

# METHODS OF PREPARATION OF ORGANOMETALLIC COMPOUNDS

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*Received July 12, 1954*

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## I. INTRODUCTION

In this review an effort has been made to collect and to discuss briefly all the reactions which have been used to synthesize organometallic compounds. For

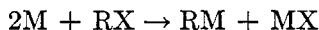
the purpose of this discussion all of the elements exclusive of the noble gases, the halogens, hydrogen, carbon, nitrogen, oxygen, phosphorus, and sulfur are considered as metals. Stable organometallic derivatives of only about half of the metals are known. The distinguishing feature of any organometallic compound is the carbon-to-metal bond. Many different reactions have been used to effect the formation of carbon-metal bonds. Some of the reactions are highly specialized, whereas others are very general and are applicable to the preparation of many different kinds of organometallic compounds. Because of the very broad scope of this subject, each reaction and method cannot be considered in detail, and all of the pertinent references cannot be included. The examples and references have been chosen only to illustrate types of reactions.

The preparative methods have been classified under twenty-eight subheadings as listed in the table of contents. Three main headings have been chosen: (1) methods involving free metals, (2) the preparation of organometallic compounds from metal salts, and (3) their preparation from other organometallic compounds of the same metal (interconversion methods). An attempt has been made to include under each subheading a discussion of, or at least a reference to, organometallic compounds of each metal to which the type reaction has been applied. Table 1 (see page 875) presents in summary the methods as they have been applied to each of the metals and serves as a convenient cross reference.

## II. PREPARATION OF ORGANOMETALLIC COMPOUNDS BY METHODS INVOLVING FREE METALS

### *A. Reactions of metals with organic halides*

Although it cannot be applied to all metals, the reaction



is perhaps the most fundamental one in organometallic chemistry. Upon it depend the syntheses, either directly or indirectly, of almost all organometallic compounds.

The reaction between lithium and organic halides is a general method for preparing RLi compounds. Grosse (182) prepared triphenylmethyllithium from 0.5 per cent lithium amalgam and triphenylmethyl chloride in ether solution. Ziegler and Colonius (464) obtained good yields of phenyllithium from lithium and iodo- or bromobenzene and of *n*-butyllithium from lithium and *n*-butyl halides in various solvents. Other studies (109, 170, 171) established the reaction as one of choice for preparing ether solutions of a large number of RLi compounds.

Metallic sodium reacts with organic chlorides under carefully controlled conditions to give satisfactory yields of RNa compounds. *n*-Amylsodium was obtained from *n*-amyl chloride and sodium sand in petroleum ether (142, 332, 336). Chlorobenzene and *p*-chlorotoluene in petroleum ether, benzene, or toluene gave, with sodium sand, high yields of the corresponding RNa compounds (143). *n*-Butylsodium and *n*-propylsodium were obtained in yields of 20-25 per cent by this method (337).

Like triphenylmethyl lithium, the corresponding triphenylmethyl rubidium and triphenylmethyl cesium were obtained from triphenylmethyl chloride and amalgams of the metals (182).

When ether solutions of certain alkyl and aryl halides were heated with beryllium powder at 80–90°C. for 15 hr. or longer, reaction took place with the formation of  $RBeX$  compounds (146). A catalyst, such as mercuric chloride or the less effective beryllium chloride, was necessary. The compounds methylberyllium iodide, ethylberyllium iodide, ethylberyllium bromide, *n*-butylberyllium iodide, and phenylberyllium iodide were prepared by this method.

Little need be said of the well-known reaction between magnesium and organic halides in ether solution to give Grignard reagents, named after their discoverer (179). Some interesting variations of this reaction have been reported. Grignard reagents have been prepared from the lower perfluoroalkyl iodides (195). An 85 per cent yield of phenylmagnesium chloride has been obtained by heating chlorobenzene with magnesium in a sealed tube at 150–160°C. (113). It has been claimed that high yields of  $RMgX$  compounds result from the reaction of magnesium with alkyl or aryl halides in the absence of any solvent if only a little ethyl orthosilicate is present (3). Dialkyl sulfates react with magnesium to give  $RMgOSO_3R$  compounds (423), but the presence of a trace of magnesium halide seems to be necessary for the reaction to occur (61, 424). Grignard reagents prepared in optically active 2,3-dimethoxybutane as the solvent underwent reaction with carbonyl reagents to give products with slight optical activity (58). The sterically hindered chloroketone 2-chloro-2,6,6-trimethylcyclohexanone reacted with magnesium to form the corresponding carbonyl-containing Grignard reagent (14).

Under the same conditions as used for the preparation of Grignard reagents, calcium reacts with organic iodides to yield  $RCaI$  compounds. This reaction, first studied by Beckmann (12), apparently is limited to aryl iodides and primary alkyl iodides (145), although a slow reaction between calcium and secondary alkyl iodides was reported to take place (173). Phenylcalcium iodide has been prepared from calcium and iodobenzene in ether solution (132).

The reactions of strontium and barium amalgams with ethyl iodide have given evidence for the formation of small quantities of ethylstrontium iodide and ethylbarium iodide (261). Other workers (147) have been unable to confirm the reaction of barium amalgam with ethyl iodide. These same investigators did, however, obtain small yields of ethylbarium iodide and phenylbarium iodide from electrolytic barium and highly purified iodides.

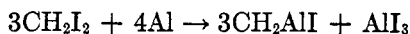
Early studies by Frankland (90) on the reaction between ethyl iodide and zinc led to the discovery of the first organozinc compound, ethylzinc iodide, which upon heating produces diethylzinc and zinc iodide. The reaction takes place more easily between ethyl iodide and a zinc-copper couple (272), and by this method Dennis and Hance (66) have prepared pure diethylzinc in high yields.

Unlike zinc, cadmium does not react easily with alkyl iodides. Wanklyn (439) probably prepared small quantities of diethylcadmium by the action of ether solutions of ethyl iodide on cadmium metal. Löhr (290) obtained only very

small amounts of impure dimethylcadmium by heating cadmium with methyl iodide.

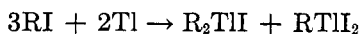
Maynard (304) has obtained high yields of methylmercuric iodide and benzylmercuric iodide from metallic mercury and the corresponding alkyl iodides. The reactions took place only in sunlight or other strong illumination. The only other organic halides which have been found to react with mercury are ethyl iodide (88, 90, 421) and methylene iodide (381); also,  $\alpha$ -bromophenylacetonitrile has been reported to react with mercury and give the compound  $C_6H_5CH(CN)HgBr$  (271).

Methylene iodide with aluminum, on long standing, gave a white reaction product (433). The reaction has been represented by the following equation (84):



Aluminum, activated with iodine, reacted readily with methylene bromide to give an organoaluminum compound of unknown composition. This compound, with water, evolved pure methane (262). The high-boiling oily product obtained from the reaction of ethyl iodide and aluminum at elevated temperatures (191) was thought, by Cahours (33), to be  $(C_2H_5)_2Al \cdot AlI_3$ . More recently, this product has been separated by fractional distillation (180) into  $(C_2H_5)_2AlI$  and  $C_2H_5AlI_2$ . Spencer and Wallace (417) observed reactions between aluminum and a variety of organic halides with the probable formation of organoaluminum compounds, but in all cases the reaction products were treated with water, and consequently no organoaluminum derivatives were isolated. Other investigations (183, 215) have shown that the reaction of aluminum with organic halides is a method of choice for making organoaluminum compounds. Aluminum-copper alloy (8 per cent copper) and methyl chloride (215), with 0.1 per cent aluminum chloride as catalyst, reacted to give an equimolar mixture of dimethylaluminum chloride and methylaluminum dichloride in an almost quantitative yield. Similar reactions took place between aluminum and methyl bromide, methyl iodide, ethyl halides, *n*-propyl iodide, iodobenzene, and *p*-iodotoluene (183). When methanol vapor was passed over aluminum filings at 270°C., the liquid condensate contained aluminum and was apparently  $(CH_3)_6Al_2$  (435).

Indium and thallium showed evidence of reacting when heated with iodobenzene and  $\alpha$ -bromonaphthalene, but no products were isolated (417). Schumb and Crane (403) observed a very slow reaction between methylene iodide and indium, but they isolated no organoindium compounds. Under certain conditions metallic thallium reacted with organic iodides, apparently according to the following equation:



This reaction will be considered in a later section.

Methyl chloride has been found to react at high temperatures with silicon in the presence of copper as a catalyst to form a mixture of the methylsilicon chlorides (220). The same type of reaction occurs between silicon and chloro- (378) or bromobenzene (434) to give phenylsilicon halides. An analogous reaction takes place when methyl chloride is passed over germanium in the presence of copper

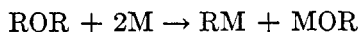
at temperatures above 300°C. to yield a mixture of methylgermanium chlorides (377). Frankland (89) discovered that metallic tin reacts with ethyl iodide to give diethyltin diiodide. In the same way, methyl iodide and tin yielded dimethyltin diiodide (34). Reaction of methyl chloride, bromide, and iodide and ethyl chloride with molten tin gave the dialkyltin dihalides,  $R_2SnX_2$  (413, 414). Finely divided metallic lead and ether solutions of organic iodides appeared to react readily. The conditions for these reactions will be considered in detail later.

At 160–200°C. methyl iodide and arsenic reacted to produce  $(CH_3)_4AsI$ , which, upon distillation over solid potassium hydroxide, gave trimethylarsine (36). Methyl iodide and ethyl iodide with antimony in sealed tubes heated to 140°C. reacted to give the  $R_3SbI_2$  compounds (30). The reaction of selenium with methyl iodide at 180°C. led to the formation of  $(CH_3)_3SeI \cdot I_2$  (407). Tellurium, in sealed tubes with methyl iodide (65, 73) and with ethyl iodide (101), reacted, upon heating, to yield the corresponding  $R_2TeI_2$  compounds.

An organoiron compound,  $(C_2H_5)_2FeBr \cdot C_2H_5FeBr_2$ , was said to be formed by the reaction of ethyl bromide with specially prepared metallic iron (2).

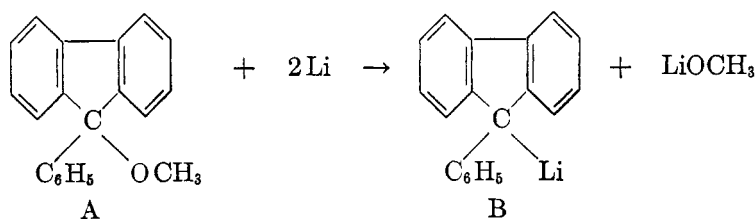
### B. Cleavage of ethers

Analogous to the reactions just described between metals and organic halides are the reactions of ethers with metals to give organometallic compounds and metal alkoxides.

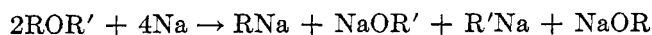


These reactions are apparently confined to the alkali metals.

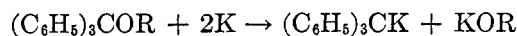
Schlenk and Bergmann (385) studied the action of lithium on several methyl ethers. For example, compound A reacted with lithium to give the organolithium compound B.



Apparently, also, a small quantity of  $(C_6H_5)_2C(OCH_3)Li$  resulted when lithium stood in contact with  $(C_6H_5)_2C(OCH_3)_2$  for 3 weeks (386). Sodium cleaved diphenyl ether, when heated to 180°C., to give phenylsodium and sodium phenoxide (400). With the ethyl naphthyl ethers and ethyl phenyl ether all four possible sodium compounds were formed by cleavage.



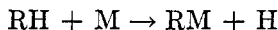
Ziegler and Thielmann (471) cleaved various ethers with potassium. For example, triphenylmethylpotassium resulted from the following reaction:



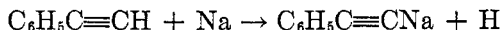
Sodium-potassium alloy was found to cleave a variety of methyl ethers of the type  $\text{ROCH}_3$  to give the corresponding  $\text{RK}$  compounds (470).

*C. Direct metalation of hydrocarbons*

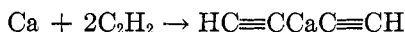
The displacement of hydrogen from a hydrocarbon by a metal according to the reaction



occurs only if the metal is highly reactive and the hydrocarbon contains an active hydrogen atom. When acetylene was passed into a solution of sodium in liquid ammonia, hydrogen was evolved and a quantitative yield of ethynylsodium resulted (210). Sodium reacts with phenylacetylene also according to the following equation:



This same type of reaction has been used to prepare the phenylethynyl derivatives of potassium, rubidium, and cesium (169). Lithium was found to be inert toward phenylacetylene (169). The reaction between calcium and acetylene in liquid ammonia gave good yields of diethynylcalcium (437).

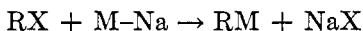


Triphenylmethane reacted readily with the alkali metals in liquid ammonia solution with the evolution of hydrogen and the formation of the triphenylmethylmetallic compounds (250).

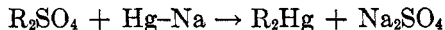
A remarkable reaction between iron and cyclopentadiene at  $375^\circ\text{C}$ . is reported to yield bis(cyclopentadienyl)iron (322).

*D. Reactions of alloys with organic halides*

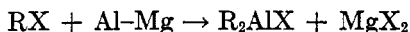
In some cases, where metals react only slowly or not at all with organic halides, it has been found advantageous to employ an alloy containing an alkali metal, usually sodium. The reaction may be represented by the following equation:



Frankland and Duppa (92), long ago, used sodium amalgam to prepare  $\text{R}_2\text{Hg}$  compounds from organic halides; more recently alkyl sulfates have been used (100).



The reaction of alkyl halides with an aluminum-magnesium alloy (30 per cent magnesium) gave high yields of  $\text{R}_2\text{AlX}$  compounds (183).

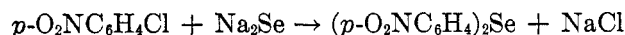


Sodium-tin alloy reacted with methyl and ethyl iodides to produce the  $\text{R}_3\text{SnI}$  and  $\text{R}_4\text{Sn}$  compounds (36, 193). A sodium-tin alloy and bromobenzene gave tetraphenyltin (368).

The commercial production of tetraethyllead from ethyl chloride and sodium-lead alloy need not be discussed here. This same type of reaction was used by Cahours (35) to prepare tetramethyllead from methyl iodide, and by Polis (367) to make tetraphenyllead from bromobenzene. A rather unexpected reaction between sodium-lead alloy and acetone has been reported to yield triisopropyllead (177). High yields of alkyllead compounds are claimed from reactions of alkyl halides with lead and magnesium mixtures (41).

Sodium and potassium alloys of the Group V metals, arsenic, antimony, and bismuth, have been employed for the preparation of organometallic compounds of these elements. Sodium arsenide heated with ethyl iodide (277) and with methyl iodide (38) gave the corresponding  $R_3As$  compounds. *p*-Bromoanisole and sodium antimonide at high temperatures formed tris(*p*-methoxyphenyl)-antimony but in rather poor yields (292). Potassium-antimony alloys with alkyl iodides were used in the first studies on organoantimony compounds (276, 296). Trialkylbismuth compounds were formed in the reaction of alkyl iodides with potassium-bismuth alloys (22, 74, 296). Sodium-bismuth alloys have been used in the synthesis of triaryl bismuth derivatives (172, 316, 318).

Aliphatic iodides heated with sodium hydroselenide yielded the corresponding  $RSeH$  compounds (436). A similar reaction was shown to take place between sodium ethyl sulfate and sodium hydroselenide (411, 412). *p*-Nitrochlorobenzene reacted with sodium selenide in the following manner (9):



In 1840 Wöhler (456) obtained diethyltellurium by distilling a sodium or potassium alloy of tellurium with potassium ethyl sulfate.



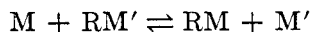
Aluminum telluride has been used to prepare organotellurium compounds from alkyl halides. By this reaction, for example, tellurocyclohexane



was made from pentamethylene bromide (325).

#### *E. Metal-metal displacement reactions*

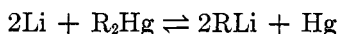
The displacement of a metal from one of its organometallic compounds by another metal is a very general reaction. This method has been used to prepare organometallic compounds of most of the metals. Reactions of this type are usually reversible and should be written



although in many cases the point of equilibrium lies far to one side or the other. Usually, a more reactive organometallic compound is formed in the reaction of a metal with a less reactive organometallic compound. In most of the studies involving this reaction,  $R_2Hg$  compounds have been employed as starting materials. Three reasons for this choice are obvious. First, organomercury compounds are of a low order of reactivity, and this favors the formation of organo-

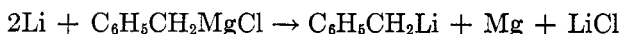
metallic compounds of most other metals. Second, a large variety of  $R_2Hg$  compounds are relatively easily available. Third, the separation of the reaction products, in this case mercury and the new  $RM$  compound, is often easier because of the liquid nature of mercury.

Schorigin (399) allowed lithium to react with a benzene solution of diethylmercury and obtained ethyllithium, as evidenced by the formation of propionic acid upon carbonation. Schlenk and Holtz (388) prepared methyllithium, ethyllithium, propyllithium, and phenyllithium by the action of lithium on the corresponding  $R_2Hg$  compounds.



