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Relative reactivities of some organometallic compounds

Lester D. Apperson
Iowa State College

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RELATIVE REACTIVITIES OF SOME
ORGANOMETALLIC COMPOUNDS

by

Lester D. Apperson

A Thesis Submitted to the Graduate Faculty
for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject Organic Chemistry

Approved:

Signature was redacted for privacy.

In charge of Major work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State College

1940

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INTRODUCTION

Organometallic compounds are probably the most important group of compounds used in organic synthesis. They include all compounds which contain a direct union of carbon with a metal. The two main classes of organometallic compounds are commonly known as "simple" and "mixed". A simple organometallic compound is one which has only R groups attached to the metal (R_nMg) while a mixed organometallic compound has both R and X groups attached to the metal ($RMgX$). The X group is usually a halogen although it may be an acid radical, hydrogen, hydroxyl, amino or one of a variety of other groups depending upon the reactivity of the selected organometallic compound. The R group is generally an alkyl or aryl radical and it may contain a large variety of substituents, but the substituents are obviously limited to those which will not react with the chosen organometallic compound.

The simple organometallic compounds may be further classified into symmetrical $\left[(C_2H_5)_4Pb \right]$ and unsymmetrical $\left[(C_2H_5)_3PbC_6H_5 \right]$ groups. An additional classification is based upon the valence of the metal in the organometallic compound. The term "organometallic radical" is given to those organometallic compounds which contain the metal in a lower valence state than is normal for the metal. Such compounds are characterized by their tendency to revert to compounds containing the metal in its

normal valence state.

A knowledge of the relative reactivities of organometallic compounds is not only of theoretical interest, but it also aids in the selection of the proper organometallic compound for use in a particular synthesis. Syntheses often involve the use of selective reactions. The wide range of reactivities exhibited by organometallic compounds should make them excellent reagents for effecting preferential reactions with polyfunctional compounds. First, of course, experimental data on the relative reactivities of the individual organometallic compounds must be compiled before the proper selections for preferential reactions can be made.

The present work with organoaluminum halides was undertaken with the view of comparing their reactivity with simple organoaluminum compounds and with organometallic compounds in general. The possibility of the intermediate formation of organoaluminum halides in the Friedel-Crafts reaction has also been considered.

The studies on divalent organolead radicals were undertaken with the dual purpose of devising improved methods for their preparation and determining their reactivity in comparison with trivalent and tetravalent organolead compounds.

A. ORGANOALUMINUM HALIDES

HISTORICAL

The chemistry of organoaluminum halides was inaugurated in 1859 by Hallwachs and Schafarik (1) when they heated ethyl iodide and aluminum in a sealed tube at 180° for two days, and obtained a reactive organic liquid which contained aluminum. Although they did not isolate or definitely identify their products, they undoubtedly had prepared a mixture of ethylaluminum iodides. The following year Cahours (2) reported the same reaction, in which the reactants were heated in a sealed tube for twenty-four hours at 130°. A liquid was obtained which fumed in the air and to it was assigned the structure $\text{Al}(\text{C}_2\text{H}_5)_3 \cdot \text{AlI}_3$. The methyl analog was also prepared. Both compounds were decomposed by water and burned in an atmosphere of oxygen or chlorine. Treatment of the ethyl derivative with an ethylzinc compound gave zinc iodide and an inflammable liquid which was probably triethylaluminum.

Mouneyrat (3) and later Fürstenhoff (4) investigated the reaction between aluminum and ethylene bromide. A compound, formulated as $\text{AlBr}_3 \cdot \text{Al}(\text{C}_2\text{H}_4\text{Br})_2$, was obtained which reacted very violently with water and exerted a catalytic effect on the

(1) Hallwachs and Schafarik, Ann., 109, 207 (1859).

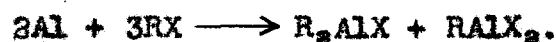
(2) Cahours, Ann. chim. phys., [3] 56, 20 (1860).

(3) Mouneyrat, Bull. soc. chim., [3] 19, 183 (1898).

(4) Fürstenhoff, Bull. soc. chim. Belg., 17, 414 (1903).

synthesis of other organometallic halides. It was capable of starting the reaction between aluminum and ethyl bromide to give a compound designated as $\text{Al}_2\text{Br}_3(\text{C}_2\text{H}_5)_3$. It was used also as a catalyst in reactions between zinc and alkyl halides (5).

Spencer and Wallace (6) were the first to present the true equation for the formation of mixed organoaluminum compounds from the reaction between aluminum and alkyl halides.

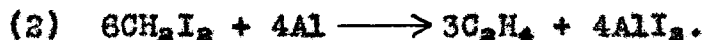
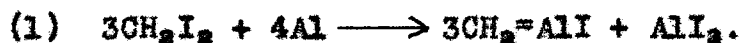


They carried out a number of reactions between organic halides and aluminum, but they did not separate or conclusively identify their products. The resulting crude reaction products were hydrolyzed to give hydrocarbons which generally contained the same number of carbon atoms as in the original halides. Evidence for the formation of hydrocarbons with twice the number of carbon atoms was found only in the case of the halogen substituted anilines. The halides investigated were methyl iodide, isoamyl chloride, isoamyl bromide, isoamyl iodide, sec.-octyl iodide, iodobenzene, chlorobenzene, p-chloroaniline, p-bromoaniline and α-bromonaphthalene. The first two were heated in sealed tubes at 270° and only decomposition gases were obtained. The others with the exception of chlorobenzene were heated in flasks fitted with condensers. Chlorobenzene was heated in a sealed tube for nine hours at 270° to give a charred product which contained a few white crystals. Hydrolysis of the mixture

- (5) Job and Reich, Bull. soc. chim., [4] 33, 1424 (1923).
(6) Spencer and Wallace, J. Chem. Soc., 93, 1827 (1908).

gave a thirty-nine per cent yield of benzene. Halogen acids were liberated in most of the reactions.

Thomas (7) reported that methylene iodide reacted with aluminum after a long period of standing to form a white crystalline product. Grosse (8) studied the reaction between methylene bromide and aluminum and found the reaction to be much more rapid if it was activated with iodine. There resulted a white organoaluminum compound in addition to aluminum bromide which was removed by high vacuum sublimation at 200°. Hydrolysis of the remaining organoaluminum compound gave pure methane. According to Faillebin (9) the course of the reaction between methylene iodide and aluminum in the presence of ether proceeded in the following manner:



In the case of methylene bromide the second reaction took place to a considerably lesser extent. The addition of iodine to the postulated methylenealuminum bromide apparently proceeded according to the equation, $\text{CH}_2=\text{AlBr} + \text{I}_2 \longrightarrow \text{CH}_2\text{I}\cdot\text{AlBrI}$, since hydrolysis gave only methyl iodide and basic aluminum bromide.

In 1925 Grignard and Jenkins (10) made an outstanding

- (7) Thomas, Compt. rend., 174, 464 (1922).
(8) Krause und von Grosse, "Die Chemie der metallorganischen Verbindungen", Gebrüder Borntraeger, Berlin (1937), p. 227.
(9) Faillebin, Compt. rend., 174, 113 (1922).
(10) Grignard and Jenkins, Bull. soc. chim., [4] 37, 1376 (1925).

contribution to the chemistry of organoaluminum halides. The mixed ethylaluminum iodides were prepared from ethyl iodide and aluminum by employing a technique similar to that used in the preparation of Grignard reagents. No ether was used, however. The resulting product was a mobile liquid which was separated by fractionation into diethylaluminum iodide (b.p., 118-120°/4-5 mm.) and ethylaluminum di-iodide (b.p., 158-160°/4 mm.; m.p., 35-37°). Molecular weight determinations showed that the compounds were bimolecular. They were soluble in ether and formed stable mono-etherates which were not destroyed by heating. Both were soluble in benzene and diethylaluminum iodide was soluble in chloroform. The compounds were very sensitive to oxygen and were instantly inflammable in the air. Water hydrolyzed them quite violently to ethane. No reaction was reported with carbon dioxide, but they brought about condensation of acetone to mesityl oxide, and with benzaldehyde unidentifiable complex condensation products resulted. Mercuric chloride and mercurous chloride were partially reduced to metallic mercury.

The ethylaluminum bromides were prepared by initiating the reaction between ethyl bromide and aluminum with a small crystal of iodine. The bromides could not be fractionated satisfactorily.

At about the same time Leone (11a) reported extensive

- (11) (a) Leone, Gazz. chim. ital., 55, 294 (1925);
(b) Leone and Braicovic, ibid., 55, 301 (1925).

studies on the reactions between alkyl halides and aluminum, in which small amounts of ether were used to initiate the reactions and additional ether was added to keep the reactions going whenever they slowed down appreciably. The mixed organo-aluminum etherates were prepared in this manner from ethyl iodide, ethyl bromide, n-propyl iodide, isocamyl iodide, n-octyl bromide and iodobenzene. The crude products were not purified but were reacted directly with ketones, acid chlorides and alkyl iodides (11b). Ketones were condensed, acetone giving mesityl oxide and acetophenone giving triphenylbenzene. The mixed ethylaluminum iodide etherates and benzoyl chloride gave a small amount of propiophenone, a small amount of α , α -dibenzoylethane, ethane, hydrogen chloride and a tarry residue. Small yields of alkylated benzenes, together with larger amounts of resinous material, were obtained from reactions between alkyl iodides and the mixed phenylaluminum iodides.

These mixed organoaluminum compounds were found also to react with ammonia, aliphatic primary and secondary amines and aryl primary amines in the manner of the corresponding magnesium compounds (12). The N-alkylanilines did not react.

Early in 1937 Walker and Willson (13) showed that methyl chloride reacts with aluminum in the presence of a small amount

(12) Leone and Braicovic, ibid., 55, 306 (1935).

(13) Walker and Willson, Refrig. Eng., 34, 89 (1937).

of iodine or aluminum chloride to form an unidentified product which is probably a mixture of dimethylaluminum chloride and methylaluminum dichloride. Later in the same year, Hall and Nash (14) isolated the mixed ethylaluminum chlorides from the products of the polymerization of ethylene by a mixture of aluminum and aluminum chloride. Ethylaluminum dichloride formed an insoluble double salt with sodium chloride at 200°, leaving the liquid diethylaluminum chloride which was decanted and distilled (b.p., 85-86.5°/9.5 mm.). Oxidation of the mixed ethylaluminum chlorides gave some ethyl alcohol and treatment with acetyl chloride yielded methyl ethyl ketone.

A better method of preparing alkylaluminum chlorides has been described by Hnizda and Kraus (15). The gaseous halide is passed into an aluminum-copper alloy which has been activated by iodine or aluminum chloride, and an equimolecular mixture of the mixed organoaluminum halides results. The description applied specifically to methyl chloride, but it was stated that ethyl chloride and methyl and ethyl bromides could also be used.

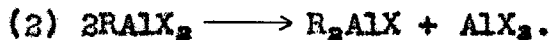
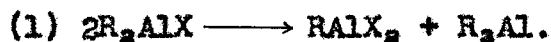
Grosse and Mavity (16) have prepared aluminum compounds of the types R_2ALX , $RALX_2$, R_2ALOR , $Al(OR)_2$, $ROALX_2$ and $(RO)_2ALX$ (R = alkyl or aryl radical, X = halogen). They were found to ignite spontaneously in air and to be decomposed

(14) Hall and Nash, J. Inst. Petroleum Tech., 23, 679 (1937).

(15) Hnizda and Kraus, J. Am. Chem. Soc., 60, 2276 (1938).

(16) Grosse and Mavity, J. Org. Chem., 5, 106 (1940).

immediately by water or alcohol into the corresponding RH compounds. Some of the compounds were reported to disproportionate easily according to the following equations:



Alkali metal halides added to the organoaluminum halides to produce white crystalline solids. For example, diethylaluminum bromide added potassium bromide to give white prisms (m.p., 55°) which were formulated as $KAl(C_2H_5)_2Br_2$. The physical constants of these aluminum compounds are given in Table I.

The preparation of these aluminum compounds is discussed by Grosse and Mavity who state that organoaluminum halides are most conveniently prepared through the reaction of alkyl halides and aryl iodides with aluminum. The reaction, which is practically quantitative, has been successfully applied using methyl and ethyl chlorides, bromides and iodides, and the n-propyl, phenyl, and p-tolyl iodides. The reactions were carried out in pyrex flasks with mechanical stirrers or, in cases where the alkyl halides are gases, in rotating or stirrer-equipped autoclaves. It was usually necessary to catalyze the reaction with iodine, an aluminum halide, or a previously prepared alkylaluminum halide. The two compounds produced were separated either by physical methods (fractional

TABLE I

Physical Constants of Some Organoaluminum Compounds

<u>ALUMINUM COMPD.</u>	<u>M.P.</u>	<u>B.P. (760 mm.)</u>	<u>d₄ (vac.) 20°</u>
1. (CH ₃) ₂ AlCl			
2. (CH ₃) ₂ AlBr	-19.1	152.4	1.4101
3. (CH ₃) ₂ AlI			
4. (C ₂ H ₅) ₂ AlCl	-82	214.5	0.9868
5. (C ₂ H ₅) ₂ AlBr	-74 to -72		1.2703
6. CH ₃ AlCl ₂	72.7		
7. CH ₃ AlBr ₂	80	211.3	
8. C ₂ H ₅ AlCl ₂	32	201.7	
9. <u>n</u> -C ₂ H ₇ AlI ₂	0 - 1.5		
10. C ₆ H ₅ AlCl ₂	93 - 95.5		
11. C ₆ H ₅ AlBr ₂	73.5 - 87		
12. C ₆ H ₅ AlI ₂	106 - 111		
13. <u>p</u> -CH ₃ -C ₆ H ₄ AlI ₂			
14. (CH ₃) ₂ AlOCH ₃	35.5		
15. CH ₃ Al(OCH ₃) ₂	>275		
16. (C ₂ H ₅) ₂ AlOC ₂ H ₅	5	247.5	0.8666
17. CH ₃ OAlCl ₂	84.3 - 84.5		
18. C ₂ H ₅ OAlCl ₂	35.5 - 35.7		
19. (C ₂ H ₅ O) ₂ AlBr	275 - 300		

distillation or crystallization), or the mixture was converted to one or the other of the two constituents by adding the stoichiometric quantity of the aluminum trihalide or trialkylaluminum compound. These last-named reactions are examples of a more general reaction between two aluminum compounds to produce a third.



By such a reaction phenylaluminum dichloride and phenylaluminum dibromide were prepared from triphenylaluminum. In an analogous manner mono- and dimethylaluminum methoxides and mono- and diethylaluminum ethoxides were prepared by combining alkylaluminum compounds with aluminum alkoxides.

Controlled reaction of alkylaluminum halides with oxygen or with alcohols gave alkoxyaluminum halides.



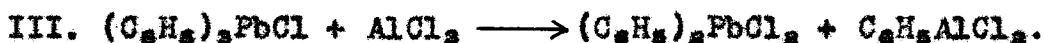
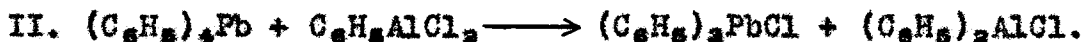
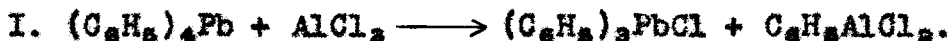
Alkyl halides reacted with magnesium (70% Al, 30% Mg) to give dialkylaluminum halides in ninety to ninety-five per cent purity and in yields up to ninety-four per cent.



Trialkylaluminum compounds were readily prepared in yields of forty to sixty per cent by refluxing either dialkylaluminum halides or the crude equimolecular mixture of the mono- and dialkylaluminum halides with alkali metals (sodium or sodium-potassium alloy).



Organoaluminum halides have also been prepared by treating organolead compounds with aluminum chloride (17). The essential reactions in petroleum ether (b.p., 90-115°) or hexane appear to be the following for phenyllead compounds:



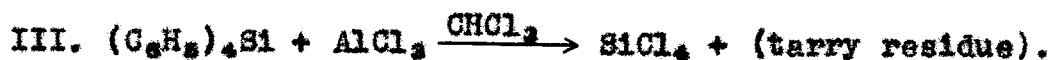
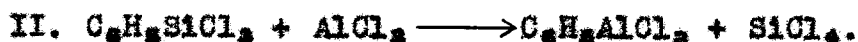
The reaction is halted at the diphenyllead dichloride stage, and this compound was shown to be unaffected when treated separately with aluminum chloride. The organoaluminum compounds were qualitatively analyzed by the color test (18), and semi-quantitatively determined both by measuring the benzophenone after treatment with benzoyl chloride, and by formation of benzene upon hydrolysis.

Evison and Kipping (19) obtained similar reactions by cleaving phenylsilicon compounds with aluminum chloride. The presence of aluminum compounds was indicated by the formation of benzene upon hydrolysis, the isolation of ethylated benzenes when ethyl bromide was present in the reaction mixture, and the isolation of acetophenone upon the addition of acetyl chloride. The three reactions were formulated as follows:

(17) Gilman and Apperson, *ibid.*, 4, 162 (1939).

(18) Gilman and Schulze, *J. Am. Chem. Soc.*, 47, 3002 (1925).

(19) Evison and Kipping, *J. Chem. Soc.*, 2774 (1931).



Ethyllead compounds (17) were cleaved by aluminum chloride to give essentially the same three reactions as reported for the phenyl derivatives. However, with ethyllead compounds, the diethyllead dichloride in equation (III) was not isolated. The aluminum compounds accelerate its decomposition to lead chloride, ethyl chloride and disproportionation products of the ethyl radicals. The organoaluminum compounds formed were chiefly diethylaluminum chloride and ethylaluminum dichloride, together with occasional small quantities of triethylaluminum. These ethylaluminum compounds appeared to form complexes with the various ethyllead compounds, and the complexes were broken up by hydrolysis, by distillation or by reaction with acyl halides. Incidental to the formation of ethyl chloride, it was significant that small quantities of hexaethylbenzene were isolated when benzene was used as the reaction medium. Of course, this Friedel-Crafts product may have come from the disproportionation of ethyl radicals to ethylene.

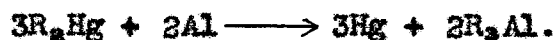
The ethylaluminum compounds were isolated by distillation, and their physical constants checked those of ethylaluminum compounds prepared both from the reaction of ethyl chloride and aluminum turnings (using a crystal of iodine or a few drops of ethyl iodide as a catalyst) and from the addition of aluminum chloride to triethylaluminum. The mixed

ethylaluminum compounds could not be fractionated satisfactorily. The boiling point of the mixed ethylaluminum chlorides was 63°/3 mm.

Unidentified organoaluminum compounds were obtained from the cleavage of triphenyl- and tri-o-tolyllead by aluminum chloride.

Simple Organoaluminum Compounds (R₃Al)

The chemistry of simple organoaluminum compounds began in 1865 when Buckton and Odling (20) prepared trialkylaluminum compounds from the corresponding mercurials and aluminum.



The methyl and ethyl compounds were prepared and both were liquids which were inflammable in the air. They distilled undecomposed in an atmosphere of hydrogen, the methyl compound boiling at 130° and the ethyl compound at 194°. Triethylaluminum added iodine to give ethyl iodide and a mixture probably containing the mixed ethylaluminum iodides and aluminum iodide. Vapor density measurements indicated that the compounds were bimolecular.

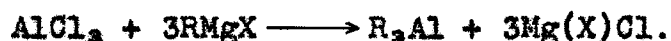
The normal propyl (b.p., 348-252°) and butyl derivatives were prepared in 1873 by Cahours (21) who used the procedure of Buckton and Odling.

Somewhat later, Roux and Louise (22) investigated the

- (20) Buckton and Odling, Ann. chim. phys., [4] 4, 492 (1865).
(21) Cahours, Jahresber., 518, 522 (1873)
(22) Roux and Louise, Bull. soc. chim., (2) 50, 497 (1888).

molecular weights of the methyl-, ethyl-, n-propyl- and iso-amylaluminum compounds and found them to be best represented as bimolecular compounds both in solution and in the vapor phase. Heating the substances above their boiling points decreased their vapor densities and the compounds decomposed more and more into the simple molecules (23).

Grignard reagents have also been used for the preparation of trialkylaluminum compounds, but an etherate is always formed. Krause and Wendt (24) prepared the etherates of trimethyl-, triethyl- and tri-n-propylaluminum by adding aluminum chloride to an ether solution of the corresponding Grignard reagent.



The resulting product was distilled in the presence of additional Grignard reagent to insure the complete removal of halogens. The etherates were designated as containing four molecules of aluminum compound and three molecules of ether. However, in some later work, it was suggested that the compounds probably formed mono-etherates (25). The etherates were very stable thermally and did not lose their ether on distillation. The boiling points of the etherates of trimethyl-, triethyl- and tri-n-propylaluminum are 68°/15 mm., 112°/16 mm., and 135°/18 mm., respectively. The etherates were prepared also from a magnesium-aluminum alloy and the corresponding alkyl bromides

(23) Quincke, Z. physik. Chem., 3, 164 (1889).

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

(25) Ref. 8, p. 221.

in ether solution.

