1943

Free radicals in the decomposition of organometallic compounds

Lauren Albert Woods
Iowa State College

Recommended Citation

Woods, Lauren Albert, "Free radicals in the decomposition of organometallic compounds " (1943). *Retrospective Theses and Dissertations*. 14180.
https://lib.dr.iastate.edu/rtd/14180

FREE RADICALS IN THE DECOMPOSITION OF ORGANOMETALLIC COMPOUNDS

by

Lauren A. Woods

A Thesis Submitted to the Graduate Faculty
for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject: Organic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State College
1943

ACKNOWLEDGMENT

The author wishes to express his sincere respect and appreciation to Dr. Henry Gilman for the assistance and encouragement given during this work.

TABLE OF CONTENTS

Page

LIST OF TABLES

INTRODUCTION

Some of the most urgent needs and desires in organometallic chemistry call for a wider application in industrial and synthetic work. The utility of most of the known organometallics has been explored rather extensively. Accordingly, it appears to be advantageous to have recourse to organometallic derivatives which are relatively unknown at present. This group includes compounds of a number of the more commonly available metals such as iron, cobalt, nickel, copper and others. From the point of view of cost, usable organometallic compounds of the more common metals would be the solution to a number of industrial problems.

The use, particularly in synthesis, of an organometallic compound is often restricted to its participation as a reaction intermediate. It is unnecessary to isolate the derivative as such. The ideal example is the Grignard reagent which can be prepared in a solvent and then used in the same medium. More difficulties are encountered, however, with the thermally unstable derivatives. Since the primary reaction, as well as the secondary reactions which give by-products, may operate through free radicals, the study of free radicals in the decomposition of organometallic compounds is of prime importance.

Free radicals are generally considered to be neutral bodies which participate in reactions *per se*. These fragments do not possess an electrical charge, but do contain an unpaired electron. As a result of the magnetically non-compensated electron these bodies are paramagnetic. This fact serves as a basis for one method of detection of free radicals.

This work considers free radicals to be operating in the various coupling reactions which take place in the presence of metallic salts. Thermally unstable organometallic compounds can be considered as intermediates. These compounds decompose to give free radicals which undergo the usual characteristic reactions.

HISTORICAL

The concept of free radicals has played a dominant role in the chemistry of organometallic compounds. In his quest for free radicals in the cacodyl series, Bunsen (1) treated cacodyl chloride with zinc and thus liberated cacodyl, $(CH_3)_2As-As(CH_3)_2$. In addition, Bunsen (2) attempted to obtain alkyl radicals by heating alkyl chlorides with metals. These experiments were unsuccessful. A few years later, as a result of an endeavor to prepare the free ethyl radical, Frankland (3) reacted ethyl iodide with metallic zinc and obtained diethylzinc. Frankland (4) also found that, by heating ethyl iodide with metallic zinc to 150° C. in a sealed glass tube, gas with the empirical formula C_2H_5 was formed. Although he considered this gas to be the free ethyl radical, it actually was butane. Nevertheless, this type of pyrolysis provided the essential means, a number of decades later, for the preparation of free radicals.

For a long time it was maintained that there were two series of paraffin hydrocarbons; one series consisting of

---

(1) Bunsen, Ann., 37, 1 (1841).
(2) Bunsen, Ann., 42, 14 (1842).
(3) Frankland, Ann., 71, 213 (1849).
(4) Frankland, Ann., 71, 171 (1849); 74, 41 (1850); 77, 221 (1851).

"radical twins", and the other of the hydrides of the radicals. Thus, ethyl hydride, $C_2H_5 . H$, and dimethyl, $(CH_3)_2$, were suposed to be isomeric. Even Baeyer's (5) initial work seemed to confirm the difference between methyl chloride and chlorinated methane. With the advent of the theory of valence in 1858, the supposition of the quadrivalent nature of carbon was made the foundation of the whole of structural organic chemistry, and the idea of free radicals deteriorated. However, it remained for Schlorlemmer (6) to finally clear up the matter of the isomerism between "radical twins" and "hydrides." He showed that both series underwent the same reactions and yielded the same products.

In 1900 the interest in free radicals was rejuvenated when Gomberg (7) isolated the triphenylmethyl radical. The next three decades were marked by prodigious endeavor which culminated in the classical researches of Paneth and coworkers (8). The identity and existence of the free methyl and ethyl radicals were now firmly established, and evidence has been presented for the existence of the phenyl and benzyl radicals.

The historical review is most suitably presented by separating the material into the following divisions:

---

(5) Baeyer, *Ann.*, *103*, 181 (1857).
(6) Schorlemmer, *J. Chem. Soc.*, *16*, 425 (1863); *ibid.*, *17*, 262 (1864).
(7) Gomberg, *J. Am. Chem. Soc.*, *22*, 757 (1900).
(8) See later references.

Identification of Free Radicals, Thermal Decomposition, Photochemical Decomposition, Electrolytic Decomposition, Organometallic Radicals and Redistribution Reaction. There is, of course, overlapping in the material included under these headings. For example, it is possible that some photochemical decomposition may take place in a decomposition primarily of a thermal nature.

Identification of Free Radicals

Most of the methods of identification of free radicals involve the use of chemical means. Reaction of a metal mirror with the corresponding formation of an organometallic compound has been used extensively. The physical constants of the products were observed and in some cases derivatives of the products were prepared. In addition, the free radical has been reacted with a halogen molecule and the resulting halide derivatized by conversion to a suitable onium compound with a tertiary amine.

In the first positive work done with free radicals, the free methyl fragment was identified by combination with metallic zinc (9). The dimethylzinc was identified by its melting and boiling points, and the spontaneous combustion in air with the separation of zinc oxide. This work also included the reaction of the free methyl radical with an antimony

---

(9) Paneth and Hofeditz, Ber., 62, 1335 (1929).

mirror. However, although antimony alkyls were apparently formed, a satisfactory identification was not possible since the product was a mixture and was obtained only in small amounts.

Paneth and Lautsch (10) identified the free ethyl radical prepared from tetraethyllead by the reaction with zinc to give diethylzinc. By a controlled partial oxidation, the diethylzinc was converted to the compound, $C_2H_5OOZnC_2H_5$. This compound precipitated as a white powder which was readily hydrolyzed. The resulting ethyl alcohol formed by the hydrolysis was identified by the iodoform test.

More recently, the reaction of free radicals with metallic sodium and with carbon tetraiodide has been used as a means of identification (11). In these experiments, tetramethyllead, without any carrier gas, was passed through a furnace at a temperature of about 900° C. and a pressure of a few hundredths of a millimeter. In one trial, the fragments were allowed to come in contact with sodium, the mixture of sodium and alkylsodium was treated with alcohol and the gases analyzed. The only hydrocarbon product present in detectable amounts was methane. Ethane was the only product when tetraethyllead was used. In another experiment, the free methyl fragments were reacted with carbon tetraiodide. The resulting alkyl iodides

---

(10) Paneth and Lautsch, Ber., 64, 2702 (1931).
(11) Simons and Dull, J. Am. Chem. Soc., 55, 2696 (1933).

were then combined with quinoline, and the resulting quinoline methiodide was identified by the method of mixed melting points. The ethyl radicals obtained from tetraethyllead were identified in a similar manner.

A number of difficulties were encountered with the above three methods of identification of free radicals, reactions with metallic zinc, metallic sodium and carbon tetraiodide. Often an excess of undecomposed starting material was mixed with decomposition products, thus giving a mixture which was difficult to separate. Most of these obstacles were obviated by permitting the free radicals to react with metallic mercury (12, 13). The dialkylmercury compounds are volatile, but are not sensitive to oxidation. These derivatives react quantitatively with mercuric chloride, or mercuric bromide, and produce the corresponding alkylmercuric halides. The alkylmercuric halides are well-defined crystalline compounds with definite melting points (14). It was further possible to react the RHgX compounds with a solution of iodine in aqueous potassium iodide to give the corresponding alkyl iodides which were distilled off. By using a method introduced by Willstätter and Utzinger (15), it was possible to react the alkyl iodide with trimethylamine to give the trimethylalkylammonium iodide. This

---

(12) Rice and Evering, _Ibid._, _56_, 2105 (1934).
(13) Rice and Rodowskas, _Ibid._, _57_, 350 (1935).
(14) Whitmore, "Organic Compounds of Mercury," Chemical Catalog Co., New York (1921).
(15) Willstatter and Utzinger, _Ann._, _382_, 148 (1911).

method serves to differentiate the methyl and ethyl radicals. The tetramethylammonium iodide is insoluble in water, acetone, chloroform and absolute alcohol, all of which dissolve trimethylethylammonium iodide very readily.

Several publications have postulated the presence of free alkyl radicals by the removal of lead mirrors (16, 17). It was found that cadmium, arsenic, antimony and bismuth mirrors were also removed (18).

Paneth and Lautsch (19) observed that tellurium mirrors were removed by free radicals. In addition, these mirrors were not deactivated by traces of oxygen. In a few selected experiments, free methyl fragments were found to be very suitably identified by these mirrors (13, 20). A deep red liquid, dimethylditelluride, $CH_3TeTeCH_3$, was the only product. This compound has a low vapor pressure at room temperature and can usually be easily separated from the excess of undecomposed starting materials used to produce the free radicals. The compound is stable in air and melts sharply at -19.5°. It is only necessary to use a few special precautions to retain the volatile compound.

Dull and Simons (21) have reported the existence of free phenyl radicals in the gaseous phase. That conclusion was based on the formation of diphenylmercury, ostensibly by the reaction of the phenyl radical with metallic mercury. A

---

(16) Paneth and Herzfeld, Z. Elektrochem., 37, 577 (1931).
(17) Paneth and Lautsch, Naturwissenschaften, 18, 307 (1930).
(18) Paneth, Trans. Faraday Soc., 30, 179 (1934).
(19) Paneth and Lautsch, Ber., 64, 2708 (1931).
(20) Rice and Glasebrook, J. Am. Chem. Soc., 56, 2472 (1934).
(21) Dull and Simons, ibid., 55, 3898 (1933).

general statement has been advanced by Hey and Waters (22) to the effect that phenyl radicals in solution invariably react with the solvent. This could serve as a method of identification.

The free benzyl radical has been detected and identified by reactions with selenium, tellurium and mercury mirrors (23).

It has been mentioned previously that mirrors of arsenic, antimony and bismuth are removed by free radicals. However, the products were not investigated thoroughly. Paneth and Loleit (24) found that the free methyl radical attacks an arsenic mirror at room temperature to give bis(dimethylarsenic)--cacodyl--as the main product, accompanied by some trimethylarsenic. Free ethyl radicals gave analogous compounds. Cold and hot mirrors of antimony with free methyl gave predominantly trimethylantimony, and a small amount of bis(dimethylantimony). With the ethyl radical, triethylantimony was formed almost exclusively in the cold; heat was necessary to form any bis-(diethylantimony). Cold bismuth mirrors gave only the R_3Bi compounds.

It has been found that beryllium is attacked by free radicals (24). Previously it has been reported that under selected conditions ethyl radicals did not react with a beryllium mirror (25).

---

(22) Hey and Waters, Chem. Rev., 21, 169 (1937).
(23) Paneth and Lautsch, J. Chem. Soc., 380 (1935).
(24) Paneth and Loleit, ibid., 366 (1935).
(25) Gilman and Brown, Rec. trav. chim., 50, 184 (1930).

More recently, physical methods involving the use of the mass spectrometer have been used for the detection of free radicals (26, 27).

Apropos of the identification of the free alkyl radicals, it would be well to mention in a qualitative manner the estimation of the "half-life" period. From a measurement of the relative rates at which standard mirrors were removed at various distances from the source, the "half-life" period of the methyl radical was calculated to be of the order of 0.006 second at a pressure of 2 mm. in hydrogen; this indicates that one-half of the total amount of free methyl radicals will be decomposed in that length of time. The "half-life" of the ethyl and benzyl radicals are of the same order of time as the methyl radical.

Thermal Decomposition

In this section are included all decompositions which may be attributed to heat. Because of the probable formation of a thermally unstable intermediate organometallic compound, coupling reactions in the presence of metallic salts are noted.

Group I.

The thermal decomposition of ethylsodium in the solid

---

(26) Eltenton, J. Chem. Phys., 10, 403 (1942).
(27) Hipple and Stevenson, Phys. Rev., 63, 121 (1943).

phase produced ethane and ethylene (28). The primary transitory product was probably the ethyl radical which then disproportionated. In a more thorough investigation, Carothers and Coffman (29) verified the general observations above and found that the ratio of ethylene to ethane was eighty-five to fifteen. Sodium hydride was also formed, probably resulting from the abstraction of a hydrogen atom from a free ethyl radical.

On heating methylpotassium or -sodium, it was found that the decomposition was in accordance with the following equation (30):

$$4\ MCH_3 \longrightarrow 3\ CH_4 + M_4C$$

Alkyl halides have been treated with sodium vapor by Polanyi and co-workers (31) at a temperature of 210° to 290°, producing free radicals in yields of 2 to 7 per cent.

In general,the Wurtz-Fittig reaction is considered to operate without intermediate free radical formation (32). However, a free radical mechanism was proposed to account for the products of the reaction between sodium and chlorobenzene--namely, benzene, biphenyl, 4-phenylbiphenyl, 2-phenylbiphenyl, 2,2'-diphenylbiphenyl and triphenylene (33). In view of the

---

(28) Shorigin, *Ber.*, *43*, *1931* (1910).
(29) Carothers and Coffman, *J. Am. Chem. Soc.*, *51*, 588 (1929).
(30) Carothers and Coffman, *Ibid.*, *52*, 1254 (1930).
(31) Hartel and Polanyi, *Z. physik. Chem.*, *B11*, 97 (1930); Polanyi and Hartel, *Ibid.*, *B11*, 13 (1930); Polanyi and Style, *Naturwissenchaften*, *20*, 401 (1932); Hartel, *Trans. Faraday Soc.*, *30*, 187 (1934); Horn, Polanyi, and Style, *Ibid.*, *30*, 189 (1934).
(32) Goldschmidt and Schon, *Ber.*, *59*, 948 (1926).
(33) Bachmann and Clarke, *J. Am. Chem. Soc.*, *49*, 2089 (1927).

recent work by Wittig and Witt (34) concerning the Wurtz-Fittig reaction, it is apparent that the formation of the above products could be explained on the basis of halogen-metal interconversion and metalation.

Buckton (35), in 1859, reported the action of diethylzinc on cuprous chloride giving a gas. Cuprous chloride and cuprous iodide were reacted with diethylzinc and gave a mixture of ethane, ethylene and hydrogen (36).

The action of alkylmagnesium halides on copper salts gave both disporportionation and coupling. For example, the ethyl Grignard gave ethane and ethylene, while propylmagnesium bromide gave propane (37). Bibenzyl was produced in good yields in this manner (38, 39).