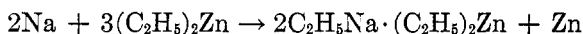
The reversibility of this reaction was demonstrated by shaking a cyclohexane solution of *n*-butyllithium with metallic mercury. Di-*n*-butylmercury and lithium amalgam were formed (464). Likewise, dibenzylmercury was formed by shaking an ether solution of benzyllithium with mercury (466).

The preparation of benzyllithium has been reported (466) by the reaction of lithium with benzylmagnesium chloride.



The reaction of lithium with an excess of diethylzinc led to the formation of a solution of ethyllithium in diethylzinc (203). In the same way, solutions of ethyllithium in diethylcadmium and triethylaluminum have been prepared. Phenyllithium has been reported from the reaction of lithium with triphenylbismuth and with tetraphenyllead (429).

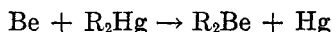
The double compound ethylsodium-diethylzinc was prepared by Wanklyn (440) from diethylzinc and metallic sodium.



By the action of sodium on a benzene solution of diphenylmercury, Acree (1) obtained phenylsodium and sodium amalgam. The  $RNa$  compounds were not isolated in a pure state until 1917, when Schlenk and Holtz (388) prepared a series of organosodium compounds from sodium metal and  $R_2Hg$  compounds. These same workers carried out reactions of sodium with  $R_4Pb$  compounds and obtained organosodium derivatives, but the products were impure and could not be separated from the finely divided lead produced by the reactions. Alkylcadmium and alkylaluminum compounds have been heated with sodium to produce the corresponding  $RNa$  derivatives (203).

Not only lithium and sodium, but also, as Grosse (182) has shown, potassium, rubidium, and cesium react with diethylzinc to give the double compounds of the formula  $C_2H_5M \cdot (C_2H_5)_2Zn$ .

Dimethylberyllium was reportedly formed in a reaction of beryllium with dimethylmercury (279). Diphenylberyllium and di-*p*-tolylberyllium were readily prepared in an analogous manner (148).



Diethylmercury and di-*n*-butylmercury, however, failed to react with beryllium.

Good yields of a number of symmetrical  $R_2Mg$  compounds have been obtained



by heating magnesium with the corresponding  $R_2Hg$  derivatives in sealed tubes (85, 115, 291, 391). From a reaction between magnesium, mercury, and the double compound  $C_2H_5Na \cdot (C_2H_5)_2Zn$ , Wanklyn (441) obtained diethylmagnesium and sodium amalgam. The same reaction applies to zinc. A mixture of zinc, mercury, and ethylsodium–diethylzinc reacted to give sodium amalgam and diethylzinc. With mercury alone, ethylsodium reacted to give diethylmercury and sodium amalgam. These reactions, like those mentioned between  $RLi$  compounds and mercury, are examples of organometallic compounds of high reactivity reacting with metals to yield compounds of a lower order of reactivity. Other related examples will be mentioned later. In each case, the energy involved in forming an amalgam seems to be sufficient to cause the reaction to take place.

Phenyllithium has been reported to react with magnesium, tin, lead, arsenic, and antimony, as well as with mercury, to give phenyl derivatives of these metals (429). The fate of the lithium in these reactions was not disclosed. Possibly free radicals (Section II,H) were involved, since the reactions were carried out in ether–xylene solutions at 100–110°C.

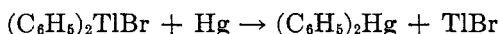
A diethylzinc solution of diethylcalcium was obtained by warming metallic calcium with an excess of diethylzinc (203). An organostrontium compound,  $(C_2H_5)_2Sr \cdot (C_2H_5)_2Zn$ , has been prepared by heating strontium with diethylzinc in benzene (138). Schulze (401), however, found no definite evidence for the formation of organometallic compounds of calcium, strontium, or barium when these metals were heated with  $R_2Hg$  compounds in sealed tubes.

The production of dialkylzinc derivatives takes place readily when metallic zinc is heated with dialkylmercury compounds (93). Good yields of diphenylzinc have been obtained by heating an excess of zinc with diphenylmercury, either without a solvent (214) or in boiling xylene solution (241).

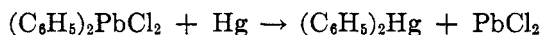
The reaction of even a large excess of metallic cadmium with dialkylmercury (93) or diarylmercury (214) compounds led to an equilibrium mixture containing both  $R_2Cd$  and  $R_2Hg$ . Actually, diphenylcadmium reacted with an excess of metallic mercury and was converted completely to diphenylmercury and cadmium amalgam (214).

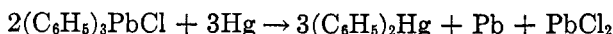
The formation of  $R_2Hg$  compounds from metallic mercury and the more reactive organolithium, -sodium, and -cadmium analogs has already been discussed. Triphenylthallium in ether solution also reacted with mercury to yield diphenylmercury and thallium amalgam (121). Triphenylbismuth and metallic mercury, when heated together, reacted until an equilibrium was reached wherein diphenylmercury and triphenylbismuth were both present (214).

Mercury reduced diphenylthallium bromide to thallos bromide with the production of a high yield of diphenylmercury (121).

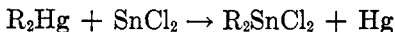


Analogous reactions between mercury and phenyllead chlorides in alcohol–acetone solutions yielded diphenylmercury. These reactions were represented by the following equations (226):





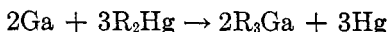
The reaction between stannous chloride and  $\text{R}_2\text{Hg}$  compounds gave good yields of  $\text{R}_2\text{SnCl}_2$  derivatives (78, 344).



This is seen to be exactly the reverse of the reaction above between diphenyllead dichloride and mercury.

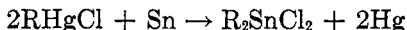
The reaction of aluminum with dialkylmercury compounds was used by Buckton and Odling (32) to prepare trialkylaluminum derivatives. This reaction was further studied by Friedel and Crafts (99), who extended it to the preparation of triphenylaluminum. More recently, other workers (213, 257, 348) have found the reaction to be a method of choice for preparing organoaluminum compounds. In boiling xylene solution, diarylmercury derivatives with aluminum gave almost quantitative yields of the  $\text{R}_3\text{Al}$  analogs (137).

Metallic gallium reacts readily with  $\text{R}_2\text{Hg}$  compounds.

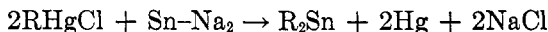


By this method good yields of trimethylgallium (446), triethylgallium (67), and triphenylgallium (122) have been obtained. In a similar manner, the syntheses of trimethylindium (68) and triphenylindium (123, 403) have been accomplished by heating metallic indium with the corresponding  $\text{R}_2\text{Hg}$  compounds.

Alkylzinc iodides and powdered tin, when heated at 150–160°C., were reported to yield  $\text{R}_4\text{Sn}$  compounds (289). Organomercuric chlorides and tin underwent the following transformation:



If a sodium–tin alloy was used, the reaction was represented as follows (338):



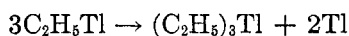
Frankland and Duppa (94) observed a reaction between bismuth and diethylmercury at 120–140°C.; triethylbismuth was obtained, but the mixture still contained diethylmercury. As mentioned previously, bismuth reacted with diphenylmercury on strong heating but an equilibrium was reached (214), and only about a 40 per cent conversion to triphenylbismuth took place. A trace of triphenylbismuth, but mostly diphenylmercury, was reported from the reaction of phenylmercuric chloride with sodium–bismuth alloy (462). Tetraphenyllead and bismuth underwent no reaction on heating at 100–130°C. for 5 hr. (167).

Krafft and Lyons (244) have shown that selenium and tellurium react with diarylmercury compounds at high temperatures and are converted to the corresponding  $\text{R}_2\text{Se}$  and  $\text{R}_2\text{Te}$  derivatives.

#### *F. Electrolysis of RM compounds to form $\text{RM}'$ compounds*

The studies of Hein and coworkers (203) on the electrolysis of solutions of ethylsodium in diethylzinc have led to some interesting and significant results. When a lead anode was used, one electrochemical equivalent of lead was dis-

solved from the anode and appeared in the solution as tetraethyllead. In an extension of this work, anodes of other metals were employed (205). The loss in weight of an aluminum electrode was 76–87 per cent based on the quantity of current which passed, and triethylaluminum was formed. A magnesium anode was strongly corroded, with the production of diethylmagnesium. The loss in weight of various other electrodes, based upon the electrochemical equivalent of current which passed, was 67 per cent for cadmium, 94–98 per cent for antimony, and 69 per cent for bismuth. In each case the normal ethyl derivatives of the metals were formed. A thallium electrode was attacked and apparently formed triethylthallium and finely divided thallium, probably by way of the following reaction:



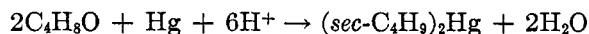
The loss in weight of a gold electrode was 1–2 per cent, and gold compounds were definitely detected in the solution. Although several forms of the metal were used, tin electrodes were entirely passive, as were also electrodes of copper, iron, platinum, and tantalum.

Kondyrev (243) carried out electrolyses of ethylmagnesium bromide solutions in ether, using zinc and aluminum anodes and a platinum cathode. The anodes lost weight equivalent to the quantity of electricity which passed; presumably diethylzinc and triethylaluminum were formed. Ether solutions of isoamylmagnesium bromide were electrolyzed with a platinum cathode and anodes of various metals (97). Anodes of aluminum, zinc, and cadmium were dissolved as a result of the electrolysis, and in the case of aluminum, the quantity dissolved was approximately equivalent to the current which passed. The products formed were probably organometallic compounds, although no search was made for them. Bismuth, gold, nickel, silver, and tin anodes were unattacked.

In these electrolytic processes, free organic radicals are probably produced on the surface of the anode, and they, in turn, may react with the metal of which the anode is made to form RM compounds, as discussed in Section II,H. The extensive studies of Evans and coworkers (80, 81, 82) on the electrolysis of Grignard solutions, using inert electrodes, substantiate the view that free radicals are produced during the process.

#### *G. Electrolysis of ketones to form RM compounds*

The preceding section was concerned with the electrolysis of organometallic compounds and the formation of new RM derivatives at the *anode*. Tafel (426) discovered that when methyl ethyl ketone in 30 per cent sulfuric acid was electrolyzed using a mercury *cathode* a 20 per cent yield of di-*sec*-butylmercury was produced. A current of 25 amp. at 7.6–8.4 v. was used, and the temperature was held at 45–50°C. The following equation represents the reaction:



Although Tafel and Schmitz (428) had reported earlier that the electrolysis of acetone in aqueous sulfuric acid using a mercury cathode gave isopropyl alcohol,

Haggerty (189) reinvestigated this work and found that little alcohol, but mostly diisopropylmercury, was produced. Results of duplicate experiments were very erratic, but from some experiments yields as high as 14 per cent were reported. From the electrolysis of menthone in sulfuric acid-alcohol-water solution, dimethylmercury has been obtained (383).

The electrolysis of a solution of acetone in 20 per cent aqueous sulfuric acid using a lead cathode gave, besides tetraisopropyllead, low yields of a red-brown oil thought to be diisopropyllead (427). This oily red product was sensitive to air and upon treatment with bromine left diisopropyllead dibromide. When aqueous sulfuric acid solutions of diethyl ketone and methyl ethyl ketone were electrolyzed, red oils were also obtained which appeared to be  $R_2Pb$  compounds (373). These materials dissolved in ether and in chloroform and were converted to diamyllead dibromide and di-*sec*-butyllead dibromide, respectively, when treated with bromine.

#### *H. Reactions of free radicals with metals*

Free methyl radicals are said to react readily with the following metals: lithium, sodium, potassium, calcium, zinc, cadmium, mercury, lanthanum, thallium, tin, lead, arsenic, antimony, bismuth, selenium, and tellurium (376). Presumably,  $CH_3M$  compounds are formed in each case. From a study of the reaction of free methyl and ethyl radicals on arsenic, antimony, and bismuth, Paneth and Loleit (353) found that compounds of the following types were formed:  $R_3As$ ,  $(R_2As)_2$ ,  $(RAs)_3$ ,  $R_3Sb$ ,  $(R_2Sb)_2$ ,  $R_3Bi$ , and  $(R_2Bi)_2$ . An interesting synthesis of trimethylbismuth, probably involving free methyl radicals, was reported to occur when a stream of methane was passed between bismuth electrodes simultaneously with an electric discharge (352).

By the action of sodium on the corresponding free triarylmethyl radicals, Schlenk and Marcus (389) prepared compounds of the type  $R_3CNa$  and  $RR'R''CNa$ . In the presence of a trace of magnesium halide to act as catalyst, magnesium reacted readily with triphenylmethyl, and a quantitative yield of di(triphenylmethyl)magnesium resulted (8, 117).

From an extensive study of the decomposition of aryldiazonium chlorides, Waters concluded that free aryl radicals were formed during the process. If certain metals were present during such decompositions, arylmetallic compounds were formed. Thus, aryl  $RHgCl$  and  $R_3SbCl_2$  compounds were produced when  $RN_2Cl$  compounds were allowed to decompose in the presence of the free metals, calcium carbonate, and acetone (298, 442). Small yields of triphenylarsine and diphenyltin dichloride were also obtained by this method (443). Earlier workers (297) had already obtained good yields of arylmercuric chlorides by allowing aqueous solutions of aryldiazonium chlorides to decompose in the presence of very finely divided mercury.

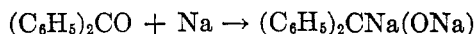
Mercury, antimony, and tellurium when heated with diphenyliodonium chloride or di-*p*-tolyliodonium chloride yielded the corresponding  $RHgCl$ ,  $R_2Te$ , and  $R_3Sb$  compounds (382). The authors suggested the possibility of a free-radical mechanism.

Nesmejanov and coworkers (345) decomposed double salts of the type

$\text{RN}_2\text{Cl} \cdot \text{SnCl}_4$  in hot ethyl acetate in the presence of metallic tin and obtained 5–20 per cent yields of  $\text{R}_2\text{SnCl}_2$  compounds. Good yields of  $\text{RHgCl}$  compounds resulted when diazonium fluoride–boron fluoride complexes,  $\text{RN}_2\text{BF}_4$ , were decomposed in water–acetone solutions of mercuric chloride in the presence of finely divided mercury (75). The mechanisms of these reactions are not well understood but perhaps, as Waters (443) believes, free radicals take part. Closely related reactions of diazonium compounds will be discussed in a later section.

#### *I. Addition of metals to double bonds*

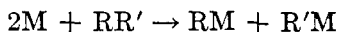
Addition to carbon–carbon, carbon–nitrogen, and carbon–oxygen double bonds is apparently characteristic only of the alkali metals. The first systematic study (384) of these addition reactions was reported in 1914. It was shown that sodium reacts with a variety of compounds containing carbon–carbon double bonds. For example, stilbene with sodium gave the compound  $\text{C}_6\text{H}_5\text{CHNaCHNaC}_6\text{H}_5$ . The  $\text{C}=\text{N}$  bond, as in benzophenone–anil, adds sodium to form compounds of the type  $\text{R}_2\text{CNaNNaR}$ . Excess sodium reacts with an aromatic ketone such as benzophenone to give the disodium derivative.



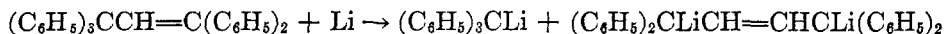
Our knowledge of these addition reactions of sodium and lithium to compounds containing double bonds has been greatly extended by the studies of Schlenk and Bergmann (387) and others (25, 460). The facility with which sodium adds to naphthalene has been increased by using dimethyl ether as a solvent; in this solvent it has been found that sodium will even add to biphenyl (408). Cesium is reported to react with ethylene to give  $\text{C}_2\text{H}_4\text{Cs}_2$  (188).

#### *J. Cleavage of carbon–carbon bonds by alkali metals*

Certain hydrocarbons having weak carbon–carbon bonds are split by alkali metals with the formation of two organometallic molecules.



The following reaction is an example of this with a hydrogen displacement (Section II,C) taking place at the same time (242).

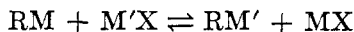


Sodium–potassium alloy, acting on symmetrical tetraphenylethane, cleaved the latter and yielded two molecules of diphenylmethylpotassium (471). Conant and Garvey (59) have studied the cleavage of a series of variously substituted ethanes, using sodium–potassium alloy and sodium amalgam. Marvel and co-workers (418) made a similar study on a large series of phenylethynyl- and *tert*-butylethynylethanes.

### III. PREPARATION OF ORGANOMETALLIC COMPOUNDS FROM METAL SALTS

#### *A. Reactions of organometallic compounds with salts of other metals*

The reactions represented by the type equation



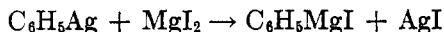
have been, by far, the most widely used to prepare all types of organometallic compounds. Because of the ease of obtaining a large variety of Grignard reagents, and because of their comparatively high reactivity, these reagents have been particularly useful in preparing a great many *less reactive* organometallic compounds. They have largely filled the position formerly occupied by organozinc compounds. As indicated in the equation, these reactions are probably essentially reversible, although in many cases this reversibility has not been demonstrated.