Tropsch and Schellenberg (26) have apparently prepared a trialkylaluminum compound by a unique method. Methyl alcohol was decomposed at 270° in the presence of aluminum. The resulting gas was condensed and found to contain an aluminum compound, probably trimethylaluminum.

The first simple arylaluminum compound was prepared by Friedel and Crafts (27) in 1888 in connection with studies on the mechanism of the reaction bearing their name. Diphenylmercury was heated with aluminum foil at 125-130° to give triphenylaluminum which reacted vigorously with water to form benzene, biphenyl and alumina. Oxidation gave some phenol, while reaction in xylene solution with sulfur produced diphenylene disulfide, phenyl sulfide and probably some phenyl mercaptan. A small amount of diphenylmethane was isolated from the reaction with benzyl chloride. No reaction occurred with chlorobenzene. Hilpert and Grüttner (28) also prepared triphenylaluminum from diphenylmercury and found the melting point to be 196-200°. It formed an etherate of white needles melting at 112-113°. Reaction with chloroform gave a yellow semi-crystalline product, but no triphenylmethane was isolated. No condensation reaction was observed with carbon tetrachloride.

- (26) Tropsch and Schellenberg, Abhdlg. z. Kenntnis d. Kohle, 7, 13 (1925) [Zentr., I, 3298 (1926)].
(27) Friedel and Crafts, Ann. chim. phys. [6] 14, 460 (1888).
(28) Hilpert and Grüttner, Ber., 45, 2828 (1912).

Tri-*p*-tolylaluminum has been prepared from the corresponding mercurial by Krause and Ditmar who described an elaborate method for the purification of triarylaluminum compounds by recrystallization from benzene or ether in a three-bulb apparatus (29). Tri-*p*-tolylaluminum was found to be a white crystalline powder which was soluble in benzene. It added ether to form a mono-etherate (m.p., 125°) as does triphenylaluminum. Treatment of the etherates with ammonia gave the corresponding ammonia addition compounds. Addition of iodine to triphenylaluminum gave aluminum iodide and iodobenzene.

Sodium added slowly to triphenylaluminum in ether, and after many hours of shaking a red-brown solution resulted. Concentration of the solution caused a brown powder to be precipitated (30).

Gilman and Marple (31) have simplified the preparation of triarylaluminum compounds by refluxing xylene solutions of the mercurials and aluminum. Previously, all preparations involved the use of sealed tubes. Refluxing in xylene solution is faster, there is no loss due to decomposition, and the resulting xylene solution of the organoaluminum compound is suitable for immediate use.

Xylene solutions of simple organoaluminum compounds were found to give positive color tests (18) after five minutes of

(29) Krause and Ditmar, Ber., 63, 2401 (1930); See also Ref. 8, p. 222, and Marple, Doctoral Dissertation, Iowa State College (1935), p. 30.

(30) Krause and Polack, Ber., 59, 1428 (1926).

(31) Gilman and Marple, Rec. trav. chim., 55, 133 (1936).

contact with Michler's ketone if the solution was one-tenth molar with respect to the organoaluminum compounds (31).

p-Toluanilide was obtained in a yield of seventy-one per cent from the reaction between phenyl isocyanate and tri-p-tolylaluminum in xylene solution. The yields of anilides from tri-n-propyl- and triethylaluminum were only eighteen and twenty-seven per cent, respectively (31).

Carbonation of tri-p-tolylaluminum with solid carbon dioxide gave no acid. A thirty-two per cent yield of p-toluic acid was obtained by refluxing an ether solution of tri-p-tolylaluminum under an atmosphere of carbon dioxide for seven days. When a boiling xylene solution of tri-p-tolylaluminum was treated for two hours with gaseous carbon dioxide, a forty-four per cent yield of acid was obtained (31).

An ether solution of tri-p-tolylaluminum gave a trace of diphenyl-p-tolylcarbinol after standing five days with benzophenone. Triphenylaluminum gave a twenty-three per cent yield of triphenylcarbinol after standing sixteen days with benzophenone at room temperature. A forty-three per cent yield of the carbinol was obtained by refluxing a xylene solution of tri-p-tolylaluminum and benzophenone for two hours. A cold xylene solution of tri-p-tolylaluminum was oxidized to give an eight per cent yield of p-cresol. A cold xylene solution of tri-p-tolylaluminum reacted completely in one hour with benzaldehyde to give a twenty-seven per cent yield of phenyl-p-tolylcarbinol.

Benzenitrile reacted with a xylene solution of tri-*p*-tolyl-aluminum after thirty minutes of refluxing to give a seventeen per cent yield of phenyl *p*-tolyl ketone. Ethyl and phenyl benzoates gave only condensation products with tri-*p*-tolyl-aluminum.

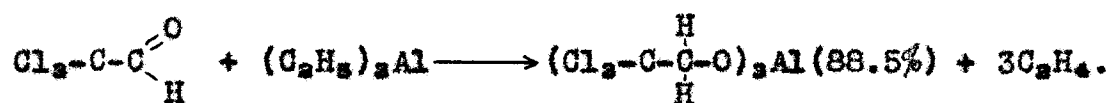
From a study of these results and results obtained by similar studies on other organometallic compounds, Gilman and Marple (31) concluded that organoaluminum compounds were more reactive than organoboron or organozinc compounds and less reactive than organomagnesium compounds.

Kirby (32) has reported that triphenylaluminum undergoes 1,4-addition with chalcone as do Grignard reagents to give a ninety-four per cent yield of β,β -diphenylpropiophenone.

Triphenylaluminum and acetophenone produced dypnone in a thirty-six per cent yield (33). No methyldiphenylearbinol was isolated, but unsymmetrical diphenylethylene and resinous products were found.

Triethylaluminum caused condensation of benzaldehyde and acetophenone to benzalacetophenone (34). Triethylaluminum exerts a reducing action also on aldehydes and ketones. Meerwein (35) has formulated the reaction as follows:

- (32) Kirby, Iowa State Coll. J. Sci., 12, 137 (1937).
- (33) Calloway and Green, J. Am. Chem. Soc., 59, 809 (1937).
- (34) Gilman and Nelson, Rec. trav. chim., 55, 527 (1936).
- (35) Meerwein, Hinz, Majert and Sönke, J. prakt. Chem., 147, 226 (1936).



Bromal reacted similarly to the extent of seventy-three and one-half per cent. Chloroacetone was reduced by triethylaluminum to give a seventy per cent yield of chloroisopropyl alcohol. Similarly, trichloroacetone and trichloroacetophenone gave sixty-five and eighty per cent yields of the corresponding reduction products. Benzil was reduced to benzoin (40% yield). Benzaldehyde and triethylaluminum in ether solution gave only twelve per cent of the reduction product, benzylalcohol, and sixty-two and one-half per cent of the normal reaction product, phenylethylcarbinol. p-Chlorobenzaldehyde gave twenty-five per cent of p-chlorobenzyl alcohol and fifty-two per cent of the carbinol. Only five per cent of the reduction product was isolated from p-methoxybenzaldehyde while cinnamic aldehyde gave only styrylethylcarbinol (95% yield). Grignard reagents also add 1,2- to cinnamic aldehyde.

Triethylaluminum is not affected by nickel-black in the presence of hydrogen (36).

A twenty per cent by volume solution of triethylaluminum n-butyl etherate (b.p., 140-141°/15 mm.) in n-butyl ether reacted with alcohols, phenols, enols, oximes, carboxylic acids, and thiols, when heated at 100° for one hour (37). Likewise,

(36) Miller and Sauerwald, Monatsh., 48, 737 (1927).

(37) Nelson, Iowa State Coll. J. Sci., 12, 145 (1937); See also Gilman and Nelson, J. Am. Chem. Soc., 59, 935 (1937).

the solution reacted with hydrogen attached to nitrogen in amines, amides and ketimides. Reaction with some secondary amines was very slow and there was practically no reaction with acetylenes. Thus, triethylaluminum n-butyl etherate may be used to differentiate hydrogen attached to oxygen, sulfur or nitrogen from that attached to the triple-bond carbon in the acetylenes. Similar investigations showed that the order of reactivity of organometallic compounds toward active hydrogen is $Zn > Al > Cd > B > Pb > Hg > Bi > Sn > Si$.

Gilman and Nelson (38) obtained allylic rearrangement products by reaction of benzyl-metallic compounds of zinc, cadmium, mercury and aluminum with formaldehyde, acetyl chloride and carbon dioxide.

A new type of aluminum compound has been prepared by Grosse and Mavity (39) which corresponds to the general formula $M^+AlR_4^-$, where M is an alkali metal (Li, Na, K) and R is an alkyl group. These compounds have been called "alumonides". They were probably prepared earlier by Hein and Pauling (40) who studied the conductivity of quaternary ammonium salts in triethylaluminum. The "alumonides" form the symmetrical counterpart of the left hand side of the periodic system to the so-called "onium compounds", $\left[N(C_2H_5)_4\right]^+ Cl^-$, of the right

(38) Gilman and Nelson, ibid., 61, 741 (1939).

(39) Grosse and Mavity, Abstracts, American Chemical Society, Milwaukee meeting, 1938.

(40) Hein and Pauling, Z. physik. Chem., A165, 338 (1933).

hand side. The tetraethyl aluminides are white, crystalline, fusible, salt-like substances which are very sensitive to oxygen or water. They are insoluble in paraffin hydrocarbons but are easily soluble in and crystallizable from aromatic hydrocarbons. The fused salts are readily electrolyzed, depositing aluminum at the cathode, and evolving gas at the anode.

They are prepared by the direct addition of alkyl alkali compounds to triethylaluminum, $C_2H_5Li + (C_2H_5)_3Al \longrightarrow Li\overline{Al(C_2H_5)_3}$, or more conveniently by the reaction of the alkali metals with triethylaluminum, $3M + 4(C_2H_5)_3Al \longrightarrow 3M\overline{Al(C_2H_5)_3} + Al$.

The lithium compound melts at 165-167° and the sodium and potassium compounds at 90-96° and 80-83°, respectively.

Direct addition of sodium ethylate to triethylaluminum produced $Na\overline{Al(C_2H_5)_2(OC_2H_5)}$ which melted at 79-83°.

EXPERIMENTAL

Preparation of Ethylaluminum Chlorides. The apparatus consisted of a 250 cc. three-necked flask equipped with a Hopkins condenser, a mercury-sealed stirrer and a delivery tube for introducing gaseous ethyl chloride. The reflux condenser outlet was connected to a U-tube filled with mercury. A pressure head of 50 mm. was maintained in order to keep the ethyl chloride in the reaction flask. The ethyl chloride was purified by passing the gas first through concentrated sulfuric acid and then soda lime. A safety tube was inserted in the sulfuric acid wash bottle. The rate of flow of gas was regulated by means of a screw clamp and the depth of immersion of the ethyl chloride container in a cooling bath.

In a typical run 7 g. (0.259 g. atom) of aluminum turnings and a crystal of iodine were placed in the three-necked flask and the flask was then swept out with nitrogen. Ethyl chloride gas was allowed to flow in slowly and at the same time the mixture was heated by means of a hot plate until the reactants began to fume. Then a water bath was substituted for the hot plate and the mixture was heated at a temperature just below the boiling point of water for about five hours. At the end of that time the aluminum had ceased taking up ethyl chloride, and the ethyl chloride bubbled out of the mercury escape-valve quite rapidly. After being cooled, the liquid was filtered

through glass wool into a Claisen flask and then was distilled in an atmosphere of nitrogen at reduced pressure. The boiling point was $63^{\circ}/3$ mm. when the product was distilled through a good column. The yield from a number of runs ranged from 50% to 90% with an average yield of 68%. The halogen analyses on distillates from a number of different runs varied from 40.4% to 44.8%. An equimolecular mixture of ethylaluminum dichloride and diethylaluminum chloride requires a halogen value of 42.4%. Addition of dry ether to the mixed chlorides gave the etherates which boiled at $95-105^{\circ}/2$ mm.

Preparation of the mixed chlorides by the addition of aluminum chloride to triethylaluminum was also effected, but it was not as satisfactory a method as the one given. Hall and Nash (14) have prepared the mixed chlorides through the reaction of aluminum, aluminum chloride and ethylene. Kraus and Hnizda (15) have prepared alkylaluminum chlorides by a procedure similar to the one described here for the preparation of the mixed ethylaluminum chlorides.

Preparation of Diethylaluminum Chloride. Except for minor changes the method used was essentially that of Hall and Nash (14). The mixture of ethylaluminum chlorides (32.4 g., 0.13 mole) and 16.6 g. (0.28 mole) of sodium chloride was heated with stirring for forty minutes at a temperature of 200° . The entire mixture solidified so it was distilled directly from the reaction flask. (It is more convenient to run the reaction in a Claisen flask.) The ethylaluminum di-

chloride remained in the residue as a double salt with sodium chloride while the diethylaluminum chloride distilled out, boiling at $58^{\circ}/3$ mm. (yield, 14 g. or 43.3%). The purity of the product was verified by halogen analysis and by evolution of a theoretical quantity of ethane upon hydrolysis.

Grosse and Mavity (16) have reported that dialkylaluminum halides may be prepared in yields up to 94% with a purity of 90 to 95% by reacting alkyl halides with an aluminum-magnesium alloy. This method of preparation was not investigated. Diethylaluminum chloride also was prepared by the addition of the theoretical quantity of aluminum chloride to triethylaluminum, but this method required repeated fractional distillations and was not so satisfactory as the method of Hall and Nash. Fractional distillation of the mixed ethylaluminum chlorides was not very satisfactory and gave only a crude separation of the chlorides. Addition of ether to diethylaluminum chloride gave the mono-etherate (b.p., $100-102^{\circ}/3$ mm.).

Anal. Calcd. for $(C_2H_5)_2AlCl \cdot (C_2H_5)_2O$: Cl, 18.25. Found: Cl, 18.30, 18.32.

Preparation of Ethylaluminum Dichloride. This product was never obtained in a state of 100% purity. The purest product was obtained by the addition of a slight excess of aluminum chloride to the mixture of ethylaluminum chlorides. The resulting liquid was subjected to several fractional distillations giving a compound of about 95 to 98% purity in a yield of approximately 50%. The low yield was due chiefly

to losses in the repeated distillations. The boiling point was approximately 60°/3 mm.

Attempts to distill ethylaluminum dichloride from the sodium chloride double salt (p. 32) by adding aluminum chloride and heating under a high vacuum were unsuccessful. Likewise, fractional distillation of the mixed chlorides was unsatisfactory giving a very poor separation.

Preparation of Ethylaluminum Iodides. The procedure of Grignard and Jenkins (10) was followed very closely. In a typical run, 7 g. (0.259 g. atom) of aluminum was placed in a three-necked flask fitted with a mercury-sealed stirrer, a condenser and a dropping funnel. The reaction flask was swept out with nitrogen and about 5 to 10 cc. of the 50 g. (0.33 mole) of ethyl iodide was added. The flask was heated by means of an oil bath to 75°. After about ten minutes of heating at this temperature, the reaction started and it was necessary to remove the oil bath and cool the flask with a cold water bath to control the vigorous reaction. After the initial reaction had subsided, the remainder of the ethyl iodide was added dropwise with occasional cooling. (In some experiments it is necessary to heat the reaction during the addition of the remaining ethyl iodide because the reaction stops and it must be started before too large an excess of ethyl iodide is added.) The oil bath was returned after all the iodide had been added and the temperature of the bath was raised slowly to 115° and maintained at that temperature for one hour.

The contents were cooled and transferred to a Claisen flask by means of a siphon tube and nitrogen pressure. Some glass wool was packed into the siphon tube to act as a filter. Distillation in an atmosphere of nitrogen gave a clear liquid boiling over a range of 110-170°/4-5 mm. The yields from a large number of runs ranged from 27 to 40 grams or an average yield of 70%. The mixed ethylaluminum iodides can be fractionated but the mixture of iodides was used in all the reaction studies.

Preparation of Butylaluminum Iodides. n-Butyl iodide (25 g., 0.135 mole) and aluminum (2.6 g., 0.10 g. atom) were heated just below the refluxing temperature of butyl iodide. After five minutes of heating, the reaction started and the liquid became yellow-green in color. The vigorous reaction was controlled by cooling the reaction flask in an ice bath. The vigorous reaction soon stopped and the color faded to gray. The flask was gradually warmed to the refluxing temperature of butyl iodide. A hydrocarbon gas was evolved, but no hydrogen iodide was liberated. A dark brown liquid remained in the reaction flask and gave a color test with Michler's ketone (18). Check runs were not as satisfactory, so the procedure was modified to produce the etherates.

About 10 cc. of n-butyl iodide (100 g., 0.544 mole) and 2 cc. of dry ether were refluxed in the presence of aluminum (9.5 g., 0.35 g. atom), and after about five minutes of heat-

ing, the reaction started. The initial vigorous reaction was controlled by cooling the reaction flask in an ice bath. The remaining butyl iodide was added dropwise. Occasionally, the reaction stopped and it was necessary to add dry ether and warm the reaction flask to start it. After all the butyl iodide had been added, additional ether was added and the solution was refluxed for two hours. The grayish-brown liquid was filtered through glass wool into a Claisen flask and then distilled in an atmosphere of nitrogen giving a colorless distillate. The boiling range was 100-170°/ 5 mm. and the yield was 45 g. or 34%.

Preparation of Mixed Butylaluminum Chloride Etherates.

A modification of the method of preparing trialkylaluminum etherates was used (24). Anhydrous aluminum chloride (75 g., 0.55 mole) was added in small amounts by means of a hopper to an ether solution of butylmagnesium chloride (0.5 mole). The reaction flask was cooled in an ice-water bath during the addition of aluminum chloride. The reaction mixture is a thick viscous paste and efficient stirring is required. After all the aluminum chloride had been added, the reaction mixture was allowed to stand at room temperature for two hours. The excess ether was distilled away and the residue was distilled directly from the reaction flask at reduced pressure (3 mm.) in an atmosphere of nitrogen. A Claisen flask was used as the receiving vessel and it was immersed in an ice bath. Liquid

began distilling over at a bath temperature of 80-100° and the bath temperature was gradually increased to 200°. The distillation required about eight hours. The light yellow distillate was redistilled boiling over a range of 100-170°/25 mm. The major portion of product distilled at 163-5°/25 mm. Fractionation studies indicated the presence of the etherates of tri-n-butylaluminum, di-n-butylaluminum chloride, n-butylaluminum dichloride and aluminum chloride. Gilman and Apperson (17) have shown that the mono-etherate of aluminum chloride can be distilled. The predominating product was n-butylaluminum dichloride. The yield of the mixture was 65 g. or 57% based upon n-butylaluminum dichloride etherate.

Preparation of Phenylaluminum Iodides. Leone (11a) has described the preparation of the mixed phenylaluminum iodides from the reaction between aluminum and iodobenzene in the presence of ether. The presence of the etherates was found to be objectionable in later reactions, so the procedure was modified slightly to produce the ether-free compounds. About 10 g. of iodobenzene was added to 7 g. (0.259 g. atom) of aluminum contained in a three-necked flask which had been swept out with dry nitrogen. The flask was heated with a hot plate and the reaction started very soon after the iodobenzene commenced to reflux. The remainder of the iodobenzene (0.4 mole) was added dropwise at a sufficient rate to keep the reaction going. It is generally necessary to continue the heating and keep the iodobenzene near its reflux temperature. At times

the reaction may become violent and the heat must be removed and in rare cases a cooling bath must be employed. After all the iodobenzene had been added, the reaction mixture was heated by a metal bath which was maintained at a temperature of 180-200° for six hours. The resulting product was a dark brown viscous paste which solidified to a sticky solid upon being cooled. It was soluble in benzene, toluene and xylene and insoluble in petroleum ether. The mixture of phenylaluminum iodides was not purified, but was used directly in reaction studies. In some experiments the aromatic hydrocarbon solutions of the mixed phenylaluminum iodides were filtered through glass wool before adding a reactant. The preparation of phenylaluminum iodides is more convenient in smaller runs. A 0.1 mole or 0.2 mole run is very satisfactory and only requires 1-2 hours of heating after all the iodobenzene has been added.

Preparation of p-Tolylaluminum Dichloride. The procedure is similar to the method which Grosse and Mavity (16) used in the preparation of phenylaluminum dibromide and dichloride. Aluminum chloride (6.7 g., 0.051 mole) was added slowly by means of a hopper to a xylene solution of tri-p-tolylaluminum (0.0254 mole) which had been prepared from di-p-tolylmercury and aluminum (31). The aluminum chloride dissolved and gave a dark brown colored solution. After the aluminum chloride had all been added, the solution was warmed for thirty minutes.

When solvents other than xylene were desired in later reactions, the *p*-tolylaluminum dichloride was prepared in xylene solution, and the xylene was removed by distillation at reduced pressure in an atmosphere of nitrogen. The desired solvent was then added.

Miscellaneous Attempted Preparations of Organoaluminum

Halides. The reactions between aluminum and the following halides were investigated: ethylene bromide, *n*-propyl chloride, *n*-butyl chloride, *n*-butyl bromide, chlorobenzene and bromobenzene. The only encouraging result was obtained with bromobenzene. The reaction started after the addition of an iodine crystal, but it soon slowed down and gave an incomplete reaction. A weak color test was obtained. The other halides with the exception of chlorobenzene evolved hydrogen halide when they were refluxed in the presence of aluminum. Iodine, ether, aluminum chloride and several organoaluminum compounds were used as catalysts without success. Chlorobenzene did not react with aluminum at the refluxing temperature of chlorobenzene. Reaction occurred in a sealed tube at 250°, but hydrogen chloride was evolved and only a tar was obtained.