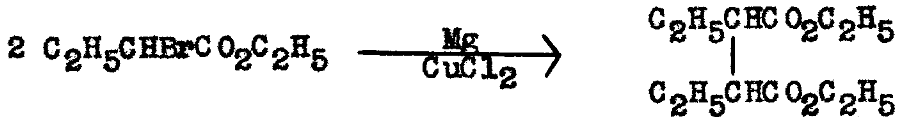
The coupling action of cupric halides has been observed with ethylenic and acetylenic Grignard reagents. Strylmagnesium bromide ($C_6H_5CH = CHMgBr$) gave 1,4-diphenylbutadiene-1,3 (40) and phenylethynlmagnesium bromide gave diphenyldiacetylene (41).

Ethyl α-bromobutyrate has been treated with magnesium and cupric chloride and supposedly gave the ethyl ester of

---

(34) Wittig and Witt, Ber., 74, 1474 (1941).
(35) Buckton, Ann., 109, 218 (1859).
(36) Wanklyn and Carius, Ann., 120, 69 (1861)
(37) Kondyrew and Fomin, J. Russ. Phys. Chem. Soc., 47, 190 (1915) [Chem. Zentr., 87, I, 832 (1916)].
(38) Miukhailenko and Protasova, ibid., 53, 347 (1921) [C. A., 18, 2338 (1924)].
(39) Gilman and Kirby, Rec. trav. chim., 48, 155 (1929).
(40) Gilman and Parker, J. Am. Chem. Soc., 46, 2823 (1924).
(41) Danehy and Nieuland, ibid., 58, 1609 (1926).

β,β'-diethylsuccinic acid (42).



$$2\ C_2H_5CHBrCO_2C_2H_5 \xrightarrow[CuCl_2]{Mg} \begin{array}{c} C_2H_5CHCO_2C_2H_5 \\ | \\ C_2H_5CHCO_2C_2H_5 \end{array}$$

Copper salts have been used very extensively for the coupling of aryl groups derived from arylmetallic compounds. The first very complete work in this series was carried out by Kondyrew and Fomin (37). They prepared bi-*p*-tolyl and biphenyl by the action of the corresponding Grignard on various cuprous and cupric halides. Turner (42) reported that phenylmagnesium bromide reacted with cupric chloride to give a good yield of biphenyl. This formation of biphenyl under the influence of copper salts has been studied by various other workers (39, 43). It has been found that the reaction with copper salts was the method of choice for the preparation of bimesityl (44).

As would be expected, phenylcopper slowly decomposed at room temperature to give biphenyl predominantly (45a, 45b). A small amount of biphenyl has been isolated in the reaction of tetraphenyllead with cupric nitrate, indicating that phenylcopper was momentarily formed (45c).

---

(42) Turner, J. Proc. Royal Soc. N. S. Wales, 54, 37 (1920) [C. A., 15, 669 (1921)]

(43) (a) Krizewsky and Turner, J. Chem. Soc., 115, 559 (1919).
(b) Sakellarios and Kyrimis, Ber., 57, 322 (1924).
(c) Miukhailenko and Zasuipkina, J. Russ. Phys. Chem. Soc. 53, 343 (1921) [C.A., 18, 2338 (1924)].

(44) Moyer and Adams, J. Am. Chem. Soc., 51, 630 (1929).

(45) (a) Reich, Compt. rend., 177, 322 (1923).
(b) Gilman and Straley, Rec. trav. chim., 55, 821 (1936).
(c) Gilman and Woods, J. Am. Chem. Soc., 65, 435 (1943).

Several investigations have been carried out on the reaction of organic halides with Grignard reagents in the presence of a catalytic amount of copper salts. Gilman and Zoellner (46) found that with an activated copper-magnesium alloy, a decrease in yield of RMgX was noted. This fact can be attributed to the reaction of the RX with the RMgX under the influence of the copper. Prior to this work, it was reported that phenylmagnesium iodide reacted smoothly with iodobenzene to give biphenyl (43a).

As with the copper halides, Buckton (35), and Wanklyn and Carius (36) reported reactions of diethylzinc with silver chloride. Grignard reagents prepared from bromobenzene and benzyl chloride have been reacted with a variety of silver salts to give yields of the coupling product varying from 0 to 100 per cent (39). In contrast to the reaction with the cupric bromide, which gave coupling, _n_-butylethynylmagnesium chloride with silver bromide gave a 60 per cent yield of _n_-butylethynylsilver (41). The butylacetylene was regenerated by refluxing with aqueous potassium cyanide.

Gardner and co-workers (47) have carried out very extensive investigations upon the action of organomagnesium halides on silver bromide. Coupling resulted with the Grignard

---

(46) Gilman and Zoellner, _ibid._, _53_, 1581 (1931).
(47) (a) Gardner and Borgstrom, _ibid._, _51_, 3375 (1929).
(b) Gardner, Joseph, and Gollub, _ibid._, _59_, 2583 (1937).
(c) Gardner and Joseph, _ibid._, _61_, 2551 (1939).
(d) Gardner and Snyder, _ibid._, _62_, 2879 (1940).
(e) Joseph and Gardner, _J. Org. Chem._, _5_, 61 (1940).
(f) Bickley and Gardner, _ibid._, _5_, 126 (1940).

derivatives prepared from bromobenzene, p-bromoanisole, p-bromotoluene, benzyl chloride, cyclohexyl bromide and n-butyl bromide (47a). When treated with silver bromide, a mixture of phenylmagnesium bromide and p-methoxyphenylmagnesium bromide gave the following products after demethylation (47b): 22 per cent biphenyl, 4.7 per cent 4-hydroxybiphenyl and 18.2 per cent, 4,4'-dihydroxybiphenyl. This reaction was extended to mixtures of phenylmagnesium bromide and various alkylmagnesium bromide compounds (47e). In all cases, except when the alkyl group was tert.-butyl, some of the unsymmetrical product was formed. The same investigators also found that the action of silver bromide on mixtures of benzylmagnesium bromide and other alkyl Grignards gave increasing yields of benzylalkanes with increasing chain length, except in the case of the tert.-butyl derivative. A mixture of p-tolysilver and p-methoxyphenylsilver, prepared from the Grignard reagents and silver bromide, gave all three possible products after heating (47f).

Krause and Wendt (48) reported the decomposition of phenylsilver to give biphenyl and metallic silver.

The reaction of silver nitrate with various R_4Pb, R_4Sn and R_3Bi compounds to give RAg derivatives has been investigated rather thoroughly. The first report of work of this nature was concerned with the reaction of triethylphenyltin with silver nitrate (49). The products in this cleavage were

---

(48) Krause and Wendt, Ber., 56, 2064 (1923).
(49) Ladenburg, Ann., 159, 251 (1871).

triethyltin nitrate, biphenyl and metallic silver. The biphenyl and metallic silver were undoubtedly the result of the decomposition of phenylsilver.

Krause and Schmitz (50) found that triphenylethyllead and -tin were very readily cleaved by silver nitrate to give a phenylsilver-silver nitrate complex.

$$C_2H_5Pb(C_6H_5)_3 + 2\ AgNO_3 \longrightarrow C_2H_5Pb(C_6H_5)_2NO_3 + C_6H_5Ag{\cdot}AgNO_3$$

These authors stated that symmetrical aryltin and -lead compounds did not react with silver nitrate. More recently, however, it has been observed that under comparatively mild conditions, tetraphenyllead and -tin will react with silver nitrate to give the intermediate phenylsilver which decomposes to silver and biphenyl (45c).

Both triphenylbismuth (51) and diphenylbismuth bromide (52) reacted with silver nitrate to give biphenyl through the transitory phenylsilver.

Trithienylantimony and -bismuth, as well as tetrathienyltin and -lead, reacted with silver nitrate apparently to give the thienylsilver-silver nitrate complex (53). An investigation of the decomposition products was not carried out.

Tetramethyllead reacts with silver to give ethane, predominantly, and a small amount of methane and ethylene

---

(50) Krause and Schmitz, Ber. 52, 2150 (1919).
(51) Challenger and Alpress, J. Chem. Soc., 119, 913 (1921).
(52) Challenger and Wilkinson, ibid., 121, 91 (1922).
(53) Krause and Renwanz, Ber., 65, 777 (1932).

(54, 45c). Tetraethyllead gave butane, ethane and ethylene under the same conditions. In the reaction of tetra-*n*-propyl lead with silver nitrate, the resulting *n*-propylsilver decomposed to give 23 per cent coupling to hexane and 77 per cent disproportionation to propane and propylene (55, 54b).

Other than for brief, general comments on the thermal stability of gold compounds, little information can be found concerning the decomposition of such derivatives. This is due, in part, to the small amount of work which has been done because of the costly nature of the materials used in such reactions. Kharasch and Isbell (56) investigated the action of aurous chloride carbonyl with the Grignard reagent of various types of organic radicals. These reactions resulted in the liberation of carbon monoxide, the precipitation of metallic gold, and the formation of the *bis*-hydrocarbon.

$$2\ RMgX + 2\ AuCOCl \longrightarrow R.R + 2\ CO + 2\ Au$$

Phenyl-, *o*-tolyl-, *p*-tolyl- and -naphthylmagnesium bromides, and benzylmagnesium chloride were used. Aurous chloride gave biphenyl with phenylmagnesium bromide.

$$2\ C_6H_5MgBr + 2\ AuCl \longrightarrow C_6H_5.C_6H_5 + 2\ MgClBr + 2\ Au$$

n-Propylgold dibromide decomposed spontaneously

---

(54) (a) Semerano and Riccoboni, *Ricerca sci.*, *11*, 269 (1940) [*C.A.*, *37*, 71 (1943)].
(b) Semerano and Riccoboni, *Ber.*, *74*, 1089 (1941).
(c) Semerano, Riccoboni, and Callegari, *Ber.*, *74*, 1297 (1941).

(55) Semerano, Riccoboni, and Götz, *Z. Elektrochem.*, *47*, 484 (1941).

(56) Kharasch and Isbell, *J. Am. Chem. Soc.*, *52*, 2919 (1930).

and quantitatively to give aurous bromide and n-propyl bromide (57).

$$n\text{-}C_3H_7AuBr_2 \longrightarrow AuBr + n\text{-}C_3H_7Br$$

This decomposition may operate through the intermediate formation of propyl and bromine radicals.

Group II.

Very little has been noted on the thermal decomposition of the organo derivatives of magnesium and the alkaline earth metals. However, the organometallic compounds of the "B" family, especially those of mercury, have been studied quite thoroughly.

Octane was formed when di-n-butylzinc was heated with a nickel catalyst (58). The statement was made that this reaction appeared to be rather complex.

Concerning dimethylcadmium, the general observation was made that it was the most stable derivative of cadmium (59). The statement that the methyl derivatives are the most stable, as for example dimethylmercury, trimethylboron and tetramethyllead, was also made.

Frankland and Duppa (60) catalyzed the decomposition of diethylmercury with metallic copper, silver and gold. The product was an inflammable gas, but an analysis was not performed.

---

(58) Zartman and Adkins, J. Am. Chem. Soc., 54, 3398 (1932).
(59) Krause, Ber., 63, 999 (1930).
(60) Frankland and Duppa, J. Chem. Soc., 17, 29 (1864); Ann., 130, 117 (1864).

Thermal decomposition of dimethylmercury at a temperature above 290° and in the absence of hydrogen gas gave ethane, methane and carbonaceous material (61). In the presence of hydrogen, there was no carbonaceous material and methane was the predominant gaseous product, indicating that the methyl radicals reacted with the hydrogen gas.

A comparison of the reaction,

$$RHgR \longrightarrow R.R + Hg$$

was carried out on the three butyl derivatives. The results showed that the stability of the carbon-mercury linkage decreases in the order: RCH_2Hg-, R_2CHHg-, and R_3CHg- (62).

Frey and Hepp (63) decomposed di-n-butylmercury at 490° and 3 mm. and found that a complex mixture resulted. The products were ethylene (57.0%), ethane (6.3%), butane (20.5%), hexane (10.6%), heptane (1.3%), and octane (2.13%). Di-sec.-butylmercury decomposed to give isopentane predominantly (64).

Diethylmercury was heated in a mixture of hydrogen and ethylene and a polymer of ethylene was the primary product (65). A small amount of saturated hydrocarbons was also produced. A proposed mechanism for the formation of the higher unsaturated and saturated hydrocarbons involved free ethyl radicals:

---

(61) Cunningham and Taylor, J. Chem. Phys., 6, 359 (1938).
(62) Marvel and Calvery, J. Am. Chem. Soc., 45, 820 (1923).
(63) Frey and Hepp, ibid., 55, 3357 (1933).
(64) Frey, Ind. Eng. Chem., 26, 198 (1934).
(65) Taylor and Jones, J. Am. Chem. Soc., 52, 1111 (1930).

$(C_2H_5)_2Hg \longrightarrow Hg + 2\ C_2H_5$, followed by the reaction,

$C_2H_5 + C_2H_4 + C_2H_4 \longrightarrow C_4H_9 + C_2H_4$, then

$C_4H_9 + C_2H_4 + C_2H_4 \longrightarrow C_6H_{13} + C_2H_4$

$C_6H_{13} + C_2H_5 \longrightarrow C_2H_6 + C_6H_{12}$ and, or

$C_6H_{13} + C_2H_4 \longrightarrow C_6H_{12} + C_2H_5$

In a sealed tube reaction at 160-170°, dibenzylmercury was decomposed with acetic acid. Surprisingly, a comparatively large amount of bibenzyl was formed (66). Dibenzylmercury decomposes thermally, with or without a catalyst, to give bibenzyl and mercury (67).

Dreher and Otto (68) catalytically decomposed diphenylmercury by distillation from powdered iron, or metallic copper, to give biphenyl. Razuvaev and Koton (67, 69) studied the effect of other catalysts, such as nickel, palladium, gold and silver, on the decomposition of diphenylmercury. All of the metals used gave biphenyl.

A series showing the relative inclination to decomposition with palladium as a catalyst was established with R_2Hg compounds (69). The increasing tendency to decompose was as follows: α-naphthyl-, p-tolyl-, p-bromophenyl-, p-phenetyl-p-anisyl-, phenyl- and benzyl-. All the mercury derivatives gave the coupled product on decomposition, except di-α-naphthyl-

---

(66) Jones and Werner, Ibid., 40, 1257 (1918).
(67) Razuvaev and Koton, Ber., 66, 854 (1933).
(68) Dreher and Otto, Ann., 154, 93 (1870).
(69) Razuvaev and Koton, Ber., 66, 1210 (1933).

mercury which gave naphthalene. In this series of decompositions, both the solvent and the catalyst markedly affected the course and extent of the breakdown (70). For example, the relative effect of catalysts in alcohol was arranged in the following decreasing order: palladium, nickel, gold, silver and copper. In tetralin the order of decreasing effect was palladium, gold, silver, nickel and copper.

Diphenylmercury was decomposed by heating in paraffin oil containing sulfur (71). The production of free phenyl radicals was inferred from the formation of diphenyldisulfide.

Group III.