Reich (372) reported the first preparation of an organocopper compound by the reaction of phenylmagnesium bromide with cuprous iodide. Methyl lithium or methylmagnesium iodide reacts with cuprous iodide to give a methylcopper compound (129). Reich, as well as other workers (151, 270), prepared phenylsilver from silver bromide and phenylmagnesium bromide. Earlier, Krause and Schmitz (268) had obtained the interesting compound  $C_6H_5Ag \cdot AgNO_3$  from the reaction of silver nitrate with triphenylethyllead and triphenylethyltin. The closely related aryl  $R_4Pb$  and  $R_4Sn$  derivatives did not react with silver nitrate. On the other hand, methylsilver was formed by the reaction of tetramethyllead with silver nitrate in alcohol at  $-80^\circ C$ . (410). Organobismuth compounds were said to react with alcoholic silver nitrate to give yellow precipitates which were thought to be organosilver compounds (50).

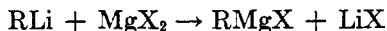
Diethylgold bromide (369) was prepared in low yields from ethylmagnesium bromide and auric chloride. Kharasch and Isbell (230) prepared several other alkylgold compounds by this method. Arylgold compounds were not formed in the reaction of aryl Grignard reagents with gold chloride. Dimethylgold iodide has been obtained (20).

Ninety per cent yields of dimethylberyllium and good yields of other  $R_2Be$  compounds have been prepared from beryllium chloride and Grignard reagents (148, 178). Ether solutions of diphenylberyllium were easily obtained from beryllium chloride and phenylmagnesium bromide (104).

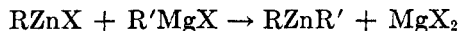
The reverse of the reaction between silver bromide and phenylmagnesium bromide, to give phenylsilver, was reported by Bickley and Gardner (16), who obtained phenylmagnesium iodide from phenylsilver and magnesium iodide in ether.



A magnesium halide apparently can be easily and completely converted to a Grignard reagent in ether solution by the action of an organolithium compound (155).

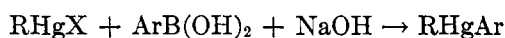


Ether solutions of  $R_2Zn$  compounds are readily made by the interaction of Grignard reagents with zinc halides (260). Krause and Fromm (258) have used the following reaction for the preparation of unsymmetrical organozinc compounds:



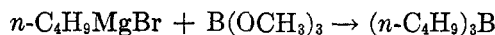
Although organocadmium compounds are difficult to obtain otherwise, they may be synthesized in good yields from Grignard reagents and cadmium halides (255). Cadmium chloride appears to be the best halide to use for this purpose (141).

Some of the early workers on organomercury compounds prepared them from  $R_2Zn$  derivatives and mercuric chloride (29, 90). Pfeiffer and Truskier (301, 364) were the first to employ the Grignard reagent for the synthesis of  $R_2Hg$  derivatives from mercuric chloride. Phenylboric acid and mercuric chloride reacted immediately in aqueous solution and yielded phenylmercuric chloride (235, 315). This is the reverse of a reaction, to be mentioned shortly, for preparing  $RBX_2$  compounds from the  $R_2Hg$  analogs. The reaction



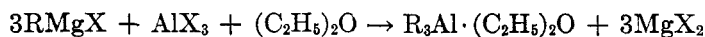
has found use as a method for making unsymmetrical organomercury compounds (96). In place of arylboric acids, diaryltin dichlorides or diarylantimony chlorides may be used. The analogous reaction between diaryltin dihalides and mercuric chloride gave high yields of diaryl-mercurials (345). These reactions between tin and mercury compounds are reversible, as will be seen later. Phenylmercuric chloride was produced by the reaction of mercuric chloride with either triphenylethyllead or triphenylethyltin in alcohol (369). More recently, it was shown that mercuric chloride reacted with *n*-amylsodium in petroleum ether, and a good yield of di-*n*-amylmercury resulted (335).

Reactions of halides of Group III elements with other RM compounds have been used to obtain organometallic derivatives of boron, aluminum, gallium, and thallium. Pure samples of trimethylboron and triethylboron were prepared by the reaction of boron chloride and the  $R_2Zn$  compounds (420). Much earlier, Frankland and Duppa (91) had used this same reaction, employing boron chloride and also ethyl orthoborate. Khotinsky and Melamed (235) applied the reaction of Grignard reagents with boric acid esters to synthesize a series of organoboric acids of the type  $RB(OH)_2$ . This reaction has more recently been investigated by Johnson and coworkers (223), who obtained tri-*n*-butylboron.



A superior method for the synthesis of  $R_3B$  compounds is the reaction of Grignard reagents on boron fluoride-etherate (263). The extensive studies by Michaelis (312, 313) on the reactions of boron chloride or boron bromide with diarylmercury compounds have shown that either  $RBX_2$  or  $R_2BX$  types can be formed, depending upon the quantity of  $R_2Hg$  compound used.

Stable etherates of organoaluminum compounds are formed by the reaction of Grignard reagents with aluminum halides (269).

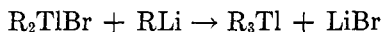


Aluminum chloride has been reported (83) to react with organosilicon compounds and yield silicon tetrachloride, together with aluminum derivatives of the type  $AlCl_2$ . Some interesting reactions between tetraphenyllead or triphenyllead

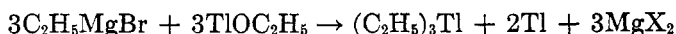
chloride and aluminum chloride gave phenylaluminum dichloride as one of the products (103). Tetraethyllead and aluminum chloride produced  $C_2H_5AlCl_2$ ,  $(C_2H_5)_2AlCl$ , and a little  $(C_2H_5)_3Al$ .

The reaction of ethylmagnesium bromide with gallium bromide was used to prepare the first organogallium compound (67). The product was an etherate of the formula  $(C_2H_5)_3Ga \cdot (C_2H_5)_2O$ . Dimethylgallium etherate was obtained in 90 per cent yield by the same method (254, 375). The reaction between gallium bromide and dimethylzinc was said to give a quantitative yield of trimethylgallium (254).

The most useful method by which organothallium compounds have been prepared is through the reaction of a thallium salt with another RM compound. Hansen (192), who first investigated the reaction of thallic chloride with diethylzinc in ether solution, thought that he obtained triethylthallium, and possibly he did. The triethylthallium, however, could not be separated, so the mixture was decomposed to give the highly stable diethylthallium chloride. Other investigators (194) believed that the reaction of diethylzinc and thallic chloride proceeded only to the diethylthallium chloride stage and that no triethylthallium was formed. Meyer and Bertheim (311) used Grignard reagents with thallic chloride to obtain compounds of the type  $R_2TlX$ . Later workers (174, 175, 259) have prepared a large number of  $R_2TlX$  compounds by means of the Grignard reaction. Goddard (174, 175) has reacted thallic chloride with several other RM compounds. For example,  $R_2TlX$  derivatives were obtained, often in good yields, from  $R_4Sn$ ,  $R_3Bi$ ,  $(C_6H_5)_2Hg$ ,  $(C_3H_7)_2Hg$ ,  $(C_6H_5)_4Pb$ ,  $(C_2H_5)_2(C_6H_5)_2Pb$ , and others. The  $R_3Sb$  and  $R_3P$  compounds and some derivatives of mercury and lead gave only thallic chloride. A smooth reaction takes place between thallic halides and arylboric acids in water solution, and either  $R_2TlX$  or  $RTlX_2$  types may be obtained depending upon the ratio of the reactants (52). This method has been used to obtain a variety of substituted diarylthallium halides (306). The only  $R_3Tl$  compounds which have been isolated were prepared by the following reaction (17, 121, 181):



Menzies and Cope (308) carried out reactions of thallic bromide and also thallic ethoxide with ethylmagnesium bromide and found that the reaction may be represented by the following equation:

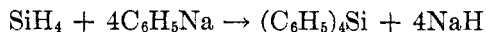


Phenyllithium (17, 124) and methyllithium have been shown to give a similar reaction with thallic halides.

In Group IV organometallic compounds of silicon, titanium, germanium, tin, and lead have been prepared by allowing halides of these elements to react with other organometallic compounds. In 1865, Friedel and Crafts (98) obtained tetramethylsilane by heating silicon tetrachloride with dimethylzinc in a sealed tube. Dimethylzinc has also been used to prepare the methylsilanes,  $CH_3SiH_3$  and  $(CH_3)_2SiH_2$ , from the corresponding chlorosilanes (419). Kipping (237)

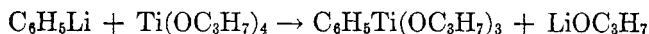


made compounds of the type  $R_4Si$ ,  $R_3SiCl$ , and  $R_2SiCl_2$  by the reaction of Grignard reagents with silicon tetrachloride. Schumb and coworkers (404, 405) obtained  $R_3SiSiR_3$  and  $R_3SiOSiR_3$  compounds from the reaction of Grignard reagents (404) and organosodium compounds (405) with the halides  $Cl_3SiSiCl_3$  and  $(Cl_3Si)_2O$ . Diarylmercury compounds and silicon tetrachloride have given products of the type  $R_2SiCl_2$  (273, 274). Esters such as methyl or ethyl orthosilicate react as do the halides (69). Thus, from these esters and a mixture of diethylzinc and sodium, Ladenburg (274) prepared  $(C_2H_5)_2Si(OR)_2$  derivatives. Acids of the type  $RSiOOH$  were obtained from aryl Grignard reagents and ethyl orthosilicate (236). A 53 per cent yield of tetrabenzylsilane has been reported from the reaction of benzylmagnesium chloride with sodium fluosilicate at high temperatures (416). The reaction of silane with phenylsodium gave tetraphenylsilane (354).



Mixed organosilicon compounds such as  $(C_6H_5)_3SiC_4H_9$  may be prepared by the reaction of a triarylsilicon halide with an alkyllithium compound (110).

An organotitanium compound has been isolated from the reaction of tetraisopropyltitanate with phenyllithium (209).



Other organotitanium compounds have been described but not isolated. The stability of these compounds appears to depend upon both the organic radicals and the other groups attached to titanium (209).

Soon after the discovery of germanium, Winkler (455) synthesized the tetraethyl derivative by the action of diethylzinc on germanium tetrachloride. The  $R_2Zn$  compounds have also been used by other workers to prepare tetraethylgermane (66) and tetraphenylgermane (248) in good yields. Although alkylmagnesium halides react with germanium tetrachloride to give good yields of  $R_4Ge$  derivatives (351, 425), it has been repeatedly observed (11, 66, 329, 425) that certain other Grignard reagents give mostly  $R_2GeX_2$  and  $RGeX_3$  compounds and very little of the  $R_4Ge$  derivative, even when a large excess of the Grignard reagent is used. Worrall (458), however, found, in the case of the phenyl compound at least, that it was only necessary to replace the ether of the reaction mixture with toluene and reflux for a short time in order to obtain an 86 per cent yield of tetraphenylgermane from germanium tetrachloride and phenylmagnesium bromide. No excess of the Grignard reagent was necessary. The reaction of phenyllithium with tricyclohexylgermanium bromide was a successful method for preparing phenyltricyclohexylgermane (222). Germanium tetrachloride reacted with diarylmercury compounds (11, 351); after hydrolysis of the reaction mixtures, products of the formula  $(RGeO)_2$  were isolated.

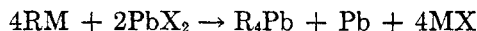
The various kinds of organotin compounds,  $R_4Sn$ ,  $R_3SnX$ ,  $R_2SnX_2$ , and  $RSnX_3$ , were synthesized from stannic halides and Grignard reagents in 1904 (363, 370). Organolithium compounds may sometimes be used to advantage in preparing  $R_4Sn$  derivatives, as shown in the synthesis of tetra-*p*-dimethylaminophenyltin

from stannic chloride and *p*-dimethylaminophenyllithium (6). Frankland and Lawrence (95) used diethylzinc to prepare tetraethyltin from stannic chloride. Diphenylmercury and stannic chloride were found to produce diphenyltin dichloride (4). In a similar way, diphenyltin dichloride has been obtained from the reactions of stannic chloride with triphenylbismuth (54) and tetraphenyllead (176). A common reaction of organometallic compounds with halides of the same metal is illustrated in the reaction of stannic chloride with tetraphenyltin to give two molecules of diphenyltin dichloride (176).

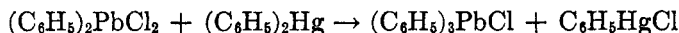


Reactions of Grignard reagents with stannous halides have given the more or less stable  $\text{R}_2\text{Sn}$  derivatives. Pfeiffer (360) reported the preparation of an impure sample of diethyltin from ethylmagnesium bromide and stannous chloride. Diaryltin compounds, stable enough to be recrystallized and handled in the air, were prepared from Grignard reagents and stannous chloride (256).

As early as 1861, Buckton (29) prepared tetraethyllead by heating lead chloride with diethylzinc. Later workers have reported 90 per cent yields of tetraethyllead from this reaction (310). Pfeiffer and Truskier (364) were the first to use Grignard reagents to prepare  $\text{R}_4\text{Pb}$  compounds from lead chloride. This reaction is a superior method for obtaining such compounds (185). In the reaction of Grignard reagents, organozinc compounds, organolithium compounds, and other  $\text{RM}$  compounds with lead halides ( $\text{PbX}_2$ ), metallic lead is always one of the products. The overall process may be represented by the following equation (364):



The reaction mechanism is, however, by no means clear (286). Under proper conditions,  $(\text{R}_3\text{Pb})_2$  compounds may be the chief products (42, 105, 265, 267). Possibly  $\text{R}_2\text{Pb}$  derivatives are first formed, for some of these (265) have actually been isolated in small quantities from the reaction of arylmagnesium halides with lead chloride at low temperatures. Diphenyllead dichloride and diphenylmercury, heated in pyridine, reacted to give only a fair yield of triphenyllead chloride (5).



Diaryllead acetates were formed by the reaction of diarylmercury compounds with lead acetate in chloroform solution (339).

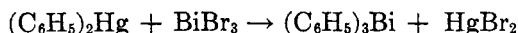
Arsenic trichloride and  $\text{R}_2\text{Zn}$  compounds react to give good yields of aliphatic  $\text{R}_3\text{As}$  derivatives (37, 216, 374), but the best and easiest method for preparing organoarsenic compounds from arsenic trihalides is probably by means of Grignard reagents (211, 358, 409). Strangely enough, arsenious oxide also reacts readily with Grignard reagents (18, 380), and good yields of triarylarsonic types have been obtained from this reaction. Tetraphenyllead and arsenic trichloride reacted in hot toluene and gave a 91 per cent yield of diphenylarsenic chloride (55).



A mixture containing diphenylbismuth chloride, diphenylarsenic chloride, and phenylarsenic dichloride was obtained by the reaction of triphenylbismuth with arsenic trichloride (55).

Organoantimony compounds, like those of arsenic, are best prepared from antimony trichloride and Grignard reagents (76, 186, 187, 211, 358). Buckton (31) reported that diethylmercury and antimony trichloride gave triethylantimony. Diphenylmercury, in reacting with antimony trichloride, gave both triphenylantimony dichloride and diphenylantimony trichloride (55). Tetraphenyllead and antimony trichloride have given a 92 per cent yield of diphenylantimony chloride (176). Antimony trichloride with triphenylbismuth yielded triphenylantimony dichloride (55). Triethylantimony diiodide was the product from the reaction of antimony pentachloride with ethylmagnesium iodide (363), and diphenylantimony trichloride was obtained from tetraphenyllead with antimony pentachloride (176). Amorphous antimony sulfide,  $\text{Sb}_2\text{S}_3$ , reacted with  $\alpha$ -naphthylmagnesium bromide to give a small quantity of tri- $\alpha$ -naphthylantimony (302). A similar reaction with antimony oxide yielded no organoantimony compounds.

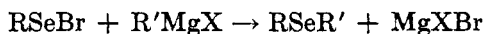
The reaction of Grignard reagents with bismuth halides, first employed by Pfeiffer (358), has been widely used to synthesize a great number of organobismuth compounds (49, 55, 164, 266). The older method, using  $\text{R}_2\text{Zn}$  compounds with bismuth halides, also apparently gave satisfactory yields of  $\text{R}_3\text{Bi}$  derivatives (299, 300). Challenger and Allpress (50) reported a quantitative yield of triphenylbismuth from the following reaction:



Later it was shown that the reaction is actually reversible, and from triphenylbismuth and mercuric chloride, phenylmercuric chloride and diphenylbismuth chloride resulted (55). Bismuth bromide and tetraphenyllead produced diphenylbismuth bromide (176), but bismuth chloride and tetraethyllead gave triethylbismuth as well as diethylbismuth chloride (103). A solution of bismuth bromide and triphenylbismuth in ether yielded diphenylbismuth bromide (187).

The researches of Hein and coworkers (197, 204, 206) on the reaction of Grignard reagents with chromium salts led to the discovery of the organochromium compounds. For example, phenylmagnesium bromide and chromic chloride reacted to yield a mixture of  $(\text{C}_6\text{H}_5)_5\text{CrBr}$ ,  $(\text{C}_6\text{H}_5)_4\text{CrBr}$ , and  $(\text{C}_6\text{H}_5)_3\text{CrBr}$ . Apparently, chromium in the form of a non-ionized salt is necessary if organochromium compounds are to be obtained (199). Molybdenum pentachloride, molybdenum trichloride, and molybdenum tribromide were said to react with phenylmagnesium bromide and give organomolybdenum compounds analogous to those of chromium (196). Organotungsten compounds have been reported from the reaction of phenylmagnesium bromide with tungsten hexachloride or hexaphenoxide (202).

