g. p-bromobenzoic acid melting at 148-150°.

The filtered ether solution was extracted with about 5% sodium hydroxide which caused a substance to separate at the interface and cause troublesome emulsions. On filtering the alkaline extract and the ether, .3 g. of tarry material was secured.

The alkaline solution on being acidified, yielded 103 g. p-bromobenzoic acid melting at 148-150°. This, with the above secured three grams, is equivalent to 63.9 % (0.64 mole) p-bromobenzoic acid.

The ether solution was concentrated to about 200 cc. and then allowed to evaporate spontaneously. A pasty solid was secured which, on recrystallization from alcohol, yielded 12 g. (.035 mole, 35.3%) 4,4'-di-bromobenzophenone melting at 168°.

The use of Anisole as a solvent:

A test with Michler's ketone could not be obtained with p-di-bromobenzene using anisole as a solvent, although iodine, bromine, and activated 2% and 12.5% copper-magnesium alloy were added. On adding about 25 cc. anhydrous ether the reaction started at once.

p-Bromophenylmagnesium bromide was prepared in an anisole-di-ethyl-ether solution from 23.6 g. (.1 mole) p-di-bromobenzene and 2.4 g. magnesium. After the reaction had gone to completion for one bromine, 2.5 g. (.1 mole magnesium) activated 2% copper-magnesium alloy was added. After being stirred for two hours no noticeable solution of the alloy had taken place. Carbon dioxide was then passed into the reaction flask for two hours.

The reaction product was then hydrolysed with iced-hydrochloric acid. After adding about 500 cc. ether there remained at the interface a small amount of white solid which on being separated and dried weighed less than .1 g. It was not investigated further.

The ether-anisole was then steam distilled to remove the anisole. The residue was then extracted with ether, when all the solid went into solution. The fine pasty solid secured from the ether was taken up in alkali. After filtering the alkaline solution the acid was reprecipitated, and the acid solution was digested on the steam plate for several hours. This caused the fine milky solid to coagulate into a more filterable form. After drying at 110° for 2 hours, 12 g. (57.5%, .058 mole) p-bromobenzoic acid was secured which melted at 149-150°.

<u>The use of dimethyl aniline as solvent:</u>

On adding 23.6 g. (.1 mole) p-di-bromobenzene to 2.4 g. (.1 mole) magnesium in dimethyl aniline as a solvent no reaction took place even after catalysing with bromine, iodine, ethyl bromide and activated copper-magnesium alloys. Fifty cc. anhydrous ether was then added. After stirring for 2 hours a positive test for the presence of the Grignard reagent was secured. Carbon dioxide was passed into the reaction flask for two hours, although no positive test could be secured after fifteen minutes. The reaction product was then decomposed with a large excess of hydrochloric acid and filtered. The residue was then taken up in alkali and steam distilled to remove the last traces of dimethyl aniline.

The alkaline solution was filtered, made acid, and then extracted with ether when all the bluish white solid went into solution. After evaporating the ether 5.2 g. (31.3%, .03 mole) p-bromobenzoic acid was secured.

B. A study of polyhalogen aromatic compounds other than p-di-bromobenzene.

p-Di-iodobenzene:

The Grignard reagent prepared in anhydrous ether from 12.2 g. (.037 mole) p-di-iodobenzene and 1.8 g. (.075 mole) magnesium was subjected to a rapid current of carbon dioxide for one and one-half hours. The reaction product was hydrolysed with iced hydrochloric acid and filtered when two and one-half g. (.0124 mole, 33.8%) terephthalic acid was secured. The ether solution on being concentrated gave a small amount of p-di-iodobenzene melting at 125-128° and about 5 g. of an intractable oil.

The terephthalic acid was converted into the dimethyl ester which melted at 137-140°.

m-Di-iodobenzene:

The meta-di-iodobenzene used in this run was not recrystallized.