The information regarding the extent and manner of the thermal decomposition of the organometallic compounds of this group is rather meager. Most of the work has been restricted to the synthesis of such compounds. Studies on decomposition were essentially neglected.

Triethylboron (b.p., 95°) slowly decomposed at 100° C. Forty-eight and nine-tenths cc. of gaseous boron derivative gave 2.1 cc. of ethane and 0.4 cc. of hydrogen after heating for fifty-eight hours (72a).

Lanthanum chloride reacted with phenyllithium to give biphenyl, and with methyllithium to give methane (72b).

---

(70) Razuvaev and Koton, J. Gen. Chem. (U.S.S.R.), 4, 647 (1934) /C.A., 28, 3661 (1935)/.

(71) Razuvaev and Koton, ibid., 5, 361 (1935) /C.A., 29, 6217 (1935)/.

(72) (a) Stock and Zeidler, Ber., 54, 531 (1921).
(b) Jones, Doctoral Dissertation, Iowa State College (1941).

When one mole of thallous chloride was refluxed with two moles of ethylmagnesium bromide, a quantitative production of metallic thallium was obtained (73). However, the gaseous products were not analyzed. Triphenylthallium decomposed to phenylthallium and biphenyl when heated in refluxing xylene (74).

Group IV.

Many attempts have been made to prepare organometallic compounds of the "A" family of Group IV. These experiments led to the conclusion that such compounds were thermally unstable.

The stability of the organo compounds of the "B" family has been studied quite thoroughly. This is especially true of the lead compounds, which served as an early source of free radicals.

Cahours (75) reported a reaction of titanium tetrachloride with diethylzinc, but an organometallic was not isolated. The gaseous products were not identified. Later investigations considered the product to be butane (76). Peternò and Peratoner (77) reported the complex, $TiCl_4 \cdot 2(C_2H_5)_2Zn$, which hydrolyzed to give n-octane, among other products.

---

(73) Menzies and Cope, J. Chem. Soc., 2862 (1932).
(74) Gilman and Jones, J. Am. Chem. Soc., 62, 2357 (1940).
(75) Cahours, Ann., 122, 48 (1862).
(76) Schumann, Ber., 21, 1079 (1888).
(77) Peternò and Peratoner, Ber., 22, 467 (1889).

Diethylmercury reacted with titanium tetrachloride to give an unidentified gas which was probably butane (78).

Challenger and Pritchard (79) observed that titanium tetrachloride reacted with phenylmagnesium bromide to give biphenyl. A mixture of sodium, chlorobenzene and titanium tetrachloride also gave biphenyl. α-Naphthylmagnesium bromide gave bi-α-naphthyl.

In a sealed tube reaction, diphenylmercury reacted with titanium tetrachloride to give phenylmercury chloride, biphenyl and titanium trichloride (80).

Titanium tetraethoxide reportedly reacted with *n*-butyllithium to give an organotitanium compound along with *n*-octane (81).

Hinsberg (82) treated zirconium tetrachloride with diethylzinc at 180° C. and observed that a gas was produced. The product was considered to be butane.

More recently, various titanium and zirconium halides and alkoxides have been treated with alkyl- and arylmetallic compounds (72b). The alkyl compounds gave the RH derivatives and the aryl compounds gave the coupling products.

Tetraethylsilicon decomposed under high hydrogen pressure and temperature according to the following equation (83):

---

(78) Levy, *Ann. Chim. Phys.*, [VI] *25*, 433 (1892).
(79) Challenger and Pritchard, *J. Chem. Soc.*, *125*, 864 (1924).
(80) Razuvaev and Bogdanow, *J. Gen. Chem.* (U.S.S.R.), *3*, 367 (1933) [*C.A.*, *28*, 2340 (1934)].
(81) Plets, *ibid.*, *8*, 1298 (1938) [*C.A.*, *33*, 4193 (1939)].
(82) Hinsberg, *Ann.*, *239*, 253 (1887).
(83) Dolgov and Vol'nov, *J. Gen. Chem.* (U.S.S.R.), *1*, 330 [*C.A.*, *26*, 2168 (1931)].

$$H_2 + 2\ (C_2H_5)_4Si \longrightarrow 2\ C_2H_6 + (C_2H_5)_3Si\text{-}Si(C_2H_5)_3$$

Phenyllithium reacted with silicon metal to give only biphenyl (84).

The decomposition of tetraethylgermanium at 420-450° gave a very complex mixture of gaseous products (85). Hydrogen (10.6%), methane (7.5%), ethane (41.5%), propane (3.3%), ethylene (21.7%), propylene and butylene (12.9%), isobutylene (1.6%), and acetylene (1.4%) were formed.

Kraus and Bullard (86) reported that the thermal decomposition of dimethyltin oxide gave tetramethyltin, ethane, stannous oxide and stannic oxide. The products would indicate the transitory formation of the free methyl radicals.

The existence of free benzyl radicals has been established in the pyrolysis of tetrabenzyltin (23). The evidence for the transitory formation of the fragments was the reaction with mirrors of selenium, tellurium and mercury.

Palladium and gold decompose tetraphenyltin to biphenyl and tin (87). The action of metals on the breakdown of tetraphenyltin in alcohol solution according to the equation,

$$R_4Sn \longrightarrow 2\ R.R. + Sn$$

was in the following order of decreasing activity: palladium, silver, nickel and gold (88).

A host of investigators have pyrolyzed tetramethyllead

---

(84) Talalaeva and Kocheshkov, ibid., 8, 1831 (1938) [C.A., 33, 5819 (1939)].
(85) Geddes and Mack, J. Am. Chem. Soc., 52, 4372 (1930).
(86) Kraus and Bullard, ibid., 51, 3605 (1929).
(87) Koton, J. Gen. Chem. (U.S.S.R.), 4, 653 (1934) [C.A., 29, 3662 (1934)].
(88) Koton, Ber., 66, 1213 (1933).

(9, 16, 24, 27, 89). Free methyl radicals were among the products in each case. The free fragments were identified by means of the methods which have been discussed previously.

Tetraethyllead has been decomposed in the usual manner to give free ethyl radicals (10, 17, 27, 65, 89e, 90). Cramer (91) carried out the thermal decomposition of tetraethyllead in benzene solution in the presence of ethylene and hydrogen. The evidence favored the assumption that the predominating reaction of ethyl radicals in solution was that of disproportionation and that the ethylene so formed was converted to higher hydrocarbons in the following manner:

$$C_2H_5- + 2\ C_2H_4 \longrightarrow C_4H_9- + C_2H_4$$

The alkyl R_4Pb compounds above methyl and ethyl break down to give free methyl and ethyl radicals. Branched chains seemed to accelerate the decomposition. Tetra-n-propyllead gave free methyl and ethylene, while tetraisobutyllead gave free methyl fragments (23).

Observations in connection with the low temperature formation of free radicals indicated that aluminum trichloride

---

(89) (a) Rice, Johnston, and Evering, J. Am. Chem. Soc., 54, 3529 (1932).
(b) Simons, McNamee, and Hurd, J. Phys. Chem., 36, 939 (1932).
(c) Paneth, Hofeditz, and Wünsch, J. Chem. Soc., 372 (1935).
(d) Romm, J. Gen. Chem. (U.S.S.R.), 10, 1784 (1940) /C.A., 35, 3880 (1941)/.
(e) Ipatiev, Razuvaev and Bogdanov, Ber., 63, 335 (1930).
(90) Minert, J. Am. Chem. Soc., 55, 979 (1933).
(91) Cramer, Ibid., 56, 1234 (1934).

reacted with tetraethyllead to give apparently free ethyl radicals (92).

Zechmeister and Csabay (93) found that, although tetraphenyllead distills unchanged at 15-20 mm. at a temperature of 240°, energetic heating at 270° gave metallic lead, some unchanged material, and a good yield of biphenyl. Dull and Simons (21) obtained evidence that tetraphenyllead was decomposed to give free phenyl radicals: namely, that the gaseous products reacted with mercury to produce diphenylmercury. Biphenyl was also produced. Later, Dull and Simons (94) found that a quantitative yield of biphenyl was obtained from tetraphenyllead at 252° in the absence of a catalyst. The yields of biphenyl were observed to decrease at lower temperatures; higher temperatures gave benzene and terphenyls. However, Koton (95) claimed that the decomposition, in absence of catalysts, of tetraphenyllead begins above the temperature of 252° reported by Dull and Simons (94). Koton found that newly prepared metallic lead catalyzed the decomposition at lower temperatures and suggested that as an explanation for the decomposition at 252°.

The catalytic decomposition of tetraphenyllead has led to interesting results. Nickel catalyzes a synthetic reaction whereby tetraphenyllead is converted quantitatively into

---

(92) Gilman and Apperson, _J. Org. Chem._, _4_, 162 (1939).
(93) Zechmeister and Csabay, _Ber._, _60_, 1617 (1927).
(94) Dull and Simons, _J. Am. Chem. Soc._, _55_, 4328 (1933).
(95) Koton, _ibid._, _56_, 1118 (1934).

biphenyl (58). A similar reaction occurred with tetra-p-tolyllead. Koton (87, 88) studied the action of a number of catalysts on this reaction. He found the activity of the metals in the decomposition in alcohol form the following series of increasing strength: palladium, gold, silver and nickel. The reaction was represented by the equation,

$$R_4Pb \longrightarrow 2\ R.R + Pb$$

Group V.

There is a paucity of information concerning the pyrogenic decomposition of the organometallic compounds of the metals of Group V. To be sure, there are innumerable known derivatives of such metals but they have been studied with other purposes in mind.

Vernon (96) observed that all halides and oxyhalides of vanadium which were studied reacted with phenylmagnesium bromide to give biphenyl.

Recently, it was reported that organotantalum compounds were assumed to have been prepared by the reaction of tantalum pentachloride with either phenylmagnesium bromide or ethylmagnesium bromide (97). Conclusive evidence for the existence of such compounds was lacking. The reaction residues were not worked up for coupling products.

When triarylbismuth compounds are heated to high temperatures, they decompose into the metal and biaryl compounds (98).

---

(96) Vernon, Ibid., 53, 3831 (1931).
(97) Afanasyev, Chemistry and Industry, 18, 631 (1940).
(98) Gilman and Yale, Chem. Rev., 30, 281 (1942).

Group VI.

As a consequence of the interest shown in the heavy metals of this group, primarily because of their radioactivity, a comparatively large amount of work on the organometallic derivatives has been carried out. This work was done in spite of the difficulty of the procedure involved.

Bennett and Turner (99a) reported that phenylmagnesium bromide reacted with chromium trichloride to give biphenyl. Duplicate results were obtained in later work (42) with this and more extensive reactions (99b). However, o-tolylmagnesium bromide reacted with the chromium halide to give only a small yield of the coupled product. Even in an atmosphere of hydrogen gas, biphenyl was produced by treating the MX_3 with the phenyl Grignard reagent (100). The metal product was the hydride.

Triphenylchromium and tetraphenylchromium, obtained as amorphous deposits in the electrolysis of triphenylchromium iodide and tetraphenylchromium iodide, respectively, in anhydrous liquid ammonia, readily split off biphenyl (101). Hein and co-workers (102) have also suggested that pentaphenylchromium hydroxide, $(C_6H_5)_5CrOH$, can eliminate a neutral phenyl radical in certain of its reactions.

---

(99) (a) Bennett and Turner, J. Proc. Roy. Soc. N. S. Wales, 53, 100 (1919) /C.A., 14, 414 (1920)/.
(b) Bennett and Turner, J. Chem. Soc., 105, 1057 (1914).
(100) Weichselfelder and Thiede, Ann., 447, 64 (1926).
(101) Hein and Markert, Ber., 61, 2255 (1928).
(102) Hein and co-workers, Ber., 54, 2711 (1921); Ber. 61, 730 (1928); Ber., 62, 1151 (1929).

Gazopoulos (103) carried out a rather extensive series of coupling reactions using molybdenum pentachloride. He treated the metal halide with the desired Grignard derivative and obtained the following coupled products: biphenyl (85%), bibenzyl (62%), bi-p-tolyl (45%), 2,5-dimethylhexane (50%), and 2,7-dimethyloctane (50%). The 2,5-dimethylhexane and 2,7-dimethyloctane were prepared, respectively, from isobutylmagnesium bromide and isoamylmagnesium bromide.

Hein (104) reported that phenylmagnesium bromide reacted with molybdenum pentachloride, trichloride and tribromide, to give compounds analogous in stability to those of chromium.

Cahours (75) reported that metallic tungsten reacted with methyl iodide to give a compound of the formula, $W(CH_3)_3I$, as evidenced by analysis. Nevertheless, it is very improbable that a carbon-metal linkage was present. Later, Turner (105) observed that all attempts to prepare organotungsten compounds by reacting the metal halides with organomagnesium halides proceeded according to the following equation:

$$WCl_y + y\ RMgX \longrightarrow WCl_{(y-2)} + 2\ MgXCl$$
$$+ (x-2)\ RMgX + R.R$$

The coupled compound was the prime reaction product. A more recent investigation of this reaction seemed to indicate that tungsten halides reacted with the Grignard reagent to give

---

(103) Gazopoulos, Praktika (Akad. Athenon), 7, 180 (1932) [C.A., 28, 4726 (1934)].
(104) Hein, Angew. Chem., 51, 503 (1938).
(105) Turner, Proc. Chem. Soc., 30, 4 (1914).

unstable intermediate organometallic compounds which were not isolated due to the ease with which they decomposed (99a). Brydowna (106) found that tungsten hexachloride reacted in ether with phenylmagnesium bromide to give a 50 per cent yield of biphenyl. Job and Rouvillais (107) reported a reaction of the tungsten hexachloride with phenylmagnesium bromide to give metallic tungsten, but the fate of the phenyl radicals was not determined. More recently, the compounds, $C_6H_5WO_3.5H_2$, $(C_6H_5W)_2O_7H_4$ and $(C_6H_5)_3W_2O_8H_7$, have been reported in the reaction of tungsten trichloride, or tungsten tetraphenylate, with phenylmagnesium bromide (108). No mention was made of decomposition products.

Group VII.

Kharasch and Fields (109) have recently reported the slight action of manganous chloride on coupling reactions. This lesser reactivity may be due to the relatively stable nature of the RMnX compounds.

In contrast to the supposed formation of trimethylrhenium (110) by the reaction of rhenium trichloride with methyl magnesium iodide, it was found that this reaction gave an almost quantitative yield of gases, composed mostly of methane with a

---

(106) Brydowna, *Bull. soc. chim.*, [4] 39, 1771 (1926).
(107) Job and Rouvillais, *Compt. rend.*, 187, 564 (1928).
(108) Hein and Nebe, *Naturwissenschaften*, 28, 93 (1940).
(109) Kharasch and Fields, *J. Am. Chem. Soc.*, 63, 2316 (1941).
(110) Druce, *J. Chem. Soc.*, 1129 (1934).

small amount of ethane (111). No organometallic compound could be isolated.