Organoselenium compounds may be prepared by means of the Grignard reagent. An example is the synthesis of unsymmetrical derivatives (13) through the reaction



Leicester (287) found that selenium tetrabromide reacted with diarylmercury compounds or arylmercuric halides to give quantitative yields of  $R_2Se$  derivatives.



Tellurium tetrachloride when heated with tetraphenyllead in toluene produced a 50 per cent yield of diphenyltellurium dichloride (176). Lederer (280, 281, 283, 284) has reacted tellurium tetrabromide and tetrachloride with aryl Grignard reagents and obtained a large number of diaryltellurides (281, 284) and triaryltellurium halides (280, 283).

There seems to be good evidence that phenylmagnesium iodide reacts with manganese iodide to form an organomanganese compound (111). This product, however, has never been isolated in a pure state.

Bis(cyclopentadienyl)iron, the only well-characterized organoiron compound so far described, was prepared by the reaction of cyclopentadienylmagnesium bromide with ferric chloride (225, 227). This organoiron compound has unusual structural features that make it remarkably stable (453). Following the discovery of bis(cyclopentadienyl)iron, similar cyclopentadienyl compounds of titanium, zirconium, vanadium (452), niobium (451), chromium, molybdenum, tungsten (450), manganese (451), cobalt (449), nickel (452), and ruthenium (448) were synthesized. The methods of synthesis have involved the reaction of metal salts with cyclopentadienyllithium, -sodium, -potassium, and -magnesium bromide. In addition, two other types of reactions have been employed for the preparation of cyclopentadienylmetallic compounds. Cyclopentadiene underwent reaction with metallic iron at 375°C. to give  $(C_5H_5)_2Fe$  (322). Chromium, molybdenum, tungsten, iron, cobalt, and nickel carbonyls, when heated with cyclopentadiene, gave the cyclopentadienylmetallic compounds (450). The discovery of the unusually stable cyclopentadienyl compounds has opened a new approach to the preparation of organometallic compounds of many of the transition metals.

Organocobalt compounds aside from those containing the cyclopentadiene nucleus have been prepared by the reaction of cobaltous halides with Grignard reagents (221).

Platinic chloride and methylmagnesium iodide yielded trimethylplatinum iodide (87, 370). It was later shown that this reaction also gave tetramethylplatinum (136). The latter compound was obtained in 46 per cent yield by the action of methylsodium on trimethylplatinum iodide.

Before leaving this section it will be well to point out, again, those cases in which inorganic compounds other than halides have been converted to organometallic compounds by means of Grignard reagents. Reactions of boric acid esters,  $B(OR)_3$ , with Grignard reagents produced  $RB(OH)_2$  (235) and  $R_3B$  compounds (223). Thallous ethoxide and ethylmagnesium bromide gave triethylthallium as one product (308). Esters of silicic acid,  $Si(OR)_4$ , reacted with  $R_2Zn$  compounds to give  $R_2Si(OR)_2$  derivatives (274), and with Grignard reagents to give  $RSiOOH$  acids (236). The reaction of arsenious oxide with Grignard reagents has been reported as a good method for preparing triarylarsonic

compounds (18). Antimony sulfide reacted with  $\alpha$ -naphthylmagnesium bromide to give tri- $\alpha$ -naphthylantimony (302). Finally, the preparation of organotungsten compounds from tungsten hexaphenoxide and phenylmagnesium bromide has been claimed (202).

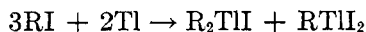
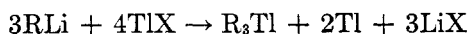
*B. Reactions of halides of metals in lower valence states with RM compounds in the presence of organic halides (128)*

In the preceding section it was mentioned that the reaction of a Grignard reagent or an organolithium compound with a thallos halide immediately produced metallic thallium and an  $R_3Tl$  compound (175). A similar reaction with lead halides was also pointed out (152).

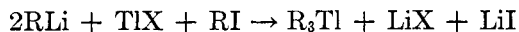


The free metals so formed are in a state of very fine subdivision and appear to react readily with organic halides, although ordinary forms of these metals do not react with such halides.

When an  $RLi$  compound is added to a suspension of a thallos halide in an ether solution containing an organic iodide, the following sequence of transformations takes place:

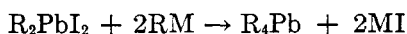
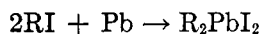


If these three equations are added, the overall reaction is seen to be



The reaction of thallos iodide, methyl lithium, and methyl iodide gave a 90 per cent yield of trimethylthallium; and from thallos chloride, phenyllithium, and iodobenzene an 80 per cent yield of triphenylthallium was obtained.

Reactions of lead halides with Grignard reagents and organolithium compounds in the presence of organic iodides can be represented by the following equations:



Addition of these equations gives the total reaction:

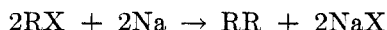


A quantitative yield of tetramethyllead was obtained from methyl lithium, lead iodide, and methyl iodide; and from methylmagnesium chloride, lead chloride, and methyl iodide the yield of tetramethyllead was in excess of 70 per cent. The reaction of phenyllithium, lead chloride, and iodobenzene gave excellent yields of tetraphenyllead, based on the above equation (152).

The halides of mercury, germanium, and tin in lower valence states might be expected to undergo reactions similar to the above reactions of thallium and lead halides.

*C. Reactions of metal halides with organic halides, using sodium as a condensing agent*

The familiar "Wurtz" type of condensation exemplified by the reaction



has been applied to the condensation of inorganic halides with organic halides. Alkylboron compounds are reported to be formed by the reaction of boron halides with alkyl halides and aluminum or zinc (24).

Polis (366) obtained  $R_4Si$  compounds (where  $R$  = phenyl, *p*-tolyl, and benzyl) from reactions of the organic halides and silicon tetrachloride with sodium in ether.

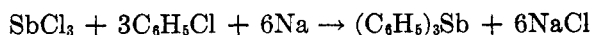


A little ethyl acetate was used to catalyze the reactions. Kipping and Lloyd (238) prepared aliphatic  $R_4Si$  derivatives by this same method. The chloride  $Cl_3Si-SiCl_3$  was cleaved with chlorobenzene and sodium and gave tetraphenylsilane rather than the expected disilane (402).

Tetraphenylgermane and tetra-*p*-tolylgermane were made through the reaction of the aryl bromides, germanium tetrachloride, and sodium in ether (425). An improvement in the yield of tetraphenylgermane was claimed when the reaction was carried out in toluene (458).

Contrary to the report of Polis (368), tetraphenyltin apparently can be prepared in good yields from the reaction of stannic chloride, bromobenzene, and sodium in ether solution (425).

One of the best methods of preparing aryl  $R_3As$  and  $R_3Sb$  compounds seems to be the reaction of the trihalides of the metals with aryl chlorides and sodium (319, 330).



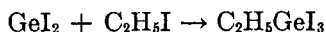
Tri-*n*-propylarsine has been made from arsenic trichloride, *n*-propyl chloride, and sodium (64).

*D. Addition of organic halides to metallic salts*

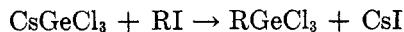
The reaction expressed in the equation



has been found applicable to the preparation of organometallic compounds of germanium, tin, and lead. A mixture of ethyl iodide and germanium diiodide heated at 110°C. in a sealed tube for 3 days has been reported to give an almost quantitative yield of ethylgermanium triiodide (86).

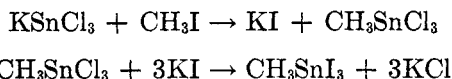


A reaction probably of this same nature, although the mechanism is not well understood, is that between alkyl or aryl iodides and the salt  $\text{CsGeCl}_3$  (431).

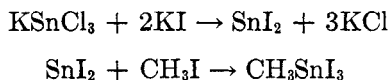


Good yields of ethylgermanium trichloride and phenylgermanium trichloride were reported.

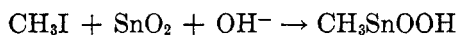
Stannous iodide and methyl iodide were found to react smoothly when heated together; the product was methyltin triiodide (361). Closely related reactions of alkyl iodides with a potassium chloride–stannous chloride double salt have been carried out in sealed tubes which were heated at about  $100^\circ\text{C}$ . for 48 hr. (430). A 44 per cent yield of methyltin triiodide was obtained when methyl iodide was used. The mechanism of the reaction was pictured as follows:



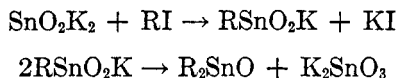
An alternative process would be



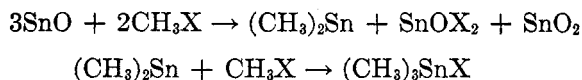
and this seems especially probable, since the second step in this mechanism is a reaction already known to take place (361). From the reaction of isopropyl iodide with  $\text{KSnCl}_3$ , however, the compound  $i\text{-C}_3\text{H}_7\text{SnCl}_3$  was actually isolated in 40 per cent yield, and this points to the first mechanism as more likely. The reactions of the potassium chloride–stannous chloride double salt are related closely to a reaction of methyl iodide with stannic oxide in basic aqueous alcohol solution. This process, first used by Meyer (309), led to the formation of methylstannic acid.



Pfeiffer (359, 363) later studied the reaction, using a series of alkyl iodides.



The reaction of tin oxide with methyl chloride or bromide at high temperatures has given the trimethyltin halides (414). Dimethyltin is a possible intermediate in the reaction.



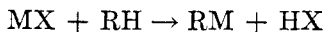
#### *E. Methylation of metallic salts with aluminum carbide*

In all of the literature there is only one report on the use of a metallic carbide for the preparation of  $\text{RM}$  compounds. This reaction, however, is important enough to require a separate section for its consideration.

It is well known that aluminum carbide reacts with aqueous acid solutions and evolves methane. Hilpert and Ditmar (212) found that when aluminum carbide was added to an aqueous acid solution of mercuric chloride, methylmercuric chloride was formed in yields as high as 30 per cent. If the acidity of the solution was not too high, dimethylmercury was also produced. A solution of bismuth chloride in 20 per cent hydrochloric acid, when treated with an excess of aluminum carbide, gave a 60 per cent yield of trimethylbismuth. Methyltin trichloride was obtained from the reaction of aluminum carbide with acid solutions of both stannous and stannic chlorides.

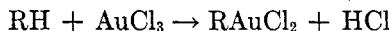
*F. Metalations with metallic salts*

The displacement of hydrogen from organic molecules, according to the reaction



is an important means of synthesizing some organometallic compounds. Moissan (323) found that potassium hydride reacted with acetylene to form potassium acetylide and hydrogen. The alkali amides, alkoxides, and hydrides, particularly the sodium derivatives, are widely used in synthetic organic chemistry. They react with a variety of compounds containing so-called "active hydrogen," such as malonic esters,  $\beta$ -ketoesters, nitriles, etc., and in many cases true organometallic compounds are formed. It is beyond the scope of this review to discuss these numerous reactions. Even diphenylmethane may be metalated with potassium amide to form diphenylmethylpotassium (461).

Equally well known are the reactions of copper (392) and silver (454) salts with acetylenes to form the acetylides. Such reactions may take place in aqueous solution. A rapid metalation of aromatic hydrocarbons was observed with anhydrous auric chloride (231). If the reaction was stopped before it proceeded too far, compounds of the formula  $\text{RAuCl}_2$  were formed.



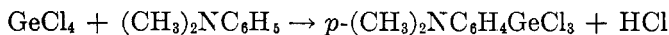
Mercuration of aromatic compounds by means of inorganic mercury salts takes place easily in many cases. Volhard (438) mercurated thiophene directly, with mercuric chloride. Mercuric acetate was found to react with benzene homologs to give organomercury compounds (70). The direct mercuration of benzene with mercuric acetate has given 80 per cent yields of phenylmercuric acetate (303). Kharasch and coworkers (229, 232) have further studied the reaction and given a theoretical discussion of the mercuration of aromatic compounds with mercuric acetate. Furan underwent prompt mercuration in the  $\alpha$ -positions; if these were blocked, substitution took place at the  $\beta$ -carbon atoms (161).

When dibenzofuran and thallic chloride were heated together in water at 165°C. for 4 hr., a low yield of bis(4-dibenzofuryl)thallium chloride was formed (102).

Trichlorosilane and silicon tetrachloride are reported to react with benzene at high temperatures to yield phenylsilicon trichloride (321). A mixture of germanium tetrachloride and dimethylaniline reacted when heated to give a good



yield of *p*-dimethylaminophenylgermanium trichloride, which upon hydrolysis produced the compound  $[p-(\text{CH}_3)_2\text{NC}_6\text{H}_4\text{GeO}]_2\text{O}$  (186).



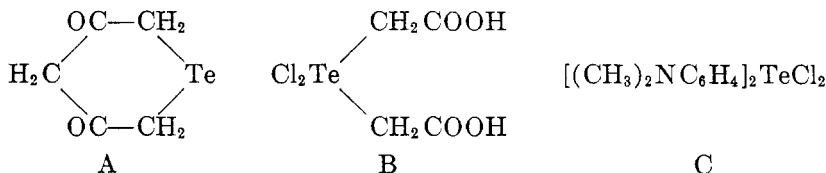
Methylaniline and diethylaniline have also been metalated with germanium tetrachloride (11).

Perhaps in this section should be mentioned the unusual reaction of cyclopentadiene with the hexacarbonyls of chromium, molybdenum, and tungsten at high temperatures to give  $(\text{C}_5\text{H}_5)_2\text{Cr}$ ,  $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_5$ , and  $\text{C}_5\text{H}_5\text{W}(\text{CO})_6$ , respectively (450). In like manner the carbonyls of iron, cobalt, and nickel react with cyclopentadiene to give cyclopentadienylmetallic compounds (450).

Wieland (447) heated arsenic trichloride and benzene in the presence of aluminum chloride as catalyst. Hydrogen chloride was evolved, and a mixture of triphenylarsine, diphenylarsenic chloride, and phenylarsenic dichloride was obtained. A reaction between selenium tetrabromide, benzene, and aluminum bromide gave a 25 per cent yield of diphenylselenium (293). By an extension of this reaction, triphenylselenium chloride has been prepared from diphenylselenium dichloride, benzene, and aluminum chloride (288).

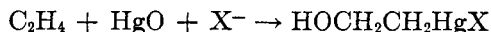


Morgan and coworkers (326, 327, 328) have studied the reactions of tellurium tetrachloride with organic compounds. With acetylacetone, hydrogen chloride was evolved and the cyclic compound A was formed (327). Excess acetic anhydride and tellurium tetrachloride in chloroform yielded compound B (328). Benzene derivatives have also been metalated. From dimethylaniline, for example, compound C resulted (326).



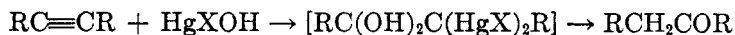
#### G. Addition of metallic salts to carbon-carbon double bonds

The addition of mercury salts to aliphatic double bonds takes place easily. Hofmann and others (217, 218, 379, 397, 459) have studied these reactions extensively with a great many ethylenic compounds. For example, ethylene, passed into an aqueous suspension of mercuric oxide in the presence of halide ions, reacted in the following manner:



A review of the reactions of mercury salts with ethylenic compounds is available (57).

The addition of mercury salts to acetylenes in basic solution leads to dimerized derivatives (341), which easily hydrolyze to give carbonyl compounds.



This reaction is the basis of the industrial production of acetaldehyde from acetylene.

Hall and Nash (190) found that a mixture of ethylaluminum dichloride and diethylaluminum chloride was formed when a mixture of aluminum and aluminum chloride reacted with ethylene under pressure at 100–200°C.

Selenium monochloride apparently underwent direct addition to ethylene (19).

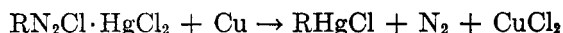


A mixture of selenium tetrachloride and red selenium underwent reaction with 1,2-dichloroethylene in the presence of aluminum chloride to yield a dialkylselenium compound (23).

#### *H. Reactions of metallic salts with aryldiazonium compounds*

The formation of organometallic compounds by the decomposition of aryldiazonium compounds in the presence of metals has been discussed in a previous section. In these reactions, it is believed that free radicals are first formed, and that they, in turn, react with the metals. The mechanism by which RM compounds are formed when aryldiazonium compounds decompose in the presence of metallic salts, or when the double salts of metal halides and aryldiazonium compounds are allowed to decompose, has not been satisfactorily explained.

Nesmejanov and others (79, 340, 342, 343) have observed that a very general method, and often the best method, for preparing aryl R<sub>2</sub>HgX compounds is to allow complex salts of the type RN<sub>2</sub>Cl·HgCl<sub>2</sub> to decompose in acetone in the presence of copper powder.



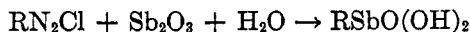
By using an excess of copper powder and adding strong ammonia, the RHgCl compound can be reduced to give a good yield of R<sub>2</sub>Hg.