Reactions of Mixed Organoaluminum Compounds

The standard apparatus consisted of a three-necked flask equipped with a condenser, a mercury-sealed stirrer and either a dropping funnel or a hopper. All reactions were carried out in an atmosphere of dry nitrogen. A mole of the mixed organo-

aluminum halides signifies $R_3Al_2X_3$ and not the average molecular weight of the two constituents R_2AlX and $RAlX_2$.

Color Test with Michler's Ketone. The procedure of Gilman and Warple (31) was followed which consisted of the addition of a 3 cc. sample of an organoaluminum halide to 3 cc. of a 1% solution of Michler's ketone in benzene. The tube was stoppered and allowed to stand over a definite period of time and then hydrolyzed by the addition of 50% ethanol. Several drops of a 0.2% solution of iodine in glacial acetic acid were added and a greenish-blue color appeared if the test was positive. All of the organoaluminum halides gave a positive color test if allowed to stand in contact with Michler's ketone for thirty minutes before hydrolysis. The alkylaluminum halides gave a weak test after standing five minutes before hydrolysis and a strong test after standing fifteen minutes before hydrolysis. A 3 cc. sample of a 0.2 molar xylene solution of the mixed ethylaluminum iodides gave a faint test after standing five minutes, a better test after ten minutes and a strong positive test after standing fifteen minutes before hydrolysis. Xylene solutions of arylaluminum halides required fifteen minutes of contact for a weak test and thirty minutes of contact for a strong test. All of the organoaluminum halides gave positive color tests when warmed for five minutes with Michler's ketone before hydrolysis.

Benzonitrile and Phenylaluminum Iodides. A xylene solution of 20.6 g. (0.2 mole) of benzonitrile was added dropwise

to a xylene solution of the mixed phenylaluminum iodides which had been prepared from 40.8 g. (0.2 mole) of iodobenzene and 3.78 g. (0.14 g. atom) of aluminum (p. 36). The color test was only slightly positive after thirty minutes of refluxing, and it was negative after one hour of refluxing. The mixture was refluxed for an additional five hours and then cooled to room temperature. It was hydrolyzed by pouring into a mixture of ice and hydrochloric acid. The mixture was filtered and the residue was boiled with dilute hydrochloric acid. The acid solution was filtered and the residue was washed with xylene which left only 1.6 g. of resinous material. All the filtrates were combined, and the xylene layer was separated and washed with dilute sodium carbonate solution and water. The xylene solution was dried over sodium sulfate and then subjected to distillation. Fifteen grams (73%) of unreacted benzonitrile was recovered. Three grams of an oily residue was left which was distilled at 2 mm. pressure yielding 3 g. of distillate which was identified as biphenyl (mixed m.p., 69°). The residue from the distillation was treated with hydroxylamine hydrochloride, and after several recrystallizations, 0.8 g. of benzophenone oxime was obtained (mixed m.p., 139-40°). This corresponds to a 3% yield of benzophenone. There was no indication that a Friedel-Crafts reaction had occurred since no traces of phenyl xylyl ketones could be detected. A Friedel-Crafts reaction would involve xylene rather than any benzene

which might be formed from the cracking of xylene.

Benzonitrile and Ethylaluminum Iodides. A xylene solution of benzonitrile (15.5 g., 0.15 mole) and the mixed ethylaluminum iodides (26.1 g., 0.05 mole) was refluxed for six hours. A 90% recovery of benzonitrile was obtained together with a small amount of resinous material. No trace of propiophenone could be detected.

Carbonation of Ethylaluminum Iodides. Dry carbon dioxide gas was bubbled into a boiling xylene solution of the mixed ethylaluminum iodides for 14 hours. The color test was positive after ten hours of refluxing, but negative at the end of twelve hours of refluxing. No acid was isolated, but some resinous material was formed. Likewise, carbonation of the mixed butylaluminum iodide etherates (p. 34) was unsuccessful in boiling xylene.

Carbonation of Phenylaluminum Iodides. Dry carbon dioxide gas was bubbled into a refluxing benzene solution of the mixed phenylaluminum iodides for twelve hours. The color test was negative after ten hours of refluxing, but no acid was isolated. Resinous materials with a strong phenolic odor were obtained.

Ketones and Organoaluminum Halides. Leone (11b) has reported that organoaluminum halides condense ketones very readily. This has been confirmed using acetone, propiophenone and benzophenone with a mixture of ethylaluminum iodides. The mixed phenylaluminum iodides also condensed acetone and propiophenone,

but a benzene solution of benzophenone and the mixed phenylaluminum iodides did not react at room temperature and an 88% recovery of benzophenone was realized.

Benzophenone-Aluminum Chloride Complex and Organoaluminum Iodides. The benzophenone-aluminum chloride complex was prepared by adding small amounts of aluminum chloride (7.35 g., 0.055 mole) to a cooled benzene solution (50 cc.) of 9.8 g. (0.054 mole) of benzophenone. A benzene solution of the mixed ethylaluminum iodides (13.1 g., 0.025 mole) was added, and the mixture was warmed just below reflux for one hour. Hydrolysis was effected by slowly pouring the reaction mixture into an ice-hydrochloric acid mixture. The benzene layer was separated, washed with sodium bisulfite solution to remove free iodine and then dried over calcium chloride. The benzene was distilled away and the crude benzophenone was recrystallized from petroleum ether (b.p., 60-68°) giving a 92% recovery. A mixed melting point with an authentic sample of benzophenone was not depressed.

Treatment of the benzophenone-aluminum chloride complex (0.025 mole) with a slight excess of the mixed phenylaluminum iodides (prepared from 12.2 g. of iodobenzene and 1.08 g. of aluminum) in benzene solution left a tarry residue after hydrolysis and evaporation of the benzene, so the benzophenone was isolated by distillation of the tar at reduced pressure. The fraction boiling at 165-175°/15 mm. was collected as

benzophenone. Recrystallization gave 4 g. of pure product or a 60% recovery of benzophenone which was identified by a mixed melting point.

Acetophenone-Aluminum Chloride Complex and Organoaluminum Iodides. To the complex, prepared by the addition of aluminum chloride (14.7 g., 0.11 mole) to a benzene solution of 12 g. (0.10 mole) of acetophenone, was added slowly 26.1 g. (0.05 mole) of the mixed ethylaluminum iodides. The mixture was heated to reflux, allowed to cool, and was then hydrolyzed by pouring into an ice-hydrochloric acid mixture. The benzene layer was separated and the aqueous layer was extracted with ether. The ether extracts were combined with the benzene layer, and the solution was washed with dilute alkali, dilute sodium thiosulfate and water. It was dried over sodium sulfate and distilled. Nine grams or a 75% recovery of acetophenone (b.p., 198-203°) was obtained. It was characterized by conversion to the semicarbazone (mixed m.p., 198°).

The acetophenone-aluminum chloride complex was also prepared from benzene, acetic anhydride (25.5 g., 0.25 mole) and aluminum chloride (80 g., 0.6 mole) in a typical Friedel-Crafts acylation. To this complex was added an excess of the mixed ethylaluminum iodides, and the mixture was warmed just below reflux for one hour. It was hydrolyzed and worked up in the customary manner, and a 52% yield of acetophenone was obtained.

Treatment of the acetophenone-aluminum chloride complex (0.05 mole) with an excess of the mixed phenylaluminum iodides (prepared from 18.4 g. of iodobenzene and 1.6 g. of aluminum) in benzene solution, using the same conditions as described for the mixed ethylaluminum iodides, gave a 64% recovery of acetophenone.

Acetophenone-Aluminum Chloride Complex and Ethylaluminum Chlorides. An excess of the mixed ethylaluminum chlorides (7.4 g., 0.03 mole) (p. 30) was added to an acetophenone-aluminum chloride complex (0.05 mole) which had been prepared by the addition of 8 g. (0.06 mole) of aluminum chloride to a benzene solution of 6 g. (0.05 mole) of acetophenone. The reaction was worked up by the same procedure that was employed in the preceding experiments. A 65% recovery of acetophenone (b.p., 198-203°) was realized. It was identified by conversion to the semicarbazone (mixed m.p., 198°). The same reaction was run at 0° and an 80% recovery of acetophenone was obtained.

Propiophenone-Aluminum Chloride Complex and Ethylaluminum Iodides. An excess of the mixed ethylaluminum iodides (15.7 g., 0.03 mole) was added to a propiophenone-aluminum chloride complex (0.05 mole) which had been prepared by the addition of 8 g. (0.06 mole) of aluminum chloride to a benzene solution of 6.7 g. (0.05 mole) of propiophenone. It was refluxed for one hour and then worked up in the usual manner. There resulted a 70% recovery of propiophenone (b.p., 210-218°) which was

characterized by treatment with semicarbazide hydrochloride to give the semicarbazone (mixed m.p., 173-4°).

Acetone-Aluminum Chloride Complex and Organoaluminum Iodides. Treatment of an acetone-aluminum chloride complex (0.034 mole) with an excess of the mixed ethyl- or phenylaluminum iodides produced chiefly tar, but a 10% recovery of acetone was obtained in both cases.

Benzoyl Chloride-Aluminum Chloride Complex and Ethylaluminum Iodides. An equivalent amount of aluminum chloride was added slowly by means of a hopper to a cooled benzene solution of 14 g. (0.1 mole) of benzoyl chloride. To this was added dropwise a slight excess of the mixed ethylaluminum iodides (28.7 g., 0.055 mole). The reaction is exothermic and it is necessary to cool with a water bath if the organoaluminum compound is added too rapidly. After all the reagent had been added, the mixture was heated slowly until the benzene began to reflux. Hydrolysis was effected by pouring into an ice-hydrochloric acid mixture. The benzene layer was separated and combined with the ether extracts of the aqueous layer. After washing with dilute alkali, sodium bisulfite and water, the solution was dried over sodium sulfate, and then the ether and benzene were distilled away leaving crude propiophenone which was converted to the semicarbazone. There was isolated 10 g. of propiophenone semicarbazone (mixed m.p., 173-4°) corresponding to a 56% yield of propiophenone.

A slight excess of the mixed ethylaluminum iodides (28.7 g., 0.055 mole) was added to a carbon disulfide solution of the benzoyl chloride-aluminum chloride complex (0.1 mole). The reaction was treated in the same manner as in the preceding experiment except the propiophenone was distilled (b.p., 210-218°). The yield amounted to 8.3 g. or 62%. It was characterized by conversion to the semicarbazone (mixed m.p., 173-4°).

Benzoyl Chloride-Aluminum Chloride Complex and Phenylaluminum Iodides. A benzene solution of the benzoyl chloride-aluminum chloride complex (0.05 mole) was added dropwise to an excess of the mixed phenylaluminum iodides (prepared from 18.4 g. of iodobenzene and 1.6 g. of aluminum) dissolved in benzene. The reaction mixture was stirred at room temperature for an hour and then hydrolyzed in the usual manner. The benzene layer was combined with the ether extracts of the aqueous layer, and washed with dilute alkali and sodium bisulfite solution. After drying over calcium chloride, the solvent was removed and the residue was distilled at reduced pressure. The portion boiling from 130-40°/8 mm. was collected as benzophenone (identified by crystallization and a mixed melting point with an authentic sample, m.p., 48°). The yield was 6 g. or 70%.

Using carbon disulfide as the reaction medium, a 72% yield of benzophenone was realized from the benzoyl chloride-aluminum chloride complex (0.05 mole).

Benzoyl Chloride-Aluminum Chloride Complex and p-Tolylaluminum Dichloride. A xylene solution of the benzoyl chloride-aluminum chloride complex (0.05 mole) was added to a xylene solution of a slight excess of p-tolylaluminum dichloride which had been prepared from 4.44 g. (0.033 mole) of aluminum chloride and 0.017 mole of tri-p-tolylaluminum (p. 37). The mixture was warmed gently for thirty minutes by means of a water bath. It was hydrolyzed and washed in the usual manner. After removal of the solvent, the residual liquid was distilled at reduced pressure. The distillate (b.p., 150-75°/10 mm.) crystallized yielding 6.5 g. or a 71% yield of phenyl p-tolyl ketone which was identified by a mixed melting point (52-4°) with a known sample.

Acetyl Chloride-Aluminum Chloride Complex and p-Tolylaluminum Dichloride. A xylene solution of the acetyl chloride-aluminum chloride complex, prepared by the addition of an equivalent quantity of aluminum chloride to a xylene solution of 3.9 g. (0.05 mole) of acetyl chloride, was added to a xylene solution of a slight excess of p-tolylaluminum dichloride which had been prepared from 4.44 g. (0.033 mole) of aluminum chloride and 0.017 mole of tri-p-tolylaluminum. The reaction was performed in the same manner as the preceding experiment. The distillate was collected over a range of 80-100°/10 mm., and it amounted to 5 g. or a 62% yield of methyl p-tolyl ketone. It was characterized by conversion to the

semicarbazone (m.p., 202-4°).

Benzoyl Chloride and Ethylaluminum Iodides. A mixture of ethylaluminum iodides (20.9 g., 0.04 mole) was added dropwise to a stirred solution of benzoyl chloride (7.75 g., 0.075 mole) in benzene. The reaction was quite exothermic, so a water bath was used to cool the reaction during the addition of the organo-metallic compound. After all the aluminum compound had been added, the solution was refluxed for thirty minutes. The contents, after being cooling, were poured into a mixture of ice and hydrochloric acid. The benzene layer was separated and the aqueous layer extracted with ether. The combined extracts were washed with dilute sodium bisulfite, dilute alkali and water. After drying over calcium chloride, the solvents were removed leaving a yellow oil which distilled from 200-230°. Redistillation gave 9 g. of propiophenone (b.p., 214-219°) or a 90% yield. It was characterized by conversion to the semicarbazone followed by a mixed melting point with a known sample (m.p., 173-4°).

Using carbon disulfide as the reaction medium, an 85% yield of propiophenone was obtained from 13.5 g. (0.096 mole) of benzoyl chloride. The reaction mixture was hydrolyzed and the product was isolated by crystallization instead of distillation. After the carbon disulfide had been removed, petroleum ether (b.p., 90-115°) was added to the oil, and upon cooling the propiophenone crystallized. The crystals were sucked dry of solvent by means of a filter stick leaving 9 g. of ketone.

The solvent was treated with semicarbazide hydrochloride and an additional 2 g. of propiophenone was isolated as the semicarbazone making a total yield of 11 g. or 85%.

Using tetrachloroethane as the reaction medium, and adding benzoyl chloride (3.5 g., 0.025 mole) to a benzene solution of the mixed ethylaluminum iodides (6.8 g., 0.013 mole), gave a 54% yield of propiophenone (isolated as the semicarbazone).

When petroleum ether (b.p., 90-115°) was used as the reaction medium under the same conditions as in the previous experiment, a 48% yield of propiophenone was isolated as the semicarbazone from 3.5 g. (0.025 mole) of benzoyl chloride.

Using ether as the solvent under the same conditions as in the preceding two experiments, gave no propiophenone, a small amount of ethyl benzoate, 4 g. of benzoic acid and about 0.3 g. of α,α -dibenzoyl ethane (m.p., 84°) which was characterized by conversion to 3,5-diphenyl-4-methylpyrazole (m.p., 223°) with hydrazine hydrate.

Reactions using nitrobenzene as the solvent were not attempted due to the vigorous reaction between nitrobenzene and the organoaluminum iodides.

Benzoyl Chloride and Phenylaluminum Iodides. To a xylene solution of the mixed phenylaluminum iodides, which had been prepared from 15 g. (0.074 mole) of iodobenzene and 1.35 g. (0.05 g. atom) of aluminum, was added 5.3 g. (0.038 mole) of benzoyl chloride. The solution was refluxed for one hour,

allowed to cool, and was then hydrolyzed by pouring into an ice-hydrochloric acid mixture. The xylene layer was separated and washed with dilute sodium carbonate, dilute sodium bisulfite and water. The xylene was dried over sodium sulfate and then distilled away leaving a yellow-black oil which was converted to an oxime by means of hydroxylamine hydrochloride. The oxime did not depress the melting point of a known sample of benzophenone oxime (m.p., 138-41°). The yield of oxime was 3.5 g. or 47.5%.

Benzoyl Chloride and Triphenylaluminum. Triphenylaluminum was prepared in xylene solution from aluminum and diphenylmercury according to the directions of Gilman and Marple (31). Twenty-one grams (0.15 mole) of benzoyl chloride was added dropwise to a xylene solution of triphenylaluminum (0.05 mole). The solution was refluxed for one hour, allowed to cool and then hydrolyzed by pouring into an ice-hydrochloric acid mixture. The xylene layer was separated and washed with dilute sodium carbonate solution and water. The xylene was dried over sodium sulfate and then distilled away. The residual oil finally crystallized upon standing in the ice box for several days. It was very impure, so it was subjected to steam distillation. The oil layer in the distillate was separated, dissolved in ether, dried over sodium sulfate and distilled. The portion boiling at 155-165°/10 mm. crystallized and was identified as benzophenone by a mixed melting point (47-8°). The

yield was 10 g. or 36.5% based on benzoyl chloride. The residual solid from the steam distillation was recrystallized from alcohol and melted at 161°. It showed no depression with a known sample of triphenylcarbinol. The yield was 1.5 g. or 11.5%.

Benzoyl Chloride and Diethylaluminum Chloride. Fourteen grams (0.10 mole) of benzoyl chloride was added dropwise to 6.13 g. (0.05 mole) of diethylaluminum chloride (p. 31) dissolved in 50 cc. of benzene. The solution was refluxed for one hour, allowed to cool, and then hydrolyzed by pouring into an ice-hydrochloric acid mixture. The benzene layer was separated and washed with dilute sodium carbonate solution and water. It was dried over sodium sulfate and distilled. The portion boiling at 210-218° was collected as propiophenone. It was identified by conversion to the semicarbazone (mixed m.p., 173°). The yield was 9 g., or 67% based on benzoyl chloride which indicated both ethyl groups in diethylaluminum chloride reacted to some extent. There was no evidence of the formation of diethylphenylcarbinol.

Benzoyl Chloride and Ethylaluminum Dichloride-Sodium Chloride Double Salt. To a benzene suspension of 9.5 g. (0.05 mole) of the ethylaluminum dichloride-sodium chloride double salt (p. 31) was added 7 g. (0.05 mole) of benzoyl chloride. The mixture was refluxed for one hour, cooled and then hydrolyzed in the usual manner. The benzene layer was

worked up in exactly the same manner as in the previous experiment. The amount of residual oil was so small that it was treated with semicarbazide hydrochloride and the propiophenone was isolated as the semicarbazone (mixed m.p., 173°). The yield of semicarbazone was 1.9 g. which corresponds to a 20% yield of propiophenone. The low yield is probably due to the insolubility of the complex.

Benzoyl Chloride and p-Tolylaluminum Dichloride. Benzoyl chloride (7 g., 0.05 mole) was added to a xylene solution of a slight excess of p-tolylaluminum dichloride which had been prepared from 4.44 g. (0.033 mole) of aluminum chloride and 0.017 mole of tri-p-tolylaluminum. The mixture was warmed slightly and then allowed to stand at room temperature for two hours. After hydrolysis, the xylene layer was separated and washed with dilute sodium carbonate solution and water. The xylene solution was dried over sodium sulfate and distilled. The portion boiling from 160-80°/10-15 mm. amounted to 8 g., and redistillation at 157-8°/8 mm. gave 5.5 g. or a 60% yield of phenyl p-tolyl ketone which was identified by a mixed melting point with an authentic specimen (m.p., 53-5°).

Using the same procedure in petroleum ether (b.p., 90-115°) solution, a 30% yield of phenyl p-tolyl ketone was realized. There was considerable tar formed in this reaction.

Benzoyl Iodide and Phenylaluminum Iodides. Benzoyl

iodide (41) was prepared by passing dry hydrogen iodide over 70 g. (0.5 mole) of benzoyl chloride over a period of seven hours. The product was distilled slowly at reduced pressure (b.p., 94-6°/5 mm.). Iodine was removed from the product by shaking with mercury and redistilling just before using. The yield was 105-110 g. or 90-95%.

To a slight excess of the mixed phenylaluminum iodides (prepared from 18.4 g. of iodobenzene and 1.6 g. of aluminum) in petroleum ether (b.p., 90-115°) was added 11.6 g. (0.05 mole) of benzoyl iodide. The mixture was stirred for two hours at room temperature and then hydrolyzed by pouring into an ice-hydrochloric acid mixture. The petroleum ether layer was combined with the ether extracts of the aqueous layer and then washed with dilute sodium carbonate solution, dilute sodium bisulfite solution and water. The ether-petroleum ether layer was steam distilled leaving a residual tar which was vacuum distilled. The distillate crystallized and did not depress the melting point of a known sample of benzophenone (mixed m.p., 47-8°). The yield of benzophenone was 3 g. or 33%. A considerable amount of tar was left in the distilling flask.