Group VIII

Numerous experiments have been carried out in attempts to prepare organometallic compounds of the metals of Group VIII. Some preparations have been successful, notably those of the platinum compounds (112), but most have lead to coupling products.

Organoiron compounds aroused the interest of the early synthetic organic chemists. Wanklyn and Carius (36) reported the reaction of diethylzinc with iron iodide to give ethane, ethylene and hydrogen. This reaction has been checked and the formation of the products mentioned above was verified (113).

In a reaction reminiscent of the preparation of the Grignard reagent, Spencer and Harrison (114a) reacted iodobenzene with metallic iron. However, instead of the expected phenyliron iodide, there was produced excellent yields of biphenyl. In a similar experiment, Zeltner (114b) was of the opinion that an organoiron compound was formed as an intermediate in the reaction of iron metal with p-iodotoluene to give bi-p-tolyl.

---

(111) Gilman, Jones, Moore, and Kolbezen, J. Am. Chem. Soc., 63, 2525 (1941).

(112) Lichtenwalter, Doctoral Dissertation, Iowa State College (1938).

(113) Job and Reich, Compt. rend., 177, 1439 (1923).

(114) (a) Spencer and Harrison, Proc. Chem. Soc., 26, 118 (1910).
(b) Zeltner, J. prakt. Chem., 77, 393 (1908).

There was a variety of experiments involving alkyl derivatives. Ferrous chloride, ferric chloride and ferric thiocyanate reacted with ethylmagnesium bromide to give ethane and ethylene, and with propylmagnesium bromide to give propane (37). The synthesis of ethyliron iodide was claimed in a reaction between ethylzinc iodide and ferrous iodide by refluxing in ether (115). It is very improbable that an organoiron compound was formed. Ferric chloride promoted the coupling of substituted ethynylmagnesium halide compounds (41). In this way, bis(n-butylacetylene) was prepared in a 50 per cent yield. Miukhailenko and Protasova (38) found that the addition of ferric halides promoted quantitative yields of bibenzyl from benzyl chloride and magnesium in ether. Bibenzyl was synthesized by other workers using similar procedures (99b, 116).

Phenylmagnesium bromide reacted with ferric chloride to give good yields of the coupled product (116). Kondyrew and Fomin (37) prepared biphenyl and bi-p-tolyl by the action of the respective Grignard reagents with iron halides and pseudohalides. Bromobenzene refluxed with magnesium and a catalytic amount (4 mole per cent) of ferric chloride gave a quantitative yield of biphenyl (43c). Weichselfelder and Thiede (100) observed that phenylmagnesium bromide reacted with ferric chloride in an atmosphere of hydrogen gas to give one mole of biphenyl, one mole of benzene, and iron hydride. Ferrous

---

(115) Job and Reich, Compt. rend., 174, 1358 (1922).
(116) Oddo, Gazz. chim. ital., 44, 268 (1914).

chloride, however, gave only benzene under the same conditions.

In the formation of biphenyl in the reaction of ferric chloride with the phenyl Grignard reagent (117), Champetier (118) postulated a two-stage reaction:

$$2\ C_6H_5MgBr + 2\ FeCl_3 \longrightarrow C_6H_5 \cdot C_6H_5 + 2\ FeCl_2 + 2\ MgClBr \quad (I)$$

$$2\ C_6H_5MgBr + 2\ FeCl_2 \longrightarrow C_6H_5 \cdot C_6H_5 + 2\ Fe + 2\ MgClBr \quad (II)$$

The synthesis of phenyliron iodide was reported with the following reaction (118):

$$2\ C_6H_5ZnCl + FeI_2 \longrightarrow 2\ C_6H_5FeI + ZnCl_2 + ZnBr_2$$

The evidence presented for the existence of this organoiron compound was the hydrolysis of the product to give ferrous hydroxide.

$$2\ C_6H_5FeI + 2\ H_2O \longrightarrow 2\ C_6H_6 + Fe(OH)_2 + FeI_2$$

Obviously, the conclusion drawn as to the existence of this compound involved a good deal of conjecture.

More recently, the coupling reactions of Group VIII metals were investigated thoroughly (119). In the reactions of phenylmagnesium iodide with the anhydrous metal halides, practically quantitative yields of biphenyl were obtained with iron, cobalt, nickel, ruthenium, rhodium and palladium. Markedly reduced yields were observed with the chlorides of osmium, iridium and platinum. Nickelous cyanide gave 30 per cent biphenyl. Cobaltous bromide and 2,4,6-trimethylphenylmagnesium bromide gave 20 per cent bimesityl.

---

(117) Job and Champetier, Compt. rend., 189, 1089 (1929).
(118) Champetier, Bull. soc. chim., [4] 47, 1131 (1930).
(119) Gilman and Lichtenwalter, J. Am. Chem. Soc., 61, 957 (1939).

A series of questionable organometallic compounds was prepared for use in anti-knock studies with gasoline. Sims and Mardles (120) claimed to have prepared α-naphthylcobalt, xylylcerium, phenylchromium and tungsten, as well as uranium and iron phenyls. None of these compounds was isolated or identified.

Kharasch and co-workers (109, 121, 122) have studied the catalytic effect of iron, nickel, and especially cobalt halides, on coupling reactions. They found that excellent yields of biaryls were obtained when an aryl Grignard reagent, or lithium compound, was treated with an organic halide, preferably a bromide, in the presence of 3-10 mole per cent of the metal halide. The following chain mechanism was suggested:

$$C_6H_5MgBr + CoCl_2 \longrightarrow C_6H_5CoCl + MgClBr$$

$$2\ C_6H_5CoCl \longrightarrow C_6H_5{\cdot}C_6H_5 + 2\ CoCl$$

$$CoCl + C_6H_5Br \longrightarrow CoClBr + C_6H_5{\cdot}$$

$$X\ (C_6H_5{\cdot}) \longrightarrow C_6H_5H,\ C_6H_5{\cdot}C_6H_5\ \text{(trace)},\ C_6H_5{\cdot}C_6H_4{\cdot}C_6H_5,$$

and so on.

Wanklyn and Carius (36) treated nickel halides with diethylzinc and obtained a mixture of ethane, ethylene and hydrogen. In a hydrogen atmosphere, nickel chloride reacted with phenylmagnesium bromide to give benzene and nickel

---

(120) Sims and Mardles, *Trans. Faraday Soc.*, *22*, 368 (1926).
(121) Kharasch, Lewis, and Reynolds, *J. Am. Chem. Soc.*, *65*, 493 (1943); Kharasch, Nundenberg, and Archer, *ibid.*, *65*, 495 (1943); and Kharasch and Fuchs, *ibid.*, *65*, 504 (1943).
(122) Kharasch and Reynolds, *ibid.*, *63*, 3239 (1941).

hydride (123). Jones (124) reported that nickel tetracarbonyl gave biphenyl and benzoin with phenylmagnesium bromide. Similarly as with iron, iodobenzene reacted with nickel metal to give excellent yields of biphenyl (114). Biphenyl was isolated in the reaction of the phenyl Grignard reagent with nickel chloride in the presence of ethylene (125). Nickel cyanide was observed to give coupling with the phenyl and benzyl Grignard reagents (39).

Electrolytic Decomposition

But few of the available organometallic compounds have been subjected to electrolysis. This is primarily due to the lack of interest in such an investigation. In addition, due to solubilities and reactivities, very few such compounds are suitable for a study of this nature.

Hein (126) found that a solution of ethylsodium in diethylzinc behaved as a true electrolyte. An investigation of possible products was not carried out. Later work showed that this electrolysis gave zinc at the cathode and a mixture of hydrocarbons, chiefly ethylene and ethane, but also small amounts of methane, propane and butane, at the anode (127).

---

(123) Schlenk and Weichselfelder, Ber., 56, 2230 (1923).
(124) Jones, Chem. News, 90, 144 (1904).
(125) Job and Reich, Compt. rend., 179, 330 (1924).
(126) Hein, Z. Elektrochem., 28, 469 (1922).
(127) Hein, Petzchner, Wagler, and Segitz, Z. anorg. allgem. Chem., 141, 161 (1924); Wooster, Chem. Rev., 11, 1 (1932).

The transient existence of free ethyl groups was proved by the use of lead anodes in an experiment in which an electrochemical equivalent of lead was lost and tetraethyllead appeared in solution.

Ethylpotassium was observed to conduct better than ethylsodium and that compound better than ethyllithium (127). Benzyllithium was the best conductor of all the lithium alkyls. Diethylcalcium and diphenylmercury were non-conducting in diethylzinc.

Further proof for the existence of the free ethyl radicals in the electrolysis of ethylsodium in diethylzinc was the formation of the corresponding metal alkyls when cathodes of aluminum, cadmium, antimony, bismuth and thallium were used (128). Tin, copper, iron, platinum, tantalum and gold electrodes were passive.

Rodebush and Peterson (129) electrolyzed diethylzinc with a voltage of 110 and found that zinc was deposited, and although the products at the anode were not identified, there "could be little doubt that the ethyl radical was liberated at the anode."

Electrolytic studies have been carried out quite extensively on Grignard reagents, but only a select number included an investigation of decomposition products.

Evans and Lee (130) reported that methylmagnesium

---

(128) Hein and Segitz, Z. anorg. allgem. Chem., 158, 153 (1926).
(129) Rodebush and Peterson, J. Am. Chem. Soc., 51, 638 (1929).
(130) Evans and Lee, ibid., 56, 654 (1934).

chloride, bromide, and iodide gave methane, ethane, ethylene and isobutylene when electrolyzed at varying voltages and current densities. The reactions were considered to be as follows:

$$2n\ CH_3 \longrightarrow n\ CH_4 + (CH_2)_n$$
$$4\ CH_3 \longrightarrow C_2H_4 + 2\ CH_4$$
$$8\ CH_3 \longrightarrow C_4H_8 + 4\ CH_4$$
$$2\ CH_3 \longrightarrow C_2H_6$$

where $(CH_2)_n$ represents isobutylene and similar unsaturated derivatives. The anodic products from the electrolysis of ethylmagnesium halides were ethane, ethylene and traces of hydrogen. Propylmagnesium halides gave propane, propylene and traces of hydrogen. Mixtures of ethyl- and propylmagnesium halides gave chiefly ethane, propane, ethylene and propylene.

When a mixture of ethylmagnesium bromide and phenylmagnesium bromide was electrolyzed, only the ethyl group was discharged. In later work, Evans and Field (131) reported that high current density favored coupling. For example, the yields of ethane in the electrolysis of methylmagnesium bromide ranged from 19.5 per cent with a low current density to 84.2 per cent with a high current density.

Eighty-five per cent of the butyl radicals in n-butyl-

---

(131) Evans and Field, ibid., 58, 720 (1936).

magnesium bromide appeared as octane in the electrolysis of the Grignard reagent (132). With isobutylmagnesium bromide, 96 per cent of the isobutyl radicals coupled. The *sec.*-butyl Grignard gave 43 per cent coupling after electrolysis. The coupling tendency of the *n*-propyl radical under similar conditions was approximately 50 per cent; that of the *tert.*-butyl and isopropyl radicals was slight.

Gaddum and French (133) observed that benzylmagnesium chloride gave bibenzyl in yields exceeding 50 per cent on electrolysis. The electrolytic decomposition of phenylmagnesium bromide gave biphenyl in rather poor yields.

Dimethylmercury was prepared by the electrolysis of methylmercury acetate in the presence of pyridine (134). Free methyl radicals undoubtedly appeared in the course of this reaction.

Photochemical Decomposition

Although photochemical decomposition has been observed in a general way in a number of compounds, only a few critical experimental studies have been made concerning such decompositions.

Diethylzinc was dissociated by light to give ethane and some hydrogen (135a). Usually no ethylene was formed. A more

---

(132) Evans, Braithwaite, and Field, *ibid.*, *62*, 534 (1940).
(133) Gaddum and French, *ibid.*, *49*, 1295 (1927).
(134) Maynard and Howard, *J. Chem. Soc.*, *123*, 960 (1923).
(135) (a) Berthelot and Gaudechon, *Compt. rend.*, *156*, 1243 (1913).

recent publication (135b) has reported that ethane, ethylene and butane, along with small amounts of hydrogen and butylene were formed when diethylzinc was photochemically decomposed. The composition of the product did not change markedly with the temperature.

Moore and Taylor (135b) also recorded the same observations with dimethylmercury as with the diethylzinc mentioned above. With ultra-violet illumination, dimethylmercury decomposed to give mercury and ethane (136). Cunningham and Taylor (61) found that the photochemical decomposition of dimethylmercury in the absence of hydrogen produced ethane practically exclusively, while in the presence of hydrogen, measurable amounts of methane were obtained in addition to the ethane.

The formation of methyl radicals in the photochemical decomposition of tetramethyllead by ultra-violet light has been proved (137a). The main products were lead and ethane. Under the same conditions tetraphenyllead decomposed to give biphenyl and metallic lead.

Organometallic Radicals

There are numerous examples of the occurrence of the so-called "organometallic radicals" in the decomposition, thermal

---

(135) (b) Moore and Taylor, J. Chem. Phys., 8, 396 (1940).
(136) Thompson and Linnett, Trans. Faraday Soc., 33, 874 (1937).
(137) (a) Leighton and Mortensen, J. Am. Chem. Soc., 58, 448 (1936).

or otherwise, of normal organometallic compounds. The evidence that these organometallic radicals are "true" free radicals is not conclusive (137b). It is probable that these derivatives are polymers which ostensibly exhibit the odd-valency. For example, triphenyllead actually exists as the dimer, hexaphenyldilead.

Methylmercury and ethylmercury have been prepared by the electrolysis of alkylmercury halides in liquid ammonia at low temperatures (12, 138a). At higher temperatures these compounds decompose to R_2Hg and Hg.

It has been postulated that diphenylthallium was formed when one equivalent of sodium was added to a solution of diphenylthallium bromide in liquid ammonia (138b). More substantial evidence was presented for the transitory formation of phenylthallium when triphenylthallium was heated in xylene (138b).

Kraus and Brown (139) prepared diphenylgermanium by the action of sodium on a diphenylgermanium dihalide.

Diethyltin was formed in the reaction of diethyltin dihalide with sodium amalgam,

$$(C_2H_5)_2SnX_2 + 2\ Na(Hg) \longrightarrow (C_2H_5)_2Sn + 2\ NaX$$

and the action of the ethyl Grignard reagent on stannous chloride (140).