Using 15 cc. of a saturated ether solution of meta-di-iodo benzene and 2.5 g. (.1 mole) magnesium, the reaction failed to start even on adding ethyl bromide, iodine, and activated magnesium, but started at once on adding one drop of liquid bromine. An ether solution of the remainder of 16.5 g. (.05 mole) meta-di-iodobenzene was then added dropwise. After the reaction mixture had been stirred for an hour carbon dioxide was led into the reaction chamber for two hours. The ether was first decanted. On evaporating the ether a small amount of pasty solid was secured, from which nothing was identifiable.

The residue from the decanted ether was hydrolysed with iced hydrochloric acid and filtered. In this manner 4 g. (.024 mole, 48.2%) iso-phthalic acid was secured. It was identified by converting it into the dimethyl ester which melted at 60-64°.

sym-Tri-bromobenzene:

12.6 g. (.04 mole) 1,3,5-tri-bromobenzene and 1.5 g. (.06 mole) magnesium were heated together for five minutes at the boiling point of the aryl halide. On adding ether there was no evidence of a reaction. No reaction took place although it was catalysed with iodine, bromine, ethyl bromide, bromobenzene, ordinary and activated 2% and ordinary and activated 12.5% copper-magnesium alloys.

After treating the reaction product with carbon dioxide for five hours it was hydrolysed and worked up in the usual manner, but no acid product was secured. However, 9 g. (71.4%, .029 moles) recrystallized tri-bromobenzene melting at 118° was recovered.

o-Di-bromobenzene:

Using bromine as a catalyst, a Grignard reagent was prepared from 11.8 g. (.05 mole) o-di-bromobenzene and 3 g. (.12 mole) magnesium. Since only a small amount of the metal went into solution toluene was added and the reaction mixture was refluxed for 12 hours at 105°. After subjecting the reaction mixture to a steady stream of carbon dioxide for two hours, the reaction product was hydrolysed with iced hydrochloric acid. No solid insoluble material remained at the interface. On evaporating the ether an oil was thrown out which could not be induced to crystallize. It was then taken up in alkali and reprecipitated as an oil on adding hydrochloric acid. It could not be induced to crystallize. On treating the oil with bromine water 1 g. (.0032 mole, 31.7%) tri-bromophenol was secured melting at 94-96°. A mixed melting point showed no depression. In this run a test for the Grignard reagent with Michler's ketone was not made.

m-Di-bromobenzene:

Run I.--The Grignard reagent prepared from 11.8 g. (.05 mole) m-di-bromobenzene and 3 g. (.12 mole) magnesium was diluted with dry toluene and refluxed for 14 hours at 100°. After treating the reaction mixture with carbon dioxide and working it up the same as in the previous run, nothing but a tarry product was secured. In this run a test for the Grignard reagent with Michler's ketone was not made.

Run II.--11.8 g. (.05 mole) m-di-bromobenzene was heated to its boiling point with 1.2 g. (.05 mole) magnesium for five minutes. On adding ether the reaction started at once and nearly all the magnesium was used up before the reaction subsided. Then 1 g. (.04 mole) more magnesium was added, but the reaction flask continued to cool. Then .5 g. 12.5% copper-magnesium alloy was added, but no further reaction was apparent. The reaction mixture was treated with carbon dioxide for two hours. The ether solution was decanted, treated with hydrochloric acid, dried and evaporated, leaving about 1 cc. of a halogen-containing oil.

The residue in the reaction flask was then hydrolysed with iced hydrochloric acid. The insoluble product was filtered, taken up in ether and after numerous recrystallizations from alcohol, acetic acid and ether, 4 g. (.002 mole, 40%) m-bromobenzoic acid was secured melting at 152-153°. A mixed m. p. showed no depression.

CONCLUSIONS

1. It has been shown that there is no analogy between Grignard formation with polyhalogen compounds and Fry's electronic formula.

2. Among the best catalysts in use for starting Grignard reagents, none is capable of inducing more than one halogen to react to form the Grignard reagent with polyhalogen aromatic compounds, that are not formed without the catalyst.

