1935

The relative reactivities of some organometallic compounds

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Recommended Citation

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THE RELATIVE REACTIVITIES OF SOME
ORGANOMETALLIC COMPOUNDS

by

124
12-06

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A Thesis Submitted to the Graduate Faculty
for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject Organic Chemistry

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Iowa State College

1935

ACKNOWLEDGEMENT

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

TABLE OF CONTENTS

Page

INTRODUCTION 5

A. THE COLOR TEST WITH ORGANOMETALLIC COMPOUNDS 9

  INTRODUCTION 9

  EXPERIMENTAL 12

  DISCUSSION OF RESULTS 18

  SUMMARY 19

B. SOME REACTIONS OF ORGANO-ALUMINUM COMPOUNDS 20

  INTRODUCTION 20

  EXPERIMENTAL 28

    Reaction with Phenyl Isocyanate 36

    Reaction with Carbon Dioxide 37

    Reaction with Benzophenone 38

    Reaction with Oxygen 38

    Reaction with Benzaldehyde 38

    Reaction with Benzonitrile 39

    Reaction with Esters 39

  DISCUSSION OF RESULTS 40

  SUMMARY 42

C. SOME REACTIONS OF ORGANOBORON COMPOUNDS 43

  INTRODUCTION 43

  EXPERIMENTAL 51

    Reaction with Phenyl Isocyanate 57

    Reaction with Benzaldehyde 57

  DISCUSSION OF RESULTS 59

  SUMMARY 61

Page

D. SOME REACTIONS OF ORGANOZINC COMPOUNDS 62

INTRODUCTION 62

EXPERIMENTAL 65

Reaction with Carbon Dioxide 67

Reaction with Benzophenone 67

Reaction with Phenyl Isocyanate 68

Reaction with Benzonitrile 68

DISCUSSION OF RESULTS 69

SUMMARY 70

E. THE RELATIVE REACTIVITIES OF ORGANOMETALLIC COMPOUNDS OF ALUMINUM, BORON AND ZINC 71

INTRODUCTION 71

EXPERIMENTAL 80

Reaction Rates with Michler's Ketone 84

Minimum Concentration Giving the Color Test 87

Reaction Rates with Benzaldehyde, Benzophenone and Benzonitrile 89

Rate of Displacement of Mercury from Organomercury Compounds by Aluminum and Zinc 93

DISCUSSION OF RESULTS 95

SUMMARY 99

THE RELATIVE REACTIVITIES OF SOME ORGANOMETALLIC COMPOUNDS

Introduction

Organic synthesis is, in general, based upon the use of selective or preferential reactions. Organic chemistry is built upon the reaction of an organic compound with one or more other elements or compounds. The success of any reaction depends to a large extent on the reactivities of the groups involved. The ability to predict how a reaction will proceed or the best synthesis to use in each case depends upon knowledge of the relative reactivities of the compounds or groups involved. Organometallic compounds have often been used in reactions with polyfunctional compounds. Thus, Noller and Adams (1) by the proper use of a Grignard reagent on aldehyde esters obtained compounds that showed addition to the aldehyde group but not to the ester group. A large number (2) of such preferential reactions with polyfunctional compounds are found in the chemistry of organomagnesium compounds. In some cases, however, preferential reaction does not take place as the Grignard reagent reacts equally well with all functional groups present. Thus, Boyd and Ladhams (3) hoped that by the use of preferential

(1)Noller and Adams, J. Am. Chem. Soc., 48, 1074 (1926).
(2) (a) Grignard, Compt. rend., 134, 849 (1902); (b) Fordyce and Johnson, J. Am. Chem. Soc., 55, 3368 (1933); (c) Mavrodin, Bul. soc. chim. Romania, 15, 99 (1933).
(3) Boyd and Ladhams, J. Chem. Soc., 1928, 2089.

reaction they could convert methyl o-cyanobenzoate into o-cyanotriphenylcarbinol. They found, however, that phenylmagnesium bromide in ether solution reacted with both the cyano and the ester groups. No trace of o-cyanotriphenylcarbinol could be detected. Finger and Gaul (4) report that in the reaction of Grignard reagents on methyl cyanoformate both the ester and cyano groups were attacked by the Grignard reagent. It is hoped that by the use of organometallic compounds less reactive than the Grignard reagent preferential reactions of this type can be carried out without difficulty. This may open new fields whereby otherwise inaccessible compounds may be prepared through the medium of selective or preferential reactions involving organometallic compounds less reactive than the Grignard reagents.

Organometallic compounds probably constitute the most important group of compounds used in synthesis. They include all compounds which are characterized by the carbon-metal linkage and may be represented as falling into three important classes: first, those containing only like R groups attached to the metal; second, those having different R groups attached to the metal; and third, those having both R groups and halogen attached to the metal. The task of comparing the reactivities of all of these different compounds is great, and it is only through continued effort that it may be achieved.

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(4) Finger and Gaul, _J. prakt. Chem._, _111_, 54 (1923).

The proper method of approach in a study of this kind seems to be to attempt a correlation between the chemical reactivities of the organometallic compound and the position of the metal in the periodic table. The more reactive organometallic compounds seem to be formed from the metals in the lower left hand corner of the periodic table; that is, the more positive the metal the greater the reactivity, and the organorubidium and organocesium compounds appear to be more reactive than those higher in the group (5).

The organometallic compounds of the second group elements appear to be less reactive than the organoalkali compounds (6), while the alkaline earth metals and magnesium form the most active organometallic compounds of the second group metals.

In this study an attempt has been made to compare the relative reactivity of the organometallic compounds of zinc of the second group elements with those of aluminum and boron in the third group. Due to the wide range of reactivity of the many organometallic compounds, from the very reactive organoalkali compounds to the relatively stable organocompounds of tin, bismuth and lead, it is difficult, if not impossible, to find any one reaction which could be used in

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(5) For a general review and references see: Julius Schmidt, "Organometallverbindungen." Stuttgart. 1934.

(6) Gilman and Kirby, J. Am. Chem. Soc., 55, 1265 (1933).

a quantitative manner to measure all their relative reaction velocities or reactivities. In the case of the three metals chosen the reactions entered into by all three are very few. The reactions of organoaluminum and -boron compounds with compounds containing different functional groups have been little studied. Therefore, it is first necessary to investigate the reaction of organozinc, -aluminum, and -boron compounds with certain functional groups and then to choose those best suited for a comparison of the relative reactivities.

A. THE COLOR TEST WITH ORGANOMETALLIC COMPOUNDS

Introduction

The color test for reactive organometallic compounds has been of very great use in measuring the relative reactivities of such compounds. It has been used in comparing organometallic compounds of different metals with each other (6); for comparing the reactivity of organometallic compounds with different R groups with selected reactants (7); and for distinguishing between RMgX and R_2Mg compounds (8).

The color test as developed by Gilman and Schulze (9) depended upon the formation of tertiary alcohols by the interaction of Michler's ketone (tetramethyl-p-diaminobenzophenone) and an organometallic compound. The test was designated as a color test for reactive organometallic compounds, as it was thought that only the more reactive of these compounds formed by metals of the first and second group of the periodic table would give the test. The test was reported as being given by the organoalkali compounds, the Grignard reagents, organoberyllium, organocalcium, and organobarium

(7) (a) Gilman and Pickens, J. Am. Chem. Soc., 47, 2406 (1925);
(b) Gilman, Heck, and St. John, Rec. trav. chim., 49, 212 (1930);
(c) Gilman and St. John, ibid., 49, 222 (1930).

(8) Bachmann, J. Am. Chem. Soc., 52, 4412 (1930).

(9) Gilman and Schulze, ibid., 47, 2002 (1925).

compounds. Tests were not given by compounds in which the metal was attached to an element other than carbon, and the following organometallic compounds were reported as not giving the color test: ethylzinc iodide, diethylzinc, diethylmercury, di-p-tolylmercury, p-tolylmercuric iodide and tetraethyl-lead. From these results one would predict that the reaction between the above compounds and the carbonyl group does not take place.

Gilman and Schulze (10) found further that certain organomagnesium compounds did not give an immediate color test when treated with Michler's ketone. Thus tertiary-butylmagnesium chloride, bromide and iodide, tertiary-amylmagnesium iodide and tertiary-hexylmagnesium chloride gave a positive test, provided 5 minutes were allowed for the reaction between the Grignard reagent and Michler's ketone. If the hydrolysis was effected immediately after addition of the organomagnesium compound to the Michler's ketone solution the test was very faint or negligible.

In further studies of this color test Gilman and Heck (11) found that the sensitiveness of the test increased with the use of a hot saturated solution of Michler's ketone in benzene. Tertiary-butylmagnesium bromide was found to give a test when its solution was allowed to stand 3 to 4 minutes with Michler's ketone solution prior to hydrolysis. Furthermore, an immediate test was obtained when a hot concentrated

(10) Gilman and Schulze, Bull. soc. chim., 41, 1479 (1927).
(11) Gilman and Heck, Rec. trav. chim., 48, 193 (1929).

solution of Michler's ketone was used.

Work with the Grignard reagent of (β-chloro-ethyl)-methylaniline (12) showed that in this case the color only slowly developed when the Grignard reagent was treated with Michler's ketone. This sluggishness is postulated as being due to steric hindrance.

In a study of the relative rates of reaction of organometallic compounds of aluminum, boron, and zinc the first method of attack that suggested itself was use of the color test to determine the time of reaction of these organometallic compounds with selected reactants. The possibility of the use of the color test was investigated and extended to organometallic compounds other than those of the first two groups of the periodic table.

It was found that in some cases the reaction of an organometallic compound with Michler's ketone was an extremely slow reaction requiring several hours or days before sufficient reaction had taken place to give a noticeable color. This suggested the possibility that many reactions heretofore reported as not going may still be carried out if sufficient time of contact is given and conditions are right for the reaction. Thus the apparent absence of reaction between phenylmagnesium bromide and a simple olefinic linkage may be merely a limiting case of an extremely slow reaction.

Besides studying the color test with organometallic compounds of aluminum, boron, and zinc work was also begun on the possibility of a very slow reaction between Michler's ketone

(12) Gilman and Heck, Ber., 62 B, 1379 (1929).

and the less reactive organometallic compounds of the periodic system.

Experimental

The color test for reactive organometallic compounds as developed by Gilman and Schulze (9) was made as follows: "One-half to one cc. of the solution to be tested is treated, at room temperature, with an equal volume of a 1% solution of Michler's ketone in dry benzene. The reaction product is then hydrolyzed by the slow addition of one cc. of water during which the test tube is gently agitated to moderate the vigor of the reaction. The subsequent addition of several drops of a 0.2% solution of iodine in glacial acetic acid develops a characteristic greenish-blue color when Grignard reagent is present."

This test has been modified in several respects to meet the needs of the other organometallic compounds. A sample of 2 cc. was found better than a smaller sample, as in many cases a color would develop with 2 cc. where 1 cc. would not give a color. It is merely a matter of a solution which is more concentrated with regard to the organometallic compound, since the addition of 2 cc. of a sample to 2 cc. of Michler's ketone naturally gives a higher concentration of organometallic compound than the addition of 1 cc. of sample to 2 cc. of Michler's ketone solution.

The test was always carried out in a test tube which had been thoroughly cleaned and dried in an oven at 120°. Two cc. of 1% solution of Michler's ketone in dry benzene was placed in the test tube and the 2 cc. sample of the organometallic compound added to this. The test tube was then tightly stoppered and shaken for several minutes or allowed to stand over a certain period of time. In cases of a very sensitive test it was well to displace the air in the test tube with nitrogen before addition of the sample. The sample was removed in a 2 cc. pipette which had been cleaned and dried. The use of a small rubber bulb from a medicine dropper as a means of applying suction to the 2 cc. pipette was found very effective and prevented troublesome contact with solvent vapors.

The solution of the organometallic compound always gave a better color test if it was added while hot to the Michler's ketone or if the solution was heated for several minutes after addition. In either case the solution was cooled, and approximately 20 drops of a 50% alcohol solution was added to hydrolyze the reaction product. The alcohol solution was used instead of water because better contact was thus obtained between the hydrolyzing agent and the reaction product. Most of the solutions tested were xylene solutions, and hydrolysis with water alone was very slow; whereas, the use of an alcohol-water solution gave very quick results. To the solution, after hydrolysis, was added several drops of a 0.2% solution of iodine in glacial acetic acid. It was found that it was very easy to add too much iodine solution, thus masking a slight green color by the color of the excess iodine. It was found best to add a maximum of 4 to 6 drops at first. If the color was then not fully developed more was carefully added. In all cases 10 drops of the iodine solution was found to give a very characteristic greenish-blue color.

The Color Test with Organoaluminum Compounds. The triphenyl- and tri-p-tolylaluminum compounds in a xylene solution were found to give a positive color test after 5 minutes' contact with Michler's ketone if their solution was of at least 0.1 molar concentration with respect to the triarylaluminum compounds. They give a very greenish-blue color the same as that of the Grignard reagent. If a more dilute solution was used it was necessary to allow the reaction mixture to stand for longer periods of time and in some cases to heat the solution.

With the triethyl- and tri-*n*-propylaluminum compounds the color obtained was not quite as characteristic as with the aryl derivatives. Solutions of 0.1 molar concentration, or greater, gave a color test, but the color generally ranged from a deep purple through a light blue with very little green. The greater part of the color was in the lower aqueous layer, and the color seemed to vary with the concentration. That is, the more concentrated solutions were purple and violet; whereas, the more dilute samples gave a light blue coloration. Dilute solutions gave a color if allowed sufficient time of contact or were heated.