---

(137) (b) Morris and Selwood, ibid., 63, 2509 (1941).
(138) (a) Krause, ibid., 35, 1732 (1913).
      (b) Gilman and Jones, ibid., 62, 2357 (1940).
(139) Kraus and Brown, ibid., 52, 4031 (1930).
(140) (a) Lowig, Ann., 84, 308 (1852).
      (b) Frankland, Ann., 85, 329 (1853).
      (c) Pfeiffer, Ber., 44, 1269 (1911).

$$2\ C_2H_5MgBr + SnCl_2 \longrightarrow (C_2H_5)_2Sn + 2\ MgX_2$$

The diaryltin compounds have been prepared by similar methods, as well as by pyrolysis of the dihydride (141).

$$(C_6H_5)_2SnH_2 \longrightarrow (C_6H_5)_2Sn + H_2$$

As would be expected, the R_3Sn compounds may be prepared in liquid ammonia by the following reactions (141b, 142):

$$(CH_3)_3SnX + Na \longrightarrow (CH_3)_3Sn + NaX$$

$$(C_6H_5)_3SnNa + ClSn(C_6H_5)_3 \longrightarrow 2\ (C_6H_5)_3Sn + NaCl$$

Triethyllead has been prepared by the electrolysis of triethyllead hydroxide (143) and the reaction of sodium in liquid ammonia with triethyllead bromide (144). Diphenyllead, di-*p*-tolyllead, triphenyllead, tri-*p*-tolyllead, tri-*o*-tolyllead, and tri-*p*-xylxyllead have been prepared by Krause and Reissaus (145) by the reaction of lead halides with Grignard reagents.

A transitory brown to red coloration of a liquid ammonia solution of a diaryllead dihalide was observed when metallic sodium was added (145b).

---

(141) (a) Kraus and Becker, *Ber.*, *53*, 173 (1929).
(b) Chambers and Scherer, *J. Am. Chem. Soc.*, *48*, 1054 (1926).
(142) (a) Kraus and Sessions, *ibid.*, *47*, 2361 (1925).
(b) Harada, *Bull. Chem. Soc. Japan*, *4*, 266 (1929) /*C.A.*, *24*, 1340 (1930)/.
(c) Ladenburg, *Ann.* (*Suppl.*), *8*, 63 (1872).
(d) Rugheimer, *Ann.*, *364*, 51 (1909).
(143) Midgley, Hochwalt, and Calingaert, *J. Am. Chem. Soc.*, *45*, 1821 (1923).
(144) (a) Calingaert and Soroos, *J. Org. Chem.*, *2*, 535 (1938).
(b) Gilman and Bailie, *J. Am. Chem. Soc.*, *61*, 731 (1939).
(145) (a) Krause and Reissaus, *Ber.*, *55*, 888 (1922).
(b) Leeper, Doctoral Dissertation, Iowa State College (1942).

It has been observed that occasionally the pyrolysis of R_6Pb (R_3Pb) compounds gives the R_4Pb derivative with difficulty (145c).

Lithium, sodium, potassium, calcium, or barium reacted with diphenylbismuth halides in liquid ammonia according to the following equation (146):

$$(C_6H_5)_2BiX + Na \longrightarrow (C_6H_5)_2Bi + NaX$$

Evidence has also been presented for the existence of dimethylbismuth and diethylbismuth (9, 24, 147).

Triphenylchromium and tetraphenylchromium are usually considered to have free radical characteristics (101).

Redistribution Reaction

The redistribution reaction is essentially an example of the general equilibrium reaction represented by the following equation:

$$AY + BZ \longrightarrow AZ + BY$$

With the organometallic compounds, these reactions constitute liquid-phase equilibria in which an ionizing solvent is unnecessary. A catalyst is required, however. The interchange takes place purely at random, and using the law of probability one can predict in advance the composition of the product.

---

(145) (c) Baillie, Doctoral Dissertation, Iowa State College (1938).

(146) Gilman and Yablunky, *J. Am. Chem. Soc.*, *63*, 212 (1941).

(147) Denham, *ibid.*, *43*, 2367 (1921).

Although a mixture of dimethyl- and diethylzinc failed to show an appreciable amount of redistribution (148), the RR'Zn compounds are known to rearrange on heating to give a mixture of R_2Zn and R'_2Zn (149).

Dimethylmercury and diethylmercury can be mixed, when pure, without undergoing any transformation. However, in the presence of a suitable catalyst an interchange of methyl and ethyl radicals occurred according to the following equation (148):

$$(CH_3)_2Hg + (C_2H_5)_2Hg \longrightarrow 2\ CH_3HgC_2H_5$$

An equimolecular mixture of tetramethyllead and tetraethyllead, when treated with triethyllead chloride or aluminum chloride as a catalyst, gave all the five possible R_4Pb compounds in the proportions given in the following equation (150):

$$8\ Me_4Pb + 8\ Et_4Pb \longrightarrow 1\ Me_4Pb + 4\ Me_3EtPb + 6\ Me_2Et_2Pb + 4\ MeEt_3Pb + 1\ Et_4Pb$$

In a similar manner a mixture of tetramethyl-, tetraethyl-, and tetra-n-propyllead gave a mixture of the fifteen possible R_4Pb compounds in proportions corresponding to a random distribution of the three radicals (150). Other examples of this reaction of RM compounds have been given where the reactants are two or more different radicals, including methyl,

---

(148) Calingaert, Soroos, and Hnizda, ibid., 62, 1107 (1940).
(149) Krause and Fromm, Ber., 59, 931 (1926).
(150) Calingaert, Beatty, and Soroos, J. Am. Chem. Soc., 62, 1099 (1940).

ethyl, n-propyl, isopropyl, isobutyl, tert.-butyl, phenyl, and p-tolyl, bound to one or more metals, including lead, tin, silicon and mercury (148, 150).

A spontaneous redistribution of alkyl radicals occurred with the R_3PbX compounds; the reactants served as their own catalyst. Thus, a mixture of trimethyl- and triethyllead chlorides, or the single compound dimethylethyllead chloride, reacted to give all the four possible R_3PbCl compounds (151). It has been observed that R_2PbX_2 derivatives decompose at elevated temperatures in the following manner (152):

$$R_2PbX_2 \longrightarrow R_2 + PbX_2$$

An interchange of radicals has been observed with a mixture of triphenyl- and tri-α-naphthylbismuth in the absence of a catalyst and at a high temperature (153).

Compounds of two different metals react under similar conditions yielding all the possible compounds of both metals. For example, a mixture of tetramethyllead and diethylmercury reacted in the presence of an aluminum chloride catalyst to give an interchange of the alkyl radicals between the two metals according to the following equation (154, 155):

$$Me(PbR_3) + Et(HgR) \longrightarrow Me(HgR) + Et(PbR_3)$$

At the same time there was a redistribution of the radicals

---

(151) Calingaert, Soroos, and Shapiro, ibid., 62, 1104 (1940).
(152) Calingaert and Beatty, ibid., 61, 2748 (1939).
(153) Challenger and Ridgway, J. Chem. Soc., 121, 104 (1922).
(154) Calingaert, Soroos, and Thomson, J. Am. Chem. Soc., 62, 1542 (1940).
(155) Calingaert, Soroos, and Shapiro, ibid., 63, 947 (1941).

between the R_2Hg compounds, and also between the P_4Pb compounds giving two independent random equilibrium mixtures containing all eight possible compounds. However, it was observed that the equilibrium in the above equation is displaced toward the right.

Tetraethyllead and tetramethyltin gave all of the ten possible R_4M compounds (152).

EXPERIMENTAL

At the present time there are a large number of metals for which no organometallic derivatives are available. Further studies on the stabilities of such types were desirable in view of more extended attempts in their preparation. The interpretation of the decomposition of these derivatives on the basis of free radical formation was considered to be of prime importance.

The existence of the new compounds, diphenyl-α-naphthylantimony, diphenyl-p-chlorophenylantimony and diphenylmesitylantimony, has been reported (156). However, it was considered expedient to make available the procedures used in these preparations, as well as the analyses and solubilities.

Reaction of Dimethylmagnesium with Silver Bromide

A solution of 0.025 mole of dimethylmagnesium (157) in 40 cc. of ether was added to a stirred suspension of 9.4 g. (0.05 mole) of silver bromide in 20 cc. of ether cooled by an ice bath. The addition required ten minutes. The reaction

---

(156) Woods and Gilman, Proc. Iowa Acad. Sci., 48, 251 (1941) [C.A., 36, 3492 (1942)].

(157) The dimethylmagnesium was prepared from methylmagnesium chloride by the precipitation of the magnesium chlorides with dioxane using the method of Cope, J. Am. Chem. Soc., 57, 2238 (1935).

began immediately. On warming to room temperature, the mixture evolved gas rapidly. After standing for twelve hours, the mixture was heated to refluxing for five hours. The apparatus was swept out with nitrogen and the gas analyzed. There resulted 0.022 mole (88% yield) of pure ethane.

Reaction of Dimethylmagnesium with Silver Iodide

A solution of 0.02 mole of dimethylmagnesium in 33 cc. of anhydrous ether was added dropwise to a suspension of 9.4 g. (0.04 mole) of silver iodide in 20 cc. of ether cooled by an ice bath. The evolution of gas began immediately. After the mixture was allowed to come to room temperature, it was refluxed for ten hours, and the apparatus swept out with nitrogen. The analysis of the gas showed that 0.014 mole (70% yield) of ethane had been evolved.

Reaction of Methyllithium with Methyl Iodide in the Presence of a Catalytic Amount of Gold Tribromide

A solution of 7.1 g. (0.05 mole) of methyl iodide in 15 cc. of ether was added to a suspension of 1.09 g. (5 mole per cent) of gold tribromide in 15 cc. of ether. To the above mixture was added 0.05 mole of methyllithium in 40 cc. of ether over a period of twenty minutes. The suspension refluxed rapidly and the gas evolution was very apparent. After standing for five hours, the apparatus was swept out with nitrogen. A bluish-purple suspension was visible throughout the reaction; this was probably colloidal gold. There was obtained from this reaction 0.029 mole (58% yield) of ethane, and 0.013 mole (13% yield) of methane.

A "blank" was carried out on the above reaction of methyllithium with gold tribromide except that the methyl iodide was not added. Only the calculated amount of ethane (0.0025 mole) and methane (0.0024 mole) based on the gold tribromide was obtained.

A duplicate of the above reaction was performed and the same observations were made. The yield of ethane was 0.026 mole (52%), and of methane 0.021 mole (21%).

Reaction of Methyllithium with Gold Tribromide

To 60 cc. of ether contained in a 250 cc. three-necked flask--cooled to 70° by a dry ice-acetone bath and equipped with a stirrer, dropping funnel and nitrogen outlet-- was slowly added 8.74 g. (0.02 mole) of gold tribromide. A solution of 0.06 mole of methyllithium in 50 cc. of ether was added, during three hours, to the above vigorously stirred suspension. The mixture gave a negative Color Test 1. The suspension was allowed to slowly warm to room temperature and was then refluxed for two hours. The gas analysis showed that 0.023 mole (76.8% yield) of ethane, and 0.011 mole (18.4% yield) of methane were evolved.

Reaction of Zirconium Tetrachloride with Methylmagnesium Iodide

A solution of 0.073 mole of methylmagnesium iodide in 30 cc. of ether was added, during one hour, to a stirred suspension of 8.6 g. (0.0365 mole) of zirconium tetrachloride in 50 cc. of ether cooled to -15° by means of an ice-salt bath. No gas was evolved and very little decomposition was evidenced, although a reaction had apparently occurred. A green solution accompanied by a flocculent precipitate was produced. After the mixture was warmed to 0°, decomposition occurred and gas evolved. Then an additional 0.073 mole of methylmagnesium iodide was added, and the mixture allowed to stand for three days. After heating the mixture to refluxing for one-half hour, the apparatus was swept out with nitrogen. An analysis showed that 0.077 mole (52.7% yield) of methane was produced.

Reaction of Zirconium Tetrachloride with Dimethylmagnesium

A solution of 0.05 mole of dimethylmagnesium in 80 cc. of ether was added dropwise to a stirred suspension of 5.83 g. (0.025 mole) of zirconium tetrachloride in 20 cc. of ether cooled by an ice bath. A reaction occurred immediately. About two liters of gas were collected in twenty minutes. After standing for twenty hours the mixture was heated to refluxing for a few hours, and the apparatus swept out with nitrogen.

There was produced 0.074 mole (74% yield) of methane.

Reaction of Methylmagnesium Chloride with Tantalum Pentachloride

During twenty-five minutes, a solution of 0.1 mole of methylmagnesium chloride in 46 cc. of ether was added to a stirred suspension of 7.16 g. (0.02 mole) of anhydrous tantalum pentachloride (analyzed) in 28 cc. of ether while the mixture was cooled by an ice bath. Gas was evolved rapidly. After about forty minutes the reaction subsided and the ice bath was removed. The reaction mixture had become very pasty. After standing for six hours, the mixture was heated to refluxing and the usual procedure of manipulation and analysis was followed. The yield of methane was 0.062 mole (62%).

Reaction of Phenylmagnesium Bromide with Bromobenzene in the Presence of Ferric Chloride

Fifteen and seven-tenths grams (0.1 mole) of bromobenzene were added to a solution of 1.62 g. (10 mole per cent) of ferric chloride in 50 cc. of anhydrous ether. To the above solution was added 0.1 mole of phenylmagnesium bromide in 75 cc. of ether over a period of thirty minutes. When the Grignard reagent was first added, pale-yellow ferrous chloride was precipitated. The latter iron halide was reduced to metallic iron by further addition of the phenylmagnesium bromide.

Enough heat was generated to reflux the mixture during the addition. After refluxing for six hours, the mixture was hydrolyzed and steam distilled. The yield of biphenyl was 5.95 g. (38.6%). The melting point was 69-71°; the mixed melting point was 69-71°.

Reaction of Phenylmagnesium Bromide with Bromobenzene in the Presence of Ferrous Chloride

Fifteen and seven-tenths grams (0.1 mole) of bromobenzene were added to a suspension of 1.27 g. (10 mole per cent) of ferrous chloride in 50 cc. of anhydrous ether. To the above stirred suspension was added, during thirty minutes, 0.1 mole of phenylmagnesium bromide. After the addition was complete, the mixture was refluxed for four hours and hydrolyzed. The product was steam distilled and the yield of biphenyl (mixed m. p.) was 4.08 g. (26.6%).

Thermal Decomposition of Dimethylgold Bromide

A solution of 1.54 g. (0.005 mole) of dimethylgold bromide in 25 cc. of ether was refluxed for forty-eight hours. The solution turned reddish-brown in color after a short time. This change was accompanied by the appearance of metallic gold. The gas resulting from the decomposition amounted to 0.00308 mole (61.5% yield based on two methyl groups from dimethylgold bromide) of pure ethane.

The red solution was filtered and the residue washed with ether until the washings were colorless. The yield of metallic gold amounted to 0.612 g. (62.2%).

The ether was removed from the above filtrate by a distillation under reduced pressure. The residue was extracted with petroleum ether (b.p., 28-38°). The solvent was evaporated and the recovered dimethylgold bromide recrystallized. This compound amounted to 0.144 g. (9.4%).

Methylgold dibromide, identified by solubilities, was separated by an extraction of the above residue with chloroform according to Brain and Gibson (158). The yield of the compound was 0.21 g. (11.3%).