Benzoyl chloride, under the identical conditions employed in the previous experiment with benzoyl iodide, gave only a

(41) Mr. J. F. Nelson kindly furnished the directions for the preparation of benzoyl iodide. His procedure was essentially the same as Staudinger's. Staudinger and Anthes, Ber., 46, 1423 (1913).

13% yield of benzophenone.

Benzoyl Iodide and Ethylaluminum Iodides. To a slight excess of the mixed ethylaluminum iodides (13 g., 0.025 mole) dissolved in benzene was added dropwise 10 g. (0.043 mole) of benzoyl iodide. The flask was cooled with a water bath during the addition, and then it was allowed to stand at room temperature for two hours before hydrolysis. The benzene layer was separated and combined with the ether extracts of the aqueous layer. The combined extracts were washed with dilute sodium carbonate, dilute sodium bisulfite and water. The solvents were removed by distillation and an alcohol-water mixture was added to the residual oil. Upon cooling, most of the propiophenone precipitated. The mother liquor was sucked away with a filter stick and treated with semicarbazide hydrochloride to convert the remaining propiophenone to the semicarbazone. The total yield of propiophenone was 95.4%.

Reaction in ether solution, using the same procedure, produced considerable ether cleavage with the formation of ethyl benzoate. Some unreacted benzoyl iodide was recovered as benzoic acid (2.6 g. from 0.043 mole or 49.5%) and a small amount of α, α -dibenzoyl ethane was formed which was identified by a mixed melting point (m.p., 84°).

Acetyl Chloride and p-Tolylaluminum Dichloride. To a xylene solution of a slight excess of p-tolylaluminum dichloride which had been prepared from 4.44 g. (0.033 mole) of aluminum chloride and 0.017 mole of tri-p-tolylaluminum was added

3.93 g. (0.05 mole) of acetyl chloride. The mixture was allowed to stand at room temperature for two hours and was then hydrolyzed by pouring into an ice-hydrochloric acid mixture. The xylene was distilled away and the residual oil was vacuum distilled. The portion boiling from 80-100°/10 mm. was collected as methyl *p*-tolyl ketone. It was characterized by conversion to the semicarbazone (m.p., 202-4°). The yield was 75%.

Acetic Anhydride and Ethylaluminum Chlorides. Acetic anhydride (10.2 g., 0.1 mole) was added slowly to a large excess of the mixed ethylaluminum chlorides (27.3 g., 0.11 mole) in benzene solution. The mixture was heated until the benzene commenced to reflux. It was then cooled and hydrolyzed in the customary manner. The benzene layer was separated, dried over sodium sulfate and distilled from a Glinsky column. The various fractions were treated with semicarbazide hydrochloride, and the ketone was converted to the semicarbazone. The aqueous layer was neutralized and also distilled from a Glinsky column. The fractions were treated with semicarbazide reagent, and the total yield of the semicarbazone was 5.1 g. which corresponded to a 39.5% yield of methyl ethyl ketone. There was no depression of the melting point with a known sample of the semicarbazone of methyl ethyl ketone (m.p., 135°).

Benzoic Anhydride and Ethylaluminum Iodides. A benzene solution of benzoic anhydride (11.3 g., 0.05 mole) was added dropwise to a benzene solution of the mixed ethylaluminum

iodides (39.1 g., 0.075 mole). The mixture was heated until the benzene began to reflux, and then it was allowed to cool. It was hydrolyzed in the usual manner. The benzene layer was separated and combined with the ether extracts of the aqueous layer. The combined extracts were washed with dilute sodium bisulfite, dilute sodium carbonate and water. Acidification of the sodium carbonate washings gave 6 g. of benzoic acid. The solvents were removed from the benzene-ether extracts and the residual oil was distilled. The distillate, boiling at 210-218°, amounted to 6 g. or a 45% yield of propiophenone based on both carbonyl groups of benzoic anhydride. It was characterized by conversion to the semicarbazone (m.p., 173-4°).

Benzenesulfonyl Chloride and Ethylaluminum Iodides. Fifteen grams (0.085 mole) of benzenesulfonyl chloride was added dropwise to a benzene solution of the mixed ethylaluminum iodides (15.6 g., 0.03 mole). The reaction was exothermic and a cooling bath was used during the addition. The red-black colored solution was stirred overnight and then hydrolyzed in the usual manner. The benzene layer was separated and washed with dilute alkali and water. The solution was dried over sodium sulfate, and the benzene was distilled away leaving an oil which crystallized on prolonged standing. The crystals were very impure as the melting point was 35-40°. Repeated crystallizations from a benzene-petroleum ether mixture gave 3 g. of a sulfur compound which melted at 61° and did not

depress the melting point of a known sample of diphenyl disulfide. The expected sulfone (m.p., 42°) could not be isolated.

The mixed ethylaluminum iodides and *p*-toluenesulfonyl chloride, under the same conditions, gave an oil which crystallized on standing. The melting point ranged from 46-50°. Repeated crystallizations from a benzene-petroleum ether (b.p., 60-68°) mixture gave 1 g. of a sulfur compound which melted at 69-71°, and is as yet unidentified. The expected sulfone melts at 56°. It is very likely that a shorter reaction period would favor the formation of sulfones in both reactions.

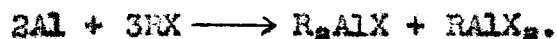
Carbon Tetrachloride and Benzene in the Presence of Ethylaluminum Chlorides. To a mixture of 30 g. (0.25 mole) of dry benzene and 7.7 g. (0.05 mole) of carbon tetrachloride, contained in a 300 cc. round bottom flask provided with a reflux condenser, was added 6.3 g. (0.025 mole) of the mixed ethylaluminum chlorides through the condenser from a dropping funnel. The reflux condenser outlet contained a two-holed stopper which held the dropping funnel and a calcium chloride tube. The flask was kept in an ice-water bath during the dropwise addition of the organometallic compound, and the bath was not removed after the addition was complete but was allowed to gradually warm up during a period of twenty-four hours. At the end of this time, 10 cc. of dry ether was added and the mixture was allowed to stand for an additional twenty-four hours. It was then hydrolyzed by pouring into

an ice-hydrochloric acid mixture which contained 5 cc. of acid and 50 g. of ice. Seventy cubic centimeters of benzene was added and the solution was refluxed for ten minutes. It was allowed to cool to 50°, and the benzene layer was separated and washed with warm water which contained a small amount of hydrochloric acid. The benzene was evaporated and the residual solid was recrystallized from alcohol. The melting point of a known sample of triphenylmethane was not depressed (mixed m.p., 92°). The yield was 35%.

The same reaction using the mixed phenylaluminum iodides gave no triphenylmethane. Likewise, no triphenylmethane was obtained using triethylaluminum as the condensing agent.

DISCUSSION OF RESULTS

Organoaluminum halides are most conveniently prepared by the interaction of aluminum and organic halides. The



reaction goes well with most organic iodides, although n-butyl iodide has a tendency to split out hydrogen iodide and form aluminum iodide which then reacts with n-butyl iodide to give hydrocarbon gases, liquids and a tarry residue. Grosse (16) likewise noted a secondary reaction in the preparation of the mixed n-propylaluminum iodides. Proper cooling and complete covering of metallic aluminum with liquid diminished the secondary reaction and gave the mixed n-propylaluminum iodides. Addition of ether aids in the prevention of hydrogen iodide liberation, but the etherate is formed and the ether cannot be removed to yield the ether-free compound.

The use of organic bromides and chlorides is very limited at the present time. Only the methyl and ethyl bromides and chlorides have yielded organoaluminum compounds and special techniques are required. An autoclave may be used, or the gaseous alkyl halide may be passed into a heated flask containing aluminum and a catalyst. The catalyst may be iodine, alkyl iodides, aluminum chloride or alkylaluminum compounds. An excess of alkyl halide is avoided by passing the gaseous halide into the reaction flask. The fact that sealed tube reactions

give only secondary reaction products indicates that an excess of alkyl halide should be avoided. Refluxing alkyl chlorides in the presence of aluminum yields only secondary reaction products.

The tendency to split out hydrogen chloride is shown least by methyl chloride and increases with chain length until finally n-butyl chloride splits out hydrogen chloride with practically no heating. However, the tendency to pull out hydrogen bromide from alkyl bromides in the presence of aluminum is not so great, and alkyl iodides split out hydrogen iodide to an even lesser extent.

Ethyl bromide behaves normally with aluminum, but refluxing n-butyl bromide or ethylene bromide in the presence of aluminum yields hydrogen bromide and hydrocarbon gases. It is very likely that the organoaluminum halides could be prepared by passing the gaseous alkyl bromides over heated aluminum. There is some evidence for the formation of the mixed phenyl-aluminum bromides when bromobenzene is refluxed in the presence of aluminum which has been catalyzed with iodine. The incompleteness of the reaction appears to be due to the low order or reactivity of bromobenzene and not to a secondary reaction of splitting out hydrogen bromide.

The mixed organoaluminum halides may also be prepared by the addition of aluminum halides to simple organoaluminum compounds. A serious disadvantage of this method is the isolation of the products since it is necessary to separate an equilibrium

mixture. For this reason the reaction has little utility in the preparation of alkylaluminum halides. However, it is of value in preparing arylaluminum halides because the equilibrium can be controlled to a certain extent since the arylaluminum halides are solids and can be precipitated by the proper choice of solvent. This reaction is the best method available for the preparation of phenyl- and p-tolylaluminum dichlorides.

Organoaluminum halide etherates are prepared by reacting aluminum chloride with Grignard reagents in ether solution, by direct reaction of organic halides and aluminum in ether solution or by adding ether to the ether-free compounds. Mono-etherates are formed and the ether is held so tenaciously that it cannot be removed to yield the ether-free compounds without total decomposition of the carbon-aluminum linkages.

Alkylaluminum halides are colorless liquids which can be distilled in an atmosphere of nitrogen without decomposition. The mixture of alkylaluminum halides which is obtained from the reaction of aluminum and alkyl halides can generally be separated by fractional distillation or crystallization. However, the mixed ethylaluminum bromides and chlorides cannot be fractionated satisfactorily, and chemical means are employed to effect a separation. Dialkylaluminum halides can be separated from alkylaluminum dihalides by adding sodium chloride and then distilling. The alkylaluminum dihalide-double salt does not distill while the dialkylaluminum halide is distillable and can be obtained in a high state of purity in this manner.

Grosse (16) adds R_2Al compounds to the mixture of organoaluminum halides (R_2AlX , $RAlX_2$) which converts the dihalide to the mono-halide ($RAlX_2 + R_2Al \longrightarrow 2R_2AlX$) and then fractionates the resulting liquid. A purer dialkylaluminum halide is obtained by the sodium chloride double salt method.

Alkylaluminum dihalides cannot be regenerated from their sodium chloride double salts. The only method available for the separation of alkylaluminum dihalides from the mixture of alkylaluminum halides is the conversion of the dialkylaluminum halide to the alkylaluminum dihalide by means of aluminum halide and fractionation of the resulting liquid. This does not give an entirely pure product, but Grosse (16) has found that fractional distillation followed by fractional crystallization will yield a pure product.

All the mixed alkylaluminum compounds react violently with water and alcohol, fume in the air and often ignite spontaneously. They are soluble in most organic solvents with which they do not react. The alkylaluminum dihalides are less soluble than the dialkylaluminum halides, but the difference is not very well marked.

Arylaluminum halides are solid compounds which cannot be easily distilled. The mixed phenylaluminum iodides cannot be distilled, but phenylaluminum dichloride and dibromide are distillable at very low pressures. The arylaluminum halides are soluble in benzene, toluene, xylene and ether, but are almost insoluble in petroleum ether. They fume in air and react with

water and alcohol but not quite as violently as do the alkyl-aluminum halides.

It appears that organoaluminum halides are endowed with the same general order of reactivity as the simple organoaluminum compounds. The relative reactivity of simple organoaluminum compounds has been determined by Gilman and Marple (31) who found that they are less reactive than organomagnesium and -beryllium compounds and more reactive than organoboron and -zinc compounds. It would be helpful if there were a general rule concerning the relative reactivities of simple and mixed organometallic compounds, but a brief review of the literature indicates that the order of reactivity depends to a great extent upon the choice of reagent.

According to Gilman and Schulze (42) alkylberyllium halides are generally less reactive than dialkylberyllium compounds. However, in the case of organomagnesium compounds, the relative reactivities of R_2Mg and $RMgX$ compounds vary according to the reagent chosen. Schlenk and Schlenk (43) and also Bartlett and Berry (44) consider R_2Mg and $RMgX$ compounds to be equally effective in carbonyl addition reactions. $RMgX$ compounds have been found to be more reactive than R_2Mg compounds in reactions with valeronitrile (45), dimethyl sulfate (46) and diethyl sulfate (47).

(42) Gilman and Schulze, J. Chem. Soc., 2663 (1927).

(43) Schlenk and Schlenk, Ber., 62, 920 (1929).

(44) Bartlett and Berry, J. Am. Chem. Soc., 56, 2683 (1934).

(45) Gilman and Brown, ibid., 52, 1181 (1930).

(46) Cope, ibid., 56, 1578 (1934); Suter and Gerhart, ibid., 57, 107 (1935).

(47) R. H. Kirby, Master's Thesis, Iowa State College (1935), p. 30.

Dimethylmagnesium is reported to be more reactive than methylmagnesium iodide with benzonitrile (47). Triphenylmethylmagnesium bromide is carbonated more readily than ditriphenylmethylmagnesium (48). The reaction of dimethylmagnesium with enolizable ketones indicates that this substance is less reactive toward the carbonyl linkage than is methylmagnesium iodide (49).

R_2Cd and $RCdX$ compounds are reported to be essentially equal in effectiveness in the synthesis of ketones from acid chlorides (34). Phenylmercuric chloride reacts with ketene to give a twenty per cent yield of acetophenone, but there is none of this product isolated with diphenylmercury (50). Reaction with diphenylmercury was reported in this paper, but later work showed that the reaction was due to the presence of mercuric chloride as an impurity.

Simple organoboron compounds undergo addition reactions to carbonyl groups, but only two of the R groups are involved under usual conditions (51). Triphenylgallium and benzoyl chloride give a seventy-nine per cent yield of benzophenone which indicates that all three phenyl groups react to a certain extent (52). The alkyl groups of trialkylgallium compounds can be removed stepwise by cleavage with water and acidic reagents (53). The cleavage of trimethylindium with water and alcohol

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

(49) Wright, *ibid.*, 61, 1152 (1939).

(50) Gilman, Wooley and Wright, *ibid.*, 55, 2609 (1933).

(51) Gilman and Marple, *Rec. trav. chim.*, 55, 76 (1936).

(52) Gilman and Jones, *J. Am. Chem. Soc.*, 62, 980 (1940).

(53) Dennis and Patnode, *ibid.*, 54, 182 (1932).

cleaves only two methyl groups, and dilute acid is required to expel the third methyl group (54). The yield of benzohydrol from benzaldehyde and triphenylindium is eighty-three per cent. Diphenylindium iodide and phenylindium di-iodide give benzohydrol in yields of sixty-six and nineteen per cent, respectively (55). Simple organothallium compounds react with carbonyl compounds, but only one R group is involved and an R_2TlX compound is a product of the reaction (56). Therefore, simple organothallium compounds are decidedly more reactive than mixed organothallium compounds. Likewise, simple organoindium compounds appear to be more reactive than the mixed compounds, but here the difference in reactivity is not so well marked as in the case of the thallium compounds. The same applies to the organometallic compounds of gallium and boron, and in general the simple organometallic compounds of group III metals appear to be more reactive than the mixed organometallic compounds. However, it is not unlikely that the reactivity might be reversed for some particular reagents.

An investigation of organoaluminum compounds reveals that the relative reactivity between simple and mixed compounds is not very pronounced and that a variation is observed according to the choice of reagent. The color test with Michler's ketone indicates that the simple compounds are slightly more reactive.

(54) Dennis, Work, Rochow and Chamot, ibid., 56, 1047 (1934).

(55) Unpublished studies in these laboratories by Mr. R. G. Jones.

(56) Gilman and Jones, J. Am. Chem. Soc., 61, 1513 (1939).

Alkylaluminum halides give a weak test after standing five minutes before hydrolysis and a strong test after standing fifteen minutes prior to hydrolysis. Xylene solutions of arylaluminum halides require fifteen minutes of contact with Michler's ketone for a weak test and thirty minutes of contact for a strong test. A two cubic centimeter sample of a two-tenth molar xylene solution of the mixed ethylaluminum iodides gives a faint test after five minutes of contact with Michler's ketone and a strong test after fifteen minutes of contact. Xylene solutions of the simple organoaluminum compounds give a positive color test after five minutes of contact with Michler's ketone if the solution is at least one-tenth molar with respect to the organoaluminum compounds (31).

Refluxing a xylene solution of benzonitrile and tri-*p*-tolylaluminum for two hours gives a seventeen per cent yield of phenyl *p*-tolyl ketone (31), while only a two per cent yield of benzophenone is obtained when the mixed phenylaluminum iodides are treated with benzonitrile for six hours in boiling xylene. This small yield does not result from a Friedel-Crafts reaction because a reaction of that type would involve the solvent xylene rather than any benzene which might be formed from the cleavage of xylene. No evidence of phenyl xylyl ketones was detected. No propiophenone can be isolated from the reaction between benzonitrile and the mixed ethylaluminum iodides; a ninety per cent recovery of benzonitrile is realized. The rather slow reaction with benzonitrile in-

icates a fairly high order of reactivity for organoaluminum halides since it has been shown that benzonitrile, in comparison with some other functional groups, possesses a low order of reactivity toward Grignard reagents (57).

Carbonation of tri-*p*-tolylaluminum with solid carbon dioxide gives no acid, while refluxing an ether solution of tri-*p*-tolylaluminum in an atmosphere of carbon dioxide for seven days gives a thirty-two per cent yield of *p*-toluic acid. A forty-four per cent yield of *p*-toluic acid is obtained when a boiling xylene solution of tri-*p*-tolylaluminum is treated for two hours with gaseous carbon dioxide (31). The color test is still positive after bubbling dry carbon dioxide gas into a boiling xylene solution of the mixed ethylaluminum iodides for ten hours. The color test is negative at the end of twelve hours, but no acid can be isolated. Likewise, carbonation of the mixed phenylaluminum iodides in boiling benzene solution for ten hours gives no acid; only resinous products with a strong phenolic odor are obtained. The reactions of organoaluminum halides are being investigated further by Mr. A. H. Haubein of these laboratories, and he has found that the mixed phenylaluminum iodides give benzoic acid upon carbonation. Dry ice and the mixed phenylaluminum iodides in toluene solution give a five per cent yield of benzoic acid. Bubbling gaseous carbon dioxide into a boiling benzene solution

(57) Entemann and Johnson, ibid., 55, 2900 (1933).

of the mixed phenylaluminum iodides for two hours gives a thirty-five and six-tenths per cent yield of benzoic acid. The yields of benzoic acid using toluene and xylene as the solvent are forty-five and six-tenths and forty per cent, respectively. These results indicate that the mixed compounds are as reactive toward carbon dioxide as the simple compounds and even more reactive on the basis of dry ice carbonation. It also appears that the acids are destroyed upon refluxing for too long a period of time.

Acid chlorides react very readily with organoaluminum halides to give good yields of ketones. The mixed ethylaluminum iodides and benzoyl chloride give a ninety per cent yield of propiophenone in benzene solution and an eighty-five per cent yield in carbon disulfide solution. This yield is based on the per cent conversion of benzoyl chloride using an excess of the organoaluminum compound. Refluxing a xylene solution of triphenylaluminum and benzoyl chloride for one hour produces a thirty-six and one-half per cent yield of benzophenone (based on all three phenyl groups reacting). Under the same conditions, benzoyl chloride and the mixed phenylaluminum iodides give a forty-seven and one-half per cent yield of benzophenone. This does not mean that the mixed compounds are more reactive since an eleven and one-half per cent yield of triphenylcarbinol is also obtained in the reaction with triphenylaluminum. No carbinol is isolated in the reaction with the mixed phenylaluminum iodides. Perhaps benzophenone is tied up in a complex

which does not react with the mixed phenylaluminum iodides but does react with triphenylaluminum. It is known that ketone-aluminum chloride complexes are quite unreactive toward organoaluminum halides. Reaction with benzophenone is to be expected since organoaluminum halides react with benzonitrile and, therefore, should react even more readily with ketones. It is true that ketones condense in the presence of organoaluminum halides, but there should be no condensation reaction with benzophenone since there is no alpha hydrogen available for enolization. Furthermore, there should be no condensations with the expected product, triphenylcarbinol, since it has no alpha hydrogen atoms. Except where di-aryl ketones and arylaluminum halides are used, it is possible that ketones, in addition to condensing with themselves, react normally with organoaluminum halides to give carbinols which dehydrate to produce olefins which in turn polymerize to complex resinous products.

Organoaluminum halides are much better condensing agents than simple organoaluminum compounds. Acetophenone is condensed by triphenylaluminum to give dyprone (33), but only further condensation products are obtained with the mixed organoaluminum compounds. Benzaldehyde and simple organoaluminum compounds give good yields of carbinols while mixed organoaluminum halides yield only complex condensation products. Carbon tetrachloride and benzene give triphenylmethane in the presence of the mixed ethylaluminum chlorides. Triethylaluminum or the mixed phenylaluminum iodides do not catalyze this

condensation reaction.