The Color Test with Organoboron Compounds. Both the trialkyl- and the triarylboron compounds gave a very characteristic greenish-blue color when the color test was made. In order to obtain the test after 5 minutes' contact with Michler's ketone without heating, a solution of approximately 1 molar concentration was required. The triarylboron compounds in this case were hydrolyzed after considerable shaking with 50% alcohol, and on addition of the iodine solution the color developed. In some cases the color did not appear until 2 or 3 minutes after the iodine solution was added and on further standing darkened into a very deep green. When concentrated solutions of tri-*n*-propylboron were used, treatment with alcohol and water did not appear to be sufficient to hydrolyze the excess organoboron compound. On addition of iodine solution a temporary color developed which was immediately destroyed on shaking. Krause (13) states that trialkylboron compounds are very stable toward alcohol and water and cannot be easily destroyed in this manner. It was evident that an excess of the organoboron compound was interfering with the color reaction. In order to destroy the excess of the organoboron compound air was bubbled through

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(13) Krause and Nitsche, *Ber.*, *54B*, 2784 (1921).

the solution for approximately 5 minutes. The solution became very warm due to the oxidation, and after cooling, the iodine solution was added. A very good color test was obtained immediately. In the case of more dilute solutions which were allowed to stand over long periods of time or heated this oxidation was not necessary to obtain the color test.

The Color Test with Organozinc Compounds. The organozinc compounds appeared to be rather unreactive with Michler's ketone. When a 1 molar solution of the trialkyl- and triarylzinc compounds are treated with Michler's ketone a color is generally not obtained except after long standing in contact with Michler's ketone or by sufficient heating. The color developed is the characteristic greenish-blue but is not intense except after long contact between the reactants.

Miscellaneous Studies. Because of the fact that the organoboron, -aluminum and -zinc compounds showed the color test, although in some cases the reaction was very slow, it was thought possible that other less reactive organometallic compounds might also add to the carbonyl group if given the proper opportunity. For this reason saturated solutions of the following organometallic compounds in benzene were sealed in test tubes under nitrogen with a 1% solution of Michler's ketone: Diphenylmercury, di-p-tolylmercury, diethylmercury, triphenylbismuth, triphenylstibine, triethyltin chloride, triphenyltin chloride, tetraphenyltin, triphenyl-lead chloride, tetraphenyl-lead, triphenyl-lead and tetra-ethyl-lead. Two cc. of the saturated solutions of the organometallic compounds in benzene and two cc. of Michler's ketone solution were sealed in each test tube. Five tubes for each organometallic compound were prepared along with a tube containing 4 cc. of the solution of the organometallic compound to serve as a blank. The purpose of this test was to allow these reagents to stand for several years and then, working them up in the usual manner, to determine if a very slow reaction had taken place. The first of these tubes was opened 18 months after sealing. In no case was a definite color test obtained; however, the organometallic compounds of mercury and lead that were tested gave on addition of the iodine reagent a solution of a light yellow color bordering on a faint green. In most of the other cases the solutions were a light rose after the addition of the iodine. This seemed to indicate a possible slow reaction with the compounds of lead and mercury. Of the alkyl and aryl compounds the diethylmercury and tetra-ethyl-lead solutions appeared to be closer to the required greenish-blue than did the aryl compounds. A longer period of time must, however, elapse before any definite conclusions can be drawn as to the result of this experiment.

Discussion of Results

The success of the color reaction depends to a very large extent on control of conditions. The usual test as carried out for a Grignard reagent is generally very carelessly done. This may result in negative tests in some cases where an organometallic compound is present. With the less reactive organometallic compounds the color test must be carried out under very careful conditions or it may be missed entirely. Conditions should be as anhydrous as possible, and oxygen should also be excluded to a certain extent. Water and oxygen are, in general, more reactive with organometallic compounds than is the carbonyl group of Michler's ketone, so it is very easy for a small amount of either water or oxygen to spoil a color test.

The fact that organo-aluminum, -boron, and -zinc compounds gave a color reaction points to the possibility that many of the reactions we now consider as not taking place would take place if sufficient time were allowed for it. It is altogether possible that the less reactive organometallic compounds may give a color test if allowed to stand for several years under the proper conditions. It is also possible that compounds such as the substituted ethanes or the organosilicon compounds may also add very slowly to the carbonyl linkage.

Summary

1. Certain changes and modifications have been made in the color test for organometallic compounds.
2. The color test has been extended to organometallic compounds of aluminum, boron and zinc.
3. Investigation of a color test with the less reactive organometallic compounds has been begun.

B. SOME REACTIONS OF ORGANO-ALUMINUM COMPOUNDS

In a consideration of the important part played in organic synthesis by aluminum compounds, the question naturally arises as to whether organo-aluminum compounds themselves are not endowed with great reactivity. This hypothesis is well in accord with the position of aluminum in the periodic table and with the considerations of Zeltner (14). The organo-aluminum compounds have been, however, very little studied; and practically the only interest shown in them has been as a means of interpreting the Friedel and Crafts (15) reaction.

The first organo-aluminum compound was evidently prepared in 1859 by Hallwachs and Schafarik (16). They reacted ethyl iodide with aluminum at 180° and obtained a reactive liquid but did not isolate or identify their product. No doubt they had a sample of the mixed ethylaluminum iodides.

Cahours (17) in 1860 treated ethyl iodide with aluminum in a sealed tube and obtained a substance to which he gave the formula $Al\ (C_2H_5)_3.AlI_3$. The compound was probably an equimolecular mixture of ethylaluminum di-iodide and diethylaluminum iodide. The methyl derivative was also prepared.

By the action of aluminum foil on dialkylmercury compounds

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(14) Zeltner, *J. prakt. Chem.*, **77**, 393 (1908).
(15) Leone, *Atti II congresso naz. chim. pura applicata*, **1926**, 1332.
(16) Hallwachs and Schafarik, *Ann.*, **109**, 206 (1859).
(17) Cahours, *Ann. chim. phys.*, (3) **58**, 20 (1860).

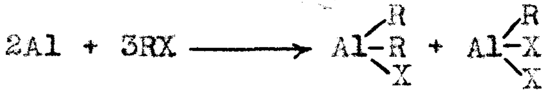
at a temperature slightly above their melting points Buckton and Odling (18) prepared the trialkylaluminum compounds

$$3R_2Hg + 2Al \longrightarrow 3Hg + 2R_3Al$$

In 1888 Friedel and Crafts (19) in an attempt to explain the mechanism of the reaction bearing their name prepared the first triarylaluminum compound. On reacting diphenylmercury with aluminum foil at 125-130° they obtained triphenylaluminum. From a study of this compound the authors considered that triphenylaluminum behaves like a mixture of benzene and aluminum chloride and that this favors the mechanism advanced that an organometallic compound, probably $C_6H_5Al_2Cl_5$, is formed temporarily in the Friedel and Crafts reaction where aluminum chloride is used.

Further studies of triarylaluminum compounds were made in 1912 by Hilpert and Grüttner (20) with their work on triphenylaluminum and its etherate, and later by Krause and co-workers (21) in their studies of the reactions of sodium and ammonia on triarylaluminum compounds.

The true equation for the formation of mixed organoaluminum compounds



$$2Al + 3RX \longrightarrow Al\begin{matrix}R\\R\\X\end{matrix} + Al\begin{matrix}R\\X\\X\end{matrix}$$

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(18) Buckton and Odling, ibid., (4), 4, 492 (1865).
(19) Friedel and Crafts, ibid., (6), 14, 433 (1888).
(20) Hilpert and Grüttner, Ber., 45, 2828 (1912).
(21) (a) Krause and Polack, Ibid., 59B, 1428 (1926);
(b) Krause and Dittmar, Ibid., 63B, 2401 (1930).

was first given in 1908 by Spencer and Wallace (22). They carried out a number of preparations of organo-aluminum compounds but did not separate or identify their products. They reported that the aliphatic derivatives lower in the series than the butyl derivative reacted with aluminum when heated in a sealed tube, while those higher in the series than butyl reacted when they were heated with aluminum in an open flask. Aluminum does not favor the Wurtz-Fittig reaction, that is, the formation of compounds containing twice as many carbon atoms as there are present in the original halogen compound, as in the case of magnesium:

$$2Al + 6RX \longrightarrow 2AlX_3 + 3R.R$$

In an attempt to find a more convenient method for the preparation of trialkylaluminum compounds, Krause and Wendt (23) studied the action of ethyl bromide in the presence of ether on an alloy of magnesium and aluminum. They obtained in this manner triethylaluminum etherate, $4Al(C_2H_5)_3,3(C_2H_5)_2O$. They reported, however, that the etherate could be more easily prepared by the action of sublimed aluminum chloride on ethylmagnesium bromide in ether. They also prepared in this manner the trimethyl- and tri-*n*-propylaluminum compounds.

Grignard and Jenkins (24) in 1924 prepared the mixed organo-aluminum compounds from ethyl iodide and aluminum,

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(22) Spencer and Wallace, *J. Chem. Soc.*, *93*, 1827 (1908).
(23) Krause and Wendt, *Ber.*, *56B*, 466 (1923).
(24) Grignard and Jenkins, *Compt. rend.*, *179*, 89 (1924).

and by fractional distillation separated the mixture into diethylaluminum iodide and ethylaluminum di-iodide. At about the same time Leone (25) reported an easy method for the preparation of these mixed compounds. He found that with the aid of a little anhydrous ether as a catalyst most of the organic alkyl iodides would react with aluminum in an open flask or even in a test tube. The bromides were easily prepared by heating the mixtures in sealed tubes.

The mixed organo-aluminum compounds were generally viscous liquids, and they were extremely reactive toward oxygen or water, thus being very difficult to handle. When the mono- and diethyl compounds were separated, the diethylaluminum iodide was obtained as a colorless liquid boiling at 118-120°/4 mm. It was readily soluble in benzene and chloroform and dissolved easily in ether to give the mono-etherate. The ethylaluminum di-iodide distilled at 158-160°/4 mm. and melted in a sealed tube filled with nitrogen, at 35-37°. It formed well-defined crystals which were soluble in benzene and gave the mono-etherate with ether. Both of these compounds were instantly inflammable in air, giving a reddish flame and great clouds of iodine vapor.

The trialkylaluminum compounds were generally colorless mobile liquids, and they took fire rather easily in air. They were violently decomposed by water, sometimes taking fire. The

(25) Leone, Gazz. chim. ital., 55, 294 (1925).

mono-etherates were easily formed, and the compounds were quite soluble in benzene and its homologues. The aryl compounds are, in general, solids and, although they react rapidly with oxygen, they do not take fire. Water decomposes them rapidly; but, as in most cases the aryl derivatives react less violently than the alkyl derivatives.

In a search for a method of comparison of the relative reactivities of organic compounds of aluminum, boron and zinc further work was done on the reaction of these compounds with different functional groups. The reactions of organozinc compounds have been extensively studied, as they were used largely in organic synthesis before the development of the Grignard reagent. The reactions of aluminum and boron compounds with functional groups have, however, not been greatly studied. They are of interest as a means of comparing chemical reactivities, and they may be distinctive and valuable in their reactions with polyfunctional compounds.

Previous work on organo-aluminum compounds reports that they act as powerful condensing agents. The normal reactions of organometallic compounds were not observed, and generally only the products of condensation were isolated. The reaction of mixed alkyl organo-aluminum compounds with acetone gave mesityl oxide; acetophenone gave triphenylbenzene (26); while with benzaldehyde, Grignard and Jenkins (24) reported nothing but

(26) Leone and Braicovic, Gazz. chim. ital., 55, 301 (1925).

complex condensation products. The mixed ethylaluminum iodides and benzoyl chloride (26) gave small amounts of propiophenone along with α-α-dibenzoylethane and ethane. The reaction with ammonia and amines (27) proceeded similarly to that of the Grignard reagent. Triphenylaluminum (19) reacts vigorously with water forming benzene, diphenyl, and alumina. Oxidation gave some phenol, while reaction of a xylene solution with sulfur produced diphenylene disulfide, phenyl sulfide and probably some phenyl mercaptan. Some diphenylmethane was isolated from the reaction of benzyl chloride on triphenylaluminum, but no reaction was obtained with chlorobenzene. Chloroform gave a yellow semi-crystalline product, but no triphenylmethane was detected. Iodine reacted with triphenylaluminum in the proportions necessary to give aluminum iodide and iodobenzene. Triarylaluminum compounds react with sodium to give R_3Al. Na (21 a); while treatment of the etherates with ammonia yielded the ammine R_3Al. NH_3 (21 b).

In a study of the mechanism of the Friedel and Crafts reaction Leone (15) pointed out that the ketone synthesis could hardly be interpreted by use of organometallic compounds, as he showed that organo-aluminum compounds exerted on ketones a very energetic condensing action not observed in ketone synthesis. In the synthesis of hydrocarbons, however, he presented evidence in support of the view that organometallic

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(27) Leone, *ibid.*, *55*, 306 (1925).

compounds were formed on treatment of aromatic hydrocarbons with aluminum chloride. Phenylaluminum iodide and alkyl halides yielded homologues of benzene.

The author was interested mainly in the simple organo-aluminum compounds, and most of the work thus far has been done with triphenyl- and tri-p-tolylaluminum of the aryl series and tri-*n*-propylaluminum of the alkyl series. Under certain conditions they were found to react with numerous functional groups. In ether or benzene solutions the reaction was very slow, but in boiling xylene reaction was effected quite rapidly and in fair yields. Entemann and Johnson (28) have shown that the nitrile group reacts less rapidly with phenylmagnesium bromide than the other functional groups studied. Since organo-aluminum compounds react normally with benzonitrile, we may assume that they should also react with the more reactive functional groups. In the case of esters, however, none of the expected product has as yet been isolated.

Oxidation of organo-aluminum compounds was also of interest since very poor yields are obtained in the oxidation of aryl Grignard reagents (29); it was hoped that, due to the great affinity of organo-aluminum compounds for oxygen, they might be used to produce substituted phenols. The yields, however, were not satisfactory.

It has been found that triarylaluminum compounds can be

(28) Entemann and Johnson, *J. Am. Chem. Soc.*, *55*, 2900 (1933).
(29) Gilman and Wood, *ibid.*, *48*, 806 (1926).

prepared by the method given by Nesmeyanov and workers (30) for the preparation of diarylzinc compounds. Previously all preparations had been made by heating the organomercury compound slightly above its melting point in the absence of a solvent and with an excess of aluminum. The reaction was carried out either in a sealed tube or in a flask under nitrogen or some other inert gas. The preparation in a xylene solution is much to be preferred as it is considerably faster, prevents loss by sublimation and decomposition and gives a xylene solution of the organometallic compound suitable for use immediately.

