REDUCTIONS INVOLVING UNIPOSITIVE MAGNESIUM

MARVIN D. RAUSCH, WILLIAM E. McEWEN AND JACOB KLEINBERG

Department of Chemistry, University of Kansas, Lawrence, Kansas

CONTENTS

I. INTRODUCTION

Reductions effected by metals are of considerable significance. The present review is concerned with reductions brought about by the use of magnesium, but specifically with the unipositive form of this substance. Examination of the literature reveals that such reductions fall into two main categories: (a) those by means of unipositive magnesium anodically generated, and (b) reductions with magnesium–magnesium halide mixtures. In addition to a discussion of these topics, the effects on massive magnesium of a variety of organic radical-ions generated by unipositive magnesium are described.

II. REDUCTIONS WITH UNIPOSITIVE MAGNESIUM ANODICALLY GENERATED

A. Inorganic reductions in aqueous solution

There have been a number of reports in the early literature to the effect that a significant quantity of hydrogen is evolved from the anode when aqueous sodium chloride solutions are electrolyzed between magnesium electrodes (13, 16). Such behavior is indeed unusual, since the primary electrochemical process at an anode is one of oxidation, and hydrogen can be produced from water only by a process of reduction. The suggestion was made, but not proved, that unipositive magnesium was formed as an unstable intermediate, oxidation of this species to the common dipositive state by water being responsible for evolution of hydrogen (61). The initial mean valence number, V_i, for magnesium entering solution was calculated from the loss in weight of the anode and the amount of current passed through the cell, as measured by means of a copper coulometer,

417

by the equation

$$V_i = \frac{\text{weight of copper deposited in coulometer} \times 24.32}{31.77 \times \text{weight of magnesium lost from anode}}$$

Values of V_i in the neighborhood of 1.3 were found and were stated to be independent of current density, temperature, concentration, and composition of the electrolyte (3). It was also noted that permanganate and dichromate ions were reduced at a magnesium anode in neutral solution.

What appears to be conclusive evidence for the existence of unipositive magnesium has been provided in some recent work (53). In electrolyses of aqueous sodium sulfate solutions carried out between magnesium electrodes in a divided cell, the anodic evolution of hydrogen was found to correspond satisfactorily to that expected from oxidation by water of magnesium from the measured mean valence state (ca. 1.4) to the familiar dipositive state. In the presence of a strong oxidizing agent such as chlorate ion, another reduction product in addition to hydrogen is formed in the anolyte, and the quantity of anodic hydrogen is found to be decreased. The anodic oxidation of magnesium to the unipositive state was further demonstrated by reduction of permanganate ion to manganese dioxide and silver ion to elementary silver under conditions which did not permit the oxidizing agent to come directly in contact with the anode. It should be emphasized that in the absence of electrical current the magnesium is not attacked by any of the electrolytic solutions employed.

B. Anodic reductions of organic substances in pyridine solution

In the anodic oxidation of magnesium in aqueous solutions (and of other very active metals in water, acetic acid, and liquid ammonia (14, 15, 50, 54)) evidence for the existence of lower oxidation states is obtained only when the electrolyte contains an oxidizing agent which is reduced by the species of metal of lower valence, or when the solvent itself undergoes reduction. Recently, the anodic behavior of magnesium in pyridine as solvent has been investigated. This solvent has the advantage over those cited above in that it is reduced only with great difficulty but is nevertheless a fair electrolytic medium. Therefore the behavior of dissolved oxidants can be studied without the interference of complicating solvent effects.

In the anodic oxidation of magnesium in sodium iodide–pyridine medium the metal enters solution with an initial mean valence number of two (55). However, the presence in solution of any one of a number of potential organic oxidants (for example, benzophenone, 4,4'-dimethylbenzophenone, 2'-methoxy-2,4,6-trimethylbenzophenone, benzil, nitrobenzene, azoxybenzene, azobenzene, bromobenzene, benzonitrile, benzaldehyde, and ethyl benzoate) caused the magnesium to dissolve with an initial mean valence number significantly less than two (51, 55, 56, 57, 62). Only with nitrobenzene and azoxybenzene was the magnesium attacked nonelectrolytically by the original solutions employed.

When the initial mean valence number was less than two, a reduction product(s) of the organic additive was isolated from the anolyte. Furthermore, in the majority of the cases studied, the quantity of reduction product isolated on

TABLE 1

"Anodic reduction" of organic compounds by unipositive magnesium in pyridine
(Sodium iodide electrolyte)

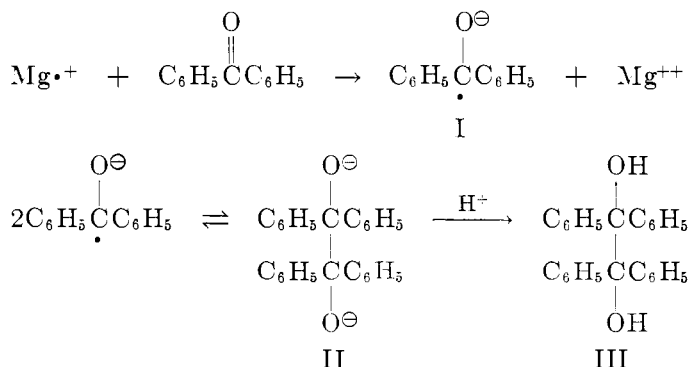| Organic Additive	V_i	Reduction Product	Yield	Reference
			per cent	
Benzophenone....................	1.67–1.83	Benzopinacol	92–98	(55)
4,4'-Dimethylbenzophenone........	1.54	1,1,2,2-Tetra-p-tolyl-1,2-ethanediol	84	(51)
Benzil...........................	1.48	Benzoin	92	(51)
Azoxybenzene....................	1.05	*trans*-Azobenzene	94	(51)
2'-Methoxy-2,4,6-trimethylbenzo-phenone	1.90	2,2'-Dimesitoylbiphenyl*	38	(57)
trans-Azobenzene.................	1.57	Hydrazobenzene	87	(62)
Benzaldehyde†....................	1.00			(56)
Bromobenzene†...................	1.68			(56)
Benzonitrile†....................	1.72			(56)
Ethyl benzoate†..................	1.90			(56)
Nitrobenzene†...................	0.27‡			(56)

* In addition to this compound a relatively large amount of unidentified polymeric material was isolated.
† No attempt was made to isolate reduction products.
‡ This extremely low V_i is due in part to nonelectrolytic corrosion by products formed during electrolysis.

hydrolysis of the anolyte corresponded essentially quantitatively to that expected from oxidation by the organic additive of the metal from its initial mean valence state to its common +2 state. Pertinent data are given in table 1.

In view of the low V_i values found in the presence of the organic additives, and in analogy with the behavior in aqueous solution cited earlier, there appears to be little doubt that the reducing agent formed electrochemically is unipositive magnesium. Since the latter is a one-electron reductant it would appear that the first step in the reduction of any of the additives consists in the transfer of an electron from the +1 magnesium to the organic molecule. Thus in the specific case of benzophenone the electron transfer would lead to the formation of the familiar ketyl radical-ion I. Two ketyl radical-ions formed in this manner dimerize to yield the pinacolate ion II. The latter on hydrolysis gives the pinacol III. It should not be inferred from the equations shown below that the magnesium ions exist in the free (or solvated) state. They may very well be coördinated with pinacolate ions and thus drive the dimerization equilibrium to the right.

$$\text{Mg}^{\cdot+} + \ \underset{\substack{\text{C}_6\text{H}_5\overset{\displaystyle\text{O}}{\overset{\|}{\text{C}}}\text{C}_6\text{H}_5}}{} \ \rightarrow \ \underset{\substack{\text{C}_6\text{H}_5\overset{\displaystyle\text{O}^{\ominus}}{\underset{\cdot}{\text{C}}}\text{C}_6\text{H}_5}}{} \ + \ \text{Mg}^{++}$$

$$\text{I}$$

$$2\,\underset{\substack{\cdot}}{\text{C}_6\text{H}_5\overset{\text{O}^{\ominus}}{\text{C}}\text{C}_6\text{H}_5} \ \rightleftharpoons \ \begin{matrix}\text{C}_6\text{H}_5\overset{\text{O}^{\ominus}}{\text{C}}\text{C}_6\text{H}_5 \\ | \\ \text{C}_6\text{H}_5\overset{}{\text{C}}\text{C}_6\text{H}_5 \\ | \\ \text{O}^{\ominus}\end{matrix} \ \xrightarrow{\ \text{H}^+\ } \ \begin{matrix}\text{C}_6\text{H}_5\overset{\text{OH}}{\text{C}}\text{C}_6\text{H}_5 \\ | \\ \text{C}_6\text{H}_5\overset{}{\text{C}}\text{C}_6\text{H}_5 \\ | \\ \text{OH}\end{matrix}$$

$$\text{II} \qquad\qquad\qquad \text{III}$$

Similar mechanisms may be visualized for other "anodic reductions."