Mixed organoaluminum compounds do not react with N-alkylanilines (12) while simple organoaluminum compounds react quite readily (37).

On the basis of the evidence presented it appears that the mixed organoaluminum compounds possess an order of reactivity comparable to the simple organoaluminum compounds, but perhaps are a little less reactive as evidenced by the color test, reaction with benzonitrile and reaction with N-alkylanilines. It should be mentioned that there is the added complication that one may be measuring the reactivity of an equilibrium mixture in the case of the mixed compounds rather than the reactivity of a single compound.

Apparently there is not much difference in reactivity between R_2AlX compounds and $RAlX_2$ compounds. Both R groups of diethylaluminum chloride react with benzoyl chloride to give a sixty-seven per cent yield of propiophenone. Under the same conditions, a sodium chloride-ethylaluminum dichloride double salt gives a twenty per cent yield of propiophenone. The low yield is due, undoubtedly, to the insolubility of the complex and not to a lower reactivity of the ethylaluminum dichloride. No carbinol was isolated in either reaction.

No definite conclusions can be made concerning the relative reactivities of alkyl- and arylaluminum halides. Alkylaluminum halides give better yields of ketones with acid chlorides than do arylaluminum halides. However, this may be due to the fact

that the alkylaluminum compounds are in a higher state of purity since they are purified by distillation. The color test is slightly quicker with alkylaluminum halides, but this again may be due to a higher state of purity. Benzonitrile reacted with the mixed phenylaluminum iodides but not with the mixed ethylaluminum iodides. Likewise, the mixed phenylaluminum iodides are carbonated to give benzoic acid, but no acid is isolated upon carbonation of the mixed ethylaluminum iodides.

The proper choice of solvent has considerable effect on the yield of product in organoaluminum halide reactions. This is shown very well in reactions between benzoyl chloride and the mixed ethylaluminum iodides. The yields of propiophenone are ninety, eighty-five, fifty-four and forty-eight per cent in benzene, carbon disulfide, tetrachloroethane and petroleum ether (b.p., 90-115°), respectively. Aromatic hydrocarbons are the best solvents. In addition to benzene, toluene and xylene have been employed with good results. There appears to be no reaction with carbon disulfide under the mild conditions employed in acid chloride reactions. The yields in petroleum ether are generally poor and a considerable amount of tar is always formed. The petroleum ether was always washed with fuming sulfuric acid, dried, and then distilled before using.

The yield of propiophenone is practically negligible when diethyl ether is used as the reaction medium in the reaction between benzoyl chloride and the mixed ethylaluminum iodides.

The main product is probably a condensation product of ethyl benzoate. Some α,α -dibenzoyl ethane is also formed. Leone (11b) has given the following interpretation for the preparation of this compound. Propiophenone is formed in the normal way and it then reacts with benzoyl chloride under the influence of aluminum salts to give α,α -dibenzoyl ethane. A small amount



of ethane is formed in the reaction, supposedly due to the cleavage of the organoaluminum compound by hydrogen chloride.

It is not surprising that ethyl benzoate is formed in reactions with benzoyl chloride in ether solution because aluminum chloride catalyzes this type of reaction, and organoaluminum halides are expected to act in a like manner (58). Benzoyl iodide and ether will give ethyl benzoate without a catalyst (59). It is surprising that the ether cleavage reaction proceeds more rapidly than the acid chloride reaction. Ether unquestionably diminishes the reactivity of organoaluminum halides.

Benzoyl iodide appears to be more reactive than benzoyl chloride with organoaluminum iodides. Benzoyl iodide and the mixed phenylaluminum iodides give a thirty-three per cent yield of benzophenone in petroleum ether solution, and benzoyl chloride under the same conditions gives only a twelve per cent yield. Benzoyl iodide and the mixed ethylaluminum

(58) Meerwein, *J. prakt. Chem.*, 134, 51 (1932).

(59) Kishner, *J. Russ. Phys. Chem. Soc.*, 41, 651 (1909) /C. A., 5, 883 (1911)/

Iodides give a ninety-five per cent yield of propiophenone in benzene solution. The yield of propiophenone using benzoyl chloride is ninety per cent. In general, benzoyl iodide is more reactive than benzoyl chloride with organometallic compounds. Gilman and Nelson (60) have found that the relative reactivities of benzoyl halides in their reactions with di-*p*-tolylmercury are benzoyl iodide > benzoyl bromide > benzoyl chloride > benzoyl fluoride. This same order of reactivity is found with phenylzinc chloride (61). The reverse order is found with Grignard reagents (57). It has been suggested that the mechanism of the reaction between acid chlorides and Grignard reagents involves carbonyl addition while the mechanism of the reaction between acid chlorides and the less reactive organometallic compounds involves metathesis.

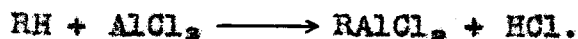
Organoaluminum Compounds and the Friedel-Crafts Reaction

The Friedel-Crafts reaction has been extended so widely since its discovery that it is very likely that no one mechanism will be able to account for all the reactions that can be induced by aluminum chloride. In order to find a mechanism or mechanisms, it is logical to first study the fundamental Friedel-Crafts reactions, namely, the hydrocarbon and ketone syntheses and then investigate the variations as they may possibly reduce to the fundamental reactions.

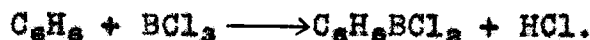
(60) Gilman and Nelson, *J. Am. Chem. Soc.*, 61, 743 (1939).

(61) Gilman, "Organic Chemistry", John Wiley and Sons, New York (1938) Vol. I, p. 418.

One of the several mechanisms which has been proposed involves the intermediate formation of organoaluminum compounds. This theory was introduced by Friedel and Crafts (27) and requires the formation of an organoaluminum compound according to the following equation:



At the present time no organoaluminum compound has been prepared in this manner. However, it is possible, under drastic conditions, to effect the following reaction between boron trichloride and benzene (62):



Leone (63) suggested that the reaction between benzene and aluminum chloride is an equilibrium reaction in which the equilibrium is greatly displaced to the left and that the organoaluminum compound is formed little by little as it reacts with alkyl halides.

Even if it is granted that organoaluminum compounds can be prepared in a Friedel-Crafts reaction, it is still necessary to consider the reactivities of the mixed organoaluminum compounds. There were no mixed arylaluminum compounds available at the time Friedel and Crafts announced the theory of intermediate organoaluminum formation. Therefore, they conducted some studies with triphenylaluminum and found that some di-

- (62) Pace, Atti accad. Lincei, 10, 193 (1929) [C.A., 24, 1360 (1930)]
(63) Leone, Atti II Congresso naz. chim. pura applicata, 1332 (1926) [Chem. Zentr. I, 2174 (1928)].

phenylmethane was formed from reaction with benzyl chloride but no Friedel-Crafts reaction occurred with chloroform (27). Hilpert and Grüttner (28) reported no condensation of triphenylaluminum with chloroform or carbon tetrachloride.

Leone (11) prepared several mixed organoaluminum compounds (etherates) and investigated their reactivity toward alkyl iodides, benzoyl chloride and ketones. Phenylaluminum iodides were found to react with alkyl iodides to give small quantities of benzene homologs. However, the reaction did not proceed with the smoothness or effectiveness of typical Friedel-Crafts alkylations. The reactivity of organoaluminum compounds is of a relatively low order and alkylations of the Wurtz type are restricted to the more reactive organometallic compounds. Therefore, if hydrocarbon synthesis involves intermediate organoaluminum compounds, then the mixed organoaluminum compounds and alkyl halides should give the same order of yields which result from the reaction of aromatic hydrocarbons and alkyl halides in the presence of aluminum chloride. Since Leone reported no definite yields of alkylated benzenes, it is worth while to investigate hydrocarbon syntheses further before ruling out organoaluminum formation as a mechanism. This work is now being investigated by Mr. A. H. Haubein of these laboratories.

With benzoyl chloride and ethylaluminum halides in ether solution, Leone (11b) found only small amounts of propiophenone and α,α -dibenzoylethane together with larger amounts of a tarry

residue. Only rapid condensation reactions occurred with ketones. Thus, acetone produced mesityl oxide with ethylaluminum iodides and acetophenone yielded triphenylbenzene with phenylaluminum iodides. From these reactions Leone concluded that it was impossible to interpret ketone synthesis by means of intermediate organoaluminum compounds.

However, in ketone synthesis, there always results a complex between the ketone and aluminum chloride and it is necessary to hydrolyze this complex to obtain the free ketone. It has now been found that these ketone-aluminum chloride complexes do not give condensation products when treated with organoaluminum halides under the moderate conditions existing in Friedel-Crafts ketone syntheses and that the ketones can be recovered upon hydrolysis. These reactions are summarized in Table II. In the case of acetophenone, the complex in reaction (5) was prepared as it is actually formed in a Friedel-Crafts synthesis. That is, acetic anhydride was reacted with benzene in the presence of aluminum chloride. The mixed ethylaluminum iodides were added to the reaction mixture, and a fifty-two per cent yield of acetophenone was obtained upon hydrolysis.

Since acid chlorides also form complexes with aluminum chloride, it was of interest to see if these complexes would react with organoaluminum halides under mild Friedel-Crafts conditions to produce ketones. The expected reactions take place very readily and give good yields of ketones. A summary of the results is given in Table III.

TABLE II

Ketone-AlCl₃ Complexes and Organoaluminum Halides

<u>Ketone-AlCl₃ Complex</u>	<u>Organoaluminum Halide</u>	<u>Per cent recovery of ketone.</u>
1. Benzophenone	$\text{[C}_6\text{H}_5\text{AlI}_2 + (\text{C}_2\text{H}_5)_2\text{AlI]}$	92
2. Benzophenone	$\text{[C}_6\text{H}_5\text{AlI}_2 + (\text{C}_2\text{H}_5)_2\text{AlI]}$	60
3. Propiophenone	$\text{[C}_6\text{H}_5\text{AlI}_2 + (\text{C}_2\text{H}_5)_2\text{AlI]}$	70
4. Acetophenone	$\text{[C}_6\text{H}_5\text{AlI}_2 + (\text{C}_2\text{H}_5)_2\text{AlI]}$	75
5. Acetophenone	$\text{[C}_6\text{H}_5\text{AlI}_2 + (\text{C}_2\text{H}_5)_2\text{AlI]}$	52
6. Acetophenone	$\text{[C}_6\text{H}_5\text{AlI}_2 + (\text{C}_2\text{H}_5)_2\text{AlI]}$	64
7. Acetophenone	$\text{[C}_6\text{H}_5\text{AlCl}_2 + (\text{C}_2\text{H}_5)_2\text{AlCl]}$	65
8. Acetone	$\text{[C}_6\text{H}_5\text{AlI}_2 + (\text{C}_2\text{H}_5)_2\text{AlI]}$	10
9. Acetone	$\text{[C}_6\text{H}_5\text{AlI}_2 + (\text{C}_2\text{H}_5)_2\text{AlI]}$	10

TABLE III

Reactions of Acid Chloride-AlCl₃ Complexes and Organoaluminum Halides

<u>Complex</u>	<u>Organoaluminum Halide</u>	<u>Solvent</u>	<u>Product</u>	<u>Per cent Yield</u>
1. Benzoyl Chloride	$\text{[C}_6\text{H}_5\text{AlI}_2 + (\text{C}_6\text{H}_5)_2\text{AlI]}$	benzene	propiophenone	56
2. Benzoyl Chloride	$\text{[C}_6\text{H}_5\text{AlI}_2 + (\text{C}_6\text{H}_5)_2\text{AlI]}$	carbon disulfide	propiophenone	62
3. Benzoyl Chloride	$\text{[C}_6\text{H}_5\text{AlI}_2 + (\text{C}_6\text{H}_5)_2\text{AlI]}$	benzene	benzophenone	70
4. Benzoyl Chloride	$\text{[C}_6\text{H}_5\text{AlI}_2 + (\text{C}_6\text{H}_5)_2\text{AlI]}$	carbon disulfide	benzophenone	72
5. Benzoyl Chloride	$p\text{-CH}_3\text{C}_6\text{H}_4\text{AlCl}_2$	xylene	phenyl <i>p</i> -tolyl ketone	71
6. Acetyl Chloride	$p\text{-CH}_3\text{C}_6\text{H}_4\text{AlCl}_2$	xylene	methyl <i>p</i> -tolyl ketone	62

Acid chlorides react alone with organoaluminum halides to give good yields of ketones as is shown in Table IV. In fact, organoaluminum halides may be reagents of choice in the preparation of ketones. No large run synthesis has been tried with organoaluminum halides, but it is to be expected that even better yields of ketones will be obtained than is now realized with small scale experiments.

Acid anhydrides are used very frequently in preparing ketones by means of a Friedel-Crafts synthesis. They react quite readily with organoaluminum halides to give ketones, but only one carbonyl group is involved in the reaction. Acetic anhydride reacts with the mixed ethylaluminum chlorides in benzene solution to give a forty per cent yield of methyl ethyl ketone. Benzoic anhydride and the mixed ethylaluminum iodides give a forty-five per cent yield of propiophenone in benzene solution. A forty-five per cent yield of benzoic acid is also obtained. Mr. A. H. Haubein of these laboratories is continuing these studies on acid anhydrides and a resume of his present progress is given in Table V.

The effect of solvents on the yields of products in organoaluminum halide reactions has already been discussed (p. 71). It was stated that aromatic hydrocarbon solvents were the best solvents, and it is interesting to note that aromatic hydrocarbons are often used as solvents in Friedel-Crafts reactions. Generally an excess of the reacting aromatic hydrocarbon is used as the solvent although it is possible to prepare

TABLE IV

Reactions of Acid Chlorides and Organoaluminum Halides

<u>Acid Chloride</u>	<u>Organoaluminum Halide</u>	<u>Solvent</u>	<u>Product</u>	<u>Per cent Yield</u>
1. Benzoyl chloride	$\underline{\underline{C_6H_5AlI_2 + (C_2H_5)_2AlI}}$	benzene	propiophenone	90
2. Benzoyl chloride	$\underline{\underline{C_6H_5AlI_2 + (C_2H_5)_2AlI}}$	carbon disulfide	propiophenone	85
3. Benzoyl chloride	$\underline{\underline{C_6H_5AlI_2 + (C_2H_5)_2AlI}}$	tetrachloroethane	propiophenone	54
4. Benzoyl chloride	$\underline{\underline{C_6H_5AlI_2 + (C_2H_5)_2AlI}}$	petroleum ether	propiophenone	48
5. Benzoyl chloride	$\underline{\underline{C_6H_5AlI_2 + (C_6H_5)_2AlI}}$	petroleum ether	benzophenone	12
6. Benzoyl chloride	$\underline{\underline{C_6H_5AlI_2 + (C_6H_5)_2AlI}}$	xylene	benzophenone	47.5
7. Benzoyl chloride	$p\text{-CH}_3\text{C}_6\text{H}_4\text{AlCl}_2$	xylene	phenyl <i>p</i> -tolyl ketone	60
8. Benzoyl chloride	$p\text{-CH}_3\text{C}_6\text{H}_4\text{AlCl}_2$	petroleum ether	phenyl <i>p</i> -tolyl ketone	30
9. Benzoyl chloride	$(C_2H_5)_2AlCl$	benzene	propiophenone	67
10. Benzoyl iodide	$\underline{\underline{C_6H_5AlI_2 + (C_6H_5)_2AlI}}$	petroleum ether	benzophenone	33
11. Benzoyl iodide	$\underline{\underline{C_6H_5AlI_2 + (C_2H_5)_2AlI}}$	benzene	propiophenone	95.4
12. Acetyl chloride	$p\text{-CH}_3\text{C}_6\text{H}_4\text{AlCl}_2$	xylene	methyl <i>p</i> -tolyl ketone	75

TABLE V

Reactions of Acid Anhydrides and Organoaluminum Halides

<u>Acid Anhydride</u>	<u>Organoaluminum Halide</u>	<u>Solvent</u>	<u>Product</u>	<u>Per cent Yield</u>
1. Acetic anhydride	$\text{[C}_2\text{H}_3\text{AlI}_2 + (\text{C}_2\text{H}_5)_2\text{AlI]}$	toluene	acetophenone	41
2. Acetic anhydride	$\text{p-CH}_3\text{C}_6\text{H}_4\text{AlCl}_2$	toluene	methyl p-tolyl	42.5
3. Acetic anhydride	$\text{[C}_2\text{H}_3\text{AlI}_2 + (\text{C}_2\text{H}_5)_2\text{AlI]}$	toluene	methyl ethyl ketone	39.5
4. Benzoic anhydride	$\text{[C}_6\text{H}_5\text{AlI}_2 + (\text{C}_2\text{H}_5)_2\text{AlI]}$	toluene	benzophenone	14
5. Succinic anhydride	$\text{[C}_6\text{H}_5\text{AlI}_2 + (\text{C}_2\text{H}_5)_2\text{AlI]}$	toluene	β -benzoyl- propionic acid	86
6. Phthalic anhydride	$\text{[C}_6\text{H}_5\text{AlI}_2 + (\text{C}_2\text{H}_5)_2\text{AlI]}$	toluene	o -benzoyl- benzoic acid	94

α-naphthoylbenzoic acid in benzene solution since phthalic anhydride reacts more readily with naphthalene than benzene. Other common solvents which are used quite extensively in Friedel-Crafts reactions are carbon disulfide, tetrachloroethane and nitrobenzene. A glance at the various summarized tables reveals that carbon disulfide and tetrachloroethane can be used satisfactorily as solvents in ketone syntheses using organoaluminum halides. No mention of nitrobenzene as a solvent has been made because organoaluminum halides and nitrobenzene react quite violently. For this reason no experiments of this type were attempted. However, in later studies by Mr. A. H. Haubein (64), a competitive reaction was run between a mixture of benzoyl chloride and nitrobenzene and the mixed phenylaluminum iodides in petroleum ether solution. Benzoyl chloride (0.2 mole) and nitrobenzene (0.2 mole) were dissolved in two hundred cubic centimeters of petroleum ether and cooled to zero degrees. To this mixture was added the mixed phenylaluminum iodides (0.1 mole). A rather mild reaction took place in comparison to the reaction of organoaluminum halides and nitrobenzene along. The products isolated were benzophenone (34.8%) and benzoic acid (53%). A seventy per cent recovery of nitrobenzene was realized. Therefore, organoaluminum halides react with acid halides before they react with nitrobenzene, and the fact that there is a violent reaction between organoaluminum halides and nitrobenzene does not

(64) Unpublished studies in these laboratories by Mr. A.H. Haubein.

signify that organoaluminum halides cannot be intermediates in ketone syntheses when nitrobenzene is used as a solvent.

In conclusion, it can no longer be said that ketone synthesis of the Friedel-Crafts type cannot involve intermediate organoaluminum compounds because of the known marked condensations between organoaluminum halides and ketones. It is true that this condensing action exists, but it is also true that ketone-aluminum chloride complexes do not react appreciably with organoaluminum halides under the mild conditions of Friedel-Crafts acylations. Furthermore, ketones are always tied up in aluminum chloride complexes in Friedel-Crafts acylations and the free ketone is never obtained till after hydrolysis of the reaction mixture. In addition, organoaluminum halides react with acid halides and anhydrides under the moderate conditions employed in Friedel-Crafts reactions to give good yields of ketones. Solvents which are generally used in Friedel-Crafts reactions also may be used with equal success in reactions involving organoaluminum halides. Therefore, on the basis of the relative reactivity of organoaluminum halides, there is no question but what they may exist as intermediates in Friedel-Crafts acylation reactions. However, it is still a matter of speculation whether intermediate organoaluminum compound formation is the true mechanism, since it has never been demonstrated that organoaluminum halides can be prepared from an aromatic hydrocarbon and aluminum chloride.

Nevertheless, until it can be decisively proved that organo-aluminum compounds cannot be synthesized in a Friedel-Crafts ketone synthesis, there is no reason to exclude intermediate organoaluminum compounds as a mechanism in Friedel-Crafts acylations.

SUMMARY

The literature of organoaluminum compounds has been reviewed.

The preparation of organoaluminum halides has been investigated.

Organoaluminum halides give a positive color test with Michler's ketone if they are warmed for five minutes prior to hydrolysis.

Reactions between organoaluminum halides and the following reagents have been studied: benzonitrile, carbon dioxide, ketones, acid chlorides and acid anhydrides.

The relative reactivities between simple and mixed organometallic compounds has been discussed.

Organoaluminum halides are of the same order of reactivity as the simple organoaluminum compounds but are perhaps slightly less reactive as shown by reactions with Michler's ketone, benzonitrile and N-alkylanilines.

R_2AlX and $RAlX_2$ compounds possess approximately the same order of reactivity.

Benzoyl iodide is more reactive than benzoyl chloride toward organoaluminum halides.

The possibility of the intermediate formation of organoaluminum halides as a mechanism for the Friedel-Crafts reaction has been investigated.

B. DIVALENT ORGANOLEAD RADICALS

HISTORICAL

Divalent organometallic radicals of germanium, tin and lead have been prepared. In the case of lead, the yields are very unsatisfactory, and, moreover, it is apparently impossible to obtain the compounds consistently. Consequently, other methods of preparing divalent organolead radicals are desirable, and this study was directed toward that goal.