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(30) Kocheshkov, Nesmeyanov and Potrosov, Ber., 67B, 1138 (1934).

Experimental

Preparation of Materials. In this work the triphenyl- and tri-p-tolyl- and tri-n-propylaluminum compounds were used. The first two are best prepared by heating the corresponding mercury compounds (21) with aluminum in the absence of a solvent or using xylene as a solvent. The tri-n-propylaluminum is best prepared by the action of aluminum chloride on the corresponding Grignard reagent (23).

Di-p-tolylmercury was obtained from Eastman Kodak Company and was used without further purification. The diphenylmercury was prepared by the method given by Nesmeyanov and Kahn (31) by decomposition of the diazonium-mercury chloride double salt with copper powder. This double salt was best prepared in a one-gallon earthenware crock equipped with an efficient stirrer. To 450 cc. of concentrated hydrochloric acid and 500 cc. of water was added 94 grams (1 mole) of aniline. The suspension of amine-hydrochloride was cooled by the addition of 500 grams of cracked ice. When the temperature reached 5°, solid sodium nitrite (approx. 69 grams) was added slowly until starch-iodide paper showed an excess. During the diazotization about 600 grams of ice was added to keep the temperature at 5°. The cold solution was quickly filtered to remove suspended matter and then returned to the

(31) Nesmeyanov and Kahn, Ber. 62B, 1018 (1929).

crock. A solution of 271 grams (1 mole) of mercuric chloride in 300 cc. of concentrated hydrochloric acid was mixed with 300 grams of ice and added slowly to the rapidly stirred solution. A heavy white precipitate separated, and the stirring was continued for one-half hour after all the mercuric chloride had been added. The complex was filtered on a 20 inch Büchner funnel, sucked as dry as possible, and washed first with two-400 cc. portions of water and then with two-150 cc. portions of acetone. The solid was air-dried at 20°, and the yield was 330 grams or 80%. It is best to use this complex immediately after preparation. It should never be stored in a closed container or near heat or light, as it is rather unstable. An attempt to store a large amount of the double salt in a stoppered bottle resulted in a sudden explosion with considerable force which caused the total decomposition of the entire amount of the double salt.

The decomposition of the diazonium-mercury chloride double salt was carried out in a two-liter three-necked flask equipped with a heavy stirrer. In this was placed 206 grams (0.5 mole) of the double salt and 700 cc. of acetone. 189 grams (3 moles) of copper powder was added to this and the solution quickly cooled to 20°. After being stirred rapidly for about 5 minutes the reaction commenced and unless cooled sufficiently it became extremely vigorous. The solution was stirred rapidly for one hour after the reaction began and then 700 cc. of concentrated ammonium hydroxide (sp. gr. 1.09) was added. This solution was allowed to stand for at least 12 hours, preferably with heating in order to obtain diphenylmercury which is free from halogen (32). The supernatant liquid was decanted and the solid collected on a Büchner funnel where it was washed successively with 25 cc. portions of water, acetone, and ether. After air-drying, the crude product was crystallized from either xylene or a chloroform-alcohol mixture, using decolorizing charcoal. The pure product, free of halogen, and melting at 121.5° was obtained in 51% yields by this method.

The aluminum used was in the form of small chips approximately 0.2 mm. thick, 2 mm. wide, and 1 cm. long. This gave better results than the granulated or powdered aluminum. Five times the required amount of aluminum was generally used.

The reactants were usually purified once, the solids being recrystallized and the liquids redistilled. The solvents were distilled from sodium and stored over bright sodium wire.

Preparation of the Arylaluminum Compounds. Without Solvent. In a 250 cc. three-necked flask provided with an inlet for dry nitrogen and an outlet connected to an oil trap (33) were placed 14.35 grams (0.0385 mole) of di-p-tolylmercury and 3.38 grams (0.125 mole) of aluminum chips. The flask had previously been

(32) Hein and Wagler, Ber., 58, 1499 (1925).
(33) Gilman and Hewlett, Rec. trav. chim., 48, 1124 (1929).

thoroughly dried and swept out with dry nitrogen. The nitrogen used was purified by passage through sodium hydroxide (40%), potassium pyrogallate (25%), sulfuric acid (conc.), and phosphorous pentoxide.

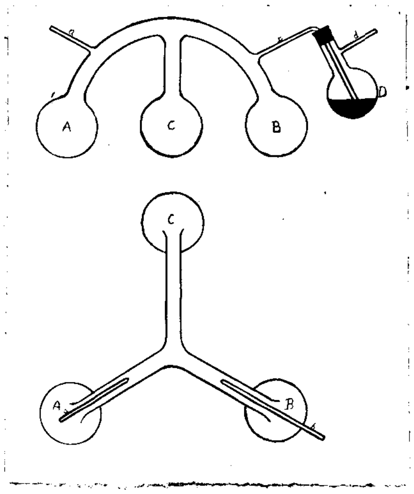

Fig. I

After all air had been replaced by nitrogen the nitrogen inlet was closed and the flask heated with a free flame. Reaction set in as soon as the mercury compound began to melt. At the first sign of reaction the flame was removed, and the reaction proceeded to completion with the evolution of considerable heat. This left a yellow mass of the tri-p-tolylaluminum along with the free mercury and the excess aluminum. The organometallic compound was dissolved in the appropriate solvent and forced by nitrogen into another flask or into the 3-bulb apparatus (Fig. I) of Krause and Polack (21 a). This apparatus consists of three-200 cc. distilling flasks , A, B, and C, of which A and B carry side tubes a and b. These flasks were sealed together at their necks so that they formed a half circle. Tube a was closed at its end, while b was bent so that it could be connected with a distilling flask containing the organometallic compound. The apparatus was first cleaned and dried and then evacuated with a vacuum pump while warming with a luminous flame. It was then filled with pure nitrogen.

The bent exit tube b was connected by means of a rubber stopper to the flask D containing either the solution of the organometallic compound or the solid compound. The flask was attached in such a manner that it was perpendicular. The apparatus was again evacuated through d, the organometallic compound melted if it was a solid, tube b warmed with a free flame, and the organometallic compound forced over into B by nitrogen entering d. If the solvent was not already present the organometallic compound was cooled and 150 cc. of a suitable solvent (usually anhydrous ether) was added in a similar manner and distributed into the 3 flasks. The tube b was then drawn to a capillary, the apparatus evacuated until all nitrogen was displaced by ether, and the tube b sealed off.

The compound was next recrystallized without danger of loss of solvent or compound. The ether was poured by suitable inclination of the apparatus into B and the 3 bulbs placed in a water bath at about 45°. When the ether was saturated with the organometallic compound it was decanted into A and by proper cooling of B most of the ether was distilled back into B and saturated anew with the organometallic compound.

This process was repeated until all the organometallic compound had been carried over into A. Bulb A was then cooled with an ice-salt mixture and the mother liquor run into C. The crystals were washed again with a little ether distilled back into A and the process repeated until a pure white crystalline compound was obtained.

Instead of preparing the organo-aluminum compound in a separate flask, it has been prepared in the 3-bulb apparatus and recrystallized without need of transferring. Very pure organometallic compounds can be prepared by either method.

With Solvent. A 250 cc. three-necked flask was equipped with a nitrogen inlet, a Hopkins condenser connected to an oil trap, and an outlet for the removal of a sample. Cork stoppers coated with collodion were used throughout whenever xylene was used as a solvent. The flask was thoroughly dried and swept out with nitrogen and then 14.35 grams (0.0385 mole) of di-p-tolylmercury, 3.38 grams (0.125 mole) of aluminum chips, and 70 cc. of dry xylene were added. The solution was heated to a gentle reflux, under nitrogen pressure, until the reaction was completed. The completion of the reaction was determined by the disappearance of all organomercury compounds. A 2 cc. sample was removed and placed in 10 cc. of alcohol. Five cc. of a solution of stannous chloride was added and the solution heated. When a hot xylene solution was treated in this manner and gave no free mercury, the reaction was considered complete but was generally heated 30 minutes longer before using. The xylene solutions were generally a straw-brown color and were removed from the excess aluminum and mercury by forcing them through a glass wool filter with nitrogen. The yield of the organo-aluminum compounds was determined by hydrolyzing a measured sample with water, precipitating the aluminum hydroxide, and determining the aluminum as Al_2O_3. In all cases the yields from the xylene solutions were practically quantitative.

Preparation of Tri-n-propylaluminum. One and one-half moles of n-propylmagnesium bromide was prepared from 1.5 moles (36.5 grams) of magnesium turnings and 1.5 moles (185 grams) of n-propyl bromide. The reaction was carried out in a one-liter three-necked flask with a mercury sealed stirrer, dropping funnel, and reflux condenser. The condenser was connected to the top of the dropping funnel and then to an oil trap in order to maintain an equal pressure throughout the system. The magnesium was covered with 125 cc. of anhydrous ether containing 5 grams of n-propyl bromide. After the reaction started the remainder of the bromide in 375 cc. of anhydrous ether was added dropwise. After complete addition of the bromide the solution was stirred for fifteen minutes and then transferred with nitrogen through a glass tube with a glass wool filter into another one-liter flask previously swept out with nitrogen. This flask was immediately connected to the same stirrer and condenser and the dropping funnel replaced by a hopper for the addition of solids. For this purpose the holder for a Gooch crucible was found best. It was fitted with a large rubber stopper carrying a solid glass rod just large enough to fill the exit tube. It must be air tight and must fit rather easily. Fifty grams (approximately 20% less than theoretically necessary) of sublimed aluminum chloride was crushed in a hot mortar and pestle and added to the hopper as quickly as possible. The aluminum chloride was then added slowly through the hopper to the well-stirred Grignard reagent. A period of one and one-half hours was necessary for the complete addition. After each addition a very vigorous reaction took place and at the end a dark thick solution was obtained. The flask was removed and connected through a distillation head to a condenser with a receiver immersed in ice-water. The solution was heated on an oil bath to remove the ether, approximately four hours being required for complete removal. The last traces were removed under the vacuum of a water pump for one hour. The ether receiver was then removed and a 250 cc. modified Claisen flask (35) with a 25 cm. fractionating side-arm put in its place. An oil pump was connected and the receiver cooled by an ice-salt mixture. The oil bath was heated to approximately 180° and at 8 mm. pressure the tri-n-propylaluminum began to distill over. Practically all of the distillate came over between 104-107°/8 mm. The distillation was very slow, requiring 6 to 8 hours, but if the temperature of the oil bath was raised further considerable decomposition occurred. The crude product thus obtained was treated with more n-propylmagnesium bromide to remove any aluminum halides present or the tri-n-propylaluminum was separated by fractional distillation. The receiver containing the tri-n-propylaluminum was connected to a condenser having an adapter suitable for receiving two fractions under reduced pressure. The apparatus had previously been swept out with dry nitrogen.

(35) Gilman, "Organic Syntheses," Coll., Vol.I, John Wiley and Sons, Inc., New York, 1932, p.125.

A water pump was connected through a trap of soda-lime and calcium chloride and the tri-n-propylaluminum was fractionally distilled. The fraction boiling at 137-138°/22 mm. was collected as tri-n-propylaluminum. It was dissolved in a suitable solvent and transferred to another flask. The yield was 27 grams or 46%. The product was a perfectly clear liquid, which fumed strongly in contact with air and took fire very easily. It did not contain halogen and was sufficiently pure without further treatment.

Reaction of Organo-aluminum Compounds with Phenyl Isocyanate. Both triphenyl- and tri-p-tolylaluminum react with phenyl isocyanate to give the expected products. To 0.02 mole of tri-p-tolylaluminum in 50 cc. of dry xylene was added 7.86 grams (0.066 mole) of phenyl isocyanate in 20 cc. of dry xylene and the solution heated to reflux. The reaction was carried out under a pressure of dry nitrogen. Fifteen minutes after addition of the phenyl isocyanate the solution failed to give a color test when a sample was allowed to stand in contact with Michler's ketone for 5 minutes before hydrolysis. The solution was heated for one hour and then hydrolyzed with dilute sulfuric acid (1:20) and extracted with ether. The ether-xylene layer was dried over anhydrous magnesium sulfate and the solvent removed. The oily product was recrystallized from ligroin (b.p. 95-115°) and from alcohol. It melted at 146.5-147° and showed no depression on mixed melting point with p-tolyl anilide prepared from aniline and p-methylbenzoyl chloride. The yield was 9.2 grams or 71%. Check runs were made with triphenyl- and tri-p-tolylaluminum compounds in all of these reactions.

When tri-n-propyl- and triethylaluminum (36) were treated with phenyl isocyanate, the expected anilides were obtained in 18% and 27% yields respectively. The low yields were probably due to the rapid decomposition of the alkylaluminum compounds. No attempt was made to obtain better yields of these anilides.

The Reaction of Organo-aluminum Compounds with Carbon Dioxide. Triarylaluminum compounds in ether-benzene or xylene solutions gave fair yields of the expected acids when refluxed for several days in an atmosphere of carbon dioxide. Fifty cc. of a 0.176 molar tri-p-tolylaluminum solution in ether gave a 32% yield of p-toluic acid when refluxed for seven days. Reaction with solid carbon dioxide gave no acid, probably due to the relatively short time of contact between the organo-aluminum compounds and the carbon dioxide. When a boiling xylene solution of tri-p-tolylaluminum was treated with gaseous carbon dioxide, a negative color test was obtained in two hours, and a 44% yield of p-toluic acid was obtained. It appeared as if the best yields of acids from organo-aluminum compounds could be obtained by use of carbon dioxide at high temperatures and pressures. The shorter the time of heating required to get complete reaction the better the yields obtained. On prolonged heating these organometallic compounds tended to decompose. The action of carbon dioxide on alkylaluminum compounds was not studied.