A STUDY OF ANTIKNOCK COMPOUNDS

INTRODUCTION

Everyone is familiar with the so-called "knock" in engines laboring at low speed while in high gear, or accelerating from low speed. It is the result of detonations of the highly compressed fuel in the cylinder head.

There are two prevailing theories which endeavor to account for this phenomenon.

The first theory explains the knock as being due to a sudden high increase of pressure in the cylinder head. The first portion of the gas ignited raises the pressure to such a point that some of the unburnt gas condenses. As the temperature is raised, due to the combustion of the burnt gas, the condensed gas suddenly explodes, resulting in the familiar knock.

The second theory explains the knock as being due to high-velocity, high-pressure waves hitting the walls and head of the cylinder.

Experience has shown that detonations can be eliminated by adding a negative catalyst which will cut down the reaction velocity of the combustion.

Dr. O. R. Sweeney, head of the Chemical Engineering Department, has been interested for a number of years in antiknock compounds. From among a large number of aromatic compounds investigated, naphthalene was found to be very satisfactory. Soon after the completion of these experiments, Midgley and Boyd[1a] published the results of some of their experiments with aliphatic organo-metallic derivatives.

Since lead tetraethyl proved to be an exceptionally good negative catalyst to cut down the reaction velocity, while naphthalene alone was very satisfactory, it was thought desirable to test the effectiveness of some lead tetraaryl derivatives.

HISTORY OF THE PREPARATION OF LEAD TETRA-ALKYL AND ARYL DERIVATIVES

Lead tetra-ethyl was first prepared by Löwig[2a] by treating ethyl iodide with a sodium-lead alloy. A slight modification of this method is being used at the present time by the Du Pont Company at Wilmington to prepare the lead tetra-ethyl for the General Motors Chemical Company.

1a. Midgley and Boyd, Ind. Eng. Chem., 14, 849, 894 (1922).

2a. Löwig, Ann., 88, 318 (1853).

Buckton[3a] secured lead tetra-ethyl by treating lead chloride with zinc di-ethyl. In a later communication he secured lead di-ethyl in the above manner, which he could not isolate as a pure product, because it was no doubt contaminated with lead tetra-ethyl[4a].

Lead tetra-phenyl was first prepared by Polis[5a] by heating an ethyl acetate solution of bromobenzene and a 4-6% sodium lead alloy in an oil bath for sixty hours. He also prepared lead tetra-tolyl by this method, however, it failed to give lead tetra-benzyl. A similar result has been observed by Mr. C. E. Adams in this laboratory when he endeavored to prepare lead tetrabenzyl by means of benzylmagnesium chloride and lead chloride.

The further study of organo-lead derivatives remained dormant until after the discovery of the Grignard reagent. In 1904 Pfeiffer and Trusken[6a] were the first to prepare lead tetra-aryl, tetra-alkyl, and tetra-aryl alkyl derivatives by means of the Grignard reagent.

[3a] Buckton, ibid., 109, 222 (1859).
[4a] Buckton, ibid., 112, 226 (1859).
[5a] Polis, Ber., 20, 717, 3332 (1887).
[6a] Pfeiffer and Trusken, Ber., 37, 1125 (1904).

Grüttner[7a], after an extensive study of organo-lead derivatives, recommends Pfeiffer's method, using the Grignard reagent, because the zinc alkyls and sodium-lead alloy methods are too expensive.

Lederer[8a] prepared a number of mixed tetra-aryl derivatives. Krause and Maira Schmitz[9a] prepared a number of mixed tetra-alkyl-aryl lead derivatives. They[10a] also prepared tri-aryl lead derivatives in which the lead is analogous to carbon in tri-phenylmethyl.

EXPERIMENTAL

To the Grignard reagent prepared from 236 g. (1.5 mole) bromobenzene and 36.5 g. (1.5 mole) magnesium there were added in small portions 139 g. (.5 mole) lead chloride. The reaction mixture was diluted to about 1-l. with anhydrous benzene and the whole was then refluxed with stirring for about eight hours. The reaction mixture, after cooling, was decomposed with dilute hydrochloric acid. Lead, in small compact balls, remained in the bottom of the flask, while a small amount of unchanged

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[7a] Grüttner, Ber., <u>44</u>, 1415 (1911); <u>49</u>, 1125 (1916); <u>51</u>, 1293, 1298 (1918).