Incidental to the studies of "anodic reductions" the nature of the products formed at the magnesium cathode was also determined. In two cases, namely with benzophenone and 4,4'-dimethylbenzophenone, products different from those found in the anolyte were isolated from the catholyte. In both instances the corresponding benzhydrols were obtained in good yield after hydrolysis of the catholyte mixture. Cathodic reduction of benzil, trans-azobenzene, and azoxybenzene yielded the same products as those found in the anolyte (table 1).

III. PROPOSED MECHANISMS FOR THE ANODIC OXIDATION OF MAGNESIUM

It has been suggested (63) that in aqueous medium magnesium is oxidized anodically to a mixture of unipositive and dipositive states. Ordinarily the $+1$ magnesium rapidly transfers its remaining valence electron to the anode and goes into solution in the dipositive state. However, if some material (e.g., the solvent itself or some other oxidizing agent) is present which reacts with the unipositive magnesium, then the latter is oxidized to its familiar $+2$ state and "anodic reduction" products are obtained,—for example, hydrogen gas from reduction of the solvent in electrolyses in aqueous solution.

All the data so far accumulated on the anodic oxidation of magnesium can be equally well interpreted in terms of an alternative hypothesis: namely, that the metal is converted initially solely to the unipositive state. This primary electrochemical step is followed by the secondary processes cited above. The observed V_i value is then the result of the relative rates at which the two possible secondary competing reactions occur. This implies that the value of V_i obtained with a specific oxidant present in solution can be altered by a change in conditions which affects its relative oxidizing power, and theoretically a V_i of 1 should be attainable even under conditions where no nonelectrolytic corrosion occurs.

Although no unambiguous case in support of the second mechanism for magnesium can be cited at the present time, only this mechanism appears to be valid for the anodic oxidation of copper in aqueous medium. Thus, at 25°C. the V_i of copper in aqueous potassium chlorate is 1.58; however, with a fixed concentration of electrolyte, constant current density, and essentially constant voltage, but with increase in temperature of the anolyte, there is a progressive decrease in V_i, until at 70°C. a value of 1.00 is obtained (58). In this temperature range nonelectrolytic corrosion is negligible. Since the nature of the primary anodic process depends primarily on the applied potential and not on the temperature of the anolyte, the decrease in V_i observed with increase in temperature appears to be attributable only to an increased rate in oxidation of copper(I) by chlorate ion, and the fact that a V_i value of 1 is attained supports the hypothesis that the copper is oxidized electrochemically solely to the $+1$ state over the whole temperature range. It should be pointed out that when a V_i value of 1 was found, chlorate ion was reduced to chloride in quantity corresponding to oxidation of the copper(I) to the $+2$ state.

IV. CORROSION OF MASSIVE MAGNESIUM BY ORGANIC RADICAL-IONS GENERATED BY UNIPOSITIVE MAGNESIUM (48)
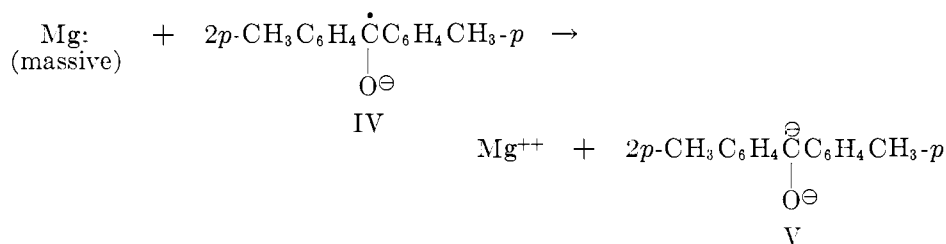
It is to be noted in table 1 that an abnormally low V_i value is found for magnesium when the sodium iodide–pyridine solutions contain nitrobenzene as

organic additive. This fact obviously requires additional comment, since a V_i value no lower than 1 would be anticipated as a result of a strictly electrochemical process. The explanation for this anomalous behavior lies in the fact that following electrolysis the anolyte, in contrast to the behavior of a control mixture, attacked massive magnesium readily. Evidently some reduction product(s) of nitrobenzene, unlike nitrobenzene itself, is able to react with the massive magnesium anode in an oxidation–reduction process and bring some of it into solution.

Even in those cases where the V_i values lie between 1 and 2 it is entirely conceivable that the products originally produced by interaction of +1 magnesium and organic additive are capable of corroding massive magnesium, and that the V_i values in reality may be a measure of both electrochemical and nonelectrochemical effects. It should be stressed again that of the additives listed in table 1 only nitrobenzene and azoxybenzene attack magnesium in the absence of current.
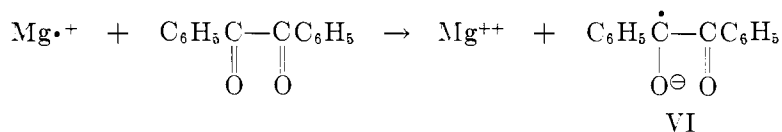
The effects on massive magnesium of the products originally formed by the interaction of unipositive magnesium and a variety of organic additives in pyridine have been investigated. With every additive thus far studied evidence has been accumulated which shows that reactive products capable of attacking massive magnesium are formed. There is also strong evidence that in every case the nonelectrolytic corrosion proceeds by way of a chain reaction, with an organic radical-ion and unipositive magnesium functioning as chain carriers. The additives examined include benzophenone, 4,4'-dimethylbenzophenone, benzil, *trans*-azobenzene, and azoxybenzene.

Particularly informative examples are found in the corrosion experiments with the reactive intermediates formed from benzophenone and 4,4'-dimethylbenzophenone. In normal electrolyses with either of these ketones as additive and a magnesium anode, the corresponding pinacol is the only reduction product isolated from the anolyte after hydrolysis. However, if, after electrolysis, the anolyte solution is allowed to remain for some time in contact with the anode or with a fresh piece of magnesium, the metal is corroded and the corresponding benzhydrol, as well as the pinacol, is isolated following hydrolysis. Furthermore, the quantity of magnesium going into solution as a result of nonelectrolytic corrosion exceeds to a *considerable* extent that expected from attack on magnesium by the ketyl radical-ion (formed by interaction of the original ketone and unipositive magnesium anodically generated), in accordance with the equation shown for 4,4'-dimethylbenzophenone:

$$\begin{array}{l} \underset{\text{(massive)}}{\text{Mg:}} \quad + \quad 2p\text{-}CH_3C_6H_4\overset{\bullet}{\underset{\underset{\text{IV}}{O^{\ominus}}}{\overset{|}{C}}}C_6H_4CH_3\text{-}p \quad \rightarrow \\[3em] \qquad\qquad\qquad Mg^{++} \quad + \quad 2p\text{-}CH_3C_6H_4\overset{\ominus}{\underset{\underset{\text{V}}{O^{\ominus}}}{\overset{|}{C}}}C_6H_4CH_3\text{-}p \end{array}$$

The amount of ketyl radical-ion (IV) formed can be calculated from the V_i

value and coulometric data. It should be pointed out that the ketyl radical-ion originally produced undoubtedly exists in equilibrium with its dimer, but the latter serves as a reservoir for the reactive monomer.