(36) The author is indebted to J. F. Nelson for the preparation of this compound.

The Reaction of Organo-aluminum Compounds with Benzophenone. An ether solution of tri-p-tolylaluminum gave after standing 5 days at room temperature with benzophenone a trace of diphenyl-p-tolylcarbinol. Triphenylaluminum gave 23.1% yields of triphenylcarbinol after standing 16 days at room temperature in an inert atmosphere with benzophenone. One one-hundredth of a mole of tri-p-tolylaluminum in 50 cc. of xylene was placed in a 200 cc. three-necked flask with reflux condenser, a nitrogen inlet, and an outlet connected to an oil trap. To this was added 0.033 mole of benzophenone, and the solution was heated to a gentle reflux. After 2 hours the color test was negative, so the solution was hydrolyzed, extracted with ether and the xylene-ether layer dried over anhydrous magnesium sulfate. After removal of the solvent a dark oil remained which would not crystallize. By cooling greatly and adding a crystal of diphenyl-p-tolyl carbinol the crude product came down in 43% yields. The carbinol was recrystallized from ligroin and identified by mixed melting point with an authentic sample.

No reactions of alkylaluminum compounds with benzophenone were attempted.

Oxidation of Organo-aluminum Compounds. Tri-p-tolylaluminum (0.01 mole) was oxidized according to the method of Gilman and Wood (29) in a cold xylene solution. The p-cresol was isolated in 8% yields.

The Reaction of Organo-aluminum Compounds with Benzaldehyde. When tri-p-tolylaluminum (0.01 mole) was treated with redistilled benzaldehyde in 50 cc. of xylene the reaction was completed in the cold, and a negative color test was obtained in one hour. Phenyl-p-tolyl carbinol was separated in 27% yields and identified by a mixed melting point with an authentic sample.

The Reaction of Organo-aluminum Compounds with Benzonitrile. One one-hundredth of a mole of tri-p-tolylaluminum was treated with 0.033 mole of redistilled benzonitrile. The reaction was completed after approximately 30 minutes of boiling; from the reaction mixture was obtained 17% yields of phenyl-p-tolyl ketone.

The Action of Organo-aluminum Compounds on Esters. Ethyl Benzoate. Tri-p-tolylaluminum and ethyl benzoate gave a yellow residue insoluble in ether. It probably consisted of condensation products.

Phenyl Benzoate. In an attempt to obtain a reaction between an organo-aluminum compound and an ester, phenyl benzoate was used instead of the ethyl benzoate. Here again, however, condensation products were the only ones obtainable.

Discussion of Results

Organo-aluminum compounds are evidently endowed with a reactivity such as would be expected from the position of aluminum in the periodic table. The evident lack of reaction previously reported was most probably due to the use of the wrong conditions. In almost all cases reported where reactions were attempted with organo-aluminum compounds the mixed alkyl compounds were used and generally in very concentrated solutions. These alkyl compounds naturally lend themselves more readily to condensation reactions than do the simple aryl derivatives. On using the triarylaluminum compounds very little condensation was observed, and the reaction with esters was the only case where the expected product was not obtained. Since small amounts were used in all of these runs it was difficult to determine the amount and nature of the by-products. It appears as if the best conditions for reaction with organo-aluminum compounds is in a boiling xylene solution, that is not of greater than 1 molar concentration.

Since the organo-aluminum compounds have reacted in the few cases thus far studied, it seems reasonable to predict that they might react with any functional group if given the proper conditions of temperature, solvent, and length of contact. Thus Berlingozzi (37) reports the reaction between nitrobenzaldehyde and a Grignard reagent to give a carbinol. The

(37) Berlingozzi, Atti accad. Lincei, 19, 332 (1934).

reaction was carried out in the cold, and although the first expected reaction would be with the nitro group, he has been able by proper control of conditions to effect a reaction with the aldehyde group without reacting with the nitro group. Similarly Mavrodin (2 c) obtained a diketone from the reaction of an organomagnesium compound on cyano-acetophenone. On the basis of previous work (28) we would expect the organomagnesium compound to react first with the carbonyl linkage and then less rapidly with the cyano group. Thus the less reactive organoaluminum compounds may be useful in this same type of reaction where two or more functional groups are involved.

The best method for the preparation of the tri-arylaluminum compounds seems to be through the use of xylene as a solvent.(38) This gives a clean, easily controlled reaction with very good yields of the organometallic compound.

(38) The author has found that continued use, especially in a pipette, of xylene solution soon tends to produce headaches and general nausea in the worker. Contact with the vapors can largely be prevented by use of rubber bulbs on small pipettes and a gas aspirator on larger pipettes. Care should be used in other transfers and in heating of xylene solutions.

Summary

1. The reaction of organo-aluminum compounds with several different functional groups has been observed.
2. The preparation of organo-aluminum compounds has been discussed.

C. SOME REACTIONS OF ORGANOBORON COMPOUNDS

Introduction

In Group III of the periodic table the only elements that form true organometallic compounds are boron, aluminum, indium, and thallium. Boron is generally considered a metalloid and forms a larger variety of organocompounds than do the other three metals. The study of these organic compounds of boron dates back to the year 1860 when Frankland and Duppa (39) first reported the preparation of some trialkylboron compounds. They prepared them by the interaction of the dialkylzinc compounds and ethyl borate according to the reaction:

$$B(OC_2H_5)_3 + 3R_2Zn \longrightarrow R_3B + 3Zn\begin{matrix} R \\ OC_2H_5 \end{matrix}$$

The Grignard reagent was first used in the synthesis of organoboron compounds in 1909 by Khotinsky and Melamed (40):

$$3RMgX + B(OC_2H_5)_3 \longrightarrow R_3B + 3C_2H_5OMgX$$

Stock and Zeidler (41) in 1921 reported yields of organoboron compounds which were almost quantitative by use of a 40% excess of dialkylzinc compounds in their reaction with boron trichloride:

$$3R_2Zn + 2BCl_3 \longrightarrow 2R_3B + 3ZnCl_2$$

The method in common use today and perhaps the best general method of preparation for the organoboron compounds

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(39) Frankland and Duppa, *Ann.*, *115*, 319 (1860).
(40) Khotinsky and Melamed, *Ber.*, *42*, 3090 (1909).
(41) Stock and Zeidler, *Ber.*, *54B*, 531 (1921).

is the interaction of the Grignard reagent with boron trifluoride, used first in 1921 by Krause and Nitsche (13):

$$3RMgX + BF_3 \longrightarrow R_3B + 3Mg<^{X}_{Cl}$$

This may be applied equally well to the preparation of both the trialkyl- and the triarylboron compounds, and a large number of different organoboron compounds have been prepared in this manner. When an excess of the Grignard reagent was not present, it was found that some of the substituted boron difluoride and monofluoride were also formed (42).

In 1915 Scharrnbeck (43) in his Doctor's Dissertation reported the formation of triphenylboron by the action of boric oxide on an ether solution of phenylmagnesium bromide. The compound he reported as triphenylboron had a melting point of 67° and was recrystallized several times from alcohol. Krause (42) reported 136° as the melting point of triphenylboron, and it could not be crystallized from alcohol without change. Evidently Scharrnbeck had some boron compound other than triphenylboron. In a later account of this work published in 1930 by König and Scharrnbeck (44) no mention was made of the preparation of triphenylboron from phenylmagnesium bromide and boric oxide.

A large number of mixed organoboron compounds are known.

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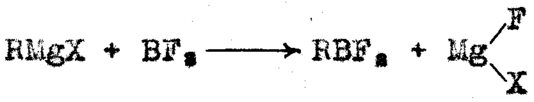
(42) Krause and Nitsche, Ber., 55B, 1261 (1922).
(43) Scharrnbeck, Doctor's Dissertation, Dresden, 1915.
(44) König and Scharrnbeck, J. prakt. Chem., 128, 153 (1930).

The first compound of this type was prepared in 1894 by Michaelis (45) when he studied the action of boron tribromide on diphenylmercury:

$$(C_6H_5)_2Hg + 2BBr_3 \longrightarrow 2C_6H_5BBr_2 + HgBr_2$$

Other compounds of this type were also obtained in 1923 by Krause (42) by use of the proper concentration of the Grignard reagent and boron trifluoride:



$$RMgX + BF_3 \longrightarrow RBF_2 + Mg\begin{matrix}F\\X\end{matrix}$$

In 1929 Pace (46), an Italian, reported the formation of phenylboron dichloride by passing the hot vapors of benzene and boron trichloride over palladium black at 500-600°:

$$C_6H_6 + BCl_3 \longrightarrow C_6H_5BCl_2 + HCl$$

The reaction between phenylboron dichloride and diphenylmercury (45) when they were heated in a sealed tube at 300-320° for twenty-four hours gave diphenylboron chloride:

$$C_6H_5BCl_2 + (C_6H_5)_2Hg \longrightarrow (C_6H_5)_2BCl + C_6H_5HgCl$$

The only other method of preparation of the monohalide is that given by Michaelis and Richter (47) when they obtained a small amount of diphenylboron chloride from the reaction between boron tribromide and diphenylmercury:

$$(C_6H_5)_2Hg + BBr_3 \longrightarrow (C_6H_5)_2BBr + HgBr_2$$

A large number of substituted boric acids have also been prepared. They may be obtained by hydrolysis of either the

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(45) Michaelis, Ber., 27, 244 (1894).
(46) Pace, Atti accad. Lincei, 10, 193 (1929).
(47) Michaelis and Richter, Ann., 315, 26 (1901).

substituted boron halides or the substituted borates, which are easily obtained by oxidation of the simple organoboron compounds.

Boro-aniline, $C_6H_5BH_2$, was prepared in 1929 by Pace (46). He treated phenylboron dichloride with dry hydrogen iodide gas in the presence of iodine and obtained phenylboron di-iodide. Ethyl alcohol was added to this product and reacted as follows:

$$C_6H_5BI_2 \cdot HI + 2C_2H_5OH + 2H_2 \longrightarrow C_6H_5BH_2 + 2C_2H_5I + 2HI + 2H_2O$$

By the slow addition of phenylboron dichloride to boro-aniline in an atmosphere of hydrogen, Pace obtained borobenzene, $C_6H_5B{:}BC_6H_5$. The reaction was quite violent and highly exothermic.

The trialkylboron compounds are generally gases or liquids and are very hard to handle due to their great reactivity with oxygen. Trimethylboron is a gas, while those with larger alkyl groups are liquids. The compounds have a very pungent odor which is described as reminiscent partly of tertiary alkyl phosphines, and partly of radishes and onions. They oxidize readily in the air with considerable evolution of heat; the lower members of the series ignite in air, while those of higher molecular weight ignite only when dropped from a capillary. In a sealed tube under nitrogen they are stable indefinitely even in light; in spite of the relatively high boiling points of some of these compounds they are strikingly volatile and quickly evaporate in an atmosphere of nitrogen. On heating they undergo slow decomposition with the evolution of hydrogen and a hydrocarbon. They are only slightly soluble in water and show very slow decomposition on prolonged treatment. On heating triethylboron with concentrated hydrochloric acid over mercury at 99° the following reaction took place (48):

$$(C_2H_5)_3B + HCl \longrightarrow (C_2H_5)_2BCl + C_2H_6$$

Most of the trialkylboron compounds form additive compounds with ammonia (48). These ammines are very unstable, however, and very little work has been done with them. Oxidation, hydrolysis, and formation of ammines are the only reactions reported of the trialkylboron compounds.

The triarylboron compounds are solids which quickly oxidize in air, fume, but never ignite. They are stable in nitrogen and carbon dioxide and dissolve without change in benzene, toluene, and other benzene hydrocarbons, are less soluble in ether and react with alcohol to form esters. In ether with the alkali metals (49) or with their amalgam a colored solution is obtained which gives crystals of an alkali derivative. Thus, triphenylboron forms yellow compounds of the type Ph_3BNa, with sodium, potassium, lithium, rubidium, and cesium. These alkali triphenylboron compounds retain ether with great tenacity. The mono-etherates of the sodium and lithium compounds have been isolated, whereas, the remaining compounds lose ether too easily to be isolated. The sodium compound is converted by iodine in an ethereal solution into triphenyl

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(48) Frankland, Ann., 124, 129 (1862).
(49) Krause, Ber., 57B, 216 (1924).

boron and sodium iodide (50). Removal of the sodium can also be effected by prolonged treatment with a large excess of pure mercury; whereas, reaction between an ethereal solution of triphenylboron and sodium amalgam containing more than 2.9% of sodium produces sodium triphenylboron. Triphenylmethyl chloride and sodium triphenylboron yield triphenylmethyl and triphenylmethylsodium; the latter compound is also obtained from sodium triphenylboron and triphenylmethyl. Triphenylboron and triphenylmethyl yield an intensely red crystalline compound. Sodium triphenylboron reacts instantaneously with alkyl halides and carbon dioxide. Ethereal solutions of sodium triphenylboron conduct electricity, but to a lesser degree than triphenylmethylsodium. Tricyclohexyl- and tri-*n*-propyl boron do not react with sodium, whereas tri-p-tolylboron resembles the phenyl derivative (51).

Tri-α-naphthyl boron has been found (52) to add two atoms of sodium giving a compound of the formula R_3BNa_2. This type of compound is not generally known and is of particular interest from the standpoint of the valence theory.

Because of the addition of sodium to triphenylboron and tri-α-naphthyl boron, Bent and Dorfman (53) suggest that these compounds behave like free radicals. They found, however, that

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(50) Krause and Polack, *Ber.*, *59B*, 777 (1926).
(51) Krause and Polack, *ibid.*, *61B*, 271 (1928).
(52) Bent and Dorfman, *J. Am. Chem. Soc.*, *54*, 2132 (1932).
(53) Bent and Dorfman, *ibid.*, *57*, 1259 (1935).

the free energy change for the reaction is considerably smaller than that for triphenylmethyl.