[8a] Lederer, Ber., <u>49</u>, 349 (1916).

[9a] Krause and Schmitz, <u>ibid</u>., <u>52</u>, 2120 (1919).

[10a] Krause and Schmitz, <u>ibid</u>., <u>52</u>, 2165 (1919).

lead chloride was suspended at the interface. The benzene-ether layer was drawn off, dried over potassium carbonate, and concentrated to a small volume when 49.5 g. of lead tetra-phenyl melting at 224° separated out. On further concentrating the solution an additional 10 g. were secured, making a total yield of 59.5 g. (0.127 mole, 50.5%).

In several previous runs where the time of refluxing was not as long, or where the reaction was carried out at the temperature of boiling ether the yields were poorer, being as low as 16%.

Owing to the fact that it was deemed desirable to combine the value of the lead derivative and that of nitrobenzene it was found necessary to determine the solubility of lead tetra-phenyl in nitrobenzene, for no quantitative data could be found in the literature. For this purpose one gram of lead tetra-phenyl was added to 100 cc. nitrobenzene and the whole digested at 110° for an hour, there being an excess of lead tetra-phenyl. After standing at room temperature for 24 hours the excess was filtered off, dried and weighed. It was thus found that .574 g. lead tetra-phenyl was soluble in 100 cc. at approximately 25° C.

Preparation of Lead Tetra alpha-Naphthyl

Run I.--To 0.8 mole alpha-naphthylmagnesium bromide prepared in anhydrous ether from 165.6 g. alpha-naphthyl bromide and 19.5 g. magnesium there were added in small portions 69.3 g. (0.25 mole) lead chloride. Each addition of chloride caused a mild refluxing of ether. After refluxing for five hours the reaction mixture was decomposed with iced dilute hydrochloric acid and then extracted with a large volume of benzene. On concentrating the benzene ether extract to about 150 cc. and cooling about one gram of a dark grey product came down which did not melt below 300°. When heated on a crucible cover it behaved similar to lead tetra-phenyl.

Run II.--After several unsuccessful attempts to increase the yield of this derivative the following run was made using the same quantities as above. However, after adding all the lead chloride 500 cc. benzene were added. Then about 200 cc. low boiling solution was distilled off when the whole became too solid to stir. Enough benzene was added to bring the total volume to 1200 cc. and upon warming the thick mass went into solution. After refluxing for 10 hours the reaction mixture was decomposed in the conventional manner. No lead had collected in balls as was the case with the preparation of lead tetraphenyl. The insoluble product was then removed by filtration and divided into two approximately equal portions and placed in thimbles of ordinary Soxlet extraction flasks. Into one flask the benzene from the reaction was added while toluene was added to the other. After extracting for five hours the solvents were removed, distilled, and returned to the extraction apparatus. This was repeated three times. From the combined extracts about 2 grams were secured. The solvents were then replaced by nitrobenzene but after 10 hours extracting the amount of product extracted was negligible.

In conclusion it must be said that if lead tetra-alphanaphthyl was formed it is too insoluble in ordinary solvents to be of any value as an anti-knock derivative.

TECHNICAL APPLICATION

Solutions of lead tetra-phenyl in nitrobenzene were made up in such strengths that when added to a ten-gallon tank of gasoline the concentrations of lead tetra-phenyl were 1 part in 5,000, 1 part in 50,000, 1 part in 100,000, 1 part in 250,000, and 1 part in 500,000, and given to Dr. Sweeney who had various people try them out.

Although the work on testing solutions of lead tetra-phenyl was not of a quantitative nature, the reports were that it was apparently as good as Ethyl gas.

CONCLUSIONS

1. Lead tetra-phenyl was found to be a good antiknock compound.

2. Owing to the small solubility of the products obtained from alpha-naphthylmagnesium bromide, it cannot be considered as an antiknock compound.