What appears to be a valid mechanism for attack of massive magnesium by the ketyl radical-ion is the following chain of reactions:

$$(a) \quad Mg: \quad + \quad p\text{-}CH_3C_6H_4\overset{\bullet}{\underset{\underset{O\ominus}{|}}{C}}C_6H_4CH_3\text{-}p \quad \rightarrow$$

$$\underset{IV}{} \qquad Mg\cdot^+ \quad + \quad p\text{-}CH_3C_6H_4\overset{\ominus}{\underset{\underset{O\ominus}{|}}{C}}C_6H_4CH_3\text{-}p$$

$$\underset{V}{}$$

$$(b) \quad Mg\cdot^+ \quad + \quad p\text{-}CH_3C_6H_4\underset{\underset{O}{\|}}{C}C_6H_4CH_3\text{-}p \quad \rightarrow \quad Mg^{++} \quad + \quad IV$$

Of course, V on hydrolysis affords the corresponding benzhydrol. It is only by the above sequence of reactions that the quantity of massive magnesium brought into solution after electrolysis can be explained. Although the attack of the ketyl radical-ion (IV) on the massive metal is depicted to show the formation of uni-positive magnesium, the question can be raised as to whether the latter is actually formed in the free state. It is entirely conceivable that as the ketyl radical-ion abstracts an electron from one magnesium atom on the surface of the metal, a molecule of ketone accepts an electron from the metal at another point on the surface to form a new ketyl radical-ion. In any event, unless these two processes are synchronous, the active form of the metal is still essentially unipositive magnesium.

In electrolyses with benzophenone or 4,4'-dimethylbenzophenone as additive, there is evidence that the magnesium anode is *not* attacked nonelectrochemically. Thus, if the anolyte is hydrolyzed immediately after electrolysis, none of the corresponding benzhydrol is ever obtained. Since it has been shown that the ketyl radical-ion formed during electrolysis is capable of corroding massive magnesium, it is evident that the anodic process protects the metal from attack by the reactive ketyl species.

In contrast to the behavior described above for benzophenone and 4,4'-dimethylbenzophenone, in which only the pinacol is formed in simple "anodic reduction" and a mixture of pinacol and benzhydrol is formed in corrosion following electrolysis, a single product is obtained in each case under both circumstances with benzil, *trans*-azobenzene, or azoxybenzene as additive. Thus the "anodic reduction" of benzil gives, after hydrolysis, benzoin as the sole product. The latter is also obtained as the only product when the anolyte following electrolysis is permitted to stand in contact with massive magnesium. As with the ketones cited above as additives, and also in the cases of the other additives noted, the quantity of magnesium consumed as a result of nonelectrolytic attack exceeded to a considerable degree that expected merely from reaction of the

metal with active intermediate produced electrochemically. There appears to be little doubt that reaction between unipositive magnesium anodically generated and benzil occurs in the following fashion:
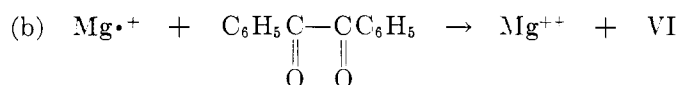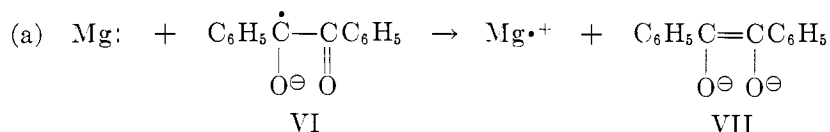
$$Mg\cdot^+ \;+\; C_6H_5\overset{\displaystyle \|}{\underset{\displaystyle O}{C}}-\overset{\displaystyle \|}{\underset{\displaystyle O}{C}}C_6H_5 \;\rightarrow\; Mg^{++} \;+\; C_6H_5\overset{\displaystyle \cdot}{\underset{\displaystyle O\ominus}{C}}-\overset{\displaystyle \|}{\underset{\displaystyle O}{C}}C_6H_5$$

<div align="center">VI</div>

Species VI can eventually yield benzoin by one of three possible routes: (a) it may disproportionate in pyridine solution to form benzil and the conjugate base (VII) of benzoin;

$$C_6H_5\overset{\displaystyle}{\underset{\displaystyle O\ominus}{C}}=\overset{\displaystyle}{\underset{\displaystyle O\ominus}{C}}C_6H_5$$

<div align="center">VII</div>
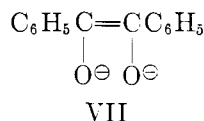
(b) it may react further with a second $Mg\cdot^+$ ion to give VII; or (c) it may disproportionate to form benzoin and benzil only after accepting a proton during hydrolysis. There is no question that VI possesses an appreciable half-life in pyridine solution, in view of the fact that the solution following electrolysis is capable of attacking massive magnesium. No other substance conceivably present in the anolyte could possibly react with massive magnesium under the experimental conditions. It is known from control experiments that benzoin itself is unreactive toward the massive metal, and attack by VII would lead, after hydrolysis, to the isolation of a reduction product of benzoin such as hydrobenzoin or desoxybenzoin.

In the light of the above discussion, nonelectrolytic corrosion can best be interpreted in terms of the chain mechanism:

$$(a) \quad Mg\colon \;+\; C_6H_5\overset{\displaystyle \cdot}{\underset{\displaystyle O\ominus}{C}}-\overset{\displaystyle \|}{\underset{\displaystyle O}{C}}C_6H_5 \;\rightarrow\; Mg\cdot^+ \;+\; C_6H_5\overset{\displaystyle}{\underset{\displaystyle O\ominus}{C}}=\overset{\displaystyle}{\underset{\displaystyle O\ominus}{C}}C_6H_5$$

<div align="center">VI   VII</div>

$$(b) \quad Mg\cdot^+ \;+\; C_6H_5\overset{\displaystyle \|}{\underset{\displaystyle O}{C}}-\overset{\displaystyle \|}{\underset{\displaystyle O}{C}}C_6H_5 \;\rightarrow\; Mg^{++} \;+\; VI$$

The "anodic reduction" of *trans*-azobenzene and of azoxybenzene yields, after hydrolysis of the anolyte, hydrazobenzene and *trans*-azobenzene, respectively. On the basis of products isolated and the extent of nonelectrolytic reaction with magnesium metal after electrolysis, the reactive intermediates formed during electrolysis are thought to have the structures VIII and IX, respectively.

$$C_6H_5\overset{\displaystyle \cdot}{N}-\overset{\displaystyle \ominus}{N}C_6H_5 \qquad\qquad C_6H_5\overset{\displaystyle \cdot}{N}-\overset{\displaystyle \overset{O\ominus}{|}}{N}C_6H_5$$

<div align="center">VIII   IX</div>

The effect on massive magnesium of products formed by cathodic reduction

has also been examined in a limited number of cases. After electrolyses with benzil or azoxybenzene present in the pyridine solution, the catholyte (as well as the anolyte) contained a substance which attacked magnesium metal extensively. However, during the course of electrolysis the magnesium cathode suffered no loss in weight. It would appear that during electrolysis the metal cathode is protected against corrosion by the ready availability of electrons at the surface. It has been pointed out previously that the ketyl radical-ion formed in the anolyte when benzophenone or 4,4'-dimethylbenzophenone was additive did not corrode the magnesium anode during electrolysis, since no benzhydrol was obtained. Inasmuch as corrosion following electrolysis yielded no characterizable products in the anolyte other than those obtained merely on electrolysis with either benzil or azoxybenzene in the solution, it is not possible to state whether nonelectrolytic attack of the magnesium anode occurs during electrolysis in the presence of these additives.