An excellent review of organometallic radicals has been presented by Bailie (1), and for that reason this discussion has been limited to the chemistry of the divalent organometallic radicals of germanium, tin and lead.

Diphenylgermanium dichloride is ammonolyzed in liquid ammonia but is stable in ethyl amine. Kraus and Brown (2) attempted the preparation of diphenylgermanium by reducing diphenylgermanium dichloride with lithium in ethyl amine solution. A resinous compound was obtained which contained from twenty-nine and two-tenths to thirty-one and two-tenths per cent germanium. The germanium content of diphenylgermanium is thirty-two per cent. It is evident that the product consisted largely of diphenylgermanium. Eatough (3) has shown

- (1) Bailie, Doctoral Dissertation, Iowa State College (1938); see also Gilman and Bailie, J. Am. Chem. Soc., 61, 731 (1939).
- (2) Kraus and Brown, ibid., 52, 4031 (1930).
- (3) Eatough, Thesis, Brown University (1929).

that triphenylsilicon forms an addition compound with ethyl amine. Ethyl amine is very likely retained by diphenylgermanium in this same manner. Reduction of diphenylgermanium dichloride in boiling xylene solution by sodium gave a yellow resinous product which was apparently an impure polymer of diphenylgermanium. Cooling the xylene solution precipitated a ten to twenty per cent yield of diphenylgermanium. Molecular weight determinations indicated the compound was a polymer which contained four molecules of diphenylgermanium. It was only slightly soluble in cold benzene, toluene or chloroform. Its solubility in hot solvents was very limited, and it was insoluble in petroleum ether. Slow crystallization from benzene gave white crystals which melted at 294-295° and were stable in air. Addition of sodium to diphenylgermanium in liquid ammonia solution produced disodium diphenylgermanium. Treatment of the disodium compound with ammonium bromide gave hydrogen and complex germanium compounds. It is possible that diphenylgermanium dihydride was formed initially and then decomposed.

In 1852 Löwig (4) prepared diethyltin by the action of ethyl iodide on a sodium-tin alloy and observed that it added oxygen and halogens. Later, Frankland (5) obtained diethyltin from the reduction of diethyltin dichloride by metallic zinc,

(4) Löwig, Ann., 84, 320 (1852).

(5) Frankland, Ann., 85, 329, 338 (1852).

and reported its spontaneous decomposition to tetraethyltin and tin. Attempts to prepare diethyltin from the reaction between diethylzinc and stannous chloride were unsuccessful, but the reaction apparently involved the intermediate formation of diethyltin (6).

Pfeiffer (7) found that diethyltin could be prepared either by the reduction of diethyltin dichloride with sodium amalgam or from the reaction between ethylmagnesium bromide and stannous chloride. Diethyltin was decomposed upon distillation into tetraethyltin and metallic tin. It was a yellow oil which readily oxidized in air to form diethyltin oxide and added halogens to give the corresponding diethyltin dihalides. Addition of ethyl iodide gave triethyltin iodide. Treatment of diethyltin with mercuric chloride formed diethyltin dichloride and mercury. In a like manner, diphenylmercury was converted to mercury and diethyldiphenyltin (8).

Deeply colored products, probably polymers of dialkyltin compounds, were reported to be formed in reactions between alkylmagnesium halides and stannous chloride (9). Krause and Weinberg (10) found that tertiary alkyl Grignard reagents and

- (6) Frankland, J. Chem. Soc., 35, 130 (1879).
(7) Pfeiffer, Ber., 44, 1269 (1911).
(8) Nesmeyanov, Kocheshkov and Puzyreva, J. Gen. Chem. (U.S.S.R.), 7, 118 (1937) [C.A., 31, 4290 (1937)].
(9) Krause und von Grosse, "Die Chemie der metallorganischen Verbindungen", Gebrüder Borntraeger, Berlin (1937), p. 354.
(10) Krause and Weinberg, Ber., 63, 382 (1930).

stannic chloride did not form tetra-alkyltin compounds as did the normal alkyl compounds. Instead, deeply colored products were obtained which added bromine to give the corresponding di-tert.-alkyltin dibromides. Stannic chloride and triphenylmethylsodium gave colored products which could not be identified.

Kraus and Greer (11) prepared polymers of dimethyltin from the reduction of dimethyltin dibromide by means of sodium in liquid ammonia. Addition of two atoms of sodium to the solid yellow polymeric dimethyltin in liquid ammonia solution gave disodium tetramethylditin as evidenced by its reaction with methyl iodide to give hexamethylditin. Addition of two atoms of sodium to disodium tetramethylditin in liquid ammonia yielded disodium dimethyltin, verified by its conversion to tetramethyltin by reaction with methyl iodide. Treatment of disodium dimethyltin in liquid ammonia with dimethyltin dibromide formed a polymer of dimethyltin which was more sensitive toward oxygen than the polymer prepared by the direct reduction of dimethyltin dibromide with two atoms of sodium. However, the two polymers were alike in appearance, and both gave dimethyltin oxide on oxidation and dimethyltin dibromide on bromination.

Diaryltin radicals are more stable than the dialkyltin compounds, and they can be prepared from the reaction of

(11) Kraus and Greer, J. Am. Chem. Soc., 47, 2568 (1925).

stannous chloride with arylmagnesium halides (12). Addition of stannous chloride to an ether solution of phenylmagnesium bromide at 0° produced a deep red-brown solution which was stirred for one hour at room temperature and then hydrolyzed by adding small pieces of ice. Benzene was added and a gold colored solution resulted. The benzene layer was separated and the yellow diphenyltin precipitated upon the addition of absolute alcohol. The yield was sixty-four per cent. Freshly prepared samples of diphenyltin were monomolecular, but polymerization took place upon standing. Diphenyltin melted in a capillary tube at 130° to give a dark red liquid which decomposed into metallic tin at 205°.

In a like manner, di-p-tolyl-, di-p-xylyl- and di-α-naphthyltin were prepared, and they were all very similar to diphenyltin. Treatment with bromine gave the corresponding diaryltin dibromides and oxidation gave the corresponding diaryltin oxides. The stability toward oxygen increased in the order phenyl, p-tolyl, p-xylyl, α-naphthyl. They all reduced alcoholic silver nitrate instantly. Diphenyltin was converted to triphenyltin when heated at 100° in the presence of excess phenylmagnesium bromide. The other diaryltin compounds did not undergo this transformation.

Dicyclohexyltin (13) has been prepared from the reaction

(12) Krause and Becker, Ber., 53, 173 (1920).

(13) Krause and Pohland, Ber., 57, 532 (1924).

between stannous chloride and cyclohexylmagnesium bromide. It was found to be unusually stable and very similar in its properties and reactions to the diaryltin compounds. A unique reaction occurred with excess cyclohexyl bromide to give di-cyclohexyltin dibromide and an oil which was probably di-cyclohexyl.

Chambers and Scherer (14) investigated the reduction of diphenyltin dichloride by two atoms of sodium in liquid ammonia solution and found that an insoluble yellow powder was obtained. It decomposed without melting at 206°, added bromine to give diphenyltin dibromide and oxidized slowly in air to yield diphenyltin oxide. These properties suggested that it was probably a polymer of diphenyltin.

The addition of four atoms of sodium to diphenyltin dichloride in liquid ammonia gave disodium diphenyltin. Treatment of the disodium compound with ammonium bromide gave diphenyltin dihydride which decomposed above the temperature of liquid ammonia into hydrogen and diphenyltin. The general appearance of this sample of diphenyltin was very similar to the diphenyltin which had been prepared by the addition of two atoms of sodium to diphenyltin dichloride. However, it was much more soluble and sensitive toward air. It was monomolecular in benzene solution, but was not as reactive toward oxygen as the monomolecular diphenyltin which Krause and Becker (13) prepared

(14) Chambers and Scherer, J. Am. Chem. Soc., 48, 1054 (1926).

from phenylmagnesium bromide.

Divalent organolead radicals have been found to be very unstable, and only diphenyl- and di-*p*-tolyllead have been isolated. However, the electrolytic reduction of a sulfuric acid solution of acetone using a lead cathode gave a dark red oil which probably contained an appreciable amount of di-isopropyllead (15). The oil was very sensitive toward oxygen, and treatment with bromine gave both tri-isopropyllead bromide and di-isopropyllead dibromide.

The deep red-brown color which is developed at the beginning of reactions between lead chloride and alkyl Grignard reagents has been attributed to the formation of dialkyllead compounds (16). However, Calingaert (17) was not able to isolate any dialkyllead compounds from such reactions. Likewise, Calingaert was unsuccessful in attempts to prepare diethyllead by the reduction of diethyllead dichloride in liquid ammonia solution.

Krause and Reissaus (18) have reported the isolation of diphenyl- and di-*p*-tolyllead from the reaction of lead chloride and the corresponding Grignard reagents. The diaryllead compounds were found to be dark red, amorphous powders which dissolved readily in ether and benzene to produce blood-red colored solutions. Addition of alcohol precipitated the original diaryllead radical unchanged. The molecular weight, determined by the freezing point lowering of a benzene solution, indicated

- (15) Tafel, Ber., 44, 323 (1911).
(16) Grüttner and Krause, Ber., 49, 1415 (1916).
(17) Calingaert, Chem. Rev., 2, 43 (1925).
(18) Krause and Reissaus, Ber., 55, 888 (1922).

simple molecules. Oxidation gave an unidentified four valence lead compound. Iodine added instantly in the cold, and silver nitrate was reduced at once to metallic silver. The diaryllead compounds retained their red color for weeks when protected from light and oxygen. They decomposed upon heating, but the exact manner of decomposition was not ascertained. Diphenyllead lost its color at about 100° when heated in a melting point tube. The decomposition products developed a yellow color at 120° and melted above 200°. There was no appearance of black metallic lead at temperatures as high as 260°. Warming diphenyllead in the presence of excess phenylmagnesium bromide produced triphenyllead and metallic lead. For this reason it was necessary to control the reaction conditions rigorously in order to prepare diphenyllead. In spite of such precautions, the yield was only two grams or three and one-half per cent. The use of a benzene-ether reaction medium increased the yield to three grams. The reverse addition of the Grignard reagent to lead chloride gave a yellow solution and triphenyllead was the only product isolated.

Krause and Reissaus (18) stated that the yield of product varied with different samples of lead chloride, and that only crystalline Kahlbaum lead chloride gave a good yield of product. It was suggested that Kahlbaum lead chloride may contain certain isotopes of lead which are responsible for the formation of diphenyllead.

EXPERIMENTAL

Phenylmagnesium Bromide and Lead Chloride. The procedure of Krause and Reissaus (18) was followed exactly. Phenylmagnesium bromide was prepared in 400 cc. of dry ether from 50 g. (0.318 mole) of bromobenzene and 8 g. (0.329 g. atom) of magnesium. The ether solution was filtered through glass wool into a two liter three-necked flask. The mixture was stirred vigorously throughout the reaction, and a pressure head of nitrogen gas was maintained so that nitrogen passed through the flask quite rapidly whenever a stopper was removed. An ice-salt cooling bath was regulated so that the temperature inside the reaction flask was maintained at 2°. Forty-four grams (0.158 mole) of dry powdered lead chloride was added in 0.3 g. portions over a period of three-quarters of an hour. The reaction mixture developed a deep golden color which gradually darkened, and finally became dark brown after the addition of lead chloride was complete. A dark red-brown color was developed at this stage of the reaction in the experiment conducted by Krause and Reissaus. It was then stirred vigorously for two hours at 0° during which time a small amount of lead precipitated. The mixture was cooled to -10° and hydrolyzed by adding small pieces of ice. The entire reaction mass was then transferred into a large nitrogen filled separatory funnel. Benzene was added and the mixture was shaken thoroughly. The benzene-ether layer was

separated, and the solution was concentrated at reduced pressure under an atmosphere of nitrogen to 50 cc. The resulting orange solution (blood-red in experiments by Krause and Reissaus) was allowed to stand for thirty minutes and was then forced through a sintered filter by means of nitrogen pressure into 50 cc. of absolute alcohol which decolorized the droplets and precipitated a yellow powder. The yellow powder was redissolved in benzene, filtered and then precipitated by adding alcohol. A white crystalline compound was obtained which was dried in a vacuum desiccator and analyzed for lead. The analysis indicated it was triphenyllead with benzene of crystallization.

Anal. Calcd. for $(C_6H_5)_3Pb \cdot C_6H_6$: Pb, 40.1. Found: Pb, 40.0.

This was confirmed by allowing it to stand in air whereupon it lost its benzene and changed to a powder which was identified as triphenyllead (darkens at 160° and melts at 225°).

The reaction was repeated using benzene as the solvent, and the same results were obtained. Running the reaction at -2° instead of $+2^\circ$ gave the same results with no indication whatsoever for the formation of diphenyllead.

An experiment was run at -10° and worked up in the usual manner. There was practically no precipitation of lead, but a light yellow solution was obtained which yielded only traces of triphenyllead. Reaction at -5° gave the same results.

The same reaction at 0° developed a reddish-brown color which changed to orange-red upon hydrolysis. Addition of

alcohol to the concentrated orange-red solution precipitated an orange colored powder. The yield was about 0.5 g. It was dried and gave a lead value of 42.3%. Triphenyllead with benzene of crystallization contains 40.1% lead and diphenyllead with two molecules of benzene of crystallization contains approximately the same percentage. The orange powder was redissolved in benzene and filtered. Alcohol was added and a light yellow powder precipitated. The same process was repeated and a white crystalline compound was obtained which was presumed to be triphenyllead with benzene of crystallization. It is very likely that the small amount of color was due to the presence of a minute amount of diphenyllead.

p-Tolylmagnesium Bromide and Lead Chloride. Seventy grams (0.25 mole) of lead chloride was added in small portions over a period of one hour to an ether solution of p-tolylmagnesium bromide which had been prepared from 85.5 g. (0.50 mole) of p-bromotoluene and 13 g. (0.535 g. atom) of magnesium. The reaction mixture was maintained at -2 to 0° throughout the addition of lead chloride and was stirred for an additional hour at this temperature. After being cooled to -10°, it was hydrolyzed by the addition of small pieces of ice. The entire mixture was transferred to a nitrogen filled separatory funnel and shaken with additional ether. The ether layer was separated and concentrated at reduced pressure to 50 cc. which left a dark red solution. After standing for thirty minutes, about 0.5 g. of an orange powder precipitated. The clear red solution

was filtered away and added dropwise to 50 cc. of absolute alcohol. A small amount of an orange powder was precipitated. This was dissolved in 25 cc. of benzene giving a red solution which was allowed to stand for fifteen minutes. It was filtered, and the filtrate was added dropwise to 25 cc. of alcohol. The precipitated orange powder was filtered off and dried in a nitrogen filled vacuum desiccator over phosphorus pentoxide. Lead analysis showed that it was tri-p-tolyllead.

Anal. Calcd. for $(\text{CH}_3\text{C}_6\text{H}_4)_3\text{Pb}$: Pb, 43.2. Found, Pb, 44.0, 43.8.

The reaction was repeated and a dark red-brown solution resulted after the lead chloride was added. After hydrolysis, the red ether layer was separated and concentrated at reduced pressure to 50 cc. The resulting blood-red solution was allowed to stand for fifteen minutes during which time about a gram of orange colored tri-p-tolyllead settled out. The red solution was filtered, and the filtrate was evaporated to dryness at reduced pressure. The red solid was dissolved in 25 cc. of dry ether. The red solution was filtered and the filtrate was evaporated to dryness at reduced pressure. The red powder was dried in a nitrogen filled vacuum desiccator over phosphorus pentoxide. The dried compound (0.2 g.) was pink and its lead content was 44.7%. Tri-p-tolyllead contains 43.2% lead, and di-p-tolyllead contains 53.3% lead.

Several identical experiments were run and in each case a red solution resulted, but no di-p-tolyllead could be iso-

lated. It was concluded that the amount of di-p-tolyllead formed was too small to allow its separation from tri-p-tolyllead.

Cyclohexylmagnesium Chloride and Lead Chloride. Seventy grams (0.25 mole) of lead chloride was added in small portions to a 400 cc. ether solution of cyclohexylmagnesium chloride (0.5 mole, titration value). The reaction was maintained at a temperature of -2 to 0° during the addition of lead chloride. It was then stirred vigorously for two hours at 0° . After being cooled to -10° , the solution was hydrolyzed by adding small pieces of ice. The entire mixture was transferred to a nitrogen filled separatory funnel and shaken with ether. The red ether layer was separated and concentrated at reduced pressure to 50 cc. The color of the concentrated ether solution was dark red. The color was discharged when the solution was added dropwise to 100 cc. of absolute alcohol, and a reddish-brown precipitate settled upon standing. The liquid was filtered away, and the reddish-brown solid was dissolved in benzene giving a red solution which was allowed to stand for fifteen minutes and was then filtered through a sintered plate into alcohol. This process was repeated and 1 g. of a rose colored compound was obtained. It lost its color very rapidly in air and reduced alcoholic silver nitrate instantly. The rose color changed to yellow at about $80-90^{\circ}$ when the compound was heated in a capillary tube. The yellow compound decomposed at 126° which is the decomposition temperature of tricyclohexyl-

lead. Lead analysis of the rose colored compound indicated that it was a mixture of dicyclohexyllead and tricyclohexyllead.

Anal. Calcd. for $(C_6H_{11})_2Pb$: Pb, 55.6. Found: Pb, 50.6, 51.0.

Tricyclohexyllead contains 45.4% lead. Attempts to separate the two compounds resulted in the isolation of 0.3 g. of tricyclohexyllead and decomposition of the dicyclohexyllead.

Check experiments were not as satisfactory although red solutions were obtained in every experiment. The use of benzene as the reaction medium gave 3 g. of a pink compound which was apparently tricyclohexyllead with one molecule of benzene of crystallization. It was unusually soluble due to the benzene of crystallization. It decomposed at 126° , the decomposition point of tricyclohexyllead.

Anal. Calcd. for $(C_6H_{11})_2Pb \cdot C_6H_6$: Pb, 38.7; C, 53.8; H, 7.3. Found: Pb, 39.0, 39.2; C, 53.0, 53.2; H, 8.0, 8.5.

Calcd. for $(C_6H_{11})_2Pb \cdot 2C_6H_6$: Pb, 39.2; C, 54.4; H, 6.4.

The compound did not reduce alcoholic silver nitrate solution immediately, and it was not very sensitive toward air although it changed to yellow tricyclohexyllead when exposed for several hours to air.

Reactions in Liquid Ammonia Between R_2PbX_2

Compounds and Two Equivalents of Metal

Dicyclohexyllead Dibromide and Sodium. Dicyclohexyllead dibromide was prepared by adding a chloroform solution of

bromine to a chloroform suspension of tricyclohexyllead which had been prepared from lead chloride and cyclohexylmagnesium bromide (19). Two equivalents (0.46 g., 0.02 g. atom) of sodium were added in small pieces to a liquid ammonia suspension of 5.33 g. (0.01 mole) of dicyclohexyllead dibromide. The first addition of sodium produced a black color which remained throughout the addition of metal. After one-half of the liquid ammonia had evaporated, dry ether was added which produced a yellowish-green colored solution. The reaction flask was swept out with nitrogen while the remainder of the ammonia evaporated. The resulting mixture was filtered under nitrogen. The ether insoluble material was extracted with warm benzene, but no product was obtained upon evaporation of the benzene. The benzene insoluble portion was washed with water and then treated with warm ammonium acetate solution which almost completely dissolved it. Treatment of the ammonium acetate solution with potassium dichromate solution gave 3 g. of lead chromate or a 62% conversion of lead in dicyclohexyllead dibromide to lead in lead chromate.

A 59% yield of inorganic lead compounds was obtained using dicyclohexyllead dichloride (19) and two equivalents of sodium under the same conditions as described in the experiment with dicyclohexyllead dibromide.

Diphenyllead Difluoride and Lithium. Diphenyllead difluor-

(19) Krause, Ber., 54, 2060 (1927).

ide was prepared by the addition of an aqueous solution of potassium fluoride to an alcoholic solution of diphenyllead di-iodide (20). Fourteen-hundredths of a gram (0.02 g. atom) of lithium was added to a liquid ammonia suspension of 4 g. (0.01 mole) of diphenyllead difluoride. The solution became red and almost immediately turned black. Ether was added, and the ammonia was allowed to evaporate while a stream of nitrogen was passed through the reaction flask. The resulting mixture was filtered under nitrogen. Upon evaporation of the ether, the filtrate left a trace of triphenyllead. The ether insoluble portion was extracted with chloroform and filtered. The filtrate gave 0.61 g. or 14% of triphenyllead upon evaporation of the chloroform. The chloroform insoluble material was washed with water and then dissolved in ammonium acetate solution. Addition of potassium dichromate solution yielded 1.8 g. of lead chromate or a 56% yield of inorganic lead compounds. There was no indication of metallic lead.

Diphenyllead Dichloride and Lithium. Diphenyllead dichloride was prepared by passing dry hydrogen chloride gas into a benzene solution of tetraphenyllead (21). The addition of 0.14 g. (0.02 g. atom) of lithium to a liquid ammonia suspension of 4.32 g. (0.02 mole) of diphenyllead dichloride

(20) Setzer, Leeper and Gilman, *J. Am. Chem. Soc.*, 61, 1609 (1939).