When salts of the type RN<sub>2</sub>Cl·SnCl<sub>4</sub> were decomposed with powdered tin in hot ethyl acetate, yields of from 5 to 20 per cent of R<sub>2</sub>SnCl<sub>2</sub> were produced (345). Similarly, C<sub>6</sub>H<sub>5</sub>N<sub>2</sub>Cl·PbCl<sub>2</sub>, when decomposed with copper powder, gave a very small quantity of diphenyllead oxide. The salt C<sub>6</sub>H<sub>5</sub>N<sub>2</sub>Cl·PbCl<sub>4</sub> produced a small yield of triphenyllead chloride when it was decomposed with zinc in ether (345).

The reaction of an aryldiazonium chloride with sodium arsenite, often called the Bart reaction, is a general method for preparing arylarsonic acids (393). For example, benzenediazonium chloride and sodium arsenite react according to the following equation:



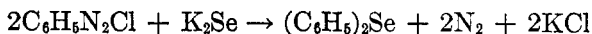
Arylantimony compounds have been synthesized conveniently by the action of aryldiazonium chlorides on antimony oxide in the presence of alkali and copper powder (26, 394).



The preparation of *p*-fluorophenylstibonic acid by the diazonium method has been broken down into two stages (77). *p*-Fluorobenzenediazonium chloride and antimony trichloride first formed a yellow complex, which upon treatment with dilute sodium hydroxide solution evolved nitrogen and gave the  $\text{RSbO}(\text{OH})_2$  compound.

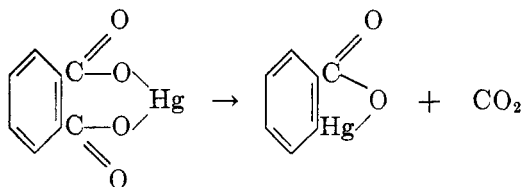
Bismuth chloride forms complex salts with aryldiazonium halides, and these complexes have been utilized for the preparation of organobismuth compounds (153, 166). When  $\text{RN}_2\text{Cl} \cdot \text{BiCl}_3$  salts were decomposed with copper powder in the appropriate solvents,  $\text{RBiCl}_2$  and  $\text{R}_2\text{BiCl}$  derivatives were obtained, usually in rather low yields.

Challenger and Peters (53) have prepared the compound  $\text{C}_6\text{H}_5\text{SeCN}$  by the reaction of benzenediazonium chloride with aqueous potassium selenocyanate. Through a similar reaction, a 72 per cent yield of diphenylselenium has been obtained (288).

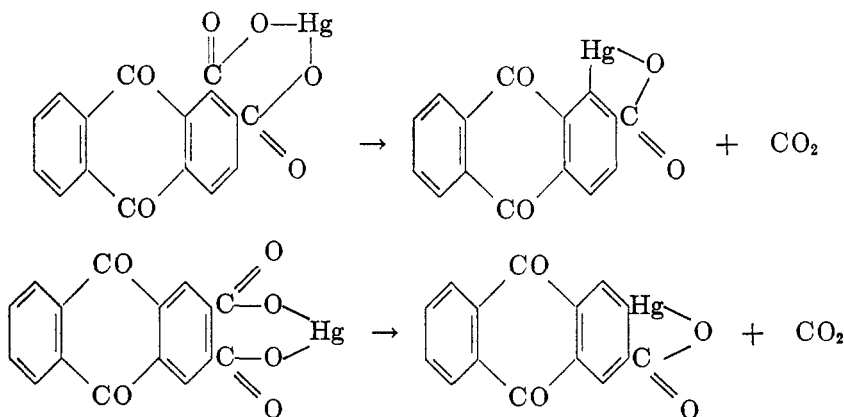


#### *I. Elimination of carbon dioxide from metal salts of organic acids*

Mercury salts of certain aromatic acids lose carbon dioxide when heated and form organomercury compounds. Pesci (356) first discovered this reaction when he heated sodium phthalate with mercuric acetate in water solution.

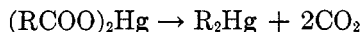


Whitmore and Carnahan (444) carried out the two following reactions at temperatures above  $200^\circ\text{C}$ .



Bis(2,4,6-trinitrophenyl)mercury and bis(2,4-dinitrobenzyl)mercury were prepared by heating the mercury salts of the corresponding acids (228). Kharasch

and Staveley (233) have found that, in general, if an organic acid easily loses carbon dioxide upon heating, its mercury salt will also lose carbon dioxide and yield an organomercury compound.

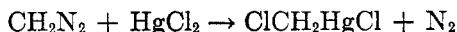


The organolead salt  $(\text{C}_6\text{H}_5)_3\text{PbOOCCH}_2\text{COOC}_2\text{H}_5$  was said (240) to lose carbon dioxide when heated at  $160^\circ\text{C}$ . under reduced pressure to give  $(\text{C}_6\text{H}_5)_3\text{PbCH}_2\text{COOC}_2\text{H}_5$ .

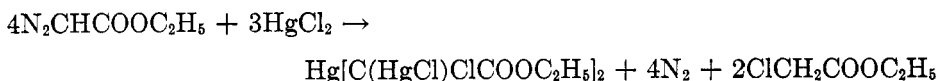
### *J. Miscellaneous methods*

The reactions discussed in this section have been applied mainly to the preparation of organomercury compounds, but possibly only because similar reactions have not been much investigated with other metals.

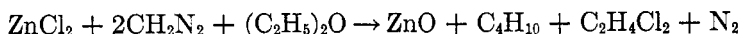
Hellerman and Newman (208) allowed diazomethane to react with mercuric chloride and obtained a quantitative yield of chloromethylmercuric chloride.



A second molecule of diazomethane reacted to give  $(\text{ClCH}_2)_2\text{Hg}$ . Other  $\text{RHgCl}$  derivatives were converted to the  $\text{RHgCH}_2\text{Cl}$  compounds by diazomethane. Diazodiphenylmethane and mercuric chloride yielded the compound  $(\text{C}_6\text{H}_5)_2\text{CClHgCl}$ . A similar reaction between mercuric chloride and diazoacetic ester (349) took place as follows:



The reaction of zinc chloride with diazomethane in ether was believed to yield the compound  $(\text{ClCH}_2)_2\text{Zn}$  as an unstable intermediate (48). This, then, reacted with the ether to give the final products represented in the following equation:



Reaction of arsenic trichloride with diazomethane gave the compounds  $\text{ClCH}_2\text{AsCl}_2$  and  $(\text{ClCH}_2)_2\text{AsCl}$  (21).

A general method for preparing aryl- $\text{HgCl}$  compounds consists in heating an arylsulfinic acid with an aqueous solution of mercuric chloride (357).



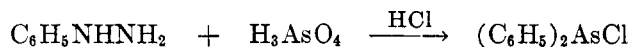
Probably a mercury salt,  $\text{RSO}_2\text{HgCl}$ , is first formed and this, when heated, loses sulfur dioxide in much the same way as mercury salts of carboxylic acids lose carbon dioxide.

A reaction between aryl iodoxy compounds and mercuric oxide in water led to the production of organomercury compounds (347). The reaction was most satisfactorily carried out in the presence of silver oxide.



By treating the reaction mixtures with an alkali halide such as sodium chloride, the  $\text{RHgCl}$  compounds were precipitated and isolated.

An interesting and unique reaction is that between phenylhydrazine and arsenic acid in the presence of hydrochloric acid to yield diphenylarsenic chloride (10).

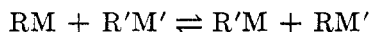


#### IV. PREPARATION OF ORGANOMETALLIC COMPOUNDS BY INTERCONVERSION METHODS

In this section methods will be discussed for converting an organometallic compound of a given metal to a different organometallic compound of the same metal. In short, reactions of organometallic compounds will be considered in which the products of the reactions are also organometallic compounds.

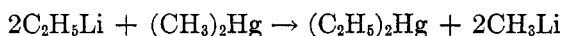
##### A. Metal-metal interconversions

Reactions of the type

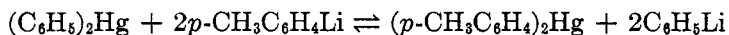


are, as indicated, reversible processes. There is a striking similarity between these reactions and the classical ionic reactions of inorganic chemistry. In general, the most negative organic radicals will migrate to the most positive metals. Often, however, the course of a reaction is influenced by the insolubility of one of the products in the solvent used.

The exchange between ethyllithium and dimethylmercury in petroleum ether (388) or in benzene (203) has been used to prepare methyllithium, which is insoluble and precipitates.



In the same way, phenyllithium was obtained from ethyllithium and diphenylmercury (203, 388). Pure samples of benzyllithium have been prepared from dibenzylmercury and ethyllithium in benzene solution (203), and from dibenzylmercury and *n*-butyllithium in ether solution (468). The reversibility of the reaction



has been demonstrated (125).

Reaction between phenyllithium and benzylmagnesium chloride gave benzyllithium as one product (466).

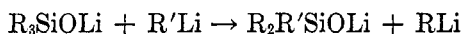
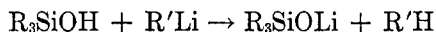


By a similar reaction, isopropyllithium was prepared from phenyllithium and isopropylmagnesium chloride (466). These reactions between Grignard reagents and lithium compounds are probably reversible, because the aliphatic deriva-

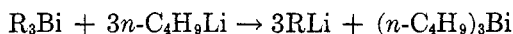
tive, *n*-butyllithium, in a reaction with diphenylmagnesium has been converted to phenyllithium (125).



*n*-Butyllithium underwent a prompt interconversion with triphenylthallium in ether solution to give phenyllithium and tri-*n*-butylthallium (124). The reaction of triarylsilanols with two equivalents of *n*-butyllithium resulted in exchange reactions (110).



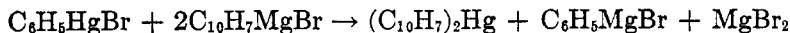
Aromatic  $\text{R}_6\text{Pb}_2$  and  $\text{R}_4\text{Pb}$  compounds (140) have been shown to undergo interchange reactions with *n*-butyllithium to form aromatic  $\text{RLi}$  derivatives and *n*-butyllead compounds. Aromatic  $\text{R}_4\text{Sn}$  compounds undergo interconversion reactions with *n*-butyllithium equally as readily as do the corresponding  $\text{R}_4\text{Pb}$  compounds (324). Triarylbismuth compounds (168) and similar derivatives of antimony (160) gave products resulting from metal-metal interchanges with *n*-butyllithium.



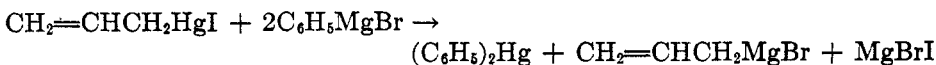
A reaction between *n*-butyllithium and diphenylselenium gave phenyllithium and phenyl-*n*-butylselenium (108). Ether solutions of *n*-butyllithium did not react with triphenylarsine or tetraphenylgermane under ordinary conditions (160).

*n*-Butylsodium, like the lithium analog, has shown a number of metal-metal interconversion reactions. A petroleum ether suspension of *n*-butylsodium with diphenylmercury gave phenylsodium and di-*n*-butylmercury (108). Similar reactions of *n*-butylsodium with aryl  $\text{R}_3\text{Bi}$  compounds yielded arylsodium derivatives and tri-*n*-butylbismuth (168).

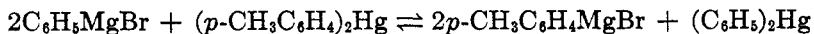
The interconversion of organomagnesium and organomercury compounds was probably first observed by Challenger and Ridgway (55). These authors found that reaction between phenylmercuric bromide and  $\alpha$ -naphthylmagnesium bromide gave di- $\alpha$ -naphthylmercury and phenylmagnesium bromide.



Kharasch and Swartz (234) obtained diphenylmercury from phenylmagnesium bromide and allylmercuric iodide.



As a matter of fact, mercury-magnesium interconversions take place quite readily in ether solution, and proof has been presented for the reversibility of the reaction between phenylmagnesium bromide and di-*p*-tolylmercury (125).

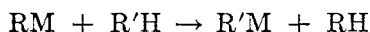


A concentrated solution of diphenylmercury in diethylzinc, on standing, was apparently partially transformed into diphenylzinc and diethylmercury (203). Diphenylmercury and tri- $\alpha$ -naphthylbismuth were heated to 200°C.; among the products were isolated di- $\alpha$ -naphthylmercury, triphenylbismuth, and diphenyl- $\alpha$ -naphthylbismuth (55). Diphenylmercury and tri-*p*-tolylbismuth underwent a similar interconversion. Unsymmetrical selenium compounds have been prepared by reaction of the symmetrical organoselenium compound with a Grignard reagent or a diarylmercury derivative (47).

Extensive studies have been reported by Calingaert and coworkers (39, 40, 43, 44, 45, 46) on reactions between two or more different organometallic compounds of the same metal. The products of such reactions are mixtures resulting from a random distribution of the organic radicals. Most of the studies have been concerned with organolead compounds (39, 40), but  $R_2Hg$ ,  $R_4Sn$ , and  $R_4Si$  systems have also been shown to undergo redistribution reactions (43). Unless the system under examination contains an organometallic halide (44), the presence of a catalyst such as aluminum chloride is usually necessary before a redistribution reaction will take place. Mixtures consisting of two different organometallic compounds also undergo exchange reactions to give all of the possible products (45, 46).

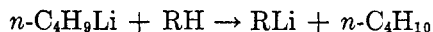
### B. Hydrogen-metal interconversions

Hydrogen-metal interconversions or metalation reactions are characteristic of the more highly reactive organometallic compounds. These reactions, represented in the equation

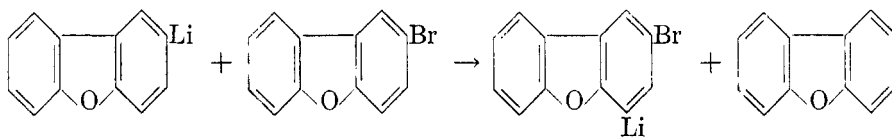


are of prime importance in the synthesis of many organometallic derivatives of lithium, sodium, and potassium.

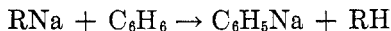
Ether solutions of *n*-butyllithium have been used extensively as metalating agents. In general, the substitution of lithium for hydrogen takes place at a carbon atom ortho to a sulfur, a nitrogen, or an oxygen linkage if these atoms are present in the aromatic molecule. *N*-Ethylcarbazole was allowed to react with *n*-butyllithium; subsequent to carbonation, a 23 per cent yield of *N*-ethylcarbazole-1-carboxylic acid was obtained (131). Metalation of such molecules as methoxydibenzofurans, diphenyl ether, anisole, diphenyl sulfide (108), phenols and methoxybenzenes (158), dibenzothiophene (118), thiophene (149), naphthalenes (422), and others (157), using *n*-butyllithium, has generally given good yields of the derivatives containing lithium in the ortho position. An interesting case in which lithium did not enter the position ortho to a sulfur linkage was the metalation of methyl phenyl sulfide using *n*-butyllithium. The chief product from this reaction was the compound  $C_6H_5SCH_2Li$ , obtained in 62 per cent yield (156). In the reaction of *n*-butyllithium with triphenylamine, the lithium atom entered the meta position (112). The other product from each of these metalation reactions using *n*-butyllithium is, of course, *n*-butane.



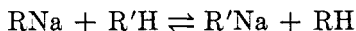
Organolithium compounds other than *n*-butyllithium are also effective metalating agents. For example, phenyllithium is used in a well-known reaction with  $\alpha$ -picoline to give  $\alpha$ -picolylithium (457). Reactions of phenyllithium and  $\alpha$ -naphthyllithium with dibenzothiophene have given 4-lithiodibenzothiophene (118). *p*-Anisyllithium reacted with *p*-anisyl bromide and formed 5-bromo-2-methoxyphenyllithium (135). A similar reaction was that of 2-lithiodibenzofuran with 2-bromodibenzofuran (135).



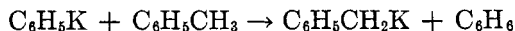
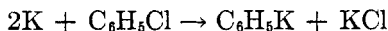
Organosodium compounds are more reactive metalating agents than the corresponding RLi compounds. Schorin (398) found that phenylsodium was readily formed by the reaction between an alkylsodium compound and benzene.



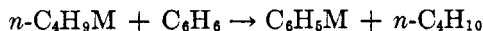
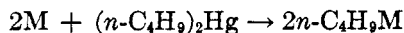
Amylsodium reacts with benzene, isopropylbenzene, and *tert*-butylbenzene to metalate the nucleus, but with toluene, the xylenes, and methylnaphthalene it reacts to metalate the side chain (333, 334). When phenylsodium was heated in toluene a lateral hydrogen atom in toluene was displaced and benzylsodium was formed (143, 331). Also, phenylsodium and *n*-butylsodium metalated  $\beta$ -methylnaphthalene laterally (143). Both phenylsodium and *n*-butylsodium have been used to metalate anisole and yield *o*-methoxyphenylsodium (108). Phenylacetylene reacted with ethynylsodium to give phenylethynylsodium (108). Conant and Wheland (60) carried out exchange reactions between hydrocarbons and both RNa and RK compounds in order to determine the relative acidities of the selected hydrocarbons.



Organopotassium compounds are highly active metalating agents. One of the best and easiest methods of preparing phenylpotassium is the reaction of an alkyl RK compound with benzene (27, 104, 130). Although phenylsodium can be prepared from sodium and chlorobenzene in toluene, the reaction of potassium with chlorobenzene in toluene, even at low temperatures, gave a high yield of benzylpotassium (143).