V. REDUCTIONS WITH MAGNESIUM–MAGNESIUM IODIDE MIXTURES

No discussion of reductions by means of unipositive magnesium would be complete without consideration of the use of magnesium–magnesium halide mixtures. When magnesium and bromine, or more importantly iodine, are brought together in an appropriate organic solvent in a ratio essentially corresponding to 1 g.-atom of metal to one of halogen, the resulting mixture contains a potent reducing agent for organic substances. The same reducing power is exhibited by a mixture of metal and magnesium(II) halide. Reductions carried out with these mixtures cannot be effected by the metal alone. Therefore, the reasonable suggestion (40) has been made that the effective reducing agent is magnesium(I) halide, formed in accordance with the following equilibrium:

$$Mg + MgX_2 \rightleftharpoons 2MgX^1$$
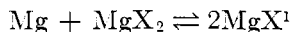
The literature contains many examples of the reduction by the magnesium–magnesium iodide mixture of a variety of organic compounds: e.g., ketones, aldehydes, and derivatives; carboxylic acids, esters, acid halides, and acyl peroxides; nitrobenzene and some of its reduction products. In the following sections the reduction of a limited number of representative examples of each of these classes of compounds is described. In addition, a number of interesting miscellaneous examples are given. Finally, table 2 presents a rather complete summary of the individual reductions effected.

A. Reduction of ketones and aldehydes

Pinacols are obtained by reduction of most aromatic ketones with the binary mixture magnesium + magnesium iodide, followed by hydrolysis of the reaction mixture. The reduction is ordinarily carried out in ether, benzene, or an ether–
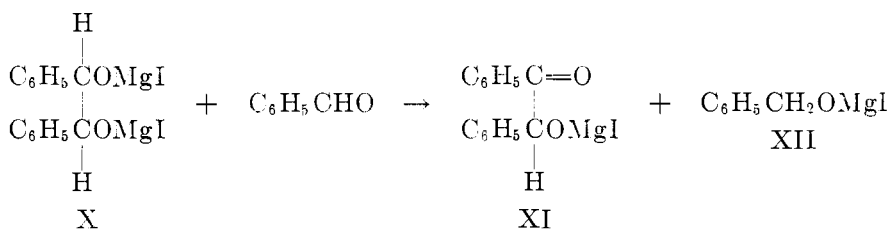
---

[1] The binary mixture magnesium–magnesium chloride is ineffectual as a reducing agent for organic compounds, as are mixtures of zinc–zinc halide, cadmium–cadmium halide, and aluminum–aluminum halide. However, the mixture beryllium–beryllium iodide has been shown to possess reducing power (40).

benzene mixture, frequently at elevated temperatures. It is proposed (40) that the active reducing agent, magnesium(I) iodide, reacts with a ketone to give an iodomagnesium ketyl; dimerization of the latter, followed by hydrolysis, yields the pinacol.
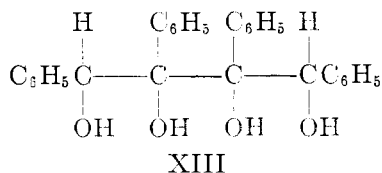
(a) $\overset{\bullet}{ArCAr}$ + $\overset{\bullet}{MgI}$ $\rightleftharpoons$ $Ar\overset{\bullet}{C}Ar^2$
$\quad\quad\quad\underset{O}{\|}$ $\quad\quad\quad\quad\quad\underset{OMgI}{|}$

(b) $2Ar\overset{\bullet}{C}Ar$ $\quad\quad$ Ar_2COMgI
$\quad\quad\underset{OMgI}{|}$ $\rightleftharpoons$ $\underset{Ar_2COMgI}{|}$

(c) $\underset{Ar_2COMgI}{\overset{Ar_2COMgI}{|}}$ + $2H_2O$ $\rightarrow$ $\underset{Ar_2COH}{\overset{Ar_2COH}{|}}$ + MgI_2 + $Mg(OH)_2$
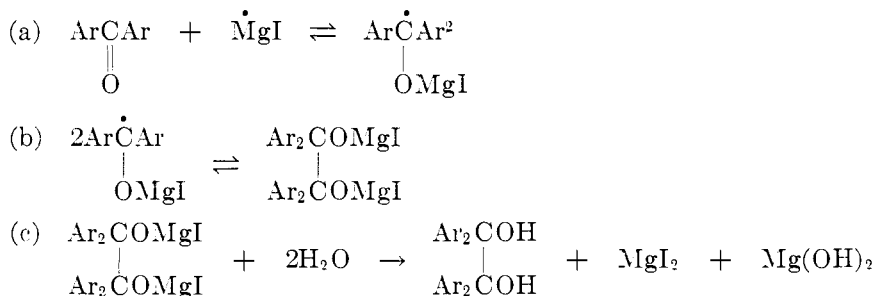
It is of interest to note that ether–benzene solutions of various aromatic ketones and magnesium–magnesium(II) iodide mixtures are highly colored, ranging from a deep red for benzophenone to an indigo blue for 4,4'-diphenylbenzophenone. Not only are these intense colors characteristic of ketyl radical-ions, but the solutions also possess other ketyl-like properties, such as extreme sensitivity to air and moisture.

Very few cases of the reduction of aromatic aldehydes by the binary mixture are on record. The reduction of benzaldehyde (43) is complex in that benzoin and benzyl alcohol are found on hydrolysis of the reaction mixture. Evidently the intermediate iodomagnesium hydrobenzoinate (X) formed in a manner analogous to that described above, for the pinacolate reacts further with benzaldehyde to produce iodomagnesium benzoinate (XI) and iodomagnesium benzylate (XII):

$\underset{X}{\underset{\overset{|}{H}}{\overset{\overset{H}{|}}{\underset{C_6H_5COMgI}{C_6H_5COMgI}}}}$ + C_6H_5CHO $\rightarrow$ $\underset{XI}{\underset{\overset{|}{H}}{\underset{C_6H_5COMgI}{\overset{C_6H_5C=O}{|}}}}$ + $\underset{XII}{C_6H_5CH_2OMgI}$

The benzoinate XI can be reduced further by the binary mixture to yield, after hydrolysis, tetraphenylerythritol (XIII)

$$\underset{XIII}{C_6H_5\underset{OH}{\overset{H}{C}}—\underset{OH}{\overset{C_6H_5}{C}}—\underset{OH}{\overset{C_6H_5}{C}}—\underset{OH}{\overset{H}{C}}C_6H_5}$$

^{2} Although the bond between magnesium and oxygen in this proposed intermediate is shown to be covalent, it is entirely likely that it possesses considerable ionic character.