The residue, remaining after the chloroform extraction, was the water-soluble hydrated gold tribromide, as evidenced by the physical properties.

Reaction of Phenylmagnesium Bromide with Bromobenzene in the Presence of Nickelous Chloride

To a stirred suspension of 1.30 g. (10 mole per cent) of nickelous chloride in 50 cc. of anhydrous ether was added 0.1 mole of phenylmagnesium bromide in 75 cc. of ether over a period of thirty minutes. The metal halide darkened, but otherwise no apparent reaction was evidenced. Then, 15.7 g.

---

(158) Brain and Gibson, J. Chem. Soc., 762 (1939).

(0.1 mole) of bromobenzene in 25 cc. of ether was slowly added. Very little heat was evolved. The mixture was refluxed for six hours and carefully hydrolyzed. The products were steam distilled, and the yield of biphenyl was 6.9 g. (44.8%).

Chromium Trichloride and Dimethylmagnesium

A solution of 0.05 mole of dimethylmagnesium in 80 cc. of ether was added to a stirred suspension of 5.28 g. (0.033 mole) of chromium trichloride in 20 cc. of ether cooled on ice. The reaction was immediate. The mixture was allowed to come to room temperature, and the reaction became more rapid. In one and one-half hours, most of the gas had been evolved. After standing for twenty hours, the suspension was heated to refluxing for ten minutes. The apparatus was swept out with several hundred cc. of dry nitrogen gas. The yield of pure methane was 0.062 mole (62.0%).

Thermal Decomposition of Diphenylcadmium

Seventy-five cc. of dry benzene was added to 5.33 g. (0.02 mole) of diphenylcadmium, and the solution was refluxed for eighty-two hours. A dark suspension slowly appeared. The mixture was hydrolyzed and the biphenyl separated by steam distillation. The yield was 0.1 g. (3.3%).

Attempted Preparation of Dibenzylcadmium

To a suspension of 18.3 g. (0.1 mole) of cadmium chloride in 150 cc. of ether was added 0.23 mole of benzylmagnesium chloride in 175 cc. of ether over a period of three-fourths of an hour. The mixture turned black quite rapidly--metallic cadmium probably separating out--and became almost pasty. The ether was distilled off using a water bath at 70°; this temperature was maintained for three and one-half hours. Then 50 cc. of dry benzene was added and the mixture refluxed for a short time. However, the supernatant liquid did not contain any cadmium. The mixture was slowly hydrolyzed, and the organic layer separated and evaporated. The residue was warmed with 15 cc. of methanol and cooled. There resulted 14.1 g. (77.5%) of bibenzyl (mixed m.p.).

Attempted Preparation of Diphenylantimony Chloride

A mixture of 5.7 g. (0.025 mole) of antimony trichloride and 17.8 g. (0.05 mole) of phenylmercury bromide was heated on an oil bath at 150° for six and one-half hours. The mixture was cooled to room temperature and then extracted, successively, with 50 cc. of petroleum ether (b.p., 60-68°), 25 cc. of ether, and 50 cc. of benzene. The three extractions were worked up separately. The ether and petroleum ether solutions contained only a trace of a non-melting solid. The benzene extraction contained the phenylmercury bromide; almost a quantitative recovery was realized.

Diphenylantimony Chloride

To a solution of 600 cc. of water and 200 cc. of 5 N sodium hydroxide at 92° was added 28 cc. of freshly-opened 30% hydrogen peroxide diluted with 200 cc. of water (159). A solution of 32.0 g. (0.09 mole) of triphenylantimony in 200 cc. of warm acetone was added to the stirred solution prepared as described above. The addition required fifteen minutes. Heat was not applied to the mixture until the temperature had dropped to 65-70°; this temperature was maintained throughout the rest of the addition of the triphenylantimony solution and the hydrogen peroxide. The mixture was stirred for five minutes and 25 cc. of 30% hydrogen peroxide added. The suspension was allowed to cool while it was stirred. The mixture was then filtered and the filtrate acidified with acetic acid. The diphenylstibonic acid was dissolved by boiling with a solution of 450 cc. of concd. hydrochloric acid in 600 cc. of water. This hot solution was filtered through a sintered glass crucible, and the filtrate slowly cooled to 55°. Then 20 g. of pulverized

---

(159) This procedure is a modification of the oxidation of triphenylantimony to diphenylstibonic acid as reported in Goddard, "Organometallic Compounds," which constitutes Part III of Vol. XI of Friend, "A Text-Book of Inorganic Chemistry," Charles Griffin Co., London (1936), p. 239.

stannous chloride ($SnCl_2 \cdot 2H_2O$) was added while stirring. Depending on experimental conditions (particularly temperature) an oil, or gray solid, appeared. The mixture was cooled and the solid material filtered. The diphenylantimony chloride was crystallized from 20 cc. of glacial acetic acid. The yield was 12.0 g. (43.0%), melting at 66.5-68°.

Diphenylantimony Iodide

This compound was prepared by the reaction of diphenylantimony chloride with sodium iodide in acetone solution according to the method of Blicke, Oakdale, and Smith (160). It was purified by crystallization from acetic acid.

Attempted Preparation of Phenyl-p-tolystibonic Acid

A solution of 28.4 g. (0.1 mole) of p-tolylantimony dichloride (161) in a mixture of 950 cc. of concd. hydrochloric acid and 500 cc. of water was cooled to 0°. A benzenediazonium chloride solution was prepared by dissolving 9.3 g. (0.1 mole) of aniline in 50 cc. of concd. hydrochloric acid, adding 125 g. of ice, and then 7.0 g. (0.1 mole) of sodium nitrite in small portions with stirring. These two solutions were mixed at 0°. A precipitate formed immediately. A small amount of frothing occurred. The complex was filtered off and partially dried.

---

(160) Blicke, Oakdale, and Smith, J. Am. Chem. Soc., 53, 1025 (1931).

(161) Blicke and Oakdale, ibid., 55, 1198 (1933).

This product amounted to 11.0 g. and seemed to slowly decompose at room temperature. The complex was treated with 500 cc. of 2 N sodium hydroxide and allowed to stand for thirty hours. No organic antimony product could be isolated.

Preparation of Tri-p-chlorophenylantimony

A solution of p-chlorophenylmagnesium bromide was prepared by adding a solution of 105.0 g. (0.55 mole) of p-chlorobromobenzene in 250 cc. of ether to a suspension of 13.3 g. (0.55 g. atom) of magnesium in 120 cc. of ether.

To the above Grignard solution was added, with stirring, a solution of 38.0 g. (0.17 mole) of antimony trichloride in 100 cc. of ether during forty-five minutes. The mixture was refluxed for eighty minutes, and then hydrolyzed by slowly pouring upon 500 g. of an ice-water suspension. The resulting mixture was filtered through a Büchner funnel, the residue washed with ether, and the ether decanted from the filtrate. The ether solution was finally filtered by gravity through fluted filter paper. The ether was distilled off and the residue dissolved in 60 cc. of warm chloroform. To this solution was added 200 cc. of hot methanol. After standing for eight hours, the mixture deposited 32.0 g. of crystals. The filtrate was slowly evaporated while cooling with ice and another 22.0 g. of material was obtained. The total yield was 54.0 g. (71.5%), melting at 99-101°.

A small amount was recrystallized as described above for analytical purposes. The maximum melting point was 101.0-101.5°.

Anal. Calcd. for $C_{18}H_{12}Cl_3Sb$: Sb, 26.69; Cl, 23.4. Found: Sb, 26.81; Cl, 23.7, 23.92.

Preparation of Tri-p-chlorophenylantimony Dichloride

Dry chlorine gas was slowly bubbled through a solution of 5.0 g. (0.011 mole) of tri-p-chlorophenylantimony in 20 cc. of chloroform cooled on ice. After the solution had turned green, it was allowed to stand, stoppered, for three hours. Then, 30 cc. of methanol was added and the mixture filtered. The precipitate was dissolved in 50 cc. of hot chloroform and 90 cc. of hot methanol was added. After cooling to room temperature, the mixture deposited a crystalline material amounting to 5.7 g. (98.0%); the melting point was 189.5-190.5°.

Anal. Calcd. for $C_{18}H_{12}Cl_5Sb$: Sb, 23.10. Found: Sb, 23.00.

Preparation of Tris(p-dimethylaminophenyl)antimony

To a solution of 6.1 g. (0.0267 mole) of antimony chloride in 60 cc. of ether was added, with stirring, 0.085 mole of p-dimethylaminophenyllithium in 64 cc. of ether during one and one-half hours. A very gentle reflux ensued. The first addition of the lithium compound to the metal halide solution resulted in a bright blue solution with a white precipitate (probably lithium chloride). On further addition of the RLi derivative, the color changed to green, then to light blue, and finally to yellow. After standing for five hours, the mixture was cooled to -15° and slowly hydrolyzed with 15 cc. of water. The ether solution was siphoned off and filtered. The solvent was evaporated off under reduced pressure. Only a slight amount of residue resulted.

The aqueous suspension, remaining after the removal of the ether, was filtered and the solid dried in a desiccator. The product was extracted with 50 cc. of hot chloroform, and the resulting solution was mixed with boiling ethyl alcohol until a saturated solution was almost formed. After cooling slowly the solution deposited crystals. The crystallization was repeated. The yield of product was 4.48 g. (35.0%), melting at 239-241°.

A small amount of the compound was recrystallized to a maximum melting point (240.5-241.5°) for analytical purposes.

<u>Anal.</u> Calcd. for $C_{24}H_{30}N_3Sb$: Sb, 25.26. Found: Sb, 25.51.

Attempted Preparation of Diphenyl-α-naphthylantimony

Into a dry 250 cc. three-necked flask equipped with a rubber seal stirrer was placed 1.77 g. (0.005 mole) of triphenylantimony and 50 cc. of anhydrous ether. To this solution was slowly added 150 cc. of liquid ammonia. Then 0.23 g.

(0.01 g. atom) of metallic sodium, cut into small pieces, was added. This addition produced a red color which changed to brown and then to brownish-black. A solution of 1.27 g. (0.005 mole) of α-iodonaphthalene in 10 cc. of ether was slowly added. No color change was observed. The ammonia was allowed to evaporate. Subsequent to extracting the residue with ether and distilling off the solvent under reduced pressure, a small amount of white solid and a dark brown oil were obtained. The only product isolated from this material was 0.02 g. (3.1%) of naphthalene. The melting point was 81.0-82.5°; the mixed melting point was 81.0-82.5°.

Another experiment was carried out under the above conditions and similar observations were recorded.

Attempted Preparation of Diphenyl-α-naphthylantimony from Diphenylantimony Chloride in Liquid Ammonia

To a solution of 1.55 g. (0.005 mole) of diphenylantimony chloride in 50 cc. of dry ether was added 150 cc. of liquid ammonia. Then 0.23 g. (0.01 g. atom) of metallic sodium, divided into little squares, was added. At first there was no apparent reaction; then a red color appeared. Occasionally a green froth could be observed. After all the sodium had been added, the solution was deep red. Because the sodium was slow in reacting, the mixture was stirred for an additional five minutes. The red color still remained. Then a solution of 1.27 g. (0.005 mole) of α-iodonaphthalene in 10 cc. of anhydrous ether was added. After stirring for forty minutes, the mixture had become a faint yellowish-brown. The ammonia was allowed to evaporate. The residue was extracted with 40 cc. of ether and the solvent removed. Only a trace of a non-melting solid was obtained.

Preparation of Diphenyl-α-naphthylantimony from Diphenylantimony Iodide in Liquid Ammonia

A solution of 2.02 g. (0.005 mole) of diphenylantimony iodide in 50 cc. of anhydrous ether was mixed with 150 cc. of liquid ammonia. A clear solution resulted. Then 0.23 g. (0.01 g. atom) of sodium metal in small pieces was slowly added. At first a yellowish-green solution appeared; then the color changed to deep red. This color remained until the end of the addition of the metal. A solution of 1.27 g. (0.005 mole) of α-iodonaphthalene in 15 cc. of anhydrous ether was added quite rapidly to the above solution (forty-five seconds were required). The deep red color was discharged immediately and a yellowish-brown solution resulted. The ammonia was allowed to evaporate, and the residue extracted with 100 cc. of ether and filtered. The ether was distilled off under reduced pressure and the residue treated with 25 cc. of methanol, shaken well, and cooled. After several hours a white crystalline material appeared. The solution was placed in an ice-box for a few hours and filtered. The solid amounted to 0.35 g. (17.5%). The crystalline compound was dissolved in 1 cc. of chloroform and 10 cc. of warm methanol was added. The solution was cooled very slowly. The resulting crystals exhibited a melting point of 98.5-99.5°. A recrystallization did not raise the melting point.

All solutions were worked up for other products. Naphthalene was separated by sublimation and amounted to 0.25 g. (39.2%). It was identified by the method of mixed melting points.

Concerning the analysis of this new compound see the next experiment.

Preparation of Diphenyl-α-naphthylantimony by the Use of the Grignard Reagent

To a stirred solution of α-naphthylmagnesium bromide--prepared by adding 10.4 g. (0.05 mole) of α-bromonaphthalene in 20 cc. of ether to 1.2 g. (0.05 g. atom) of magnesium covered with 10 cc. of ether containing a crystal of iodine, and then refluxing for one hour --was slowly added a solution of 9.33 g. (0.03 mole) of diphenylantimony chloride in 55 cc. of ether. This last addition required twenty-five minutes and barely promoted a gentle refluxing. A precipitate was formed. The flask was insulated with a towel during the addition. Stirring was continued for one-half hour. The solution was decanted and the residue was washed with 15 cc. of ether. The ether solution was hydrolyzed by slowly pouring it into 200 g. of an ice-water mixture. The ether layer was decanted and filtered. The solvent was removed by distillation under reduced pressure. A white crystalline solid remained. This residue was washed with 25 cc. of cold methanol. The compound was dissolved in 35 cc. of chloroform and 75 cc. of boiling methanol added. After the solution was allowed to cool very slowly, a crystalline product appeared. The solid amounted to 7.1 g. (58.4%), melting at 97-98.5°.

One gram of the above material was recrystallized for analytical purposes by dissolving in 3 cc. of chloroform and adding 30 cc. of hot methanol. The melting point was 98.5-99.5°.

Anal. Calcd. for $C_{22}H_{17}Sb$: Sb, 30.15. Found: Sb, 30.14, 30.18.

This product gave a mixed melting point of 98.5-99.5° with that from the liquid ammonia reaction.

Preparation of Diphenylmesitylantimony

To a solution of 0.02 mole of mesitylmagnesium bromide in 25 cc. of ether was slowly added a solution of 6.22 g. (0.02 mole) of diphenylantimony chloride in 50 cc. of ether. The addition required thirty minutes, and the mixture was stirred for thirty minutes more. The solution was hydrolyzed by pouring on 150 g. of mixed ice and water. The hydrolysis mixture was filtered. The ether layer was separated, dried over sodium sulfate, and the ether distilled off under reduced pressure. The semi-crystalline residue was treated with 15 cc. of cold methanol and filtered. The residue was dissolved in 10 cc. of chloroform and the solution diluted with 30 cc. of hot methyl alcohol. After the solution cooled to room temperature, the crystals which separated out amounted to 3.0 g. The melting point was 92-93°. The filtrate was set aside to evaporate slowly. After eight hours the crystals were filtered and amounted to 1.15 g., with a melting point of 92-93°.