All triarylboron compounds form addition products (54) with nitrogenous bases such as:

$$(C_6H_5)_3B + NH_3 \longrightarrow (C_6H_5)_3B{\cdot}NH_3$$

There is a large number of such compounds formed, the most common uniting bases being: ammonia, methyl amine, ethyl amine, propyl amine, trimethyl amine, aniline, pyridine, quinoline, quinaldine, piperidine, and phenyl hydrazine.

These compounds are rather insoluble and generally exhibit simple molecular weights (55). They are not attacked by atmospheric oxygen and are generally capable of existence above the melting point of the triarylboron compound from which they are derived. The addition compounds have melting points slightly, but as a rule, distinctly separated from their decomposition points. Some of them do not decompose in solution and can be recrystallized and are found to contain one mole of nitrogen base, the boron having a coördination number of four. Krause (54) states that the striking indifference of most of these addition compounds to atmospheric oxygen is probably due in part to the fact that by satisfying the coördination number the vacancies in the molecule are so filled out that the oxygen can, to a certain degree, no longer

(54) Krause, Ber., 57B, 813 (1924).
(55) Krause and Dittmar, Ber., 63B, 2347 (1930).

penetrate the carbon-boron union. This would also explain the differences in stability of the various compounds; there is apparently a certain "optimum of space filling," the addition of amines with excessively large molecular volumes decreasing the stability because of lack of space.

When these addition compounds are reduced by means of alkali metals in suitable solvents, Kraus and Brown (56) reported the addition of an atom of metal, forming compounds of the type $NaB(C_6H_5)_3NH_3$. They also reported the combination of triphenylboron with the amides of the alkali metals.

In an attempt to prepare compounds of the type R_4BM Thomson and Stevens (57) heated triethyl- and triphenylboron with ethyl-lithium, phenyl-lithium, methylsodium, ethylsodium, and benzylsodium. They were unable, however, to isolate any new organoboron compounds.

The reactions of organoboron compounds were up to now confined to simple oxidation, hydrolysis, and addition of alkali metals and nitrogen bases. Before comparing the relative reactivities of organoboron compounds with those of aluminum and zinc the reactions of triphenyl- and tri-n-propylboron with certain functional groups were studied to see if the organoboron compounds resemble in this way the more reactive organometallic compounds.

(56) Kraus and Brown, J. Am. Chem. Soc., 51, 2690 (1929).
(57) Thomson and Stevens, J. Chem. Soc., 1933, 556.

Experimental

The organoboron compounds selected for this study were triphenylboron of the aryl series and tri-*n*-propylboron in the alkyl series. The triphenylboron was selected as being the most representative and best known of the aryl compounds. An attempt was made to use triethylboron of the alkyl series, but in its purification by fractional distillation considerable decomposition occurred, and so the next higher derivative was used. The best method found for the preparation of these compounds was by the action of boron trifluoride on the appropriate Grignard reagent.

Preparation of Boron Trifluoride. The boron trifluoride used in these preparations was prepared by the method of Bowlus and Nieuwland (58) and obtained and used as the etherate. A four-liter Erlenmeyer flask was connected through a one-holed rubber stopper by means of an 8 mm. glass tube to two drying towers, the first containing 200 cc. of concentrated sulfuric acid, and the second being empty. The second drying tower was connected by means of a 75 cm. length of 8 mm. tubing through a two-holed rubber stopper to the bottom of a 500 cc. Florence flask. The second outlet in the rubber stopper carried a calcium chloride tube to exclude all moisture. In the Erlenmeyer flask was placed 400 grams of

(58) Bowlus and Nieuwland, *J. Am. Chem. Soc.*, *53*, 3835 (1931).

calcium fluoride and 200 grams of powdered boric oxide. The flask was then well shaken to obtain an intimate mixture of the two compounds. To this mixture was added 1300 cc. of concentrated sulfuric acid and the flask again shaken. This mixture was allowed to stand for 15 minutes under a hood until all silicon tetrafluoride had distilled off. The flask was then connected to the drying train and heated with a Bunsen burner until a steady stream of gas was passing through the drying towers. In the clean, dry Florence flask was placed 350 cc. of anhydrous ether and the flask, after connecting to the outlet tube, was surrounded with ice water. The stream of boron trifluoride evolved was regulated, by adjusting the burner, so that the bubbles passing through the sulfuric acid could just be counted. The heating was continued for about 5 hours, at the end of which time the evolution of gas was so slow that the ether started to climb up the outlet tube. Because of this the outlet tube must be very long and the reaction must be carefully watched toward the last to prevent the ether from sucking back into the drying train. The Florence flask was disconnected and the boron trifluoride-etherate distilled under atmospheric pressure from an ordinary distilling flask. The boron trifluoride-etherate distilled at 125.5-126.5^{o} and was stored in a glass-stoppered brown bottle. It is fairly stable and can be stored for a long time if kept away from light and heat. From the above preparation 260 grams or 86% yield of pure boron trifluoride-etherate was prepared.

Preparation of Triphenylboron. The preparation of triphenylboron was best carried out in a modified Claisen flask from which it could be distilled after preparation. The Claisen flask had a 200 cc. round-bottomed flask sealed onto its side-arm as a receiver. The seal was made about 3 cm. from the neck of the flask and in such a manner that the neck was parallel with the neck of the Claisen flask and exactly vertical. The flask was equipped with an efficient mercury seal stirrer at the one outlet and a condenser and dropping funnel at the other. Dry nitrogen was allowed to enter through the 200 cc. receiver to prevent distillation of ether into it. The condenser was connected to the top of the dropping funnel and then to an oil trap.

In the Claisen flask was placed 24.3 grams (1 atom) of magnesium turnings. To this was added 5 grams of bromobenzene in 200 cc. of anhydrous ether. After the reaction had begun the rest of 78 grams (0.5 mole) of bromobenzene in 250 cc. of anhydrous ether was added over a period of 4 hours. To 78 grams (0.5 mole) of bromobenzene in 200 cc. of anhydrous ether was added 39.7 grams (0.28 mole (59)) of boron trifluoride-etherate, and this solution was added slowly to the well-stirred Grignard reagent over a period of about 4 hours.

(59) Approximately 15% less than was theoretically necessary was used in order to prevent formation of the mixed organometallic compounds.

As each drop of this solution came in contact with the Grignard reagent a vigorous reaction took place. After approximately three-fourths of this solution had been added a very vigorous reaction took place, and the solution separated into two layers. It is best to cool the solution at this point in a pan of water or the reaction may leave the flask. After cooling slightly, the remainder of the boron trifluoride reagent was added and the solution refluxed for one-half hour. The stirrer was then replaced with a nitrogen inlet, the condenser and dropping funnel by a thermometer, and the outlet of the 200 cc. receiver connected by means of 8 mm. glass tubing to a 500 cc. three-necked flask carrying a Hopkins condenser. The Claisen flask was then heated on an oil bath until ether would no longer distill over. The outlet of the condenser was connected to a water pump and the remainder of the ether distilled under a pressure of 25 mm. After all ether had been distilled the 500 cc. flask was removed and replaced with another of the same size. The Hopkins condenser was replaced by a 20 cm. length of 12 mm. tubing. This was connected through a stopcock to an oil pump. All of these operations were carried out under an atmosphere of nitrogen, as the triphenylboron oxidizes very readily.

The distillation of the triphenylboron was best carried out by use of an oil bath. The bath was large enough to cover the entire bulb of the Claisen flask, and the top of the oil bath was covered with two thicknesses of asbestos paper to prevent loss of heat. The two necks of the Claisen flask were also covered with asbestos. The oil bath was heated to 240-260° before the triphenylboron began to distill over. The triphenylboron came over very slowly, and it was necessary to fan the side-arm with a free flame in order to prevent solidification. Small amounts of triphenylboron sublimed over into the 500 cc. flask but were condensed there. The triphenylboron distilled at 165-167°/4 mm. and was collected in the 200 cc. receiver. Any previous fraction that had collected in this receiver had been distilled into the 500 cc. flask. The entire distillation required about 3 hours, and at the end of this time the stopcock on the last receiver was closed and nitrogen slowly admitted to the apparatus. The triphenylboron solidified in the flask into long yellow crystals. The melting point was determined by melting the entire mass and placing a thermometer in it to determine the temperature of solidification. The temperature generally fell to about 134° before crystallization began and then rose to 137° and remained there until all of the liquid had solidified. Krause (42) reports a melting point of 136° while Bent and Dorfman (53) give 137°.

In order to obtain a pure white crystalline compound the triphenylboron was transferred to the 3-bulb apparatus (See page 31) and recrystallized several times from anhydrous ether. The compound thus obtained melted at 137° and was pure white. The yield was 42.3 grams or 62%. The solid was generally dissolved in xylene and this solution used in all reactions.

Preparation of Tri-n-propylboron. In a 1-liter Claisen flask equipped with a mercury seal stirrer, condenser, and dropping funnel was placed 26.75 (1.1 atoms) of magnesium turnings along with 150 cc. of anhydrous ether containing 5 grams of *n*-propyl bromide. After reaction had begun 95 grams of *n*-propyl bromide in 250 cc. of anhydrous ether was added slowly over a period of 3 hours. The remainder of 1.1 moles (135.3 grams) of *n*-propyl bromide with 42.6 grams (0.3 mole) of boron trifluoride-etherate in 200 cc. of anhydrous ether was then added over a period of 3 hours. A sudden vigorous reaction also occurred here when about three-fourths of the solution had been added. After complete reaction the ether was removed, using a water pump to remove the last traces. A 250 cc. modified Claisen flask with a 25 cm. fractionating side-arm was connected as a receiver and was cooled in an ice-salt mixture. Using a water pump and heating in an oil bath at 100-120° the tri-*n*-propylboron distilled at 60-70°/25 mm. This fraction was distilled again under reduced pressure and the fraction boiling at 64-65°/25 mm. retained. The yield was 33.5 grams or 80%. The tri-*n*-propylboron as obtained was a clear, colorless liquid which fumed greatly in contact with air and took fire if poured from its container. A xylene solution was found to be the most convenient method of handling this sensitive compound.

Reactions of Organoboron Compounds. The technique used in working up reactions of organoboron compounds was slightly different from that of other organometallic compounds. Treatment of the reaction products with dilute acids did not remove the boron compounds present as it does with the other organometallic compounds. Two of the radicals of the trialkyl- and triarylboron compounds seemed to react, leaving on hydrolysis substituted boric acids. Thus, triphenylboron gave phenylboric acid which was best removed by extracting the xylene solution with 10% potassium hydroxide.

Phenyl Isocyanate. It was necessary to heat 30 cc. of a xylene solution of triphenylboron containing 0.005 mole of the organometallic compound for 10 hours with 1.20 grams (0.01 mole) of phenyl isocyanate in order to obtain 16.2% yields of benzanilide. The anilide was identified by mixed melting points with an authentic sample. When tri-n-propylboron was heated 3 hours with phenyl isocyanate a negative color test was obtained, but on working up the product no anilide could be isolated. The large amounts of diphenyl urea formed from the excess phenyl isocyanate made working up of the product difficult. The reaction is being investigated further.

Benzaldehyde. When 50 cc. of a solution of triphenylboron in xylene containing 0.01 mole of triphenylboron was heated for 3 days at 140-150° with 3.18 grams (0.03 mole) of redistilled benzaldehyde a 10% yield of benzohydrol was isolated. Similar treatment of tri-n-propylboron gave a small amount of product boiling at 110-111°/23 mm. which gave a positive test for boron when treated with sulfuric acid and methyl alcohol. It has not as yet been identified and no phenylpropylcarbinol has been obtained from it. Treatment of all fractions with α-naphthyl isocyanate failed to give any of the α-naphthyl urethane of phenylpropylcarbinol. The reaction is being investigated further.

Discussion of Results

Organoboron compounds appear to possess a reactivity somewhat similar to that of organo-aluminum compounds. Although the only reactions where the expected products have been isolated were between triphenylboron and phenyl isocyanate and benzaldehyde it appears as if reaction took place in several other cases. When the organoboron compounds were treated with benzonitrile, benzophenone, or with carbon dioxide the color test disappeared after prolonged treatment, but none of the expected products could be obtained. The removal of the boron residues with 10% potassium hydroxide is not satisfactory, as it does not give complete removal except after prolonged treatment, and some of the reaction product may be destroyed here also or removed with the substituted boric acids. Steam distillation of the reaction products has proved quite satisfactory, as treatment with steam usually hydrolyzes the substituted boric acids, and the boric acid (free of organic radicals) may then be removed with water. The working up of the trialkylboron compounds is even more difficult than with the aryls. It seems, however, that if organoboron compounds react with benzaldehyde and phenyl isocyanate they should also react with other functional groups if sufficient time is given for the reaction and the proper conditions maintained.

The relative stability of tri-_n_- propylboron toward the action of alcohol or water suggests the possibility of carrying out a reaction between benzaldehyde and tri-n-propylboron in an alcohol solution. This reaction would be quite unusual and is altogether possible if the proper conditions for the reaction between tri-n-propylboron and benzaldehyde can be found.

Summary

1. The preparation of two organoboron compounds has been described.
2. The reaction of organoboron compounds with two different functional groups has been observed.

D. SOME REACTIONS OF ORGANOZINC COMPOUNDS

Introduction

The organozinc compounds, which were the first true organometallic compounds reported (60), have been largely supplemented in organic synthesis by the organomagnesium compounds. The zinc compounds are still used somewhat, because of their seemingly non-reactivity toward the carbonyl linkage, in the preparation of ketones.

The preparation of the alkylzinc compounds is usually carried out by the action of zinc, or a zinc-copper couple (61) on an alkyl halide, usually the iodide or a mixture of the iodide and the bromide. They may also be prepared by the action of zinc chloride etherate (62) on a Grignard reagent, or by the displacement of the mercury in organomercury compounds by metallic zinc. The diarylzinc compounds are best prepared by the latter method which takes place very easily when diarylmercury compounds are heated in contact with metallic zinc, using xylene as a solvent (30).

The reactions of organozinc compounds are very numerous, and a review of them is totally unnecessary (5). The author was particularly interested in the reactions of organozinc compounds with carbon dioxide, ketones, and nitriles.