TABLE 2

Reductions by means of the binary mixture magnesium–magnesium iodide

Substance Reduced	Product(s)	Melting Point	Yield	References
		°C.	per cent	
A. *Ketones and aldehydes:*				
Benzophenone	Benzopinacol	192–194	99.6	(40)
4-Methylbenzophenone	1,2-Diphenyl-1,2-di-*p*-tolyl-1,2-ethanediol	173–175	98	(40)
4,4'-Dimethylbenzophenone	1,1,2,2-Tetra-*p*-tolyl-1,2-ethanediol	183–184	94	(40)
4-Chlorobenzophenone	1,2-Diphenyl-1,2-di-*p*-chlorophenyl-1,2-ethanediol	172–178	94	(40)
4-Phenylbenzophenone	1,2-Diphenyl-1,2-di-*p*-biphenylyl-1,2-ethanediol	198–199	97	(40)
4,4'-Diphenylbenzophenone	1,1,2,2-Tetra-*p*-biphenylyl-1,2-ethanediol	200–203	95	(40)
9-Fluorenone	[9,9'-Bifluorene]-9,9'-diol	190–192	99	(40)
Xanthone	Xanthonepinacol	185–187	92	(40)
Anthrone	Anthronepinacol	184–185	83	(40)
4,4'-Bis(dimethylamino)benzophenone	1,1,2,2-Tetra-*p*-dimethylaminophenyl-1,2-ethanediol	196–197	53	(40)
4-Bromobenzophenone	1,2-Diphenyl-1,2-di-*p*-bromophenyl-1,2-ethanediol	178	94	(44)
3-Bromobenzophenone	1,2-Diphenyl-1,2-di-*m*-bromophenyl-1,2-ethanediol	147	85	(44)
2-Bromobenzophenone	1,2-Diphenyl-1,2-di-*o*-bromophenyl-1,2-ethanediol	160–165	Trace[a]	(44)
2-Chlorobenzophenone[b]	1,2-Diphenyl-1,2-di-*o*-chlorophenyl-1,2-ethanediol			(44)
		181	Small	(46)
		164	Small	(46)
4,4'-Dibromobenzophenone	1,1,2,2-Tetra-*p*-bromophenyl-1,2-ethanediol	179–180	94	(44)
3,3'-Dibromobenzophenone	1,1,2,2-Tetra-*m*-bromophenyl-1,2-ethanediol	152–156	40	(44)
3,4'-Dibromobenzophenone	1,2-Di-*m*-bromophenyl-1,2-di-*p*-bromophenyl-1,2-ethanediol	160–163	35	(44)
4-Chloro-4'-bromobenzophenone	1,2-Di-*p*-chlorophenyl-1,2-di-*p*-bromophenyl-1,2-ethanediol	169	60	(44)
4-Bromo-4'-phenylbenzophenone	1,2-Di-*p*-bromophenyl-1,2-di-*p*-biphenylyl-1,2-ethanediol	158–159	90	(44)
3-Bromo-4'-phenylbenzophenone	1,2-Di-*m*-bromophenyl-1,2-di-*p*-biphenylyl-1,2-ethanediol	175	64	(44)
2-Bromo-4'-phenylbenzophenone[a]				(44)
4-Methyl-4'-phenylbenzophenone	1,2-Di-*p*-tolyl-1,2-di-*p*-biphenylyl-1,2-ethanediol	180–182	93	(8)
		175–176	ca. 100	(11)
3-Methylbenzophenone	1,2-Diphenyl-1,2-di-*m*-tolyl-1,2-ethanediol	151–152	82	(8)
		147–148	ca. 100	(11)
3-Methyl-4'-phenylbenzophenone	1,2-Di-*m*-tolyl-1,2-di-*p*-biphenylyl-1,2-ethanediol	174–175	96	(8)
2-Methylbenzophenone	1,2-Diphenyl-1,2-di-*o*-tolyl-1,2-ethanediol	167	22	(8)
		156	ca. 100	(11)
2-Methyl-4'-phenylbenzophenone	1,2-Di-*o*-tolyl-1,2-di-*p*-biphenylyl-1,2-ethanediol	182–183	35	(8)
4-Methoxybenzophenone	1,2-Diphenyl-1,2-di-*p*-anisyl-1,2-ethanediol	173–174	45	(8)
4-Methoxy-4'-methylbenzophenone	1,2-Di-*p*-anisyl-1,2-di-*p*-tolyl-1,2-ethanediol	175–176	4	(8)
4-Methoxy-4'-phenylbenzophenone	1,2-Di-*p*-anisyl-1,2-di-*p*-biphenylyl-1,2-ethanediol	172–174	22	(8)
4-Chloro-4'-methylbenzophenone	1,2-Di-*p*-chlorophenyl-1,2-di-*p*-tolyl-1,2-ethanediol	175–176	89	(8)

TABLE 2—*Continued*

Substance Reduced	Product(s)	Melting Point	Yield	References
		°C.	*per cent*	
4-Chloro-4'-phenylbenzophenone	1,2-Di-p-chlorophenyl-1,2-di-p-biphenylyl-1,2-ethanediol	190–191	98	(8)
4-Ethoxybenzophenone	1,2-Diphenyl-1,2-di-p-ethoxyphenyl-1,2-ethanediol	141–142	27	(7a)
4-Ethoxy-4'-methylbenzophenone	1,2-Di-p-tolyl-1,2-di-p-ethoxyphenyl-1,2-ethanediol	168–169	22	(7a)
3-Methoxy-4'-phenylbenzophenone	1,2-Di-p-biphenylyl-1,2-di-m-methoxyphenyl-1,2-ethanediol	172–173	45	(7a)
3-Chloro-4'-phenylbenzophenone	1,2-Di-p-biphenylyl-1,2-di-m-chlorophenyl-1,2-ethanediol	174–175	77	(7a)
4-n-Propoxybenzophenone	1,2-Diphenyl-1,2-di-p-n-propoxyphenyl-1,2-ethanediol	146–147	62	(63)
4-n-Butoxybenzophenone	1,2-Diphenyl-1,2-di-p-n-butoxyphenyl-1,2-ethanediol	143–147	54	(63)
4-n-Amyloxybenzophenone	1,2-Diphenyl-1,2-di-p-n-amyloxyphenyl-1,2-ethanediol	119–121	42	(63)
4-Isoamyloxybenzophenone	1,2-Diphenyl-1,2-di-p-isoamyloxyphenyl-1,2-ethanediol	127–128	52	(63)
2,2'-Dimethylbenzophenone	2,2'-Dimethylbenzhydrol	118–119.5	ca. 25	(46)
4-Ethylbenzophenone	1,2-Diphenyl-1,2-di-p-ethylphenyl-1,2-ethanediol	162–163	ca. 100	(11)
4-Isopropylbenzophenone	1,2-Diphenyl-1,2-di-p-isopropylphenyl-1,2-ethanediol	161–162	ca. 100	(11)
4-Methyl-4'-ethylbenzophenone	1,2-Di-p-tolyl-1,2-di-p-ethylphenyl-1,2-ethanediol	155–156	ca. 100	(11)
1-Naphthyl p-tolyl ketone	1,2-Di-p-tolyl-1,2-di-1-naphthyl-1,2-ethanediol	150	ca. 100	(11)
2-Methoxybenzophenone	1,2-Diphenyl-1,2-di-o-anisyl-1,2-ethanediol	168–169	ca. 100	(11)
3-Methoxybenzophenone	1,2-Diphenyl-1,2-di-m-anisyl-1,2-ethanediol	139–141	ca. 100 / 20	(11) / (7a)
1-Naphthyl phenyl ketone	1,2-Diphenyl-1,2-di-1-naphthyl-1,2-ethanediol	220	46	(9)
2-Naphthyl phenyl ketone	1,2-Diphenyl-1,2-di-2-naphthyl-1,2-ethanediol	175	91	(9)
2,2'-Dibenzoylbiphenyl	9,10-Dihydro-9,10-diphenyl-9,10-phenanthrenediol	202 / 179–180	55 / 32	(6)
2,2'-Di-p-toluylbiphenyl	9,10-Dihydro-9,10-di-p-tolyl-9,10-phenanthrenediol	213	50	(6)
2,2'-Di-p-anisoylbiphenyl	9,10-Dihydro-9,10-di-p-anisyl-9,10-phenanthrenediol	188–190	43	(6)
1,8-Dibenzoylnaphthalene	cis-1,2-Diphenyl-1,2-acenaphthenediol	177.5–178	95	(12)
β-Benzopinacolone	Tetraphenylethylene	221	92	(7)
α,β-Epoxy-β-p-biphenylylpropiophenone[c]	1,2-Diphenyl-1,2-di-p-biphenylyl-1,2-ethanediol	198	46	(10)
α,β-Epoxy-β-phenylpropiophenone[c]	Benzopinacol	192–194	53	(10)
Benzil	Benzoin	135–136	95	(41)
p-Tolil	p-Toluoin	88–89	90	(45)
Anisil	Anisoin	113	62	(45)
4,4'-Dichlorobenzil	4,4'-Dichlorobenzoin	85–87	91	(45)
α-Naphthil	α-Naphthoin	138–139	91	(45)
4,4'-Diphenylbenzil	4,4'-Diphenylbenzoin	168–170	88	(45)
4-Phenylbenzil[d]	4-Phenylbenzoin	148–151	Good	(45)
Mesitil	2,2',4,4',6,6'-Hexamethyl-α,α'-stilbenediol	144–145	60	(21, 33)
2',4',6'-Trimethylchalcone	1,4-Dimesitoyl-2,3-diphenylbutane[e]			(18)