The total yield of pure product was 3.45 g. (43.7%).

Anal. Calcd. for $C_{21}H_{21}Sb$: Sb, 30.83, Found: Sb, 30.9.

Preparation of Diphenyl-p-chlorophenylantimony

To a stirred solution of 0.0115 mole of freshly prepared p-chlorophenylmagnesium bromide in 40 cc. of ether at 0° was added, during forty-five minutes, 3.11 g. (0.01 mole) of diphenylantimony chloride in 50 cc. of ether. After the halide had been added, the ice-cooled (162) mixture was stirred for two hours and then poured into 150 g. of ice and water. This mixture was filtered through a Büchner funnel and the residue washed carefully with ether. The combined ether extracts were filtered through a double thickness of fluted filter paper which contained some sodium sulfate. After the solvent was removed under reduced pressure, the residue was treated with 25 cc. of ethyl alcohol. The oil solidified after the mixture

---

(162) Earlier experiments had proved that the use of external heat at any time, or even allowing the mixture to reflux of its own accord, resulted in an oil which could not be crystallized.

was agitated. The solid material was filtered off and dissolved in 10 cc. of chloroform, and 40 cc. of hot methanol was added. After cooling to room temperature, the solution deposited crystals amounting to 2.0 g. (51.5%); the melting point was 52-53°. Further recrystallizations did not elevate the melting point.

Anal. Calcd. for $C_{18}H_{14}ClSb$: Sb, 31.44. Found: Sb, 31.46.

Attempted Preparation of Di-α-naphthyl-p-tolylantimony

To a solution of 1.42 g. (0.005 mole) of p-tolylantimony dichloride in 50 cc. of ether was added 150 cc. of liquid ammonia. A milky suspension resulted. Then 0.46 g. (0.02 g. atom) of metallic sodium was carefully added. A brown color immediately appeared which changed to deep red as more sodium was added. This red color remained after the last addition of the metal. A solution of 2.54 g. (0.01 mole) of α-iodnaphthalene in 10 cc. of ether was slowly added to the above suspension. A vigorous reaction was not apparent which probably indicated an absence of free sodium. The red color reverted to brown. The mixture was stirred and the ammonia allowed to evaporate. The residue, remaining after the evaporation, was extracted with 50 cc. of ether leaving a white solid which did not melt. The ether extract was evaporated to dryness, and the residue dissolved in 35 cc. of alcohol. After the evaporation of the alcohol, only a trace of material melting at

130-135° was obtained. A mixed melting point with tri-p-tolylantimony was 105-118°. Two g. (79%) of crude α-iodonaphthalene was recovered, and was identified as the picrate.

Reaction of Diphenylantimony Chloride with Hydrazine Hydrate

To a solution of 2.0 g. (0.04 mole) of hydrazine hydrate (163) in 60 cc. of absolute alcohol, contained in a 200 cc. three-necked flask equipped with a stirrer, was added 2.5 g. (0.008 mole) of diphenylantimony chloride. The reaction began immediately. The mixture was stirred for one hour, heated to boiling, filtered, and the filtrate was poured into 75 cc. of water. This aqueous suspension was extracted with 150 cc. of ether. The ether solution was dried over sodium sulfate, and the ether distilled off. The oily residue slowly solidified. The melting point was 71-74°. A mixed melting point with authentic triphenylantimony was 40-55°. The solid was crystallized from 1.5 cc. of glacial acetic acid. The melting point was 128-132°. The first product, melting at 71-74°, was bis-(diphenylantimony)oxide (164) and the second, melting at 128-132°, was diphenylantimony acetate (165). The yield of the oxide was 1.39 g. (61.5%).

---

(163) Hydrazine hydrate had previously been used to convert arylbismuth halides to R_3Bi compounds by Gilman and Yablunky, ibid., 62, 665 (1940).

(164) Michaelis and Gunther, Ber., 44, 2316 (1911).

(165) See Goddard, "Organometallic Compounds," which forms Part III of Vol. XI of Friend, "A Text-Book of Inorganic Chemistry," Charles Griffin Co., London (1936), p. 218.

Reduction of Triphenylantimony Dichloride with Hydrazine Hydrate

To a stirred suspension of 2.13 g. (0.005 mole) of triphenylantimony dichloride in 60 cc. of 95% alcohol was added 2.0 g. (0.04 mole) of hydrazine hydrate. Stirring was continued for one hour. The solution was poured into 100 cc. of water and the suspension was extracted with three 50-cc. portions of ether. The combined ether extracts were dried over sodium sulfate, and the ether distilled off under reduced pressure. The yield of triphenylantimony (mixed m. p.) was 1.68 g. (95.0%); the melting point was 51-52°.

Reduction of Tri-*p*-tolylantimony Dichloride to R_3Sb by Hydrazine Hydrate

To a suspension of 2.33 g. (0.005 mole) of tri-*p*-tolylantimony dichloride in 60 cc. of 95% ethyl alcohol was added 2.68 g. (0.054 mole) of hydrazine hydrate. An evolution of gas was immediately evident at the surface of the solid and ceased after 1-2 minutes. Very fine, dense, colorless crystals appeared after stirring for one hour. This solid was filtered. The alcohol filtrate was diluted with 30 cc. of water and the mixture extracted with ether. The ether was dried over sodium sulfate, and the solvent distilled off under reduced pressure. The residue was recrystallized from a small amount of alcohol and added to the crystals above. The yield of tri-p-tolylantimony (mixed m.p.) was 1.9 g. (96.5%), melting at 128-129°.

Reaction of p-Tolylantimony Dichloride with Hydrazine Hydrate

Hydrazine hydrate (4.0 g.; 0.08 mole) was slowly added, during ten minutes, to a solution of 4.25 g. (0.015 mole) of p-tolylantimony dichloride in 20 cc. of hot absolute ethyl alcohol. A precipitate appeared immediately. The suspension was refluxed for thirty minutes. The alcohol was evaporated off but no tri-p-tolylantimony could be isolated from the residue.

Reaction of n-Butyllithium with Triphenylantimony

To 3.53 g. (0.01 mole) of triphenylantimony (166) in 45 cc. of anhydrous ether was rapidly added 0.01 mole of n-butyllithium in 15 cc. of ether. The solution was stirred for one hour and poured on powdered dry ice. The residue was extracted with 30 cc. of 10% potassium hydroxide. The basic solution was boiled with a little Norite, filtered, acidified, and cooled on ice. The yield of benzoic acid was 0.08 g. (6.5%); the melting point was 119-121°. The mixed melting point was 119.5-121°.

---

(166) Similar metal-metal interconversions had been carried out with some of the corresponding bismuth derivatives by Gilman, Yablunky, and Svigoon, J. Am. Chem. Soc., 61, 1170 (1939).

In another experiment, 3.53 g. (0.01 mole) of triphenylantimony and 0.01 mole of n-butyllithium in 60 cc. of ether were stirred for ten minutes and carbonated. The yield of benzoic acid was 0.08 g. (6.5%).

In still another experiment, a solution of 1.77 g. (0.005 mole) of triphenylantimony and 0.005 mole of n-butyllithium in 60 cc. of ether was stirred for ten minutes and carbonated. The carbonation residue was extracted with 30 cc. of 10% potassium hydroxide. The basic solution was boiled with a little Norite, filtered, acidified with concd. hydrochloric acid, and cooled with ice. The benzoic acid (mixed m. p.) was filtered off and amounted to 0.051 g. (8.3%). The ether solution, remaining after the potassium hydroxide extraction, yielded 0.5 g. (28.2%) of triphenylantimony (mixed m. p.).

In two checks of this last experiment, yields of 0.070 g. (11.4%), and 0.060 g. (9.8%) of benzoic acid were obtained.

Reaction of Tri-p-tolylantimony with n-Butyllithium

A solution of 1.98 g. (0.005 mole) of tri-p-tolylantimony and 0.005 mole of n-butyllithium in 60 cc. of ether was stirred for ten minutes and carbonated. Before carbonation the solution exhibited a yellow color. The acid was separated by a potassium hydroxide extraction. The p-toluic acid (mixed m. p.) was crystallized from water. The yield was 0.040 g. (5.9%).

In a check experiment, there was obtained 0.044 g. (6.5%) of p-toluic acid.

Reaction of Tri-p-chlorophenylantimony with n-Butyllithium

A solution of 2.28 g. (0.005 mole) of tri-p-chlorophenylantimony and 0.005 mole of n-butyllithium in 60 cc. of ether was stirred for ten minutes and carbonated. When the butyllithium and the stibine were mixed, a deep red color appeared. This color progressively changed to deep brown, and then to deep purple at the end of the ten minute period. The carbonation residue was extracted with 30 cc. of 10% potassium hydroxide. The basic solution was boiled with a little Norite, filtered and acidified. Using a Soxhlet extractor, the p-chlorobenzoic acid was removed from the precipitate. This acid (mixed m. p.) amounted to 0.3 g. (38.0%).

In a check experiment, there resulted 0.29 g. (36.9%) of p-chlorobenzoic acid.

Reaction of Diphenyl-α-naphthylantimony with n-Butyllithium

A solution of 2.02 g. (0.005 mole) of diphenyl-α-naphthylantimony and 0.005 mole of n-butyllithium was stirred for ten minutes. A brilliant red color, which faded but slightly at the end of the above time interval, was produced. The solution was then poured on dry ice. The carbonation mixture was extracted with 10% potassium hydroxide, and the basic solution filtered and acidified. The precipitate was boiled with 100 cc. of water, the mixture filtered, and the filtrate allowed to cool. The crystals of α-naphthoic acid amounted to 0.134 g. (15.6%). The melting point was 159-160°. A trace of benzoic acid (mixed m. p.) was isolated.

Reaction of Diphenylmesitylantimony with *n*-Butyllithium

A solution of 1.98 g. (0.005 mole) of diphenylmesitylantimony and 0.005 mole of *n*-butyllithium in 60 cc. of ether was stirred for ten minutes and carbonated. After the addition of the n-butyllithium, the solution turned yellowish-green in color. The carbonation residue was extracted with 25 cc. of 10% potassium hydroxide. The basic solution was acidified, and the resulting mixture was warmed and filtered. The residue was washed with water, dried, and extracted with 25 cc. of hot petroleum ether (b.p., 85-110°). The petroleum ether contained only a small amount of non-melting material.

The aqueous filtrate above was made basic and evaporated to a volume of about 20 cc. The solution was acidified and cooled. The precipitate was filtered off and amounted to 0.062 g. (10.2%) of benzoic acid (mixed m. p.). A 12.8 per cent recovery of diphenylmesitylantimony was realized.

Reaction of Diphenyl-p-chlorophenylantimony with n-Butyllithium

A solution of 1.94 g. (0.005 mole) of diphenyl-p-chlorophenylantimony and 0.005 mole of n-butyllithium was stirred for ten minutes and carbonated. A brilliant red color appeared immediately on mixing the two compounds, but changed to brown at the end of the ten minutes. The carbonation mixture was extracted with 25 cc. of 10% potassium hydroxide. This basic solution was boiled with Norite, filtered and acidified. The warm mixture was filtered, and the filtrate extracted with ether. The ether solution yielded 0.024 g. (3.94%) of benzoic acid (mixed m. p.) after evaporation.

The residue from the above filtration was extracted with water using a Soxhlet extractor. There resulted 0.16 g. (20.2%) of p-chlorobenzoic acid.

Reaction of Tetraphenylgermanium with n-Butyllithium

To a suspension of 1.0 g. (0.0026 mole) of tetraphenylgermanium in 25 cc. of ether was added 0.011 mole of n-butyllithium in 30 cc. of ether. After standing for sixteen hours the mixture was carbonated. Ninety-seven per cent of the R_4M compound was recovered. No benzoic acid was obtained.

Reaction of tert.-Butyllithium with Tetraphenylgermanium

To 0.95 g. (0.0025 mole) of tetraphenylgermanium was added 0.065 mole of tert.-butyllithium in 100 cc. of petroleum ether (b.p., 28-38°). The mixture was refluxed for ninety-six hours and carbonated. The recovery of tetraphenylgermanium was almost quantitative. No benzoic acid was formed.

In another experiment, the low boiling petroleum was removed and petroleum ether (b.p.,79-115°) was added. The mixture was refluxed for twenty-four hours and carbonated. No reaction had occurred.

Reaction of Tetraphenylsilicon with n-Butyllithium

To a suspension of 1.12 g. (0.0033 mole) of tetraphenylsilicon in 25 cc. of ether was added 0.011 mole of n-butyllithium in 30 cc. of ether. After sixteen hours the mixture was carbonated. A 94 per cent recovery of the silicon compound was realized. No benzoic acid could be isolated.

Reaction of Triethylbismuth with Triphenylantimony

To a stirred solution of 1.79 g. (0.006 mole) of triethylbismuth in 100 cc. of dry benzene was added 2.12 g. (0.006 mole) of triphenylantimony. Very little visible change was observed when the solution was refluxed for twenty-four hours. The solution was cooled on ice and saturated with chlorine gas. Then the excess chlorine was removed by sweeping dry air through the solution. An aliquot portion was removed and 1 cc. of p-chlorophenylmagnesium bromide was added, but no color appeared. Hydrolysis of this test solution did not promote any color (167). The benzene was then distilled off under reduced pressure, and the residue dissolved in 25 cc. of benzene. Alcohol (175 cc.) was added. The solution was allowed to evaporate slowly. The crystals of triphenylantimony dichloride (mixed m.p.) amounted to 2.0 g. (78.6%).

Reaction of Tri-n-butylbismuth with Triphenylarsenic

To a solution of 3.7 g. (0.0098 mole) of tri-n-butylbismuth in 100 cc. of dry benzene was added 3.0 g. (0.0098 mole) of triphenylarsenic. The mixture, after the chlorine treatment, gave a negative test for triphenylbismuth dichloride.

---

(167) A color formation would have indicated the presence of triphenylbismuth dichloride. See Gilman and Yablunky, ibid., 63, 839 (1941).

DISCUSSION

The experiments in this work indicate quite clearly the unstable nature of the organometallic compounds of the transitional elements, such as silver, copper, gold, zirconium, tantalum, iron, nickel and chromium. The decomposition of these derivatives undoubtedly gives free radicals as the primary product. The fate of the free radicals is probably dependent on several factors.

One influence on the fate of the free radicals is the position of the metal in the A-, or B-family. For example, methylmagnesium chloride reacted with zirconium tetrachloride (A-family, Group IV) to give methane. With copper, silver and gold (B-family, Group I) halides, reactive methylmetallic compounds gave ethane, the coupling product. It seems to be quite generally true that with the lower alkylmetallic compounds, the halides of metals placed in the A-family do not give coupling, whereas the halides of metals placed in the B-family do give coupling.