(60) Frankland, J. Chem. Soc., 2, 263 (1849).
(61) Noller, J. Am. Chem. Soc., 51, 594 (1929).
(62) Blaise, Bull. soc. chim., 9, 1 (1911).

Only one case is reported of the carbonation of organozinc compounds. Schmitt (63) in 1890 reported the formation of propionic acid by the action of carbon dioxide on diethylzinc. This was carried out with liquid carbon dioxide in an autoclave at a temperature of 150-160°.

Pavlov (64) in the reaction between diethylzinc and acetone obtained mesityl oxide and higher condensation products. With acetyl chloride and diethylzinc, Freund (65) was able to obtain either the methyl ethyl ketone or the methyldiethylcarbinol. Acetaldehyde gave methylethylcarbinol on treatment with diethylzinc (66). In several other cases the apparent reaction of organozinc compounds with the carbonyl linkage is observed; but, in general, the organozinc compounds are classified as not reacting with ketones.

The alkyl esters of α-alkyl-β-ketonic acids were obtained by Blaise (67) by condensing nitriles with the alkyl esters of the α-bromo-acetic acids in the presence of zinc. He also prepared a series of alkyl allyl ketones (68) of the type $CH_2{:}CH{\cdot}CH_2{\cdot}\underset{\underset{O}{\|}}{C}{\cdot}R$ by the condensation of allyl iodide with an aliphatic nitrile in benzene solution. These may be

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(63) Schmitt, J. prakt. Chem., 42, 568 (1890).
(64) Pavlov, Ann., 188, 104 (1877).
(65) Freund, Ann., 118, 1, (1861).
(66) Wagner, Ann., 181, 261 (1876).
(67) Blaise, Compt. rend., 132, 478 (1901).
(68) Blaise, Compt. rend., 138, 284 (1904).

reactions of organozinc compounds with nitriles.

Under the proper conditions it has been found possible to react organozinc compounds with carbon dioxide, benzophenone, and benzonitrile. Most of these reactions were carried out using the diphenyl- and di-p-tolylzinc compounds rather than the alkyl types. The aryl types were used since they are much more stable toward air and water than the highly inflammable alkyl types, making them much more desirable to work with.

Experimental

The diarylzinc compounds were prepared by the displacement of the mercury in diarylmercury compounds by zinc in a boiling xylene solution. A 200 cc. three-necked flask with a reflux condenser was thoroughly swept out with dry nitrogen. In it were placed 17.75 grams (0.05 mole) of diphenylmercury, 13.08 grams (0.2 atom) of mossy zinc, and 100 cc. of dry xylene. This solution[7] was heated to a gentle reflux under nitrogen pressure until the reaction was completed. This was determined by the reduction of the organomercury compounds with stannous chloride, as described under the preparation of diarylaluminum compounds. The reaction is ordinarily completed in 6 or 8 hours, and the solution obtained is of a milky appearance. This solution was used without further purification for most reactions. In some cases, however, the hot xylene solution was filtered through glass wool, cooled in an ice-salt mixture, and the xylene decanted from the crystalline diphenylzinc. These crystals were washed twice with cold ligroin (b.p.95-115°) and dissolved in either benzene or xylene. The yield of the crystalline diphenylzinc, melting at 105-106°, was 7.7 grams or 70%.

The dialkylzinc compounds were prepared by the action of the zinc-copper couple on a mixture of the alkyl iodide and alkyl bromide. In a 200 cc. round-bottomed flask, with an inlet and outlet for a stream of dry hydrogen, was placed

120 grams (approximately 2 atoms) of zinc dust and 10 grams of copper oxide. The solids were thoroughly mixed and heated over a free flame. Dry hydrogen was passed in a steady stream through the flask and the flask shaken continually during the heating to avoid fusion. When the entire mass was a light gray color the couple was considered formed, and it was cooled in an atmosphere of hydrogen. The cool zinc-copper couple was then transferred to a 500 cc. three-necked flask equipped with a heavy mercury sealed stirrer and a Hopkins condenser connected to an oil trap. The flask had been previously swept out with dry nitrogen. Into this flask was placed 85.0 grams (0.5 mole) of n-propyl iodide and 61.5 grams (0.5 mole) of n-propyl bromide. The flask was then carefully heated with a flame and after about 20 minutes of refluxing the reaction began. The starting of the reaction was observed by the rapidly increased refluxing. The flame was removed and the reaction proceeded smoothly, with occasional cooling necessary to avoid too vigorous a reaction. The reaction was completed after 1-1/2 hours. After cooling, the flask was detached from the stirrer and condenser and connected to a distillation head and through a condenser to a 250 cc. modified Claisen flask. This receiver was cooled in an ice-salt mixture. The flask was heated in an oil bath to 90-100° and the di-n-propylzinc was distilled over at 55-65°/25 mm. On fractionation the fraction distilling over at 61-62°/25 mm. was collected as pure di-n-propylzinc.

The yield of the clear colorless liquid was 54.8 grams or 73%. The pure compound was highly inflammable and was dissolved in xylene or benzene for further use.

The diethylzinc was obtained from Eastman Kodak Company and was used without further purification.

The Reaction of Organozinc Compounds with Carbon Dioxide. Two one-hundredths of a mole of di-p-tolylzinc was prepared in an atmosphere of carbon dioxide and the xylene solution refluxed for 24 hours with carbon dioxide passing over it before a negative color test was obtained. The solution was hydrolyzed and extracted with 10% potassium hydroxide. Neutralization of this alkaline solution gave 21% yields of p-toluic acid. Diphenylzinc in a similar manner yielded 18% benzoic acid after refluxing 24 hours. No attempt was made to carbonate the dialkylzinc compounds.

The Reaction of Organozinc Compounds with Benzophenone. The reaction of 0.01 mole of di-p-tolylzinc with 3.64 grams (0.02 mole) of benzophenone gave a negative color test after refluxing for 24 hours. After hydrolysis of the reaction product and removal of solvent, a heavy oil was obtained which crystallized very slowly from ligroin (b.p. 95-115°). The product melted at 77-78° and gave no depression in mixed melting points with a known sample of diphenyl-p-tolylcarbinol. The yield was 28%. Triphenylcarbinol was obtained in 17% yields from the reaction of diphenylzinc on benzophenone.

No attempt was made to isolate reaction products in the reaction of dialkylzinc compounds with benzophenone.

The Reaction of Organozinc Compounds on Phenyl Isocyanate. When 0.004 mole of diphenylzinc in 20 cc. of xylene was treated with 0.008 mole of phenyl isocyanate at room temperature a negative color test was obtained in 40 hours. From the reaction products 44% yields of benzanilide were obtained. Diethylzinc (0.02 mole) reacted with phenyl isocyanate (0.04 mole) to give 16% yields of propionanilide. Di-*n*-propylzinc (0.01 mole) on treatment of its xylene solution with phenyl isocyanate (0.02 mole) at room temperature for 12 hours gave 18% yields of butyranilide.

The Reaction of Organozinc Compounds on Benzonitrile. When 0.05 mole of di-p-tolylzinc was heated for 2 hours at 135-140° with 0.1 mole of redistilled benzonitrile a negative color test was obtained. Hydrolysis of the reaction product and removal of the solvent gave a dark red oil. This oil gave on slow crystallization from ligroin (b.p. 95-115°) 22% yields of phenyl-p-tolyl ketone. Mixed melting points with a known sample were used to identify the product. The reaction products of the reaction between dialkylzinc compounds and benzonitrile were not worked up.

Discussion of Results

The reaction of organozinc compounds with certain functional groups seems to be another case of a somewhat slow reaction. Although it has been generally assumed that organozinc compounds would not react with carbon dioxide, ketones or nitriles, it has been shown that in each case reaction does take place; however, usually it is a very slow reaction.

This great difference in reactivity of organozinc compounds with certain functional groups is of great value. Ketones can be synthesized in good yields because of this. Many important syntheses are based on this difference of reactivity between the carbonyl linkage and other functional groups.

These slow reactions of organozinc compounds are best carried out in boiling xylene solutions. Ether and benzene solutions of diarylzinc compounds do not give the expected product even after contact for several days.

Summary

1. The preparation of some organozinc compounds has been described.
2. The reaction of organozinc compounds with carbon dioxide, benzophenone, phenyl isocyanate, and benzonitrile has been described.

E. THE RELATIVE REACTIVITIES OF ORGANOMETALLIC COMPOUNDS OF ALUMINUM, BORON AND ZINC

Introduction

Organic chemists are at the present time beginning to realize the value of studies comparing the chemical reactivities of organic compounds. A large amount of work has been done in the last few years on the comparison of the chemical reactivities of members of a series or group of compounds. Selected rate studies with a few compounds are of little value, and it is only by the correlation of a large number of studies made under a variety of conditions that the true value of this type of work can be determined.

The comparison of the relative reaction velocities of the many organometallic compounds is too great an undertaking to be accomplished in a short time. However, by the careful correlation of the scattered works now available it is possible to arrive at some rather interesting generalizations. It would be unwise to accept any of these generalizations as facts because of the widely varying conditions under which the results were obtained and the possibility that the results might be reversed if conditions were changed or different reactants used. However, the generalizations, in themselves, are very useful.

The relative chemical reactivities of organic compounds may in general (for the present) be defined only in terms of reference to the experimental method of acquiring the data used in making the comparison. The various experimental methods for the comparison of chemical reactivities may be classified upon the basis of whether the comparison is made of the extent of a reversible reaction, of the rates under identical conditions of a reversible or irreversible reaction which occurs free of side reactions, of the severity of conditions necessary to induce a given type of reaction to occur, or of the relative rates of competitive reactions as measured by the ratio of the products.

By far the greater part of all comparisons of the relative reactivities of organometallic compounds have made use of a study of the rates of reactions under identical conditions. The color test for organometallic compounds provides a means for measuring the relative rates of such reactions.

Gilman, Heck and St. John (69) have studied the rate of reaction of some Grignard reagents with selected reactants under identical conditions. A series of some fourteen Grignard reagents were prepared and reacted with an excess of azobenzene. The time of the reaction was determined by noting the time required for the disappearance of the color test. This gave a means of comparing the relative reactivity of these different Grignard reagents with azobenzene. The relative reactivities of n-butylmagnesium and phenylmagnesium bromides

(69) Gilman, Heck and St. John, Rec. trav. chim., 49, 212 (1930).

were also compared by reactions with a miscellany of compounds including: diethyl sulfate, benzyl chloride, ethyl cinnamate, nitrobenzene, acetophenone, benzalacetone, cupric chloride, phenyl isocyanate, and a group of substituted nitrocompounds. In general, it appeared that the *n*-butylmagnesium bromide was slightly more reactive than the phenylmagnesium bromide.

The rate of reaction, under similar conditions, of phenylmagnesium bromide and diphenylmagnesium with *n*-valeronitrile was observed by Gilman and Brown (70). They found that *n*-valeronitrile reacted with phenylmagnesium bromide in 5 to 6 minutes, while diphenylmagnesium required about 2 hours for completion of the reaction as shown by the color test. Bachmann (71) in his work with triphenylmethyl concludes, "The reaction between magnesium triphenylmethyl and carbon dioxide is considerably slower than carbonation of triphenylmethylmagnesium bromide."

The relative reactivities of *n*-butyl- and phenyl-lithium were compared with *n*-butyl- and phenylmagnesium bromide by Gilman and Kirby (72). In this study 0.02 mole of the organometallic compound was added to 0.022 mole of a series of typical reactants and the time recorded for the disappearance of a color test. On the basis of these reactions it seemed reasonably sure that the organolithium was more reactive than

(70) Gilman and Brown, *J. Am. Chem. Soc.*, *52*, 1181 (1930).
(71) Bachmann, *ibid.*, *52*, 4412 (1930).
(72) Gilman and Kirby, *ibid.*, *55*, 1265 (1933).

the organomagnesium compounds. It also seemed that the n-butyl-lithium was more reactive than phenyl-lithum. These statements were not given, however, as sweeping generalizations, but they should hold in the majority of cases.

Gilman and Kirby (73) have found that in the case of benzonitrile, dimethylmagnesium reacts more rapidly than does methylmagnesium iodide. On the other hand, it was observed that methylmagnesium iodide reacts more rapidly with diethyl sulfate than does dimethylmagnesium. The relative rates of reaction, in this case, appear to depend upon the reactant used. Dimethylmagnesium, however, reacted much more rapidly with benzonitrile and diethyl sulfate than did dimethylberyllium.

Catlin (74) determined the relative ease of scission of several organometallic compounds in chloroform solution by either hydrochloric acid or trichloroacetic acid. On the basis of the studies made he has given the series: Pb, Hg, Bi and Sn in which the metals are arranged in the order of the decreasing reactivity of their organometallic compounds. In the cases studied the aryl derivatives gave, in general, a higher reaction velocity than the alkyl derivatives.

An illustration of a rate study making use of the severity of conditions necessary to bring about a reaction is the work of Zartman and Adkins (75). They studied the decomposition,

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(73) Gilman and Kirby, Unpublished work.
(74) Catlin, Ph.D. Thesis, Iowa State College (1934).
(75) Zartman and Adkins, J. Am. Chem. Soc., 54, 3398 (1932).

under hydrogen, of certain organometallic compounds of lead, zinc, magnesium and antimony. Nickel was found to have a very profound influence on the rate of such a reaction. From their studies Zartman and Adkins concluded that the order of increasing stability of the metallic alkyls toward hydrogen, in the presence of catalytically active nickel, appears to be Mg, Zn, Pb and Sb, which is in the order of their decreasing metallic character.

Shurov and Razuvaev (76) have made rate studies in which they compared competitive reactions. Their work dealt with the migration of the phenyl group from one metal to another. By heating the phenylmetals (organometallic compounds having only phenyl groups attached to the metal) with finely divided metals they obtained a transference of the phenyl group. In this way they were able to obtain a series giving the metals in the order of their increasing stability. The method used consisted of placing the phenylmetals and the finely divided metal into a sealed tube, either with or without xylene. This tube was then heated somewhere between 150 and 300° for several hours and was then opened and treated with benzene in order to extract any organometallic compound. The benzene solution and the metallic residues were then analyzed to determine the amount of transference, if any.