TABLE 2—*Continued*

Substance Reduced	Product(s)	Melting Point °C.	Yield per cent	References
2,2′,4,4′,6,6′-Hexamethylchalcone	1,4-Dimesitoyl-2,3-dimesitylbutane[e]			(18)
α-Mesityl-2,4,6-trimethylacrylophenone	1,2,5,6-Tetramesityl-1,5-hexadiene-1,6-diol	207–208	94	(20)
α-Mesityl-2,3,5,6-tetramethylacrylophenone	1,6-Diduryl-2,5-dimesityl-1,5-hexadiene-1,6-diol	196	95	(24)
2,2′,4,4′,6,6′-Hexamethylbenzophenone	2,2′,4,4′,6,6′-Hexamethylbenzhydrol	150	35	(49)
4′-Bromo-2,4,6-trimethylbenzophenone	4,4′-Dimesitoylbiphenyl	221–222	55	(19)
4′-Chloro-2,4,6-trimethylbenzophenone	4,4′-Dimesitoylbiphenyl	215–222	60	(19)
4′-Bromo-2,4,6-triethylbenzophenone	4,4′-Bis(2,4,6-triethylbenzoyl)biphenyl	148–149	13	(19)
4′-Bromo-2,4,6-triisopropylbenzophenone	4,4′-Bis(2,4,6-triisopropylbenzoyl)biphenyl	190–191	18	(19)
2′-Bromo-2,4,6-trimethylbenzophenone	2,4,6-Trimethylbenzophenone	35.5		(19)
4′-Bromo-2,3,5,6-tetramethylbenzophenone	4,4′-Diduroylbiphenyl	323–326	61	(34)
2,4,6-Trimethylbenzophenone[f]	2′-(α-Hydroxy-α-mesityl-o-tolyl)-2,4,6-trimethylbenzophenone	239–240	10	(26)
2′-Methoxy-2,4,6-trimethylbenzophenone[f]	9,10-Dimesitylphenanthrene	249–250	10	(27)
	9,10-Dihydro-9,10-dimesityl-9,10-phenanthrenediol	195–196.5	22	(31)
2,4,6-Trimethylbenzophenone and 2′-methoxy-2,4,6-trimethylbenzophenone[f]	2′-(α-Hydroxy-α-mesityl-o-tolyl)-2,4,6-trimethylbenzophenone	239–240	28	(27)
2,3,5,6-Tetramethylbenzophenone and 2′-methoxy-2,4,6-trimethylbenzophenone[f]	2′-(α-Hydroxy-α-duryl-o-tolyl)-2,4,6-trimethylbenzophenone	202–203	25	(27)
2,4,6-Trimethylbenzophenone and 2′-methoxy-2,3,5,6-tetramethylbenzophenone[f]	2′-(α-Hydroxy-α-mesityl-o-tolyl)-2,3,5,6-tetramethylbenzophenone	187–188	24	(27)
2,3,5,6-Tetramethylbenzophenone and 2′-methoxy-2,3,5,6-tetramethylbenzophenone[f]	2′-(α-Hydroxy-α-duryl-o-tolyl)-2,3,5,6-tetramethylbenzophenone	262–263	23	(27)
2′-Methoxy-2,3,5,6-tetramethylbenzophenone[f]	9,10-Diduryl-9,10-dihydro-9,10-phenanthrenediol	232	23	(31)
	9,10-Didurylphenanthrene	289.5–291.5	26	
2,2′-Diduroylbiphenyl[f]	9,10-Diduryl-9,10-dihydro-9,10-phenanthrenediol	231–232	68	(31)
2,2′-Dimesitoylbiphenyl[f]	9,10-Dihydro-9,10-dimesityl-9,10-phenanthrenediol	200.5–201.5	77	(31)
1,3-Dibenzoyl-2-phenylcyclopentane[f]	2,3,7-Triphenyl-2,3-norcamphanediol	167–168		(25)
1,2,3-Indantrione	Hydrindantin	236 (d.)	60	(59)
Benzaldehyde	Benzoin	135–136	30	(43)
	Benzyl alcohol		22	
1-Naphthaldehyde	α-Naphthoin[g]	138–139	34	(43)
	1-Naphthalenemethanol	59.5–60	26	
p-Tolualdehyde	4,4′-Dimethylbenzoin[g]	88–89	23	(43)
	p-Methylbenzyl alcohol	60	25	
Anisaldehyde	4,4′-Dimethoxybenzoin[g]	113	24	(43)
	Anisyl alcohol	24–25	30	
p-Bromobenzaldehyde	4,4′-Dibromobenzoin[g]		29	(43)
	p-Bromobenzyl alcohol	77	25	

TABLE 2—*Continued*

Substance Reduced	Product(s)	Melting Point	Yield	References
		°C.	per cent	
p-Chlorobenzaldehyde	4,4'-Dichlorobenzoin[g]	88	24	(43)
	p-Chlorobenzyl alcohol	75	24	
2,4-Xylaldehyde	2,2',4,4'-Tetramethylhydrobenzoin	153–154		(36)
	2,2',4,4'-Tetramethylhydrobenzoin	129–130		
Mesitaldehyde	1,2-Dimesityl-1,2-ethanediol	214–215	20	(29)
	1,2-Dimesityl-1,2-ethanediol	160–161	54	
	1,2-Dimesitylethylene	132–133	Small	
2,4,6-Triisopropylbenzaldehyde	1,2-Bis(2,4,6-triisopropylphenyl)-1,2-ethanediol	285–286		(29)
	1,2-Bis(2,4,6-triisopropylphenyl)-1,2-ethanediol	186–187		
	1,2-Bis(2,4,6-triisopropylphenyl)-ethylene	147–148	Small	
2,3-Dimethyl-1-naphthaldehyde	1,2-Bis(2,3-dimethyl-1-naphthyl)-1,2-ethanediol	274–275.5		(29)
	1,2-Bis(2,3-dimethyl-1-naphthyl)-1,2-ethanediol	162–163.5		
B. Carboxylic acids, esters, acid halides, and acyl peroxides:				
Benzoic acid	Benzoin	135–136	30–40	(42)
	Benzil	95	4	
p-Toluic acid	4,4'-Dimethylbenzoin[h]	88–89	30	(42)
	4,4'-Dimethylbenzil[h]	102–104		
1-Naphthoic acid	α-Naphthoin[h]	138–139	31	(42)
	α-Naphthil[h]	189–190		
2-Naphthoic acid	β-Naphthoin[h]	125–126	70	(42)
	β-Naphthil[h]	157–158		
4-Biphenylcarboxylic acid	4,4'-Diphenylbenzoin[h]	228	46	(42)
	4,4'-Diphenylbenzil[h]	139–140		
Benzyl benzoate	Bibenzyl	52	70	(42)
	Benzoin	135–136	45	
Methyl benzoate	Benzoin	135–136	8	(42)
Phenyl benzoate	Phenol	43	90	(42)
Ethyl o-chlorobenzoate and phenylmagnesium bromide	1,2-Diphenyl-1,2-di-o-chlorophenyl-1,2-ethanediol[i]	163–164	5	(46)
Propionyl chloride[j]	3,4-Hexanedione		Small	(47)
Butyryl chloride[j]	4,5-Octanedione		Small	(47)
Mesitoyl chloride	2,2',4,4',6,6'-Hexamethyl-α,α'-stilbenediol	144–145	35	(21, 33)
	Mesitil	119–120	34	(33)
2,4,6-Triethylbenzoyl chloride	2,2',4,4',6,6'-Hexaethyl-α,α'-stilbenediol	154–155	30	(22,33)
	2,2',4,4',6,6'-Hexaethylbenzil	75–75.5	18	(22)
2,4,6-Triisopropylbenzoyl chloride	cis-2,2',4,4',6,6'-Hexaisopropylstilbenediol	175–176	37	(28)
	2,2',4,4',6,6'-Hexaisopropylbenzil	155–156		
4-Bromo-2,6-xyloyl chloride	4,4'-Dibromo-2,2',6,6'-tetramethylbenzil	211.5–212.5	14	(35)
	4,4'-Dibromo-2,2',6,6'-tetramethylbenzoin	143–144	10	
2,3,4,6-Tetramethylbenzoyl chloride	Isoduril	184–184.5		(30)
	2,2',3,3',4,4',6,6'-Octamethyl-α,α'-stilbenediol			