Another influence is the presence of catalytic factors. As an illustration, in some metal halide reactions with methyllithium or methylmagnesium chloride, the metal initially formed in the decomposition of the organometallic compound, or unused metal halide, may alter the course of reaction of the free methyl radicals. Also, the presence of lithium or magnesium halides may play an important role in the ultimate fate of the free methyl fragments. These reasons explain the formation of methane along with the predominant ethane.

The thermal decomposition of dimethylgold bromide is an example of a disproportionation which is somewhat related to the random redistribution reactions carried out by Calingaert and co-workers (168). The breakdown of the gold compound probably takes place in accordance with the following equations:

$$2\ (CH_3)_2AuBr \longrightarrow 2\ CH_3AuBr_2 + 2\ (CH_3)_3Au \qquad I$$

$$2\ (CH_3)_3Au \longrightarrow 6\ CH_3\cdot + 2\ Au \qquad II$$

$$6\ CH_3\cdot \longrightarrow 3\ C_2H_6 \qquad III$$

$$2\ CH_3AuBr_2 \longrightarrow (CH_3)_2AuBr + AuBr_3 \qquad IV$$

The trimethylgold, formed as indicated in equation I, shows only a transitory existence and probably decomposes to give free methyl radicals (equation II) which in turn unite to produce ethane (equation III). Since pure ethane was formed, side reactions of the free methyl radical must not be operating.

Although $RAuX_2$ compounds decompose in the absence of solvents in the following manner (57):

$$RAuX_2 \longrightarrow RX + AuX$$

in the presence of an organic solvent like ether, the methylgold dibromide can give dimethylgold bromide and tribromide in accordance with equation IV. This disproportionation is the most logical explanation for the production of gold tribromide.

---

(168) See earlier references.

The catalytic effect of the various metal halides, such as gold tribromide, nickelous chloride, ferrous chloride and ferric chloride, on the reaction of organometallic compounds with organic halides is very noticeable. This type of process has often been of synthetic value.

The bluish-purple suspension in the reaction of methyllithium with methyl iodide in the presence of gold tribromide, is probably due to the presence of colloidal gold. A plausible explanation for the formation of colloidal gold, and also the catalytic effect, may be elucidated by the following equations:

$$12\ CH_3Li + 4\ AuBr_3 \longrightarrow 4\ Au + 6\ C_2H_6 + 12\ LiBr \tag{V}$$

$$4\ CH_3I + 4\ Au \longrightarrow 2\ (CH_3)_2AuI + 2\ AuI \tag{VI}$$

$$2\ (CH_3)_2AuI + 2\ CH_3Li \longrightarrow 2\ Au + 3\ C_2H_6 + 2\ LiI \tag{VII}$$

$$2\ CH_3I + 2\ AuI \longrightarrow 2\ CH_3AuI_2 \tag{VIII}$$

$$2\ CH_3AuI_2 + 4\ CH_3Li \longrightarrow 2\ Au + 3\ C_2H_6 + 4\ LiI \tag{IX}$$

The initial colloidal gold is formed according to equation V, which need operate no longer after the first reaction. Considering equations VI to IX, inclusive, it is apparent that the essential reaction is the formation of one mole of ethane from one mole of methyllithium and one mole of methyl iodide. The methane probably results as a by-product in the catalytic decomposition of the trimethylgold.

The efficacy of the iron chlorides and nickelous chloride as catalysts in the reaction of phenylmagnesium bromide with bromobenzene was of the same relative degree as that of gold tribromide. The mechanism of these coupling reactions is best represented by the reactions postulated by Kharasch and coworkers (169). The yields of biphenyl would indicate that the bromobenzene does not enter into the formation of the coupled product, but only furnishes free phenyl radicals which are catalytically polymerized.

In view of the fact that the tetraphenylsilicon and -germanium compounds do not undergo metal-metal interconversions with n-butyllithium, it was desirable to attempt metalations with stronger metalating agents (170), such as tert.-butyllithium. However, even after a long period of refluxing with tert.-butyllithium, tetraphenylgermanium remained unchanged.

The failure of a compound to respond to a metal-metal interconversion may be an indication of its non-metallic character. Note the break between tin and lead compounds on the one hand, and the germanium and silicon compounds on the other.

Antimony compounds undergo the metal-metal interconversion quite readily, although to a lesser extent than those of bismuth. n-Butyllithium was the organometallic used as the cleaving agent. The reaction can be represented as follows:

$$R_3Sb + \underline{n}\text{-}C_4H_9Li \longrightarrow R_2SbC_4H_9\text{-}\underline{n} + RLi$$

---

(169) See p. 34.
(170) Gilman, Moore, and Baine, J. Am. Chem. Soc., 63, 2479 (1941).

The amount of RLi compound was determined by carbonation to give the corresponding acid.

The results of the cleavage of some antimony compounds are summarized in Table I.

Table I

Reactions of n-Butyllithium with Symmetrical and Unsymmetrical Triarylantimony Compounds

Antimony Compound	Acid Product	Yield of Acid (%) (a)
Triphenylantimony	Benzoic	8.3, 11.4, 9.8
Tri-p-tolylantimony	p-Toluic	5.9, 6.5
Tri-p-chlorophenylantimony	p-Chlorobenzoic	38.0, 36.9
Diphenyl-α-naphthylantimony	α-Naphthoic	15.5
	Benzoic	Trace
Diphenylmesitylantimony	Benzoic	10.2
Diphenyl-p-chlorophenyl-antimony	p-Chlorobenzoic	20.2
	Benzoic	3.9

(a) These experiments were run under conditions comparable to each other and to the corresponding experiments on bismuth (98, 166).

Judging from the cleavage of the symmetrical compounds, the ease with which the radicals are cleaved decreases in this order: p-chlorophenyl, phenyl and p-tolyl. The cleavage of the unsymmetrical compounds gives the decreasing order of lability; p-chlorophenyl, α-naphthyl, phenyl and mesityl.

The probable arrangement for the entire series of radicals in decreasing amount of cleavage is as follows: p-chlorophenyl, α-naphthyl, phenyl, p-tolyl and mesityl. This series is in entire accord with that based on the cleavage of the unsymmetrical triarylbismuth compounds (98).

On the basis of cleavage from unsymmetrical mercurials by hydrogen chloride, the above radicals possess the following order of decreasing lability: mesityl, α-naphthyl, p-tolyl, phenyl and p-chlorophenyl (171). It is very apparent that a cleavage series of this type depends both upon the metal derivative being cleaved, and also the cleaving agent. It would be unwise to use one series of cleavage as a basis for prediction in an unrelated type of reaction.

A comparison of the liquid ammonia reactions,

$$R_2SbI + 2\ Na \longrightarrow R_2SbNa + NaI$$

$$R_2SbNa + IR' \longrightarrow R_2SbR' + NaI$$

and the method using the Grignard reagent,

$$R_2SbX + R'MgX \longrightarrow R_2SbR' + MgX_2$$

for the preparation of unsymmetrical triarylantimony compounds is of value. In general, because of the expensive nature of liquid ammonia, the preparation involving that reagent is to be avoided. Also, only the diarylantimony iodide compounds may be utilized in this reaction. The preparation of the

---

(171) Kharasch, Legault, and Sprowls, J. Org. Chem., 3, 409 (1938); Kharasch and Flenner, J. Am. Chem. Soc., 54, 674 (1932).

iodide requires an additional step. The yields in liquid ammonia are generally much lower. Contrary to expectations, the use of liquid ammonia does not cause any undue difficulties, and but few precautions are necessary.

The preparation using the Grignard reagent involves the utilization of diarylantimony chlorides. This reaction gives more impurities than the ammonia reaction, but the yields are better. With the very sensitive, low-melting unsymmetrical organoantimony compounds, it is necessary to add the Grignard reagent to the diarylantimony chloride at the temperature of an ice bath. Higher temperatures give non-crystallizable oils.

The appearance of a transitory green color in the reaction of the liquid ammonia solution of diphenylantimony iodide with metallic sodium may be taken as evidence for the formation of diphenylantimony.

$$(C_6H_5)_2SbI + Na \longrightarrow (C_6H_5)_2Sb + NaI$$

The diphenylantimony then reacts with more sodium to give the red diphenylantimony sodium.

$$(C_6H_5)_2Sb + Na \longrightarrow (C_6H_5)_2SbNa$$

The same general observations were made with the corresponding bismuth compound (146).

Hydrazine hydrate serves as an excellent tool in the reduction of pentavalent antimony compounds. For example, tri-p-tolylantimony dichloride is reduced quantitatively to give pure tri-p-tolylantimony.

In contrast to the reaction with the corresponding bismuth compounds, hydrazine hydrate does not convert the $RSbX_2$ or R_2SbX derivatives to the R_3Sb compounds. This is another example of the enhanced stability of the organoantimony compounds over the derivatives of bismuth.

It is evident that the random distributions noted with compounds of tin, lead, mercury, and so on, are not as characteristic of the antimony and bismuth derivatives. For example, triphenylantimony underwent no reaction with triethylbismuth. This lack of interconversion was probably due to the mild conditions. Heating in the absence of solvent would undoubtedly promote some exchange of radicals.

The cleavage of triphenylantimony with hydrogen peroxide to give diphenylstibonic acid,

$$(C_6H_5)_3Sb + H_2O_2 \longrightarrow (C_6H_5)_2SbO_2H + C_6H_6$$

is one of the more dependable methods of dearylation of triarylantimony compounds. This reaction serves as an avenue of approach to diarylantimony compounds.

The most suitable preparation of diphenylantimony chloride is the reduction of diphenylstibonic acid, dissolved in strong hydrochloric acid, with stannous chloride. Actually, the antimony compound present in the acid solution is diphenylantimony trichloride, $(C_6H_5)_2SbCl_3$. The reactions may be represented as follows:

$$(C_6H_5)_2SbO_2H + 3\ HCl \longrightarrow (C_6H_5)_2SbCl_3 + 2\ H_2O$$

$$(C_6H_5)_2SbCl_3 + SnCl_2 \longrightarrow (C_6H_5)_2SbCl + SnCl_4$$

This method has several advantages over the other preparations of diphenylantimony chloride. The heating of triphenylantimony with antimony trichloride (172),

$$(C_6H_5)_3Sb + SbCl_3 \longrightarrow R_2SbCl + RSbCl_2$$

in an autoclave for a prolonged period is a troublesome reaction to carry out. In addition, it gives a mixture of mono- and diarylated products. Another method of preparation used by Blicke, Oakdale, and Smith (160) is a tedious and detailed procedure, involving the following sequence of reactions:

$$C_6H_5N_2Cl + SbCl_3 \xrightarrow{NaOH} C_6H_5SbO_3Na_2 \xrightarrow{HCl} C_6H_5SbO_3H_2$$

$$C_6H_5SbO_3H_2 \xrightarrow[HCl]{SO_2} C_6H_5SbCl_2$$

$$C_6H_5SbCl_2 \xrightarrow{NH_4OH} C_6H_5SbO$$

$$C_6H_5SbO \longrightarrow [(C_6H_5)_2Sb]_2O + Sb_2O_3$$

$$[(C_6H_5)_2Sb]_2O + 2\ CH_3COOH \longrightarrow 2\ (C_6H_5)_2SbO_2CCH_3 + H_2O$$

$$(C_6H_5)_2SbO_2CCH_3 + HCl \longrightarrow (C_6H_5)_2SbCl + CH_3COOH$$

Although the cleavage of triphenylantimony with hydrogen peroxide and the reduction of the diphenylstibonic acid to diphenylantimony chloride using stannous chloride leave much to be desired, this method is still the most acceptable preparation of diphenylantimony chloride.

In spite of the fact that the preparation of the phenyl-*p*-tolylstibonic acid was unsuccessful, it is worth repeating because of the theoretical interest involved. This attempted

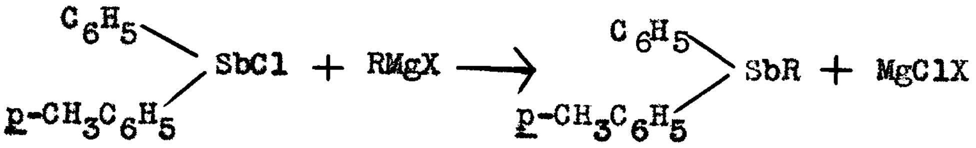
---

(172) Morgan and Vining, *J. Chem. Soc.*, *117*, 777 (1920).

preparation did not conform in procedure to the similar method of formation of diphenylstibonic acid (173). Benzenediazonium chloride in 5 N hydrochloric acid was treated with a solution of phenylantimony oxide in a small amount of acetic acid and the resulting mixture made alkaline. The essential reaction was as follows:

$$C_6H_5N_2Cl + C_6H_5SbO \xrightarrow{NaOH} (C_6H_5)_2SbO_2H$$

A successful preparation of phenyl-*p*-tolylstibonic acid would lead to the preparation of phenyl-*p*-tolylantimony chloride in a manner similar to the preparation of diphenylantimony chloride. The phenyl-*p*-tolyantimony chloride can then be treated with a suitable Grignard compound to give a completely unsymmetrical organoantimony compound.



$$(C_6H_5)(p\text{-}CH_3C_6H_5)SbCl + RMgX \longrightarrow (C_6H_5)(p\text{-}CH_3C_6H_5)SbR + MgClX$$

Such derivatives are unknown at present.

---

(173) Schmidt, *Ann.*, **421**, 233 (1920).

SUMMARY

A historical survey of the existence of free radicals in the thermal, electrolytic and photochemical decompositions of organometallic compounds has been made. Brief discussions of "organometallic radicals" and the "redistribution reaction" have been included. Methods of detecting and identifying free radicals were noted.

Silver, copper, gold, zirconium, tantalum and chromium halides were treated with methylmetallic compounds, and the gaseous products analyzed. Silver, copper and gold halides gave predominantly ethane; zirconium, tantalum and chromium halides gave methane.

Gold tribromide catalyzed the coupling of methyllithium with methyl iodide to give ethane.

Phenylmagnesium bromide reacted with bromobenzene in the presence of catalytic amounts of nickelous chloride, ferrous chloride and ferric chloride to produce biphenyl.

The cleavage action of n-butyllithium with some symmetrical and unsymmetrical triarylantimony compounds has been studied.

The detailed procedure for a new preparation of diphenylantimony chloride has been included, as well as the preparation and properties of the following new compounds: tri-p-chlorophenylantimony, tri-p-chlorophenylantimony dichloride,

tris(p-dimethylaminophenyl)antimony, diphenyl-α-naphthylantimony, and diphenyl-p-chlorophenylantimony.

Hydrazine hydrate was found to be without action on $RSbX_2$ and R_2SbX compounds. However, this reagent smoothly converted the R_3SbX_2 derivatives to the R_3Sb compounds.