From the compounds thus tested they gave the series of increasing stability as Hg, Bi, Pb, Sb, As, and Sn; that is,

(76) Shurov and Razuvaev, Ber., 65B, 1507 (1932).

any metal in this series will remove the phenyl group from the metal to the left of it, with the possible exception of lead. The products produced always consisted of the highest phenylated derivative, possibly with a lower phenylated compound as an intermediate. The migration usually occurred at a lower temperature than the dissociation of the phenylmetal derivatives. Thus, diphenylmercury dissociated 12 percent at 300°, but in the presence of Sn or Sb the migration was quantitative at 200°. The reaction was facilitated by having the metal in finely divided form.

The displacement of metals from their phenyl compounds was also studied by Hilpert and Grüttner (77). They found that magnesium, aluminum and zinc would all displace mercury when the metal was heated with diphenylmercury. Aluminum was found to react very slightly with diphenylzinc, the almost total lack of reaction possibly being due to a protecting film of oxide. When, however, the two metals were allowed to react simultaneously with enough diphenylmercury to form diphenylzinc if the zinc was present alone, it was found that the relative quantities of triphenylaluminum and diphenylzinc were in the ratio of 99 to 1. Magnesium was found to decompose completely the phenyl derivatives of aluminum and zinc, while mercury had no effect on any of the others. They concluded, therefore, that the metals Mg, Al, Zn, and Hg stand in the

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(77) Hilpert and Grüttner, Ber., 46, 1675 (1913).

same relative order of activity as in the ordinary potential series. The displacement of mercury from diphenylmercury by metallic cadmium took place with difficulty and never completely. They, therefore, placed cadmium below mercury in the series, showing the relative activity of the metals toward the formation of phenyl compounds. Bismuth resembled cadmium to some extent, but displaced mercury much more easily than did cadmium. It was, therefore, placed just ahead of mercury in the above mentioned series, and cadmium alone fell in a position different from that occupied in the ordinary potential series.

The alkali metals, as might be expected, form the most reactive organometallic compounds. They react with the usual functional groups with extreme vigor and enter some reactions that even the very active organomagnesium compounds do not show. The outstanding illustration is the olefinic linkage in some hydrocarbons. The organorubidium and organocesium compounds appear to be more reactive than those higher in the group.

Organometallic compounds of the second group elements are, in general, less reactive than the organoalkali compounds (72). The dialkylberyllium compounds appear to be less reactive than the dialkylmagnesium compounds; while the organocalcium compounds might possibly be more active than the organomagnesium halides, and the same might be true of the organostrontium and organobarium compounds. 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 organometallic compounds appear to be more active chemically than the organozincs, while the organocadmium compounds appear to be less reactive than the zinc compounds but more reactive than the organomercury compounds.

In the third group of the periodic system the reactivity of the organometallic compounds, in general, seems to decrease as the atomic weight of the metal increases, with aluminum forming fairly active compounds; while the organothallium compounds are relatively stable.

In the fourth group a transition seems to occur, and the activity of organometallic compounds formed from metals of the B family seems to increase as the atomic weight increases instead of decreasing, as is the case in groups 2 and 3. This rule seems to carry over to the B families in group 5, as it is generally considered that the organobismuth compounds are more active than the organostibines or -arsines.

Concerning the organometallic compounds formed by the metals in the first three groups of the periodic system the following generalizations may be made:

1. In the A family the relative reactivity of the organometalic compounds seems to increase as the atomic weight of the metal increases.
2. In the B family the relative reactivity of the organo-

metallic compounds seems to decrease as the atomic weight of the metal increases.

3. The A family is, in general, more active than the B family.

Concerning the organometallic compounds formed by metals in groups 4 and 5 the only statement possible is:

4. The relative activity of the organometallic compounds of metals in the B families seems to increase as the atomic weight of the metal increases.

In order to correlate better some of these generalizations concerning relative reactivities and the position of the metal in the periodic table the author has attempted to compare the relative reactivities of organozinc compounds of group 2 with organoboron and organo-aluminum compounds of group 3.

Experimental

The general procedures employed in rate studies with organoaluminum, -boron and -zinc compounds were the same as those previously employed in Grignard reaction rate studies. The organometallic compounds were prepared as described previously and were then carefully purified before being used in these rate studies. Tri-p-tolyl- and triphenylaluminum were recrystallized approximately five times from anhydrous ether and the pure white solid obtained used in these studies. The tri-n-propylaluminum was fractionally distilled and the fraction which boiled at 137-138°/22 mm. used in making the standard solutions. Triphenylboron was recrystallized approximately five times from anhydrous ether to give a pure white product melting at 137°. The tri-n-propylboron was fractionally distilled, and the fraction boiling at 64-65°/25 mm. was used in these studies. Di-p-tolyl- and diphenylzinc were crystallized from xylene and washed twice with 25 cc. portions of ligroin (b.p. 95-115°). The di-n-propylzinc was fractionally distilled and the fraction boiling at 61-62°/25 mm. used in this work.

The reactants used in these studies were either redistilled once or recrystallized from an appropriate solvent. The 1% Michler's ketone solution was prepared by dissolving recrystallized Michler's ketone in sodium-dried benzene. The iodine solution contained 0.1% iodine dissolved in glacial acetic acid. Sufficient amounts of these solutions were prepared to last during the entire study in order to have uniform reagents.

The solutions used in these studies were made by dissolving a weighed portion of the organometallic compound in enough xylene to make a known volume. By proper dilution solutions of any lower concentration could be obtained. The solutions were stored in a 400 cc. narrow-necked bottle (Fig. II), equipped so that a measured sample could be easily removed without its coming in contact with the atmosphere. The bottle A was fitted

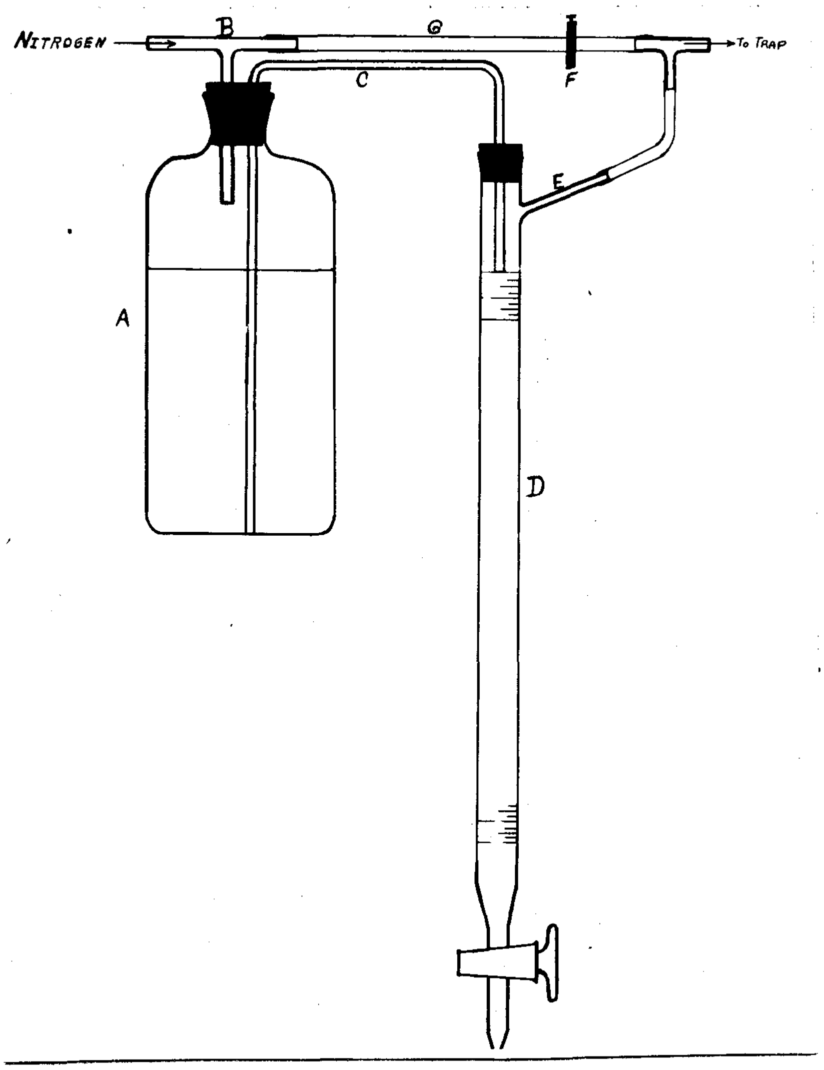

Fig. II

with a 2-holed rubber stopper having a glass T-tube B in one hole and a U-tube C in the other hole. This U-tube extended, on the one side, to the bottom of the bottle and was connected, on its other side, through a 1-holed rubber stopper with the top of a 25 cc. burette D. The burette had a small piece of 6 mm. glass tubing E sealed approximately 2 cm. from its top; this outlet was connected by means of rubber tubing with an oil trap. One side of B was also connected to the trap. In order to obtain a measured sample of organometallic compound screw clamp F was closed and nitrogen forced into the system. The solution in A was then forced into D, excess gas in D escaping through E to the oil trap. When the desired amount of solution had passed into D, the screw clamp was opened and a gentle stream of nitrogen allowed to pass through the tube G and out the oil trap. In this way a positive pressure of dry nitrogen was maintained on the solution in burette D; at any time samples of known volume could be removed. Two or more similar set-ups may be connected together, the nitrogen outlet of the one being connected to the nitrogen inlet of the other, and the outlet of the last set-up being connected to the oil trap. The operations necessary for removal of a sample in this case are the same as when only one set-up is used.

Solutions could not be stored for any length of time in the burette as the stopcock would soon become frozen. At the end of each day the excess solution of organometallic compound remaining in the burette was removed and the stopcocks greased every two or three days. Very pure nitrogen was used in this apparatus. The usual drying train (page 31) was used with two Milligan gas washing bottles filled with potassium pyrogallate to remove oxygen. The pyrogallate solution was renewed every week to obtain complete removal of oxygen, since the organometallic compounds used were very sensitive to traces of oxygen, which had to be completely removed.

When ordinary type bubbling towers were used to remove oxygen it was found that the oxygen was not completely removed. If 50 cc. of a 0.2 molar solution of triphenylboron was heated for 3 days at 135-140^{o} with a stream of nitrogen, purified in the usual manner, passing over it a negative color test was obtained. When the Milligan wash bottles were used for the potassium pyrogallate solution 50 cc. of the same solution of triphenylboron was heated for 8 days at 135-140^{o} and still gave a strong positive color test. Passage of the nitrogen over hot copper or through a solution of phenylmagnesium bromide also gave a gas sufficiently pure for this work, but these methods were more difficult to use than the one given. The pyrogallate solution was made by mixing 50 cc. of 40% potassium hydroxide solution with 150 cc. of 25% pyrogallic acid solution. This gave a concentration best suited for removal of small quantities of oxygen.

The use of solvents other than xylene was also attempted in these studies. The more volatile solvents, such as ether and benzene, gave considerable trouble from evaporation, causing a continual change in the concentration of the solution. Whenever ether solutions were used, it was necessary to jacket the container and cool the solution with running water. The only difficulty experienced with the xylene solutions was in the swelling of the rubber stoppers. All stoppers were tightly wired in, and collodion-coated cork stoppers were used when reactions required the use of boiling xylene.

Reaction Rates with Michler's Ketone. Because of the rather slow reaction between Michler's ketone and the organometallic compounds of aluminum, boron and zinc, it was possible to compare the reaction velocities of these three types of organometallic compounds by this reaction. Standard solutions of the organometallic compounds in xylene were prepared and the time that was necessary for a reaction to take place between these solutions and a 1% solution of Michler's ketone in benzene determined. The reaction was carried out in clean dry test tubes. Twelve test tubes were provided with clean corks, and into each tube was placed 2 cc. of the Michler's ketone solution. To each of these tubes was added from a burette 2 cc. of the organometallic compound. The tubes were tightly stoppered. At regular intervals a tube was opened, 20 drops of a 50% alcohol solution added, and the tubes shaken. From 4 to 10 drops of iodine were then added to the solution. During the first 12 hours solutions were tested after intervals of 5 minutes, 30 minutes, 1,2,4,6,8, and 12 hours. Thereafter, one tube was opened every 24 hours. The time recorded was the interval from the time of adding the organometallic compound to the Michler's ketone solution, to the time when hydrolysis and addition of the iodine solution gave a noticeable greenish-blue color. Slight colorations may have been noticed before this, but the test was not considered positive unless a fairly strong coloration was obtained.

Check runs were made in every case and the results duplicated in the case of the shorter time intervals, but the results with a 0.2 molar solution varied considerably with the organozinc and organoboron compounds. The development of the color test with these dilute solutions was very gradual, and since only one sample was tested every 24 hours after the first 24 hour interval, it was very easy to record differences of 24 hours in the time observed. In all cases the color developed was compared with the color given by hydrolysis and addition of iodine to a solution of the same organometallic compound which was concentrated enough to give a positive color test. The ability to recognize the proper color was very important and this human factor may account to a very large extent for the variations recorded.

Table I

Rate of Reaction of Certain Organometallic Compounds with Michler's Ketone

Time (in hours)

Organometallic Compound	Concentration of Molar Solutions							
	0.2	0.2	0.2	0.3	0.3 (a)	0.4	0.5	1.0
$(C_2H_5)_3Al$	0.5	0.5	0.5	0.5	0.08	0.08	0.08	
$(C_2H_5)_3B$	24	12	24	8	0.5	0.08	0.08	
$(C_2H_5)_2Zn$	96	48	66	12	12	6	6	
$(n-C_3H_7)_3Al$			0.5				0.08	0.08
$(n-C_3H_7)_3B$			6				0.5	0.08
$(n-C_3H_7)_2Zn$			96				36	24
$(p-CH_3C_6H_4)_3Al$			0.5					
$(p-CH_3C_6H_4)_2Zn$			48					

(a) In this series 4 cc. of the organometallic compound was added to 2 cc. of Michler's ketone.