TABLE 2—*Concluded*

Substance Reduced	Product(s)	Melting Point	Yield	References
		°C.	per cent	
2,3,5,6-Tetramethylbenzoyl chloride	Duril	250–251		(30)
	cis-2,2',3,3',5,5',6,6'-Octamethyl-α,α'-stilbenediol	167–169		
2,6-Dimethylanisoyl chloride	2,2',6,6'-Tetramethylanisil	197–198.5	38	(23)
3-Methoxymesitoyl chloride	cis-2,2',4,4',6,6'-Hexamethyl-3,3'-dimethoxystilbenediol	138.5–139.5	55	(23)
	2,2',4,4',6,6'-Hexamethyl-3,3'-dimethoxybenzil	78–79	26	
2-Methyl-1-naphthoyl chloride	cis-Bis(2-methyl-1-naphthyl)acetylene glycol	186–188	27	(32)
	2,2'-Dimethyl-α-naphthil	160–160.5	Small	
Benzoyl peroxide	Benzoin	135–136	45	(42)
C. Nitrobenzene and some of its reduction products:				
Nitrobenzene	Aniline		Small	(38)
Nitrosobenzene	Azobenzene[k]	68	71	(4)
Nitrosobenzene	Hydrazobenzene[h]	130	66	(4, 38)
N-Phenylhydroxylamine	Azobenzene	68		(38)
	Aniline			
Azoxybenzene	Azobenzene[l]	68	92	(4, 38)
Azoxybenzene	Hydrazobenzene[l]	130	92	(4)
4,4'-Dichloroazoxybenzene	4,4'-Dichlorohydrazobenzene	122	80	(4)
4,4'-Dimethoxyazoxybenzene	4,4'-Dimethoxyhydrazobenzene		Small	(4)
4,4'-Diphenylazoxybenzene	4,4'-Diphenylhydrazobenzene		50	(4)
	Xenylamine	53	20	
Azobenzene	Hydrazobenzene	130	89	(4)
	Aniline		6	
4,4'-Dimethylazobenzene	4,4'-Dimethylhydrazobenzene	133–134	43	(4)
	p-Toluidine	45	24	
4,4'-Dimethoxyazobenzene	p-Anisidine	57	20	(4)
4,4'-Diphenylazobenzene	4,4'-Diphenylhydrazobenzene		32	(4)
	Xenylamine	53	32	
D. Miscellaneous compounds:				
Di-p-anisylthioketone	Tetra-p-anisylethylene sulfide	210 (d.)	37	(60)
Benzalaniline	α,α'-Dianilinobibenzyl	137–139	100	(5)
Benzophenone anil	N-Phenylbenzohydrylamine	57–58		(5)
Fluorenone anil	N-Phenyl-9-fluorylamine	121–123	83	(5)
Benzil monoanil	α-Anilino-α-phenylacetophenone	97–98	80	(5)
Diphenylmethane	1,1,2,2-Tetraphenylethane	211	Small	(39)
N,N-Diphenylhydroxylamine	Diphenylamine	54	18	(38)
5,12-Dihydro-5,12-diphenyl-5,12-naphthacenediol[m]	5,12-Diphenylnaphthacene	207–208	73	(1)
p-(1-Chloropropyl)anisole[j]	3,4-Bis(p-hydroxyphenyl)hexane	188	100	(2)
Hexadecylmagnesium iodide	Dotriacontane	71–72	70	(52)

[a] An appreciable amount of the original ketone was "destroyed through loss of nucleus bromine."

[b] This compound behaves like its bromo analog.

[c] The reducing mixture contained magnesium, magnesium bromide, and phenylmagnesium bromide.

[d] Magnesium-magnesium bromide proved to be a more satisfactory reducing mixture than magnesium-magnesium iodide. It was not established whether the product was 4- or 4'-phenylbenzoin.

[e] Two stereoisomeric forms were isolated.

[f] The solvent employed was a mixture of toluene and n-butyl ether.

[g] The product was isolated as the corresponding benzil by oxidation, after reduction with the binary mixture.

[h] Actually, the crude reduction product consisting of both the benzoin and benzil was oxidized to the corresponding benzil. Yields reported are in terms of the benzil.

[i] Evidently phenylmagnesium bromide first reacts with ethyl o-chlorobenzoate to give 2-chlorobenzophenone, which is then reduced to the pinacol by the binary mixture. A large amount of diphenyl-o-chlorophenylcarbinol is also formed.

[j] Ethyl ether was employed as solvent.

[k] Azobenzene is obtained from the reaction of nitrobenzene, magnesium, and magnesium(II) iodide in equimolar quantities; with an excess of the binary mixture hydrazobenzene is the product.

[l] An equimolar mixture of azoxybenzene, magnesium, and magnesium(II) iodide gave azobenzene after hydrolysis; with an excess of magnesium-magnesium iodide hydrazobenzene is produced.

[m] The reducing agent was magnesium-magnesium bromide mixture.

and a polymer. Sterically hindered benzaldehydes, such as mesitaldehyde, give normal bimolecular reduction products (29).

B. Reduction of carboxylic acids, esters, acid halides, and acyl peroxides

Aromatic acids in ether–benzene solution react with the binary mixture in two stages (42): (a) quantitative conversion of the acid to the iodomagnesium salt, ArCOOMgI, with the evolution of hydrogen; and (b) bimolecular reduction of the salt to yield benzil and the further reduction product

$$ArC(OMgI)=C(OMgI)Ar$$
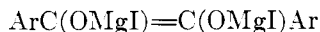
the latter giving the appropriate benzoin on hydrolysis.

Alkyl esters of aromatic acids, such as benzyl benzoate or methyl benzoate, in ether–benzene solution in the presence of the binary mixture are first cleaved by magnesium(II) iodide:

$$ArCOOCH_2R + MgI_2 \rightleftharpoons ArCOOMgI + RCH_2I$$
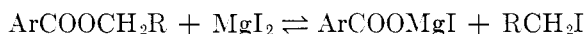
The iodomagnesium salt formed is then reduced by the binary mixture in the manner described above (42). The action of the binary mixture on one aryl ester, phenyl benzoate, has been reported (42). This compound gives iodomagnesium phenoxide, C_6H_5OMgI, and a resin, undoubtedly arising from reaction of the binary mixture with benzoyl iodide, formed in the cleavage. Phenol is the only identifiable product isolated on hydrolysis.

The reducing action of the binary mixture has been utilized for the preparation of α-diketones from aliphatic acid chlorides (47). In this manner 3,4-hexanedione and 4,5-octanedione were prepared from propionyl chloride and butyryl chloride, respectively. A number of hindered acid chlorides have been reduced. For example, mesitoyl chloride is converted, after reduction and hydrolysis, to a mixture of 2,2',4,4',6,6'-hexamethyl-α,α'-stilbenediol (XIV) and mesitil (XV) (21, 33). Other examples of the reduction of hindered acid chlorides are listed in table 2.
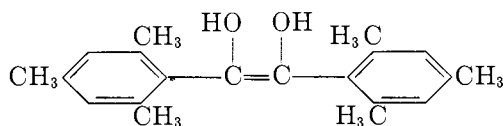
XIV
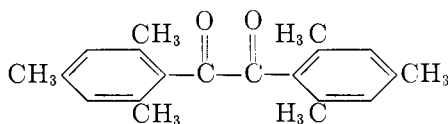
XV

Benzoyl peroxide reacts vigorously with magnesium–magnesium iodide mixtures to form the iodomagnesium salt, $C_6H_5COOMgI$, which, as with benzoic acid, yields benzoin on further reduction and hydrolysis (42).
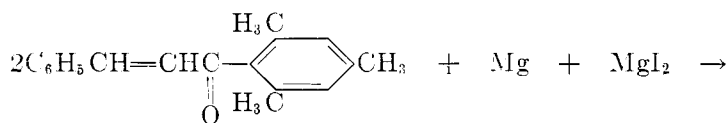
C. Reduction of nitrobenzene and some of its reduction products

It has been reported (38) that nitrobenzene undergoes slow reduction by the binary mixture to give, after hydrolysis, a poor yield of aniline. Azobenzene is obtained as the major product from the reaction of nitrosobenzene, magnesium, and magnesium(II) iodide in equimolar quantities (4). Nitrosobenzene is reduced by an excess of magnesium–magnesium iodide mixture principally to the iodomagnesium salt of hydrazobenzene, which upon hydrolysis produces hydrazobenzene (4, 38). The latter may also be produced directly from azobenzene, aniline being also formed to a small degree (4, 38). An equimolar mixture of azoxybenzene, magnesium, and magnesium iodide yields, after hydrolysis, azobenzene (4, 38). Reduction of N-phenylhydroxylamine gives azobenzene and aniline (38). Although no mention was made of the isolation of hydrazobenzene in this reaction, it appears evident that this product must also have been formed. It is of interest that when just sufficient reducing agent is employed to convert nitrosobenzene to azoxybenzene, the latter is not formed, but rather the product consists of a mixture of azobenzene and unchanged nitrosobenzene (4).