Reactions between the free metals and di-*n*-butylmercury in benzene solution have been used to prepare phenylrubidium and phenylcesium as well as phenylpotassium (119).



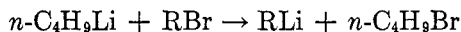


Compared with the organoalkali compound, Grignard reagents are very weak metalating agents. Alkylolithium compounds react immediately with triphenylmethane and give triphenylmethyllithium, while triphenylmethane is unchanged by Grignard reagents under the same conditions (155). Challenger and Miller (51) heated ethylmagnesium bromide with phenetole, anisole, and dimethylaniline to about 200°C. for periods of several hours. In each case, metalation occurred at the position ortho to the oxygen or nitrogen linkage. Thus, ethylmagnesium bromide with anisole gave ethane and *o*-anisylmagnesium bromide. Ethylmagnesium bromide reacted with acetylene to give ethynylmagnesium bromide (239).

Phenylcalcium iodide metalated dibenzofuran at the 4-position (132). The related reaction of phenylcalcium iodide with dibenzothiophene, however, yielded dibenzothiophene-3-calcium iodide (118, 120).

### *C. Halogen-metal interconversions*

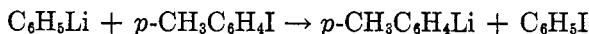
The halogen-metal interconversion reactions have been most extensively studied using organolithium compounds (224). From *n*-butyllithium and aromatic bromides or iodides, a large number of aromatic lithium derivatives have been prepared. The reactions are best conducted in ether solution.



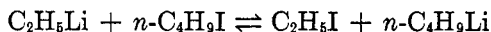
Among the halogen compounds which have been converted to the lithium derivatives by means of the above reaction are *o*-bromoanisole (133), bromodibenzofurans (159), *m*- and *p*-bromodimethylanilines (106), and a large series of aromatic bromides and iodides (134). Studies have been made of the interconversions of a number of RLi compounds with  $\alpha$ -bromonaphthalene, and the effects of solvents, time, temperature, and catalysts have been noted (139). Different methoxybromodibenzofurans with *n*-butyllithium gave, in all cases, halogen-metal interconversions rather than hydrogen-metal exchanges (154). The results of low-temperature reactions of *n*-butyllithium with 3-bromopyridine and 3-bromoquinoline were halogen-lithium exchanges rather than addition to the anil linkages (150). Subsequent to carbonation, good yields of nicotinic acid and quinoline-3-carboxylic acid were obtained.

Investigations were made (278) of the reactions of phenyl-, methyl-, and *n*-butyllithium with a series of halogenated phenyl ethers. Halogen-metal interconversions occurred with the bromo and iodo compounds but not with the chloro compounds. Only a few examples of chlorine-lithium exchanges are known at present (134). Phenylethynyl chloride reacted with *n*-butyllithium at 0°C. to give, after 30 min., a 15 per cent yield of phenylethynyllithium. A chlorine-lithium exchange took place also between *n*-butyllithium and 3-chloro-2,4,5-triphenylfuran. Two thiophene compounds, 2,5-dichlorothiophene and 2,3,4,5-tetrachlorothiophene, have been found to undergo exchange reactions with *n*-butyllithium to give 5-chloro-2-thienyllithium and 3,4,5-trichloro-2-thienyllithium, respectively (7). No fluorine-lithium interconversions have been reported.

The halogen-lithium exchanges are generally rapid and are reversible reactions. All four possible products were obtained from the reaction of either phenyllithium with *p*-iodotoluene or *p*-tolyllithium with iodobenzene (126).

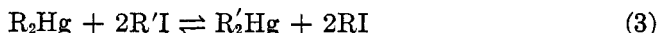
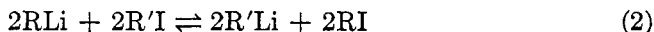
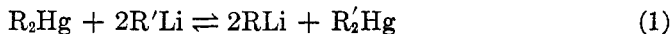


Aliphatic iodides were found to undergo iodine-lithium exchange reactions with aliphatic lithium compounds at low temperatures (126). Here, again, the reaction was reversible.



One example of a halogen-metal interconversion with an organosodium compound has been reported (126).

Ordinarily, neither Grignard reagents nor any other organometallic compounds than those of the alkali metals appear to undergo halogen-metal interconversion reactions. However, in the presence of a trace of RLi compound, halogen-mercury interconversion readily took place between aryl iodides and organomercury compounds (127). The catalytic effect of the RLi compound can be explained by the following series of reactions:

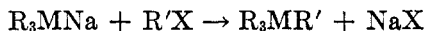


Addition of equations 1 and 2 gives equation 3. As indicated, reaction 3 is reversible. Similar interconversion reactions did not take place between aryl iodides and tetraethyllead. Probably the more reactive organometallic compounds of the metals of Groups II and III will undergo catalyzed halogen-metal exchanges.

Marquardt (300) heated triisobutylbismuth with methyl iodide to 150°C. in a sealed tube and reported that trimethylbismuth was formed. In a similar manner, triisobutylbismuth and ethyl iodide supposedly gave triethylbismuth. The trimethyl- and triethylbismuth compounds were identified only by odor.

#### *D. Reactions of RMM' compounds*

The Group IV elements, silicon, germanium, tin, and lead, form compounds of the type  $\text{R}_3\text{MNa}$ , which can react with various halogen compounds and yield  $\text{R}_3\text{MR}'$  derivatives.



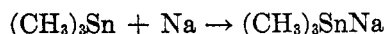
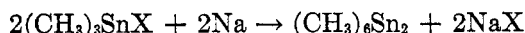
Liquid ammonia or ether are the solvents generally used for these reactions.

Kraus and coworkers (248, 249, 252, 415) prepared  $(\text{C}_6\text{H}_5)_3\text{GeNa}$  by the reaction of sodium in liquid ammonia with the compound  $(\text{C}_6\text{H}_5)_3\text{GeGe}(\text{C}_6\text{H}_5)_3$ . Triphenylgermylsodium reacted readily with alkyl halides. For instance,  $(\text{C}_6\text{H}_5)_3\text{GeNa}$  with methyl iodide, ethyl bromide (249), or other alkyl bromides (252), and polyhalides (415) formed the unsymmetrical  $(\text{C}_6\text{H}_5)_3\text{GeR}$  derivatives. The

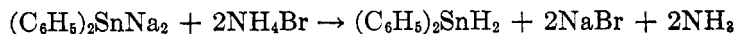
reaction of triphenylgermylsodium with trimethyltin bromide gave the compound  $(C_6H_5)_3GeSn(CH_3)_3$  (248). A similar reaction with triethylgermanium bromide, carried out in benzene, yielded the derivative  $(C_6H_5)_3GeGe(C_2H_5)_3$  (252). Potassium germyl,  $KGeH_3$ , reacted with alkyl halides to give compounds of the type  $RGeH_3$  (432).

Aryl  $R_3SiSiR_3$  compounds are readily cleaved by sodium-potassium alloy or by potassium alone to give  $R_3SiK$  derivatives (162). Ether (162) and ethylene glycol dimethyl ether (25a) appear to be the best media for these reactions. Rubidium and cesium likewise cleave hexaphenyldisilane to form the triphenylsilylmetallic compounds (162).

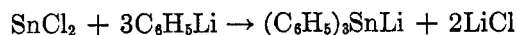
Trimethyltin halides reacted with one equivalent of sodium in liquid ammonia and quantitatively formed hexamethylditin (251). A second equivalent of sodium converted hexamethylditin to trimethyltin-sodium.



By the same reaction, triphenyltin-sodium has been prepared from triphenyltin halides and sodium (56). Triphenyltin-sodium, like the corresponding germanium compound, reacted readily with organic halides and yielded  $(C_6H_5)_3SnR$  compounds (56). Diphenyltin dichloride reacted with sodium in liquid ammonia and the product was diphenyltin-disodium,  $(C_6H_5)_2SnNa_2$ . This compound was transformed into an organotin hydride by ammonium bromide (56).

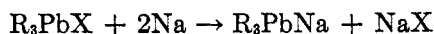


Triphenyltin-lithium has been obtained by the direct reaction of stannous chloride with phenyllithium in ether (144).

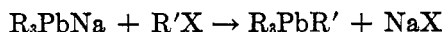


Reactions of  $(C_6H_5)_3SnLi$  with certain organic halides give  $(C_6H_5)_3SnR$  compounds.

A series of  $R_3PbNa$  compounds has been prepared (105) by the following reaction:

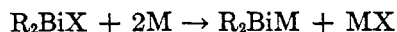


Reactions with ethyl and benzyl halides gave the unsymmetrical  $R_3PbR'$  derivatives.



Triphenylleadlithium,  $(C_6H_5)_3PbLi$ , is formed directly by the reaction of phenyllithium in ether with lead chloride at low temperatures; it undergoes the same reactions with organic halides as does the sodium analog (152).

A number of  $R_2BiM$  compounds have been prepared in liquid ammonia from aryl  $R_2BiX$  derivatives and alkali and alkaline earth metals (165).



The diarylbismuth-sodium compounds reacted, in liquid ammonia, with aryl bromides or iodides and were converted to compounds of the  $R_2BiR'$  type. These reactions have been recommended for the synthesis of unsymmetrical organobismuth compounds (165).

*E. Disproportionation of RMX compounds to give the  $R_2M$  types*

Under the proper treatment, certain mixed organometallic compounds, RMX, can be converted to the symmetrical derivatives without the aid of reducing agents.



Heating organoberyllium halides caused their disproportionation into  $R_2Be$  and  $BeX_2$  (146), and the  $R_2Be$  product could, in some cases, be distilled from the mixture.

When methylmagnesium chloride was heated in a high vacuum it was possible to distil some dimethylmagnesium from the mixture (114). A much better method of bringing about the disproportionation of Grignard reagents, however, is to precipitate the halides from the ether solution by means of dioxane (62, 63, 350, 390). The  $R_2Mg$  compound, which is normally present because of the following equilibrium

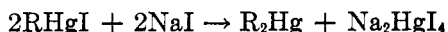


remains in solution, while  $RMgX$  and  $MgX_2$  are precipitated as insoluble dioxane complexes. When the precipitates are shaken for several hours with the ether solutions, the latter become richer in the  $R_2Mg$  compound (350).

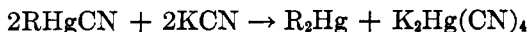
In his pioneer work on the reactions of alkyl halides with zinc, Frankland (90) found that the  $R_2Zn$  compounds could be distilled from the reaction mixtures, leaving the zinc halide behind.



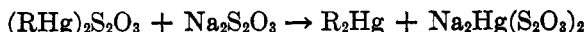
Several methods have been devised for converting arylmercuric compounds to diarylmercury derivatives by tying up part of the mercury in the form of complex salts (28, 355, 445). Heating arylmercuric iodides with sodium iodide in alcohol has given almost quantitative yields of the  $R_2Hg$  compound (445).



When Buckton (28) heated organomercuric cyanides with potassium cyanide, the following reaction took place:



A reaction similar to the above two is that of organomercuric thiosulfates with sodium thiosulfate (355).



Dreher and Otto (72) prepared  $R_2Hg$  compounds by heating  $(RHg)_2S$  compounds.



The distillation of methylaluminum diiodide caused an almost complete disproportionation to dimethylaluminum iodide and aluminum iodide (183).

A convenient synthesis of certain triarylantimony compounds consists in heating arylantimony oxides in an atmosphere of carbon dioxide (395, 396).



The reverse of the processes described in this section—namely, the reaction of a metallic halide with a symmetrical  $RM$  compound of the same metal—appears to be an entirely general reaction.

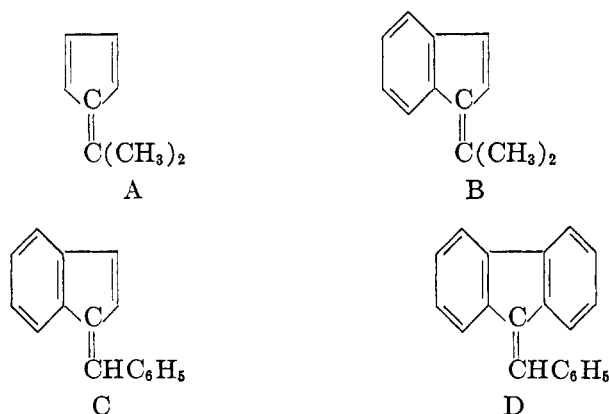


*F. Addition of organoalkali compounds to carbon-carbon double bonds*

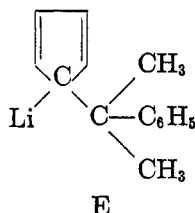
A reaction characteristic of the highly reactive organoalkali compounds is addition to carbon-carbon double bonds.



*n*-Butyllithium underwent addition to the double bond in unsymmetrical diphenylethylene and gave the compound  $(C_6H_5)_2CLiCH_2(n-C_4H_9)$  (465). A similar addition reaction took place between stilbene and *n*-butyllithium. Although phenyllithium apparently reacted slowly with unsymmetrical diphenylethylene, benzylolithium and isopropyllithium were reported (466) to add rapidly to the double bond of diphenylethylene and give the  $(C_6H_5)_2CLiCH_2R$  compounds. Ziegler and Schäfer (469) studied the addition of phenyllithium to the four fulvene compounds shown below:



From compound A the product was the new organolithium compound, E.



Compounds B, C, and D gave analogous products.

Phenylisopropylpotassium has been caused to add to the carbon-carbon double bonds of a large number of hydrocarbon compounds (463, 467).

The addition of organoalkali compounds to carbon-carbon double bonds has been postulated as the mechanism by which certain unsaturated hydrocarbons are polymerized to high-molecular-weight substances by alkali metals (15).

*G. Addition of organic halides to RM compounds of metals in lower valence states*

A few of the metals form several series of organometallic compounds in which the metals are in different states of valence. With tin, for example, compounds of the types " $R_2Sn$ ,"  $R_3Sn$ , and  $R_4Sn$  are well known. Often, the compounds containing the metals at a lower valence state will add organic halides and form derivatives in which the metals have a higher valence state.

An organogermanium compound represented as  $(C_2H_5)_2GeI$  was reported to react with ethyl iodide and yield  $(C_2H_5)_2GeI_2$  (219). This is the most satisfactory method for preparing the latter compound.

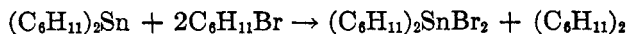
Pfeiffer (360) heated "diethyltin" with ethyl iodide in a sealed tube and prepared triethyltin iodide.



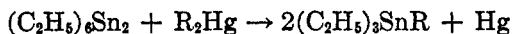
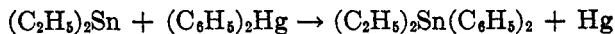
According to Grüttner (184), methyl iodide reacted with hexaethylditin at  $180^\circ C$ . and formed methyltriethyltin and triethyltin iodide.



The reactions of other alkyl iodides with  $R_3Sn$  compounds, however, did not give the same results. The products from the reaction of ethyl iodide with "triethyltin" at  $220^\circ C$ . were triethyltin iodide and butane (275). "Dicyclohexyltin" reacted with cyclohexyl bromide as follows (264):

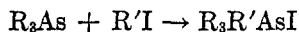


According to the following reactions, free mercury and unsymmetrical tin compounds were formed (346):



These reactions, although not strictly related to the others in this section, are included here because they are the only examples of their kind.

Michaelis and his students (314, 317) prepared many arsenic compounds of the types  $R_3R'AsI$  and  $R_2R'_2AsI$  by heating organic iodides with  $R_3As$  and  $R_2R'As$  compounds.



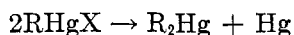
The  $R_3Sb$  compounds also add alkyl iodides and form pentavalent organo-antimony types,  $R_4SbI$  (186, 295).

Pieverling (365) found that diethylselenium added ethyl iodide to give triethylselenium iodide. Similarly, diaryltellurides add alkyl iodides; by this reaction quantitative yields of such compounds as methyl-di-*p*-anisyltellurium iodide and diphenylbenzyltellurium iodide have been prepared (282, 285).

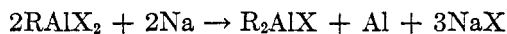
#### H. Reduction of RMX compounds

The reduction of an organometallic compound represented by the formula RMX may give the symmetrical  $R_2M$  compound, a dimerized product, RMMR, or an organometallic compound, RM, with the metal in a lower state of valence.

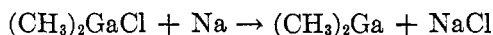
Kraus (245) electrolyzed liquid ammonia solutions of methyl-, ethyl-, propyl-, and amylmercuric chlorides and obtained the metal-like (RHg) compounds. The methyl and ethyl derivatives were the most stable, but even they decomposed rapidly at room temperature to give mercury and the  $R_2Hg$  compounds. The electrolysis of a 25 per cent water solution of methylmercuric acetate at 30–40°C. gave a 90 per cent yield of dimethylmercury (305). Almost quantitative yields of  $R_2Hg$  compounds were obtained by electrolyzing  $(RHg)_2SO_4$  solutions (307).  $R_2Hg$  compounds have been obtained from the organomercuric halides by reduction with sodium (72), sodium stannite (71), copper powder in pyridine (207), or hydrazine (107).