(21) Gilman and Robinson, *ibid.*, 51, 3112 (1929).

produced a black color immediately. The reaction was worked up in the same manner as the preceding experiment, and the results were essentially the same. The yields of triphenyllead and inorganic lead compounds were 16 and 50%, respectively.

Diphenyllead Dibromide and Lithium. Diphenyllead dibromide was prepared by adding a water solution of sodium bromide to a hot water solution of diphenyllead dinitrate which had been prepared by adding tetraphenyllead to boiling concentrated nitric acid (20). The addition of two equivalents of lithium (0.14 g., 0.02 g. atom) to a liquid ammonia suspension of 5.2 g. (0.01 mole) of diphenyllead dibromide proceeded similarly to the difluoride and dichloride. The products were 2 g. (45.5%) of triphenyllead and about 0.65 g. of lead chromate, or a 20% yield of inorganic lead compounds.

Diphenyllead Di-iodide and Lithium. Diphenyllead diiodide was prepared by adding a water solution of sodium iodide to a hot water solution of diphenyllead dinitrate (20). The addition of 0.14 g. (0.02 g. atom) of lithium to a liquid ammonia suspension of 6.15 g. (0.01 mole) of diphenyllead diiodide gave the same results as the previous reactions. The yields of triphenyllead and inorganic lead compounds were 40 and 30%, respectively.

Diphenyllead Dibromide and Lithium in Ether-Liquid Ammonia. Two equivalents of lithium (0.14 g., 0.02 g. atom) were added to one equivalent (5.2 g., 0.01 mole) of diphenyllead dibromide suspended in a mixture of 100 cc. of liquid

ammonia and 30 cc. of dry ether. The solution was cooled to -80° before the addition of lithium. The blue color, formed by the addition of lithium, was slow in disappearing but as it disappeared a red color was produced which almost immediately turned black. The products isolated were triphenyllead (23%) and inorganic lead compounds (15%).

The reverse addition was tried in which one equivalent of diphenyllead dibromide was added to a -80° cooled ether-liquid ammonia solution of two equivalents of lithium. A red solution resulted which stayed red until almost all the liquid ammonia had evaporated. There was isolated, using the customary procedure, a 37% yield of triphenyllead and a 45% yield of inorganic lead compounds. A check run using 13 g. (0.025 mole) of diphenyllead dibromide and 0.35 g. (0.05 g. atom) of lithium gave 5 g. of triphenyllead (45.5%), 40% inorganic lead compounds and 1 g. of an insoluble organolead compound which was probably impure diphenyllead oxide (10.6%).

Anal. Calcd. for $(C_6H_5)_2PbO$: Pb, 55.0. Found: Pb, 53.2, 53.8.

Treatment of the impure diphenyllead oxide with dilute hydrogen bromide gave lead bromide and an organolead halide which gave tetraphenyllead upon treatment with phenylmagnesium bromide.

The same reaction was tried at the temperature of liquid ammonia. The solution became red as the one equivalent of diphenyllead dibromide was added to the ether-liquid ammonia solution of two equivalents of lithium, but a black color

developed before all the dibromide was added. The products isolated were triphenyllead (40%), inorganic lead compounds and a trace of a compound which was probably diphenyllead oxide.

Addition of 6.5 g. (0.0125 mole) of diphenyllead dibromide to 0.175 g. (0.025 g. atom) of lithium, dissolved in an ether-liquid ammonia solution which had been cooled to -80° , turned the blue solution red and finally black before the addition was completed. An excess of ethyl bromide was added and the ammonia was allowed to evaporate while a stream of nitrogen passed through the reaction flask. The reaction mixture was not worked up in an atmosphere of nitrogen but was filtered in air. The ether filtrate gave 3 g. of a compound which was apparently triphenyllead with ethyl bromide of crystallization.

Anal. Calcd. for $(C_6H_5)_2Pb \cdot C_2H_5Br$: Pb, 37.9. Found: Pb, 38.3, 38.5.

The compound was quite soluble and contained bromine. Triphenyllead powder will not add ethyl bromide. Likewise, powdered triphenyllead will not add benzene, but triphenyllead with benzene of crystallization is formed when triphenyllead is prepared in benzene solution.

The addition of 5.2 g. (0.01 mole) of diphenyllead dibromide to 0.14 g. (0.02 g. atom) of lithium, dissolved in an ether-liquid ammonia solution which had been cooled to -80° , gave the usual black color. Addition of an excess of benzyl chloride to the black colored solution yielded a small amount of triphenylbenzyllead (mixed m.p., 92°) and an unidentified

colored organolead compound which might possibly have been triphenyllead with benzyl chloride of crystallization.

Reactions in Liquid Ammonia Between R_2PbX_2
Compounds and Four Equivalents of Metal

Diphenyllead Dibromide and Lithium. The addition of four equivalents (0.28 g., 0.04 g. atom) of lithium to a liquid ammonia suspension of 5.3 g. (0.01 mole) of diphenyllead dibromide gave a black colored solution with a slight touch of red color. Dry ether was added and the liquid ammonia was allowed to evaporate while a stream of nitrogen was passed through the reaction flask. The ether solution was filtered under nitrogen. The filtrate yielded a small amount of triphenyllead upon evaporation. The ether insoluble material was extracted with chloroform and filtered. Evaporation of the chloroform filtrate left 1.5 g. (34%) of triphenyllead. The chloroform insoluble portion was washed with water and then dissolved in warm ammonium acetate solution. Addition of potassium dichromate solution precipitated about 1 g. of lead chromate or a 31% yield of inorganic lead compounds. There was no evidence for the formation of metallic lead.

The addition of four equivalents (0.28 g., 0.04 g. atom) of lithium to a liquid ammonia suspension of one equivalent (5.3 g., 0.01 mole) of diphenyllead dibromide gave a black solution with a trace of red color. The solution was stirred for thirty minutes and an excess of ethyl bromide was added.

Dry ether was added and the mixture was stirred for an additional hour. After the liquid ammonia had evaporated, the mixture was filtered and washed with ether. The filtrate was evaporated leaving a semi-solid mass which was dissolved in methanol. A trace of oil and 2 g. (43.5%) of triphenylethyllead (mixed m.p., 42°) were obtained upon cooling the methanol solution.

The reverse addition of one equivalent (5.2 g., 0.01 mole) of diphenyllead dibromide to an ether-liquid ammonia solution of four equivalents (0.28 g., 0.01 g. atom) of lithium produced a reddish-black solution. To this solution was added an excess of ethyl bromide. After the liquid ammonia had evaporated, the mixture was filtered. The ether filtrate upon evaporation left an oil which was distilled at 8 mm. The first few drops of oil were diphenyldiethyllead.

Anal. Calcd. for $(C_6H_5)_2Pb(C_2H_5)_2$: Pb, 49.4. Found: Pb, 49.2.

The remainder of the distillate crystallized and proved to be triphenylethyllead (mixed m.p., 42°). Only a trace of inorganic material was isolated from the reaction.

The addition of 5.2 g. (0.01 mole) of diphenyllead dibromide to a liquid ammonia solution of 0.28 g. (0.04 g. atom) of lithium produced a red colored solution which was stirred for five minutes, and then an excess of ethyl bromide was added to it. The red color was discharged and the solution was stirred for fifteen minutes. Dry ether was added and the solu-

tion was stirred for an hour. As soon as the liquid ammonia had evaporated, the mixture was filtered and washed with ether. The ether filtrate left 3 g. of an oil upon evaporation of the ether. Only a trace of triphenylethyllead could be detected in the oil. The main product was diphenyldiethyllead (48%). The boiling point was 160-165°/3 mm., and the index of refraction was 1.6200 at 20°. Möller and Pfeiffer (22) gave a value of 1.5939 for the index of refraction of diphenyldiethyllead at 18° and a value of 1.6435 for the density at 20°. Diphenyldiethyllead was prepared according to the directions of Möller and Pfeiffer and was found to give an index of refraction value of 1.6128 at 18°. The boiling point was 160-162°/3 mm. and the density was 1.6410 at 20°. It was dissolved in ether and cleaved with hydrogen chloride gas to give diethyllead dichloride which gave tetraethyllead when treated with excess ethylmagnesium bromide.

The red solution, obtained from the addition of one equivalent of diphenyllead dibromide to four equivalents of lithium dissolved in liquid ammonia, was stirred for fifteen minutes and then an excess of ethyl bromide was added to it. The reaction was worked up in the customary manner and 2.5 g. of an oil was obtained ($n_D^{20} = 1.6208$). This would correspond to a 59.7% yield of diphenyldiethyllead. A trace of triphenylethyl-

(22) Möller and Pfeiffer, Ber., 49, 2443 (1916).

lead was isolated by fractional crystallization from methanol.

The same reaction, in which the red solution was stirred for thirty minutes before the addition of ethyl bromide, gave 3 g. of oil ($n_D^{20^\circ} = 1.6230$) or a 71.5% yield of diphenyldiethyllead. Check experiments gave 2.5 g. and 2.6 g. of diphenyldiethyllead ($n_D^{20^\circ} = 1.6210$).

A yield of 2.5 g. or 59.7% of diphenyldiethyllead was obtained when the red solution was stirred for forty-five minutes before the addition of ethyl bromide. The yield was only 2.3 g. or 55% when the red solution was stirred for one hour before the addition of ethyl bromide.

Diphenyllead Dibromide and Sodium. The addition of one equivalent (5.2 g., 0.01 mole) of diphenyllead dibromide to a liquid ammonia solution of four equivalents (0.92 g., 0.04 g. atom) of sodium produced a red-purple colored solution which was stirred for thirty minutes, and then an excess of ethyl bromide was added to it. Stirring was continued for fifteen minutes and then dry ether was added. The solution was stirred for an additional hour, and it was filtered as soon as the liquid ammonia had evaporated. The ether filtrate left 2.4 g. of an oil upon evaporation of the ether. This would be a 57.3% yield of diphenyldiethyllead. The oil gave an index of refraction value of 1.6206 at 20°. Cleavage in ether solution by hydrogen chloride gas gave a white solid which gave only tetraethyllead upon treatment with excess ethylmagnesium bromide.

Diphenyllead Dibromide and Potassium. The addition of 5.2 g. (0.01 mole) of diphenyllead dibromide to a liquid ammonia solution of 1.56 g. (0.04 g. atom) of potassium gave a purple colored solution. The purple solution was stirred for thirty minutes and then an excess of ethyl bromide was added. After stirring for fifteen minutes, dry ether was added and the stirring was then continued for an additional hour. The reaction was worked up in the customary manner and only 1 g. of an oil was obtained ($n_D^{20^\circ} = 1.6110$). This would be a 30% yield of diphenyldiethyllead ($n_D^{20^\circ} = 1.6128$).

Diphenyllead Dibromide and Calcium. A brown colored solution was obtained by the addition of 5.2 g. (0.01 mole) of diphenyllead dibromide to a liquid ammonia solution of 0.8 g. (0.02 g. atom) of calcium. The solution was stirred for thirty minutes and an excess of ethyl bromide was added. Ether was added and the reaction was worked up in the usual manner. The oil amounted to 2.2 g. and gave an index of refraction value of 1.6240 at 20°. A small amount of triphenylethyllead was isolated. Cleavage of the oil by hydrogen chloride in ether solution yielded a white solid which gave a mixture of phenyltriethyllead ($n_D^{20^\circ} = 1.5762$) and diphenyldiethyllead ($n_D^{20^\circ} = 1.6140$) upon treatment with excess ethylmagnesium bromide. There was no evidence of tetraethyllead, so the oil apparently contained no appreciable amount of diphenyldiethyllead, but was chiefly triphenylethyllead which would not crystallize. A known sample of triphenylethyllead gave a mixture of phenyl-

triethyllead and diphenyldiethyllead upon cleavage with hydrogen chloride and subsequent treatment with excess ethylmagnesium bromide.

Diphenyllead Dibromide and Strontium. The addition of 5.2 g. (0.01 mole) of diphenyllead dibromide to a liquid ammonia solution of 1.75 g. (0.02 g. atom) of strontium produced a brown solution. It was stirred for thirty minutes, treated with ethyl bromide, and then worked up in the same manner as the preceding calcium experiment. The resulting 2.2 g. of oil gave an index of refraction value of 1.6270 at 20°. Hydrogen chloride cleavage and subsequent treatment with excess ethylmagnesium bromide gave a mixture of phenyltriethyllead and diphenyldiethyllead indicating the oil was chiefly triphenylethyllead.

Diphenyllead Dibromide and Barium. A black colored solution was formed by the addition of 5.2 g. (0.01 mole) of diphenyllead dibromide to a liquid ammonia solution of 2.74 g. (0.02 g. atom) of barium. Treatment of the black solution with ethyl bromide in the customary manner gave 1 g. of oil which had an index of refraction value of 1.6280 at 20°. Cooling a methanol solution of the oil precipitated 0.2 g. of triphenylethyllead (mixed m.p., 42°), but the remainder would not crystallize. Hydrogen chloride cleavage and subsequent treatment with excess ethylmagnesium bromide did not give enough liquid to separate the products. The first few drops of distillate were phenyltriethyllead ($n_D^{20} = 1.5770$).

Diphenyllead Di-iodide and Lithium. The addition of 12.3 g. (0.02 mole) of diphenyllead di-iodide slowly discharged the blue color of a -80° cooled ether-liquid ammonia solution of 0.55 g. (0.08 g. atom) of lithium and formed a red colored solution. After stirring the solution for thirty minutes, an excess of ethyl bromide was added. The ether solution was filtered after the liquid ammonia had evaporated. Evaporation of the ether filtrate left 4.2 g. of oil which gave an index of refraction value of 1.6210 at 20° .

Anal. Calcd. for $(C_6H_5)_2Pb(C_2H_5)_2$: Pb, 49.4. Found: Pb, 49.2.

The oil distilled at $170-175^{\circ}/5$ mm., and the distillate gave an index of refraction value of 1.6222 at 20° and a density of 1.6400 at 20° . The lead percentages were now 48.0 and 48.9.

A check run using 5.2 g. of diphenyllead di-iodide gave 2.4 g. of oil which had an index of refraction value of 1.6222 at 20° . Cooling a methanol solution of the oil induced 0.3 g. of triphenylethyllead to crystallize. The remainder of the oil was probably diphenyldiethyllead.

The reverse addition of four equivalents (0.28 g., 0.04 g. atom) of lithium to a liquid ammonia suspension of one equivalent (6.2 g., 0.01 mole) of diphenyllead di-iodide produced a black colored solution. Addition of an excess of benzyl chloride yielded 2.7 g. (25%) of triphenylbenzyllead (mixed m.p., 93°).

Diphenyllead Difluoride and Lithium. Addition of 4 g. (0.01 mole) of diphenyllead difluoride to a liquid ammonia solution of 0.28 g. (0.04 g. atom) of lithium and subsequent treatment with ethyl bromide in the usual manner gave 2 g. of an oil which had an index of refraction value of 1.6195 at 20°. This would be a 48% yield of diphenyldiethyllead ($n_D^{18^\circ} = 1.6128$).

Diphenyllead Dichloride and Lithium. Treatment of the red solution, formed from the addition of 4.32 g. (0.01 mole) of diphenyllead dichloride to a liquid ammonia solution of 0.28 g. (0.04 g. atom) of lithium, with excess ethyl bromide in the customary manner gave 2.3 g. of an oil which had an index of refraction value of 1.6198 at 20°. This would be a 55% yield of diphenyldiethyllead ($n_D^{18^\circ} = 1.6128$).

Since the index of refraction values did not check those of known samples of diphenyldiethyllead very well, a large scale experiment was run to ascertain the exact nature of the oil which was obtained from reactions between diphenyllead dihalides and four equivalents of metal.

One equivalent (13 g., 0.03 mole) of diphenyllead dichloride was added over a period of fifteen minutes to 300 cc. of a liquid ammonia solution of four equivalents (0.84 g., 0.12 g. atom) of lithium. The red solution was stirred for fifteen minutes and an excess of ethyl bromide was added. Dry ether was then added and stirring was continued for an additional hour. After the liquid ammonia had evaporated, the mixture was filtered. The filtrate was evaporated and the 6 g. of

oil was combined with the oil from five similar runs making a total of about 35 g. of oil. The oil was fractionated at 2 mm. from a good column into seven fractions. The boiling point ranged from 50-175°/2 mm., and the index of refraction values at 20° increased from 1.5200 to 1.6420. The seven fractions were divided into three fractions according to their refractive index values. The first group contained all fractions which had an index of refraction below 1.6000, and the second group contained those fractions which had an index of refraction value above 1.6300. The fractions possessing intermediate values comprised the third group and contained the largest amount of liquid. Fractionation of this group was effected over a range of 108-175°/2-3 mm. with the majority of liquid distilling at 160-170°/2-3 mm. Refractionation of this portion gave 15 g. (20% yield) of diphenyldiethyllead, b.p., 158-161°/2 mm.

Anal. Calcd. for $(C_6H_5)_2Pb(C_2H_5)_2$: Pb, 49.4; $n_D^{18^\circ} = 1.6128$; $d^{20^\circ} = 1.6410$. Found: Pb, 49.3, 49.3; $n_D^{20^\circ} = 1.6150$; $d^{20^\circ} = 1.6401$.

The found value for the refractive index is probably more accurate than those previously reported since other samples of diphenyldiethyllead were not fractionated as well as this particular sample.

Refractionation of the second group, the triphenylethyllead fraction, gave a small amount of diphenyldiethyllead and 6 g. of triphenylethyllead (mixed m.p., 42°). This would

account for a 7.2% conversion of lead in diphenyllead dichloride to lead in triphenylethyllead.

Refractionation of the first group gave 1 g. (1.7%) of tetraethyllead which boiled at 60°/4 mm. and had an index of refraction of 1.5200 at 20° ($n_D^{20} = 1.5198$) and 2 g. (3.0%) of phenyltriethyllead which boiled at 115-116°/3 mm.

Anal. Calcd. for $C_{12}H_{18}Pb(C_6H_5)_2$: Pb, 55.8; $n_D^{20} = 1.5762$.
Found: Pb, 56.0, 56.2; $n_D^{20} = 1.5730$.

The ether insoluble material from the combined runs was washed with water and dried. The dried powder was washed with chloroform and then treated with warm ammonium acetate solution. Two grams of a brown-gray powder did not dissolve. Heating the powder gave lead oxide and lead. The powder was probably a mixture of insoluble organolead compounds and metallic lead which could not be separated. Treatment of the ammonium acetate solution with potassium dichromate solution precipitated 15 g. of lead chromate which corresponded to a 26% yield of inorganic lead compounds.

Summarizing, one equivalent of diphenyllead dibromide and four equivalents of lithium upon treatment with ethyl bromide gave 35 g. of an oil (46.5%, based on diphenyldiethyllead) and a 26% yield of inorganic lead compounds. The oil was separated into 1 g. of tetraethyllead, 3 g. of phenyltriethyllead, 6 g. of triphenylethyllead and 15 g. of diphenyldiethyllead. This would indicate that a 20% yield of dilithium diphenyllead had been prepared.

A crude yield of 32 g. of oil was obtained from the addition of ethyl bromide to the red solution which had been prepared from one equivalent of diphenyllead dichloride and six equivalents of lithium. The experiment was performed in exactly the same manner as the previous one with four equivalents of lithium. Fractionation of the oil gave 5.5 g. (9.5%) of tetraethyllead, 2 g. (3.0%) of phenyltriethyllead, 6.5 g. (7.7%) of triphenylethyllead and 9 g. (12%) of diphenyldiethyllead.

Triphenyllead and Three Equivalents of Sodium. One equivalent (4.38 g., 0.01 mole) of triphenyllead (23) was added to a liquid ammonia solution of three equivalents (0.69 g., 0.03 g. atom) of sodium. The blue solution was stirred for one hour and then treated with excess ethyl bromide. Dry ether was added and the reaction was worked up in the customary manner to give 3.2 g. of an oil which crystallized from a methanol solution. Three grams (64.5%) of pure triphenylethyllead was isolated (mixed m.p., 42°).

Dilithium Diphenyllead and Ammonium Bromide. Dilithium diphenyllead was prepared by adding 10.4 g. (0.02 mole) of diphenyllead dibromide to a liquid ammonia solution of 0.56 g. (0.08 g. atom) of lithium. The reddish-black solution was stirred for thirty minutes and 3.84 g. (0.04 mole) of ammonium bromide was added in small amounts. A deep red color developed during the early stages of the addition, but the solution

(23) Gilman and Bailie, J. Am. Chem. Soc., 61, 731 (1939).

turned black before all the ammonium bromide was added. The reaction flask was connected to a gas burette and 59 cc. of gas was collected. The gas consisted of 0.5 cc. of unsaturates and 58.5 cc. of hydrogen (13%). The presence of hydrogen could not be found in numerous check runs so it was probably formed in this reaction from free lithium and ammonium bromide. Ether was added to the black solution and the liquid ammonia was allowed to evaporate while a stream of nitrogen was passed through the flask. The mixture was filtered under nitrogen. The residue was extracted with chloroform and the extracts were combined with the ether filtrate. Removal of the solvent left 1.3 g. (15%) of triphenyllead. There was no indication of the formation of metallic lead, but a considerable amount of inorganic lead compounds was formed.