Minimum Concentration Giving the Color Test. It was found that positive color tests with the less reactive organometallic compounds could be obtained if their solution with Michler's ketone was heated for a short time. Thus, the organozinc compounds, which require several hours at room temperature to give a positive color test, gave a positive test after heating at 100-110° for 5 minutes. Better color tests could be obtained by heating for longer periods.

In determining the minimum concentration of the organometallic compounds of aluminum, boron and zinc necessary to give a positive color test 2 cc. of a standard solution of the organometallic compound was placed in a test tube containing 2 cc. of Michler's ketone solution. The test tube was then placed in an oil bath maintained at 100-110° for 5 minutes. At the end of that time it was removed, cooled under the tap, and hydrolyzed with 20 drops of 50% alcohol. To this solution was added 4 to 10 drops of the iodine solution and the color observed. A greenish-blue color was recorded as being positive, while a yellowish-green color was considered negative. The solutions tested were made up in 25 cc. volumetric flasks. These were clean and dry and flushed out with nitrogen. Ten cc. of dry xylene solution was added to the flask and then enough standard solution added from a burette to give the proper concentration, and the flask filled to the 25 cc. mark with xylene. Two cc. samples were pipetted from this into the test tubes. The last solution that gave a positive test was considered as having the minimum concentration necessary.

Table II

Minimum Concentration Required to Give the Color Test

Organometallic compounds tested	Minimum molar concentration	Remarks
$(C_6H_5)_3Al$	0.02	A 0.01 molar solution gave a faint test on heating 15 minutes.
$(C_6H_5)_3B$	0.1	This test was very weak.
$(C_6H_5)_2Zn$	0.1	This test was very weak.
$(n\text{-}C_3H_7)_3Al$	0.02	A 0.01 molar solution gave a negative test after 15 minutes' heating.
$(n\text{-}C_3H_7)_3B$	0.05	A 0.1 molar solution gave a very good test.
$(n\text{-}C_3H_7)_2Zn$	0.1	This was a weak test.

Reaction Rates with Benzaldehyde, Benzophenone, and Benzonitrile. The rate of reaction of organometallic compounds of aluminum, boron and zinc was determined with benzaldehyde, benzophenone and benzonitrile by treating the above reactants with xylene solutions of the organometallic compounds and determining the length of time required for the disappearance of the color test. The reactions were carried out at room temperature in clean dry flasks under a slight positive pressure of nitrogen. The three different organometallic compounds were run simultaneously to have as near the same conditions as possible.

It was observed in the study of reactions of simple organo-aluminum compounds that all three R groups entered into the reaction. The yields obtained were in several cases greater than were possible if only one or two of the R groups had entered into the reaction. All yields reported were calculated on the basis that one mole of the organo-aluminum compound reacted with three moles of the reactant. If less than three moles of the reactant were used the color test remained positive over very long intervals; whereas, the use of slightly more than three moles caused a fairly rapid disappearance of the color test. With organozinc compounds both R groups were found to react, and two moles of reactant were added per mole of the organozinc compound. With the organoboron compounds only two of the three R groups appeared to react. On working up of reaction products of organoboron compounds one of the products which always separated was a substituted boric acid having one R group still attached to the boron. In no case were all three R groups removed from the boron atom. When one mole of an organoboron compound was treated with slightly more than two moles of a reactant a negative color test was observed. Calculations of yields of reactions of organoboron compounds were made considering only two R groups reacting.

In all cases studied 10% excess of reactants was used. In the majority of cases 50 cc. of a 0.2 molar solution (0.01 mole) of the organometallic compound was used. In a typical experiment 3.5 grams (0.033 mole) of redistilled benzaldehyde was reacted with 50 cc. of a 0.2 molar solution of triphenylaluminum, while 2.33 grams (0.022 mole) was required for each reaction with the same amount of diphenylzinc and triphenylboron solutions. At regular intervals of time a 2 cc. sample of the solution was removed and tested for the presence of organometallic compounds. In order to obtain a color that was approximately equivalent with each solution it was found necessary to heat the solution of the organometallic compound with Michler's ketone for different intervals of time. Thus, when a 0.2 molar solution of tri-n-propylaluminum was heated with Michler's ketone for 5 minutes at 100-110° it gave a color test which was comparable to that given by a tri-n-propylboron solution that had been heated 15 minutes at 100-110°, or a di-n-propylzinc solution that had been heated 30 minutes. Therefore, samples of organoaluminum compounds removed for testing were heated 5 minutes with Michler's ketone, the organoboron compounds 15 minutes, and the organozinc compounds 30 minutes. This method differed from that used in determining the minimum concentration necessary to give a positive color test, since in that case it was desired to determine the concentration necessary to give a positive color test while all other factors remained the same. In this study the concentrations must remain the same; it was thus necessary to find the conditions required to give an equivalent positive color test with the three organometallic compounds studied. The time recorded in the table indicates the interval between the addition of the organometallic compound and the time when a sample gave a reddish color rather than the customary greenish-blue, after hydrolysis and addition of the iodine solution.

Table III

Rate Studies with Benzaldehyde, Benzophenone and Benzonitrile

Time (in hours)

Reactant	0.01 mole $(C_6H_5)_3Al$	0.01 mole $(C_6H_5)_3B$	0.01 mole $(C_6H_5)_2Zn$	0.01 mole $(n\text{-}C_3H_7)_3Al$	0.01 mole $(n\text{-}C_3H_7)_3B$	0.01 mole $(n\text{-}C_3H_7)_2Zn$
Benzaldehyde	0.5	6	8	0.5	8	8
Benzonitrile				8	14	24
Benzophenone	2	10	24	6	10	14
Benzophenone	4		14	4		16
	0.005 mole (a) $(p\text{-}CH_3C_6H_4)_3Al$		0.005 mole (a) $(p\text{-}CH_3C_6H_4)_2Zn$	0.02 mole (b) $(n\text{-}C_3H_7)_3Al$	0.02 mole (b) $(n\text{-}C_3H_7)_3B$	0.02 mole (b) $(n\text{-}C_3H_7)_2Zn$
Benzonitrile				5	24	24
Benzophenone	2		6			

(a) In this study 50 cc. of a 0.1 molar solution were used.
(b) Twenty cc. of a 1 molar solution were used.

Rate of Displacement of Mercury from Organomercury Compounds by Aluminum and Zinc. In boiling xylene solution the transference of R groups from an organomercury compound to either aluminum or zinc takes place very readily. A comparison of the time required for the formation of organo-aluminum compounds as compared to the time required for the formation of organozinc compounds gives a means of studying the relative reactivities of these two organometallic compounds.

Two three-necked 250 cc. flasks equipped with Hopkins condensers were thoroughly swept out with dry nitrogen. In the first flask were placed 5.74 grams (0.015 mole) of di-p-tolylmercury, 2.02 grams (0.075 mole) of aluminum chips, and 100 cc. of dry xylene. In the second flask were placed 3.83 grams (0.01 mole) of di-p-tolylmercury, 3.27 grams (0.05 mole) of mossy zinc, and 100 cc. of dry xylene. These two solutions were heated to a gentle reflux; then at 30 minute intervals 2 cc. samples were removed from each flask. These samples were added to 10 cc. of alcohol in a small flask. To this was added 5 cc. of a stannous chloride solution and the solution evaporated to one-half its volume. If on heating a sample, in this manner, free mercury was obtained, the transference of the R group from the mercury to the other metal present had not been completed. The time was recorded when a sample treated in this manner gave no free mercury in the bottom of the flask. Aluminum and di-p-tolylmercury gave a negative test for organomercury compounds after refluxing for 2 1/2 hours, while under the same conditions

8 hours were necessary for complete transference of the p-tolyl radical from mercury to zinc.

In a similar study using diphenylmercury, aluminum completely displaced the mercury in 2 1/2 hours, while zinc required 6 hours for complete displacement of the mercury. All of the above runs were checked and the variation in time was in no case greater than 30 minutes.

An effort was made to compare magnesium and boron, in a similar manner, with aluminum and zinc. However, no displacement of mercury from diphenylmercury was observed after refluxing a xylene solution of diphenylmercury for 24 hours with either magnesium turnings or crystalline boron. The possibility of the preparation of organoboron compounds by the reaction between organomercury compounds and both crystalline and amorphous boron is being investigated further.

Discussion of Results

The use of the color test in determining the relative reactivity of certain organometallic compounds has been extended to the less reactive organometallic compounds of aluminum, boron and zinc. Because of the very slow reaction of some of these compounds with Michler's ketone the variation in results may be considerable, but the relative rates are separated widely enough to permit a semi-quantitative determination of their relative reactivities.

On the basis of the studies made with both alkyl and aryl compounds of these three metals the relative order of decreasing reactivities is: organo-aluminum compounds, organoboron compounds, organozinc compounds.

There was little difference shown between the relative reactivities of the alkyl and aryl derivatives. However, in the study on the minimum concentration required to give a positive color test, the n-propyl derivatives seemed to give slightly better color tests with dilute solutions than did the phenyl derivatives. In general, the n-propyl derivatives and the phenyl derivatives were of approximately equal reactivity, the n-propyl compound possibly being slightly more reactive.

A comparison of the rates of reaction of the phenyl and p-tolyl compounds with benzophenone would indicate that the p-tolyl derivatives may be more reactive than the phenyl derivatives. The solutions used in the comparison were of different concentrations, but the results with the organozinc compounds seemed to warrant the prediction that the p-tolyl derivatives are more reactive than the phenyl compounds.

The studies of Entemann and Johnson (28) are supported in the study of the rate of reaction between certain functional groups and the _n_-propyl derivatives of aluminum, boron and zinc. They have shown benzaldehyde to be more reactive with phenylmagnesium bromide than benzophenone and both of these compounds to be more reactive than benzonitrile. The same general order of reactivities has been observed in these studies.

Boron, generally considered a metalloid, has been shown to yield organometallic compounds resembling closely those of aluminum and zinc. The oxides of boron also resemble very closely the oxides of aluminum, gallium and indium, in being amphoteric. These two facts are supporting evidence for the metallic state of boron.

Since boron and aluminum are generally classed in the B family of group 3 and the reactivity of the organometallic compounds in this family appears to decrease as the atomic weight of the metal increases, it would appear as if boron and aluminum were reversed in regard to the relative reactivities of their organometallic compounds. This is not unexpected. Pfeiffer and co-workers (78) have arrived at the conclusion that beryllium and magnesium exhibit properties which entitle them to be placed in the family with zinc, cadmium, and mercury, rather than with the alkaline earth metals of family A of

(78) Pfeiffer, Fleitmann, and Hansen, _J. prakt. Chem._, _128_, 47 (1930).

group II. Since the relative reactivity in family B appears to decrease as the atomic weight of the metal increases, organoberyllium compounds should be more reactive than organomagnesium compounds. It has been shown (73) that these two metals are also reversed in regard to the relative reactivity of their organometallic compounds.

It would be of interest to compare the relative reactivities of organosodium compounds with organolithium compounds. The possibility of the lesser reactivity of the organosodium compounds is suggested by the difference in reactivity between diphenylmethylsodium and the alkyl-lithium compounds (79). It would appear as if the order of reactivity of the organometallic compounds formed by metals in the first two periods of the periodic table are reversed.

It now appears generally true that the following is the order of decreasing activity of some organometallic compounds: Cs, Rb, K, (Na, Li), (Ba, Sr, Ca), Mg, Be, Al, B, Zn, Cd, Hg. (The elements in parentheses are not as yet definitely placed in this series.) A comparison between the relative reactivities of Ga, In, and Tl with B family of group 2 has not been made, but it is probable that these metals form organometallic compounds that equal or exceed organomercury compounds in reactivity.

There seems, therefore, to be a direct correlation between the position of a metal in the periodic table and the relative

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(79) Bergmann and Rosenthal, J. prakt. Chem., 135, 267 (1932); Ziegler, Crossmann, Kleiner and Schäfer, Ann., 473, 1 (1929).

reactivity of its organometallic compounds.

With the metals of the first three groups of the periodic table there appears to be a direct correlation between their positions in the electrochemical series and the relative reactivities of their organometallic compound. Mellor (80) gives the following order in the first part of his electrochemical series of elements: Cs, Rb, K, Na, Li, Ba, Sr, Ca, Mg, Al, Cr, Mn, Zn, Cd. This is the same order that has just been given for the reactivities of organometallic compounds. Every metal is in its relative position as far as present day knowledge can determine. Boron, being classed as a metalloid, is not placed in the usual electrochemical series of metals. A correlation between the position of other metals in the electrochemical series and the relative reactivities of their organometallic compounds is now in progress.

The effect of catalysts and forced conditions on the reactions of these less reactive organometallic compounds is being investigated further. The work of Gilman and St. John (81) suggests that by the proper choice of catalysts and conditions the reaction of these organometallic compounds may be either retarded or accelerated, and in this way it may be possible to develop preferential reactions with compounds having polyfunctional groups.

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(80) Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. I, Longmans, Green and Co., New York, 1922, p. 1014.

(81) Gilman and St. John, Rec. trav. chim., 49, 222 (1930).

Summary

1. The relative rates of reaction of the n-propyl and phenyl derivatives of aluminum, boron and zinc with Michler's ketone have been studied.
2. The relative reactivities of the n- propyl and phenyl derivatives of aluminum, boron and zinc have been determined by a study of the rates of reaction with benzaldehyde, benzophenone and benzonitrile.
3. The relative rates of formation of organometallic compounds of aluminum and zinc have been compared.
4. The order of decreasing reactivities has been found to be: organo-aluminum compounds, organoboron compounds, organozinc compounds.
5. A correlation has been made between the relative reactivities of some organometallic compounds and the position of the metals in the electrochemical series.
6. The possibility of the preparation of otherwise inaccessible compounds through the medium of selective or preferential reactions involving these less reactive organometallic compounds has been discussed.