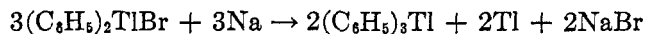
The reduction of organoaluminum halides ( $RAlX_2$ ,  $R_2AlX$ , or mixtures of the two) with either sodium or sodium-potassium alloy has given good yields of  $R_3Al$  compounds (183). By carefully controlling the quantity of sodium used, the  $RAlX_2$  compounds have been reduced to  $R_2AlX$  compounds.



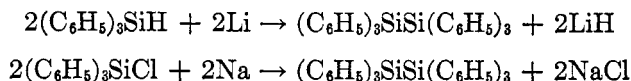
Dimethylgallium has been obtained from the reaction of sodium on dimethylgallium chloride (253).



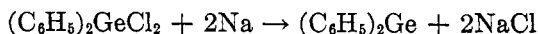
Diphenylthallium bromide reacted with sodium in liquid ammonia and gave triphenylthallium as one product (124).



Hexaphenyldisilane has been prepared by the reaction of triphenylsilane with lithium and by the reaction of triphenylchlorosilane with sodium (116).

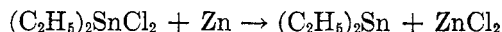


Germanium compounds of the type  $\text{R}_3\text{GeGeR}_3$  have been synthesized by heating the  $\text{R}_3\text{GeBr}$  compounds with sodium in xylene (329) or in the absence of a solvent (247). The reduction of diphenylgermanium dichloride with sodium in xylene gave 10–20 per cent yields of "diphenylgermanium" (246).



Ethylgermanium triiodide was reduced by heating with an excess of 40–60 per cent lead–bismuth alloy (219). The product was thought to have the formula  $(\text{C}_2\text{H}_5\text{GeI})_x$ .

The reduction of diethyltin dichloride with 20 per cent sodium amalgam gave "diethyltin," according to Pfeiffer (360). The same compound was obtained much earlier by Loewig (294) from the reaction of ethyl iodide with a sodium-rich tin alloy. Frankland (89) also prepared "diethyltin" by the reduction of diethyltin dichloride with zinc.

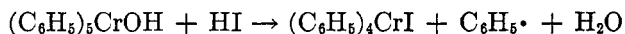


When phenyltin trichloride was reduced with sodium the products were tetraphenyltin, tin, and sodium chloride (406).

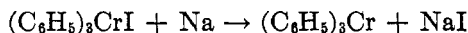
The electrolysis of triethyllead hydroxide in 95 per cent alcohol solution gave hexaethyldilead (320). Lead electrodes were used; the hexaethyldilead formed as a heavy oil at the cathode.

Other workers (163) have used hydrazine to reduce the arylbismuth halides,  $\text{RBiX}_2$  and  $\text{R}_2\text{BiX}$ , to give the  $\text{R}_3\text{Bi}$  compounds in excellent yields. Sodium in liquid ammonia reacted with diphenylbismuth bromide to give, first, diphenylbismuth-sodium (165). The diphenylbismuth-sodium then slowly decomposed and formed triphenylbismuth in 49 per cent yield.

Hein (198) found that pentaphenylchromium hydroxide spontaneously lost a phenyl group when it reacted with mineral acids or alkali halides.



When tetraphenylchromium iodide was electrolyzed in liquid ammonia, tetraphenylchromium was formed as an insoluble, red, metal-like precipitate (200). Likewise, the reduction of triphenylchromium iodide in liquid ammonia, either electrolytically or with sodium, gave triphenylchromium as a yellow-brown precipitate (201).



The authors are grateful to Dr. Helmut Merten, Richard D. Gorsich, Leonard O. Moore, and Josephine Jones for locating and checking many of the literature references.



TABLE 1

*Method of preparation of organometallic compounds*

Method	References
Lithium compounds	
$2\text{Li} + \text{RX} \rightarrow \text{RLi} + \text{LiX}$	(109, 170, 171, 182, 464)
$2\text{Li} + \text{ROR} \rightarrow \text{RLi} + \text{LiOR}$	(385, 386)
$2\text{Li} + \text{RH} \rightarrow 2\text{RLi} + \text{H}_2$	(250)
$\text{Li} + \text{RM} \rightarrow \text{RLi} + \text{M}$	(203, 388, 399, 429, 466)
$\text{Li} + \text{R} \cdot \rightarrow \text{RLi}$	(376)
$2\text{Li} + \text{RCH}=\text{CHR} \rightarrow \text{RCHLiCHLiR}$	(387)
$2\text{Li} + \text{RR}' \rightarrow \text{RLi} + \text{R}'\text{Li}$	(242)
$\text{RLi} + \text{R}'\text{M} \rightleftharpoons \text{R}'\text{Li} + \text{RM}$	(108, 124, 125, 140, 160, 203, 324, 388)
$\text{RLi} + \text{R}'\text{H} \rightarrow \text{R}'\text{Li} + \text{RH}$	(108, 112, 118, 131, 135, 149, 156, 157, 158, 422, 457)
$\text{RLi} + \text{R}'\text{X} \rightarrow \text{R}'\text{Li} + \text{RX}$	(224)
$\text{RLi} + \text{R}'\text{CH}=\text{CHR}' \rightarrow \text{R}'\text{CHRCHLiR}'$	(465, 466, 469)
Sodium compounds	
$2\text{Na} + \text{RX} \rightarrow \text{RNa} + \text{NaX}$	(142, 143, 332, 336, 337)
$2\text{Na} + \text{ROR} \rightarrow \text{RNa} + \text{NaOR}$	(400)
$2\text{Na} + 2\text{RH} \rightarrow 2\text{RNa} + \text{H}_2$	(210, 250)
$\text{Na} + \text{RM} \rightarrow \text{RNa} + \text{M}$	(1, 201, 388, 440)
$\text{Na} + \text{R} \cdot \rightarrow \text{RNa}$	(376, 389)
$2\text{Na} + \text{RCH}=\text{CHR}' \rightarrow \text{RCHNaCHNaR}'$	(384, 387, 408)
$2\text{Na} + \text{RCH}=\text{NR}' \rightarrow \text{RCHNaNNaR}'$	(384, 387)
$2\text{Na} + \text{R}_2\text{C}=\text{O} \rightarrow \text{R}_2\text{CNa}(\text{ONa})$	(384, 387)
$2\text{Na} + \text{RR}' \rightarrow \text{RNa} + \text{R}'\text{Na}$	(59, 418)
$\text{RNa} + \text{R}'\text{M} \rightleftharpoons \text{R}'\text{Na} + \text{RM}$	(108, 168)
$\text{RNa} + \text{R}'\text{H} \rightarrow \text{R}'\text{Na} + \text{RH}$	(60, 108, 143, 331, 333, 334, 398)
$\text{RNa} + \text{R}'\text{X} \rightarrow \text{R}'\text{Na} + \text{RX}$	(126)
Potassium compounds	
$2\text{K} + \text{ROR} \rightarrow \text{RK} + \text{KOR}$	(470, 471)
$2\text{K} + 2\text{RH} \rightarrow 2\text{RK} + \text{H}_2$	(169, 250)
$\text{K} + \text{RM} \rightarrow \text{RK} + \text{M}$	(182)
$\text{K} + \text{R} \cdot \rightarrow \text{RK}$	(376)
$2\text{K} + \text{RR}' \rightarrow \text{RK} + \text{R}'\text{K}$	(59, 471)
$\text{KX} + \text{RH} \rightarrow \text{RK} + \text{HX}$	(323, 461)
$\text{RK}_2 + \text{R}'\text{H} \rightarrow \text{R}'\text{K} + \text{RH}$	(104, 119, 130, 143)
$\text{RK} + \text{R}'\text{CH}=\text{CHR}' \rightarrow \text{R}'\text{CHRCHKR}'$	(463, 467)
Rubidium compounds	
$2\text{Rb} + \text{RX} \rightarrow \text{RRb} + \text{RbX}$	(182)
$2\text{Rb} + 2\text{RH} \rightarrow 2\text{RRb} + \text{H}_2$	(169, 250)
$\text{Rb} + \text{RM} \rightarrow \text{RRb} + \text{M}$	(182)
$\text{RRb} + \text{R}'\text{H} \rightarrow \text{R}'\text{Rb} + \text{RH}$	(119)
Cesium compounds	
$2\text{Cs} + \text{RX} \rightarrow \text{RCs} + \text{CsX}$	(182)
$2\text{Cs} + 2\text{RH} \rightarrow 2\text{RCs} + \text{H}_2$	(169, 250)
$\text{Cs} + \text{RM} \rightarrow \text{RCs} + \text{M}$	(182)
$2\text{Cs} + \text{RCH}=\text{CHR}' \rightarrow \text{RCHCsCHCsR}'$	(188)
$\text{RCs} + \text{R}'\text{H} \rightarrow \text{R}'\text{Cs} + \text{RH}$	(119)
Copper compounds	
$\text{CuX} + \text{RM} \rightarrow \text{RCu} + \text{MX}$	(129, 375)
$\text{CuX} + \text{RH} \rightarrow \text{RCu} + \text{HX}$	(392)

TABLE 1—*Continued*

Method	References
Silver compounds	
$\text{AgX} + \text{RM} \rightarrow \text{RAg} + \text{MX}$ $\text{AgX} + \text{RH} \rightarrow \text{RAg} + \text{HX}$	(50, 151, 268, 270, 410) (454)
Gold compounds	
$\text{Au} + \text{R}\cdot \rightarrow \text{RAu}$ $\text{AuX}_3 + 2\text{RM} \rightarrow \text{RAuX} + 2\text{MX}$ $\text{AuX}_3 + \text{RH} \rightarrow \text{RAuX}_2 + \text{HX}$	(205) (20, 230, 369) (231)
Beryllium compounds	
$\text{Be} + \text{RX} \rightarrow \text{RBeX}$ $\text{Be} + 2\text{RM} \rightarrow \text{R}_2\text{Be} + 2\text{M}$ $\text{BeX}_2 + 2\text{RM} \rightarrow \text{R}_2\text{Be} + 2\text{MX}$ $2\text{RBeX} \xrightarrow{\text{heat}} \text{R}_2\text{Be} + \text{BeX}_2$	(146) (148, 279) (104, 148, 178) (146)
Magnesium compounds	
$\text{Mg} + \text{RM} \rightarrow \text{RMgX}$ $\text{Mg} + 2\text{RM} \rightarrow \text{R}_2\text{Mg} + 2\text{M}$ $\text{Mg} + 2\text{R}\cdot \rightarrow \text{R}_2\text{Mg}$ $\text{MgX}_2 + \text{RM} \rightarrow \text{RMgX} + \text{MX}$ $\text{R}_2\text{Mg} + 2\text{R}'\text{M} \rightleftharpoons \text{R}_2'\text{Mg} + 2\text{RM}$ $\text{RMgX} + \text{R}'\text{H} \rightarrow \text{R}'\text{MgX} + \text{RH}$ $2\text{RMgX} + \text{dioxane} \rightarrow \text{R}_2\text{Mg} + \text{MgX}_2\text{-dioxane}$	(3, 61, 113, 179, 195, 423, 424) (85, 115, 291, 391, 429, 441) (8, 117, 205) (18, 155) (55, 125, 234, 450) (51, 239) (62, 63, 350, 390)
Calcium compounds	
$\text{Ca} + \text{RX} \rightarrow \text{RCaX}$ $\text{Ca} + 2\text{RH} \rightarrow \text{R}_2\text{Ca} + \text{H}_2$ $\text{Ca} + 2\text{RM} \rightarrow \text{R}_2\text{Ca} + 2\text{M}$ $\text{Ca} + \text{R}\cdot \rightarrow \text{R}_2\text{Ca}$ $\text{RCaX} + \text{R}'\text{H} \rightarrow \text{R}'\text{CaX} + \text{RH}$	(12, 132, 145, 173) (437) (203) (378) (118, 120, 132)
Strontium compounds	
$\text{Sr} + \text{RX} \rightarrow \text{RSrX}$ $\text{Sr} + 2\text{RM} \rightarrow \text{R}_2\text{Sr} + 2\text{M}$	(261) (138)
Barium compounds	
$\text{Ba} + \text{RX} \rightarrow \text{RBaX}$	(147, 261)
Zinc compounds	
$\text{Zn} + \text{RX} \rightarrow \text{RZnX}$ $\text{Zn} + 2\text{RM} \rightarrow \text{R}_2\text{Zn} + 2\text{M}$ $\text{Zn} + 2\text{R}\cdot \rightarrow \text{R}_2\text{Zn}$ $\text{ZnX}_2 + 2\text{RM} \rightarrow \text{R}_2\text{Zn} + 2\text{MX}$ $\text{R}_2\text{Zn} + 2\text{R}'\text{M} \rightleftharpoons \text{R}_2'\text{Zn} + 2\text{RM}$ $2\text{RZnX} \rightarrow \text{R}_2\text{Zn} + \text{ZnX}_2$	(66, 90, 272) (93, 214, 241, 441) (376) (258, 260) (203) (87)
Cadmium compounds	
$\text{Cd} + \text{RX} \rightarrow \text{RCdX}$ $\text{Cd} + 2\text{RM} \rightarrow \text{R}_2\text{Cd} + 2\text{M}$ $\text{Cd} + 2\text{R}\cdot \rightarrow \text{R}_2\text{Cd}$ $\text{CdX}_2 + 2\text{RM} \rightarrow \text{R}_2\text{Cd} + 2\text{MX}$	(290, 439) (93, 214) (205, 378) (141, 255)

TABLE 1—Continued

Method	References
Mercury compounds	
$\text{Hg} + \text{RX} \rightarrow \text{RHgX}$	(88, 90, 271, 304, 381, 421)
$\text{Hg-Na} + 2\text{RX} \rightarrow \text{R}_2\text{Hg} + 2\text{NaX}$	(92, 100)
$\text{Hg} + 2\text{RM} \rightarrow \text{R}_2\text{Hg} + 2\text{M}$	(121, 214, 226, 429, 441, 464, 466)
$\text{Hg} + \text{RCOR} \xrightarrow{\text{electrolysis}} \text{R}_2\text{Hg}$	(189, 383, 426, 427)
$\text{Hg} + 2\text{R}\cdot \rightarrow \text{R}_2\text{Hg}$	(75, 297, 298, 376, 382, 442)
$\text{HgX}_2 + 2\text{RM} \rightarrow \text{R}_2\text{Hg} + 2\text{MX}$	(29, 90, 98, 235, 301, 315, 335, 345, 364, 369)
$\text{HgX}_2 + \text{AlCl}_3 \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{HgX} + (\text{CH}_3)_2\text{Hg}$	(212)
$\text{HgX}_2 + \text{RH} \rightarrow \text{RHgX} + \text{HX}$	(70, 161, 229, 232, 303, 438)
$\text{HgX}_2 + \text{RCH=CHR} \rightarrow \text{RCHXCH}(\text{HgX})\text{R}$	(217, 218, 341, 379, 397, 459)
$\text{RN}_2\text{X}\cdot\text{HgX}_2 \xrightarrow{\text{Cu}} \text{RHgX} + \text{N}_2 + \text{CuCl}_2$	(79, 340, 342, 343)
$(\text{RCOO})_2\text{Hg} \rightarrow \text{R}_2\text{Hg} + 2\text{CO}_2$	(228, 233, 356, 444)
$\text{HgX}_2 + \text{CH}_3\text{N}_3 \rightarrow \text{XCH}_3\text{HgX}$	(208, 349)
$\text{RSO}_3\text{HgX} \rightarrow \text{RHgX} + \text{SO}_3$	(357)
$\text{RIO}_2 + \text{H}_2\text{O} \rightarrow \text{RHgIO}_2$	(347)
$\text{R}_2\text{Hg} + 2\text{R}'\text{M} \rightarrow \text{R}'_2\text{Hg} + 2\text{RM}$	(43, 55, 108, 125, 234)
$\text{R}_2\text{Hg} + 2\text{R}'\text{X} \xrightleftharpoons{\text{RLi}} \text{R}'_2\text{Hg} + 2\text{RX}$	(127)
$2\text{RHgX} \rightarrow \text{R}_2\text{Hg} + \text{HgX}_2$	(28, 72, 355, 445)
$\text{RHgX} \rightarrow \text{RHg}$	(245)
$2\text{RHgX} \xrightarrow{\text{reduction}} \text{R}_2\text{Hg} + \text{Hg}$	(71, 72, 107, 207, 305, 307)
Boron compounds	
$\text{BX}_3 + 3\text{RM} \rightarrow \text{R}_3\text{B} + 3\text{MX}$	(91, 223, 235, 263, 312, 313, 420)
$\text{BX}_3 + 3\text{RX} + 6\text{M} \rightarrow \text{R}_3\text{B} + 6\text{MX}$	(24)
Aluminum compounds	
$2\text{Al} + 3\text{RX} \rightarrow \text{R}_2\text{AlX} + \text{RAlX}_2$	(33, 54, 180, 183, 191, 215, 262, 433, 435)
$\text{Al-M} + 2\text{RX} \rightarrow \text{R}_2\text{AlX} + \text{MX}$	(183)
$\text{Al} + 3\text{RM} \rightarrow \text{R}_3\text{Al} + 3\text{M}$	(32, 99, 137, 213, 257, 348)
$\text{Al} + 3\text{R}\cdot \rightarrow \text{R}_3\text{Al}$	(97, 205)
$\text{AlX}_3 + 3\text{RM} \rightarrow \text{R}_3\text{Al} + 3\text{MX}$	(83, 103, 269)
$\text{AlX}_3 + \text{Al} + \text{CH}_2=\text{CH}_2 \rightarrow \text{C}_2\text{H}_5\text{AlX}_2 + (\text{C}_2\text{H}_5)_2\text{AlX}$	(190)
$2\text{RAlX}_2 \rightarrow \text{R}_2\text{AlX} + \text{AlX}_3$	(183)
$3\text{R}_2\text{AlX} \xrightarrow{\text{reduction}} 2\text{R}_2\text{Al} + \text{Al} + 3\text{X}^-$	(183)
Gallium compounds	
$\text{Ga} + 3\text{RM} \rightarrow \text{R}_3\text{Ga} + 3\text{M}$	(67, 122, 438)
$\text{GaX}_3 + 3\text{RM} \rightarrow \text{R}_3\text{Ga} + 3\text{MX}$	(67, 254, 375)
$\text{R}_3\text{GaX} + \text{Na} \rightarrow \text{R}_3\text{Ga} + \text{NaX}$	(253)
Indium compounds	
$2\text{In} + 3\text{RX} \rightarrow \text{R}_2\text{InX} + \text{RInX}_2$	(403, 417)
$\text{In} + 3\text{RM} \rightarrow \text{R}_3\text{In} + 3\text{M}$	(68, 123, 403)
Thallium compounds	
$2\text{Tl} + 3\text{RX} \rightarrow \text{RTlX} + \text{RTlX}_2$	(128, 417)
$\text{Tl} + 3\text{R}\cdot \rightarrow \text{R}_3\text{Tl}$	(205, 376)
$\text{TlX}_3 + 3\text{RM} \rightarrow \text{R}_3\text{Tl} + 3\text{MX}$	(17, 52, 121, 124, 174, 175, 181, 192, 194, 250, 306, 311)
$\text{TlX}_3 + 2\text{RH} \rightarrow \text{R}_2\text{TlX} + 2\text{HX}$	(102)
$\text{R}_2\text{Tl} + 3\text{R}'\text{M} \rightleftharpoons \text{R}'_2\text{Tl} + 3\text{RM}$	(124)
$3\text{R}_2\text{TlX} \xrightarrow{\text{reduction}} 2\text{R}_2\text{Tl} + \text{Tl} + 3\text{X}^-$	(124)