The addition of 1.92 g. (0.02 mole) of ammonium bromide to a reddish-black colored liquid ammonia solution of dilithium diphenyllead (0.02 mole) produced a deep red colored solution which stayed red for about fifteen minutes after the ammonium bromide had been added and then turned black. No hydrogen was found. The only products were triphenyllead and inorganic lead compounds.

The addition of 0.48 g. (0.005 mole) of ammonium bromide to a reddish-black liquid ammonia solution of dilithium diphenyllead (0.01 mole) produced a deep red colored solution which was filtered through a sintered plate. The red color

changed to black before all the ammonia had evaporated. The only products were triphenyllead and inorganic lead compounds. Numerous check runs gave the same results. Reactions cooled at -80° gave essentially the same results. No hydrogen was evolved at any time during the reaction.

Attempted Isolation of Dilithium Diphenyllead. Filtration of the reddish-black solutions of dilithium diphenyllead, prepared by the addition of one equivalent of diphenyllead dibromide to a liquid ammonia solution of four equivalents of lithium, gave a clear red solution which turned black after most of the liquid ammonia had evaporated. Addition of ether, benzene or tri-n-butyl amine did not stabilize the red color. Treatment of the filtered red solution with ethyl bromide gave an oil which consisted largely of diphenyldiethyllead although a small amount of triphenylethyllead was isolated. The black precipitate consisted mainly of inorganic lead compounds and a small amount of triphenyllead.

Dilithium Diphenyllead and Diphenyllead Dibromide. Dilithium diphenyllead was prepared by the addition of 5.2 g. (0.01 mole) of diphenyllead dibromide to a liquid ammonia solution of 0.28 g. (0.04 g. atom) of lithium. The reddish-black solution was stirred for thirty minutes and cooled to -80° . The addition of 5.2 g. (0.01 mole) of diphenyllead dibromide produced a black color and gave 4 g. (45.5%) of triphenyllead and a considerable amount of inorganic lead compounds.

Reduction of Diphenyllead Dihalides by Hydrogen. A

petroleum ether suspension of the diphenyllead dihalides (0.0025 mole) was shaken for one hour with 2 g. of palladium catalyst in the presence of hydrogen at atmospheric pressure. Only diphenyllead di-iodide gave any evidence of reaction. Triphenyllead was reduced completely to benzene and inorganic lead compounds. The catalyst was prepared by adding 1 g. of palladium chloride to a water suspension of 50 g. of freshly precipitated calcium carbonate. Warming the solution precipitated palladium in a finely divided state. The suspension was filtered, washed free of chlorides, dried and powdered (24).

Treatment of a petroleum ether suspension of the diphenyllead dihalides (0.0025 mole) with 2 g. of catalyst in the presence of hydrogen at 30 lbs. pressure for one hour gave benzene and probably lead halides. Diphenyllead di-iodide formed biphenyl instead of the expected benzene, probably due to the decomposition of this unstable organolead halide. The extent of the reaction was measured by the amount of lead chromate isolated after adding potassium dichromate solution to an ammonium acetate solution of the residue from the reaction. Diphenyllead di-iodide gave a quantitative yield of lead chromate, diphenyllead dibromide was reduced approximately 50% and diphenyllead dichloride and difluoride reacted almost as well as the dibromide. The values did not check (24) Busch and Stöve, Ber., 49, 1063 (1916).

very consistently for the bromides, chlorides and fluorides. A larger scale experiment was run in order to identify benzene. A petroleum ether (b.p., 90-115°) suspension of 10.4 g. (0.02 mole) of diphenyllead dibromide was shaken for twenty-four hours with 10 g. of catalyst in the presence of hydrogen at 30 lbs. pressure. The reaction mixture was filtered, and washed with petroleum ether. The filtrate was nitrated and approximately 1 g. of *m*-dinitrobenzene (mixed m.p., 90°) was obtained. The residue from the reaction was treated with warm ammonium acetate solution and filtered. Addition of potassium dichromate solution to the filtrate precipitated 3 g. of lead chromate (47%).

There was no evidence for the formation of diphenyllead which might be formed from the decomposition of diphenyllead dihydride. The solutions were never colored red.

Shaking the diphenyllead dihalides (0.0025 mole) for twenty-four hours with 2 g. of palladium catalyst in the presence of hydrogen at 30 lbs. pressure allowed complete reduction. Raney nickel (25) also gave complete reduction under these conditions. The use of Raney nickel as the catalyst produced inconsistent results when the reaction was run for one hour only.

Triphenyllead halides behaved similarly and were completely reduced after one hour of shaking at 30 lbs. pressure.

(25) Covert and Adkins, J. Am. Chem. Soc., 54, 4116 (1932).

Diphenyllead Dichloride and Aluminum. A mixture of 8.6 g. (0.02 mole) of diphenyllead dichloride, 50 cc. of two normal sodium hydroxide and 3 g. of 200 mesh activated aluminum was heated by means of a water bath for two hours. The diphenyllead dichloride was recovered unchanged. Activated lead and zinc were also used without success. The aluminum was activated by heating in alkali, the lead by heating in dilute nitric acid and the zinc by treating with hydrochloric acid.

Diethyllead dichloride and triphenyllead chloride did not react, but triethyllead chloride gave a red-yellow oil which was probably triethyllead since Hein and Klein (26) have prepared triethyllead in this manner.

Diphenyllead Dichloride and Hydrazine Hydrate. An ether suspension of 8.6 g. (0.02 mole) of diphenyllead dichloride, 3 g. (0.04 mole) of hydrazine hydrate and 3.5 g. of sodium carbonate was refluxed for two hours but no appreciable reaction occurred. Under the same conditions, 9.4 g. (0.02 mole) of triphenyllead chloride gave 0.1 g. (9.7%) of tetraphenyllead (mixed m.p., 225°). There was no indication of the formation of triphenyllead. The same reaction at 0° gave only a trace of tetraphenyllead. Reaction at room temperature without sodium carbonate produced about 0.1 g. of tetraphenyllead but no triphenyllead.

Lead Mercaptide and Phenyllithium. Lead mercaptide (27)

(26) Hein and Klein, Ber., 71, 2361 (1938).

(27) Borgstrom, Ellis and Reid, J. Am. Chem. Soc., 51, 3649 (1929).

was prepared by adding an alcoholic solution of ethyl mercaptide to a warm 50% alcoholic solution of 1/4 molar lead acetate. The solution was heated to boiling and the lead mercaptide crystallized upon being cooled. The crystals were filtered and recrystallized from chloroform. To an ether solution of phenyllithium (0.05 mole), cooled in an ice-salt bath, was added 8.3 g. (0.025 mole) of lead mercaptide. After thirty minutes of stirring, the reaction mixture began to darken, and it was black at the end of six hours. The reaction was hydrolyzed and filtered under nitrogen. The yellow ether filtrate left 2 g. of a yellow oil and 0.1 g. of a white solid upon removal of the ether. The white solid was extracted with a small amount of hot alcohol. The alcohol was evaporated and 0.06 g. of solid was left which darkened at 160° and melted at 200-225°. It was apparently a mixture of triphenyllead and tetraphenyllead. Pure tetraphenyllead (mixed m.p., 225°) was obtained from the mixture after several recrystallizations from alcohol.

The yellow liquid turned black upon distillation due to dissolved quantities of triphenyllead since traces of tetraphenyllead and metallic lead were found in the residue. The distillate amounted to 1.1 g. of an almost colorless oil which boiled at 148-152° and gave an index of refraction value of 1.5076 at 20°. Diethyl disulfide boils at 153° and has an index of refraction value of 1.5063 at 20°. It probably is formed by the oxidation of ethyl mercaptan

or lithium mercaptide.

The residue which was obtained from the filtration of the original reaction mixture was chiefly unreacted lead mercaptide, but small amounts of tetraphenyllead and 0.3 g. (11.5%) of metallic lead were isolated.

DISCUSSION OF RESULTS

All attempts to prepare diphenyllead from lead chloride and phenylmagnesium bromide, using the exact directions of Krause and Reissaus (18) were unsuccessful. A red colored solution was not obtained when the reaction was run at the specified 2°. The best temperature for obtaining a red colored solution was found to lie between -2 and 0°. The colors exhibited, both in the solutions and in the solids, were probably due to small amounts of divalent organolead radicals, but the yields were so small that a satisfactory separation from trivalent organolead compounds could not be effected.

The unusual stability of tricyclohexyllead (13) suggested the possibility that dicyclohexyllead might be stable enough to permit isolation. Cyclohexylmagnesium chloride and lead chloride gave a mixture of tricyclohexyllead and dicyclohexyllead which could not be separated.

At the present time there is no account where anyone has checked the preparation of diphenyllead. Another worker in these laboratories obtained a red solution and a small amount of red solid which was not analyzed. However, in a repeat run, he was unable to obtain a red colored solution. It is quite likely that Krause and Reissaus did prepare diphenyllead. However, they were unable to consistently obtain good results and stated that it was necessary to use Kahlbaum crystalline

lead chloride. No experiments were tried using Kahlbaum lead chloride in these laboratories. The use of benzene as the reaction medium always gave compounds which appeared to have benzene of crystallization. It is odd that Krause and Reissaus did not obtain diphenyllead with benzene of crystallization when benzene was used as the reaction solvent. Triphenyllead is isolated with benzene of crystallization under such conditions (18), and it is to be expected that diphenyllead would exhibit this tendency to even a greater extent.

It is certain that the reaction between lead chloride and phenylmagnesium bromide is of no value as a preparation for large amounts of diphenyllead for reaction studies. It might be that the use of a highly electronegative radical or the use of a large molecule would allow isolation of the divalent organolead radicals from the reaction between lead chloride and Grignard reagents.

The success of liquid ammonia reactions in the preparation of divalent organotin radicals and the fact that organolead halides are not ammonolyzed in liquid ammonia led to the investigation of the reduction of diphenyllead dihalides in liquid ammonia as a means of preparing diphenyllead. The expected reaction, $(C_6H_5)_2PbX_2 + 2M \longrightarrow (C_6H_5)_2Pb + 2MX$, either did not take place or more likely occurred, and the diphenyllead reacted further. It is possible that diphenyllead is decomposed in liquid ammonia. Decomposition of diphenyllead to triphenyllead and metallic lead did not occur unless the

metallic lead reacted with some of the substances to give inorganic lead compounds, because no metallic lead was isolated in the reactions.

Addition of two equivalents of alkali metals to one equivalent of diphenyllead dihalides in liquid ammonia produced a black colored solution which yielded triphenyllead and inorganic lead compounds upon evaporation of the liquid ammonia. There was some indication for the formation of very small amounts of diphenyllead oxide in a few experiments, supposedly due to oxidation of diphenyllead. Addition of ethyl bromide to the black colored liquid ammonia solutions gave a compound which appeared to be triphenyllead with ethyl bromide of crystallization.

The addition of four equivalents of lithium to diphenyllead dihalides in liquid ammonia yielded black colored solutions which gave triphenyllead and inorganic lead compounds upon evaporation of the liquid ammonia. Treatment of the black colored liquid ammonia solutions with ethyl bromide and benzyl chloride produced triphenylethyllead and triphenylbenzyllead, respectively. These reactions are characteristic of lithium triphenyllead (28).

The reverse addition of one equivalent of diphenyllead dihalides to four equivalents of lithium dissolved in liquid ammonia yielded red solutions which gave chiefly inorganic

(28) Unpublished studies by Mr. R. W. Leeper of these laboratories.

lead compounds and a small amount of triphenyllead upon evaporation of the liquid ammonia. Treatment of the red colored liquid ammonia solutions with ethyl bromide gave inorganic lead compounds and an oil which was about sixty per cent diphenyldiethyllead. The oil also contained twenty-five per cent triphenylethyllead, eight per cent phenyltriethyllead and four per cent tetraethyllead. It is assumed that the chief reaction was the formation of dilithium diphenyllead which reacted with ethyl bromide to give diphenyldiethyllead. The results of these reactions are summarized in Table I. The diphenyllead

TABLE I

Reactions of Diphenyllead Dihalides, Lithium and Ethyl Bromide

<u>Diphenyllead dihalide</u>	<u>Yield of oil</u>	<u>n_D^{20}</u>
Diphenyllead di-iodide	2.4 g.	1.6222
Diphenyllead dibromide	2.5 g.	1.6210
Diphenyllead dichloride	2.3 g.	1.6198
Diphenyllead difluoride	2.0 g.	1.6195

dihalides (0.01 mole) were added to four equivalents of lithium (0.04 mole) dissolved in liquid ammonia, and the resulting red solutions were stirred for thirty minutes and then an excess of ethyl bromide was added to it. The resulting oils were chiefly diphenyldiethyllead which has an index of refraction of 1.6128 at 18°. It is apparent that diphenyllead dibromide and diphenyllead dichloride are the best halides to use in the

preparation of dilithium diphenyllead based on both yield and purity of product. Lithium and sodium are the best metals to use in the preparation of R_2PbM_2 compounds. This is shown in Table II which gives the results of the addition of diphenyl-

TABLE II

Reactions of Diphenyllead Dibromide, Metals and Ethyl Bromide

<u>Metal</u>	<u>Color of Solution</u>	<u>Yield of Oil</u>	<u>n_D^{20}</u>
Lithium	red	2.5 g.	1.6210
Sodium	red-purple	3.4 g.	1.6206
Potassium	purple	1.0 g.	1.6110
Calcium	brown	2.2 g.	1.6240
Strontium	brown	2.2 g.	1.6270
Barium	black	1.0 g.	1.6280

lead dibromide (0.01 mole) to liquid ammonia solutions of various metals. The resulting solutions were stirred for thirty minutes and then an excess of ethyl bromide was added. The oil from lithium, sodium and potassium was chiefly diphenyl-diethyllead. The oil from calcium, barium and strontium was mainly triphenylethyllead.

The mechanism of the reaction between diphenyllead dihalides and four equivalents of lithium is not understood. The addition of lithium to the dihalides must have formed lithium triphenyllead since treatment with ethyl bromide gave triphenylethyllead. Diphenyllead may be formed and then de-

composes to triphenyllead since the addition of lithium develops a red color which almost immediately turns black. There is always an excess of dihalide and apparently the initially formed diphenyllead decomposed before enough lithium could be added to give the dilithium addition compound. The lithium at the end of the reaction added to triphenyllead to give lithium triphenyllead. The manner of decomposition of diphenyllead is not known. It is apparently changed to triphenyllead and complex inorganic lead compounds in liquid ammonia.

The reverse addition of one equivalent of the diphenyllead dihalides to four equivalents of lithium proceeds in a different manner. There is always a large excess of lithium and the initially formed diphenyllead adds lithium to give dilithium diphenyllead. This is the chief reaction since treatment of the red solution with ethyl bromide gives an oil which is sixty per cent diphenyldiethyllead (20% yield). Side reactions occur since the oil also contains triphenylethyllead (7.2% yield), phenyltriethyllead (3.0%) and tetraethyllead (1.7%). Random interchange (29) does not seem likely since no catalyst was present to effect such an equilibrium reaction, and the yields of product were not present in the amounts required by an interchange reaction. Furthermore, no tetraphenyllead could be isolated.

A possible explanation is the partial disproportionation

(29) Calingaert and Beatty, J. Am. Chem. Soc., 61, 2748 (1939).

of dilithium diphenyllead to give lithium triphenyllead and trilithium phenyllead. Treatment of these compounds with ethyl bromide should give the same per cent yields of triphenylethyllead and phenyltriethyllead. Actually, the yield of triphenylethyllead is more than twice the yield of phenyltriethyllead. The high yield of triphenylethyllead could be due to decomposition of the initially formed diphenyllead (p. 127), and the low yield of phenyltriethyllead could be due to disproportionation of trilithium phenyllead into dilithium diphenyllead and tetralithium lead which would account for the formation of tetraethyllead upon treatment with ethyl bromide. Cleavage of trilithium phenyllead by lithium to give tetralithium lead and phenyllithium would also account for the formation of tetraethyllead. Phenyllithium would react with the liquid ammonia to give benzene and lithium amide.

Cleavage reactions could account for other products of the reaction. For example, the main reaction could be the formation of lithium triphenyllead (p. 127) followed by successive cleavages to give the various lithium-lead compounds which would react with ethyl bromide to yield the phenylethyllead compounds. It is very unlikely that lithium triphenyllead is cleaved by lithium to yield dilithium diphenyllead, because sodium triphenyllead is not cleaved by sodium in liquid ammonia.

If dilithium diphenyllead is cleaved by lithium then the

use of six equivalents of lithium instead of four equivalents of lithium should lower the yield of dilithium diphenyllead and increase the yields of trilithium phenyllead and tetralithium lead. Treatment of the lithium-phenyl compounds, prepared from the addition of one equivalent of diphenyllead dichloride to six equivalents of lithium in liquid ammonia, with excess ethyl bromide gives triphenylethyllead (7.7%), diphenyldiethyllead (12%), phenyltriethyllead (3.0%) and tetraethyllead (9.5%). The yield of diphenyldiethyllead was reduced eight per cent and the combined yields of phenyltriethyllead and tetraethyllead were increased seven and eight-tenths per cent which would indicate that cleavage of dilithium diphenyllead may have occurred.

Diphenyltin dihydride is unstable and decomposes into diphenyltin and hydrogen (14). The corresponding reaction was tried with lead compounds but no hydrogen was evolved at any time during the preparation of dilithium diphenyllead, during the addition of ammonium bromide or during the evaporation of liquid ammonia. Hydrogen was evolved in one reaction, but this was apparently due to a bad preparation of dilithium diphenyllead in which some excess lithium reacted with the ammonium bromide to liberate hydrogen. The addition of small amounts of ammonium bromide to dilithium diphenyllead produced a blood-red colored solution, but only triphenyllead and inorganic lead compounds could be isolated. This reaction is very similar to the addition of ammonium bromide to sodium

triphenyllead (23). It is still a matter of speculation whether the highly unstable organolead hydrides can be formed, even as intermediates.

The addition of R_2SnX_2 compounds to R_2SnNa_2 compounds yielded R_2Sn compounds (14), but the addition of diphenyllead dibromide to dilithium diphenyllead gave only triphenyllead and inorganic lead compounds.

Attempts to prepare diphenyllead dihydride, or its decomposition product diphenyllead, by the reduction of diphenyllead dihalides with hydrogen and catalyst were unsuccessful. Benzene and inorganic lead compounds were the usual products of the reaction, perhaps due to cleavage of the organolead compounds by the hydrogen halide formed in the reaction. The catalyst was suspended on calcium carbonate, and it was hoped that the hydrogen halide would react first with the calcium carbonate.

Hein and Klein (26) have prepared triethyllead by the reduction of triethyllead chloride with aluminum, lead or zinc. Attempts to prepare divalent organolead compounds by the reduction of organolead dihalides with aluminum, lead or zinc did not work because the dihalides would not react.

Treatment of diphenyllead dichloride with hydrazine hydrate in boiling alcohol gives tetraphenyllead (30). The possibility of the intermediate formation of diphenyllead led to an investigation of the reaction at lower temperatures. No appreciable reaction occurred between diphenyllead dichloride and hydrazine

(30) Gilman and Barnett, Rec. trav. chim., 55, 563 (1936).

hydrate in refluxing ether solution. There was no evidence for the intermediate formation of triphenyllead in reactions between triphenyllead chloride and hydrazine hydrate in ether solution at 0° or at the refluxing temperature of ether. Only small yields of tetraphenyllead were isolated.

The ethoxide groups of ethyl borate can be replaced by R groups of organometallic compounds to produce organoboron compounds (31). The close similarity of sulfur to oxygen suggested the possibility of replacing the mercaptide radicals in lead mercaptide by R groups to form R_2Pb compounds. Lead mercaptide was chosen instead of lead ethoxide because it is stable and easily prepared. Lead mercaptide was added to an ether solution of phenyllithium, cooled in an ice-salt bath. The expected reaction, $Pb(SC_2H_5)_2 + 2C_6H_5Li \longrightarrow (C_6H_5)_2Pb + 2LiSC_2H_5$, took place but did not stop at the diphenyllead stage. Diphenyllead was decomposed to triphenyllead, tetraphenyllead and metallic lead.

(31) Frankland and Duppa, Ann., 115, 319 (1860).

SUMMARY

The literature of divalent organometallic radicals of germanium, tin and lead has been reviewed.

Attempts to prepare divalent organolead radicals by reactions of Grignard reagents with lead chloride were unsuccessful.

Reactions of the diphenyllead dihalides with metals in liquid ammonia solution were investigated. The addition of one equivalent of diphenyllead dibromide to a liquid ammonia solution of four equivalents of lithium yielded dilithium diphenyllead which gave diphenyldiethyllead upon treatment with ethyl bromide.

Miscellaneous attempted preparations of diphenyllead included reduction of diphenyllead dihalides by catalytic hydrogenation, hydrazine hydrate and aluminum metal.

Reaction of lead mercaptide with phenyllithium probably involved the intermediate formation of diphenyllead, but only triphenyllead, tetraphenyllead and metallic lead were isolated.