TABLE 1—Continued

Method	References
Silicon compounds	
$\text{Si} + 4\text{RX} \rightarrow \text{RSiX}_4, \text{R}_4\text{SiX}$	(220, 378, 434)
$\text{SiX}_4 + 4\text{RM} \rightarrow \text{R}_4\text{Si} + 4\text{MX}$	(69, 98, 110, 236, 237, 273, 274, 354, 404, 405, 419)
$\text{SiX}_4 + 4\text{RX} + 8\text{M} \rightarrow \text{R}_4\text{Si} + 8\text{MX}$	(238, 366, 402)
$\text{SiX}_4 + \text{RH} \rightarrow \text{RSiX}_3 + \text{HX}$	(321)
$\text{R}_4\text{Si} + 4\text{R}'\text{M} \rightleftharpoons \text{R}'_4\text{Si} + 4\text{RM}$	(43)
$\text{R}_4\text{SiM} + \text{R}'\text{X} \rightarrow \text{R}_3\text{R}'\text{Si} + \text{MX}$	(162)
Titanium compounds	
$\text{TiX}_4 + \text{RM} \rightarrow \text{RTiX}_3 + \text{MX}$	(209)
$\text{TiX}_4 + 2\text{RM} \rightarrow \text{R}_2\text{TiX}_2 + 2\text{MX}$	(452)
Zirconium compounds	
$\text{ZrX}_4 + 2\text{RM} \rightarrow \text{R}_2\text{ZrX}_2 + 2\text{MX}$	(452)
Germanium compounds	
$\text{Ge} + \text{RX} \rightarrow \text{RGeX}_3, \text{R}_2\text{GeX}_2, \text{etc.}$	(377)
$\text{GeX}_4 + 4\text{RM} \rightarrow \text{R}_4\text{Ge} + 4\text{MX}$	(11, 66, 222, 248, 329, 351, 425, 455, 458)
$\text{GeX}_4 + 4\text{RX} + 8\text{M} \rightarrow \text{R}_4\text{Ge} + 8\text{MX}$	(425, 458)
$\text{GeX}_2 + \text{RX} \rightarrow \text{RGeX}_3$	(86, 431)
$\text{GeX}_4 + \text{RH} \rightarrow \text{RGeX}_3 + \text{HX}$	(11, 186)
$\text{R}_4\text{GeM} + \text{R}'\text{X} \rightarrow \text{R}_3\text{R}'\text{Ge} + \text{MX}$	(248, 249, 252, 415, 432)
$\text{RGeX} + \text{RX} \rightarrow \text{R}_2\text{GeX}_2$	(219)
$\text{R}_2\text{GeX}_2 + 2\text{Na} \rightarrow \text{R}_2\text{Ge} + 2\text{NaX}$	(246)
$2\text{R}_2\text{GeX} + 2\text{Na} \rightarrow \text{R}_1\text{GeGeR}_1 + 2\text{NaX}$	(247, 329)
$\text{RGeX}_3 \xrightarrow{\text{reduction}} \text{RGeX}$	(219)
Tin compounds	
$\text{Sn} + 2\text{RX} \rightarrow \text{R}_2\text{SnX}_2$	(34, 89, 413, 414)
$\text{Sn-Na} + 4\text{RX} \rightarrow \text{R}_4\text{Sn} + 4\text{NaX}$	(36, 193, 368)
$\text{SnX}_2 + 2\text{RM} \rightarrow \text{R}_2\text{SnX}_2 + \text{M}$	(78, 344)
$\text{Sn} + 4\text{RM} \rightarrow \text{R}_4\text{Sn} + 4\text{M}$	(289, 338)
$\text{Sn} + 4\text{R}' \rightarrow \text{R}_4\text{Sn}$	(345, 376)
$\text{SnX}_4 + 4\text{RM} \rightarrow \text{R}_4\text{Sn} + 4\text{MX}$	(4, 6, 54, 95, 176, 357, 360, 363, 370)
$\text{SnX}_4 + 4\text{RX} + 8\text{M} \rightarrow \text{R}_4\text{Sn} + 8\text{MX}$	(425)
$\text{SnX}_2 + \text{RX} \rightarrow \text{R}_2\text{SnX}_2$	(309, 359, 361, 362, 414, 430)
$\text{SnX}_4 + \text{Al}_4\text{C}_3 \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{SnX}_3$	(212)
$\text{RN}_2\text{X} \cdot \text{SnX}_2 \xrightarrow{\text{Sn}} \text{R}_2\text{SnX}_2$	(345)
$\text{R}_4\text{Sn} + 4\text{R}'\text{M} \rightleftharpoons \text{R}'_4\text{Sn} + 4\text{RM}$	(324)
$\text{R}_4\text{SnM} + \text{R}'\text{X} \rightarrow \text{R}_3\text{R}'\text{Sn} + \text{MX}$	(56, 251)
$\text{R}_2\text{Sn} + \text{RX} \rightarrow \text{R}_3\text{SnX}$	(184, 360)
$\text{R}_2\text{Sn} + \text{R}'_2\text{Hg} \rightarrow \text{R}_2\text{R}'_2\text{Sn} + \text{Hg}$	(346)
$\text{R}_2\text{SnX}_2 \xrightarrow{\text{reduction}} \text{R}_2\text{Sn} + 2\text{X}^-$	(89, 360, 406)
Lead compounds	
$\text{Pb} + 2\text{RX} \rightarrow \text{R}_2\text{PbX}_2$	(128, 152)
$\text{Pb-M} + 4\text{RX} \rightarrow \text{R}_4\text{Pb} + 4\text{MX}$	(35, 41, 177, 367)
$\text{Pb} + \text{RCOR} \xrightarrow{\text{electrolysis}} \text{R}_4\text{Pb}$	(373, 427)
$\text{Pb} + 4\text{R}' \rightarrow \text{R}_4\text{Pb}$	(203, 376)
$2\text{PbX}_2 + 4\text{RM} \rightarrow \text{R}_4\text{Pb} + \text{Pb} + 4\text{MX}$	(5, 29, 42, 105, 185, 265, 267, 310, 339, 364)
$\text{RN}_2\text{X} \cdot \text{PbX}_2 \rightarrow \text{R}_2\text{PbX}_2$	(345)
$\text{R}_4\text{PbOOCR}' \rightarrow \text{R}_4\text{PbR}' + \text{CO}_2$	(240)
$\text{R}_4\text{Pb} + 4\text{R}'\text{M} \rightleftharpoons \text{R}'_4\text{Pb} + 4\text{RM}$	(39, 40, 140)
$\text{R}_4\text{PbM} + \text{R}'\text{X} \rightarrow \text{R}_3\text{R}'\text{Pb} + \text{MX}$	(105, 222)
$\text{R}_4\text{PbOH} \xrightarrow{\text{electrolysis}} \text{R}_4\text{PbPbR}_4$	(320)

TABLE 1—Continued

Method	References
Arsenic compounds	
$\text{As} + \text{RX} \rightarrow \text{R}_3\text{AsX}$	(36)
$\text{As-M} + 3\text{RX} \rightarrow \text{R}_3\text{As} + 3\text{MX}$	(38, 277)
$\text{As} + 3\text{R} \cdot \rightarrow \text{R}_3\text{As}$	(376, 443)
$\text{AsX}_3 + 3\text{RM} \rightarrow \text{R}_3\text{As} + 3\text{MX}$	(18, 37, 55, 211, 216, 358, 374, 380, 409)
$\text{AsX}_3 + 3\text{RX} + 6\text{M} \rightarrow \text{R}_3\text{As} + 6\text{MX}$	(64, 319, 330)
$\text{AsX}_3 + 3\text{RH} \rightarrow \text{R}_3\text{As} + 3\text{HX}$	(447)
$\text{Na}_2\text{HAsO}_3 + \text{RN}_2\text{X} \rightarrow \text{RAsO}_2\text{HN}_2 + \text{N}_2 + \text{NaX}$	(393)
$\text{AsX}_3 + \text{CH}_3\text{N}_3 \rightarrow \text{XCH}_2\text{AsX}_2 + \text{N}_2$	(19)
$\text{H}_3\text{AsO}_4 + \text{C}_6\text{H}_5\text{NHNH}_2 + \text{HCl} \rightarrow (\text{C}_6\text{H}_5)_2\text{AsCl}$	(10)
$\text{R}_2\text{As} + \text{R}'\text{X} \rightarrow \text{R}_2\text{R}'\text{AsX}$	(314, 317)
Antimony compounds	
$\text{Sb} + \text{RX} \rightarrow \text{R}_3\text{SbX}_2$	(30)
$\text{Sb-M} + 3\text{RX} \rightarrow \text{R}_3\text{Sb} + 3\text{MX}$	(276, 292, 296)
$\text{Sb} + 3\text{R} \cdot \rightarrow \text{R}_3\text{Sb}$	(205, 298, 376, 382, 442)
$\text{SbX}_3 + 3\text{RM} \rightarrow \text{R}_3\text{Sb} + 3\text{MX}$	(31, 55, 76, 176, 186, 187, 211, 302, 358, 363)
$\text{SbX}_3 + 3\text{RX} + 6\text{M} \rightarrow \text{R}_3\text{Sb} + 6\text{MX}$	(319, 330)
$\text{Sb}_2\text{O}_3 + \text{RN}_2\text{X} \xrightarrow{\text{Cu}} \text{RSbO}(\text{OH})_2$	(26, 77, 394)
$\text{R}_3\text{Sb} + 3\text{R}'\text{M} \rightarrow \text{R}'_3\text{Sb} + 3\text{RM}$	(160)
$3\text{RSbO} \rightarrow \text{R}_3\text{Sb} + \text{Sb}_2\text{O}_3$	(395, 396)
$\text{R}_3\text{Sb} + \text{R}'\text{X} \rightarrow \text{R}_2\text{R}'\text{SbX}$	(186, 295)
Bismuth compounds	
$\text{Bi-M} + 3\text{RX} \rightarrow \text{R}_3\text{Bi} + 3\text{MX}$	(22, 74, 172, 296, 316, 318)
$\text{Bi} + 3\text{RM} \rightarrow \text{R}_3\text{Bi} + 3\text{M}$	(94, 214)
$\text{Bi} + 3\text{R} \cdot \rightarrow \text{R}_3\text{Bi}$	(205, 352, 353, 376)
$\text{BiX}_3 + 3\text{RM} \rightarrow \text{R}_3\text{Bi} + 3\text{MX}$	(49, 50, 55, 103, 164, 176, 187, 266, 299, 300, 358)
$\text{BiX}_3 + \text{Al}_2\text{Cl}_3 \rightarrow (\text{CH}_3)_3\text{Bi}$	(212)
$\text{RN}_2\text{X} \cdot \text{BiX}_3 \xrightarrow{\text{Cu}} \text{R}_2\text{BiX}$	(153, 166)
$\text{R}_3\text{Bi} + 3\text{R}'\text{M} \rightarrow \text{R}'_3\text{Bi} + 3\text{RM}$	(168)
$\text{R}_2\text{BiM} + \text{R}'\text{X} \rightleftharpoons \text{R}_2\text{R}'\text{Bi} + \text{MX}$	(165)
$3\text{R}_2\text{BiX} \xrightarrow{\text{reduction}} 2\text{R}_2\text{Bi} + \text{Bi}$	(163, 165)
Vanadium compounds	
$\text{VX}_4 + 2\text{RM} \rightarrow \text{R}_2\text{VX}_3 + 2\text{MX}$	(452)
Niobium compounds	
$\text{NbX}_5 + 2\text{RM} \rightarrow \text{R}_2\text{NbX}_3 + 2\text{MX}$	(452)
Chromium compounds	
$\text{CrX}_3 + \text{RM} \rightarrow \text{R}_2\text{CrX}$	(197, 199, 204, 206)
$\text{R}_2\text{CrX} + \text{H}^+ \rightarrow \text{R}_2\text{CrX}$	(198)
$\text{R}_2\text{CrX} \xrightarrow{\text{electrolysis}} \text{R}_2\text{Cr}$	(200, 201)
$\text{Cr}(\text{CO})_6 + \text{RH} \rightarrow \text{R}_2\text{Cr}$	(450)
Molybdenum compounds	
$\text{MoX}_3 + \text{RM} \rightarrow \text{R}_2\text{MoX}$	(196)
$\text{Mo}(\text{CO})_6 + \text{RH} \rightarrow \text{R}_2\text{Mo}_2(\text{CO})_6$	(450)

TABLE 1—*Concluded*

Method	References
Tungsten compounds	
$WX_3 + RM \rightarrow R_3WX$	(202)
$W(CO)_6 + RH \rightarrow R_3W_2(CO)_6$	(450)
Manganese compounds	
$MnX_2 + RM \rightarrow RMnX$	(111)
$MnX_2 + 2RM \rightarrow R_2Mn + 2MX$	(451)
Selenium compounds	
$Se + 3RX \rightarrow R_3SeX \cdot X_2$	(407)
$SeHNa + RX \rightarrow RSeH + NaX$	(9, 411, 412, 436)
$Se + 2RM \rightarrow R_2Se \bullet 2M$	(244)
$Se + 2R \cdot \rightarrow R_2Se$	(376)
$SeX_4 + 3RM \rightarrow R_3Se + 3MX + RX$	(13, 287)
$SeX_4 + 3RH \xrightarrow{AlCl_3} R_3Se + 3HX + RX$	(288, 293)
$2Se_2Cl_2 + 2C_2H_4 \rightarrow (ClCH_2CH_2)_2SeCl_2 + 3Se$	(19, 23)
$K_2Se + 2RN_2X \rightarrow R_2Se + N_2 + 2KX$	(53, 288)
$R_3Se + 2R'M \rightleftharpoons R'_2Se + 2RM$	(108)
$R_3Se + RX \rightarrow R_4SeX$	(365)
Tellurium compounds	
$Te + 2RX \rightarrow R_2TeX_2$	(65, 73, 101)
$Te-M + 2RX \rightarrow R_2Te + 2MX$	(325, 456)
$Te + 2RM \rightarrow R_2Te + 2M$	(244)
$Te + 2R \cdot \rightarrow R_2Te$	(376, 382)
$TeX_4 + 3RM \rightarrow R_3Te + 3MX + RX$	(176, 280, 281, 283, 284)
$TeX_4 + 2RH \rightarrow R_2TeX_2 + 2HX$	(326, 327, 328)
$R_4Te + RX \rightarrow R_4TeX$	(282, 285)
Iron compounds	
$2Fe + 3RX \rightarrow R_3FeX + RFeX_2$	(2)
$FeX_2 + 2RM \rightarrow R_2Fe + 2MX$	(225, 227)
$Fe + 2RH \rightarrow R_2Fe + H_2$	(322)
Cobalt compounds	
$CoX_2 + 2RM \rightarrow R_2Co + 2MX$	(221)
$CoX_2 + 2RM \rightarrow R_2CoX + 2MX$	(449)
Nickel compounds	
$NiX_2 + 2RM \rightarrow R_2Ni + 2MX$	(452)
Ruthenium compounds	
$RuX_3 + 2RM \rightarrow R_2Ru + 2MX$	(448)
Platinum compounds	
$PtX_4 + 3RM \rightarrow R_3PtX + 3MX$	(87, 136, 371)

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