Three examples have been reported in which substituted azobenzenes have been subjected to reduction by the binary mixture. 4,4'-Dimethylazobenzene, 4,4'-dimethoxyazobenzene, and 4,4'-diphenylazobenzene are converted in part to the corresponding hydrazobenzenes, but reduction to the respective anilines occurs to a considerably greater extent in these cases than with azobenzene itself (4).

D. Conjugate bimolecular reductions

In addition to the simple bimolecular reductions of carbonyl compounds already described, the literature contains numerous examples of conjugate bimolecular reductions by the binary mixture (18). The latter fall into two main categories: those in which there is simply union of two molecules of the carbonyl compound and those in which union is accompanied by elimination of a small stable anion, such as methoxide or halide. A number of illustrative examples of such reductions are discussed.

$$2C_6H_5CH=CHC-\!\!\left\langle\!\!\begin{array}{c}H_3C\\ \\ H_3C\end{array}\!\!\right\rangle\!\!CH_3 \quad + \quad Mg \quad + \quad MgI_2 \quad \rightarrow$$
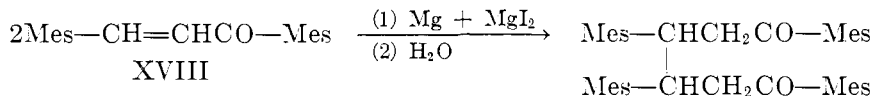
XVI
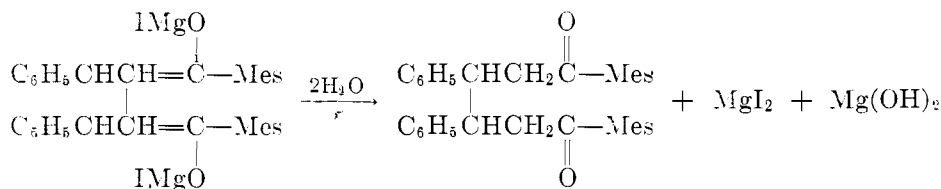
XVII

The reduction of 2',4',6'-trimethylchalcone (XVI) gives, after hydrolysis, two isomeric forms of the diketone XVII (18).

It is of interest that 2,2',4,4',6,6'-hexamethylchalcone (XVIII) behaves similarly, coupling occurring at a highly hindered carbon atom (18).

$$2\text{Mes}-\text{CH}=\text{CHCO}-\text{Mes} \xrightarrow[\text{(2) H}_2\text{O}]{\text{(1) Mg + MgI}_2} \begin{array}{c} \text{Mes}-\text{CHCH}_2\text{CO}-\text{Mes} \\ | \\ \text{Mes}-\text{CHCH}_2\text{CO}-\text{Mes} \end{array}$$

XVIII

Evidence that coupling occurs through the formation of a dienolate is provided by the behavior of α-mesityl-2,4,6-trimethylacrylophenone (XIX) toward the binary mixture. After hydrolysis, the dienol XX is isolable (20).

XIX   XX
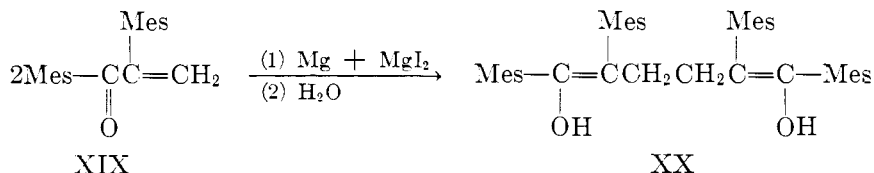
The effect of the binary mixture on highly hindered diaryl ketones sterically incapable of forming pinacols has been investigated. Conjugate bimolecular reduction of 4'-bromo-2,4,6-trimethylbenzophenone (XXI) occurs with the elimination of bromide ion and the production of 4,4'-dimesitoylbiphenyl (XXII) (34).

XXI   XXII
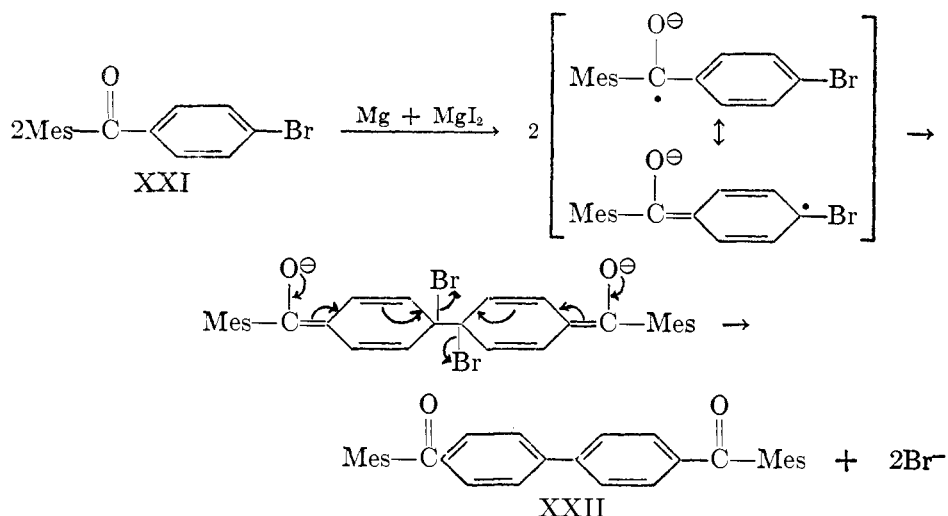
Another example of coupling with the elimination of an anion, specifically the methoxide ion, is found in the reduction of 2'-methoxy-2,4,6-trimethyl-benzophenone (XXIII) (27, 31).
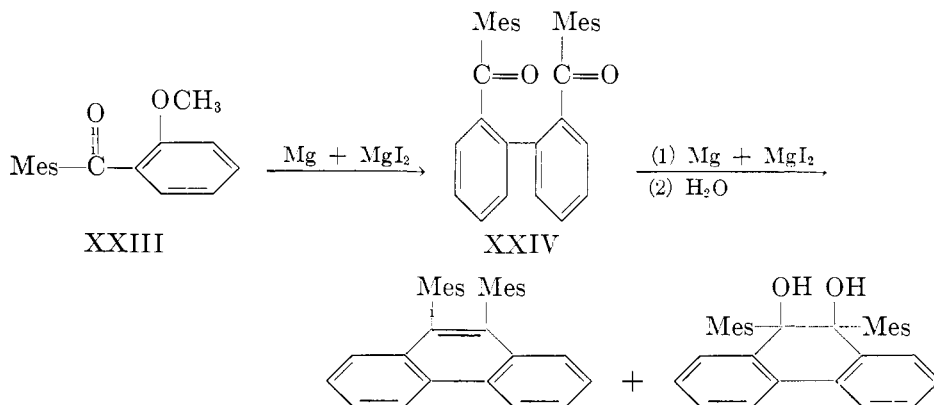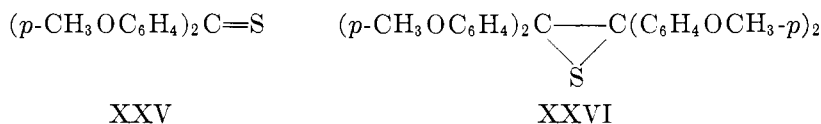
Although the proposal was made that 2,2'-dimesitoylbiphenyl (XXIV) is formed as an intermediate in the reaction, this compound was not isolated. It is worth noting that XXIV is obtained in the reduction of XXIII by means of unipositive magnesium anodically generated (table 1).
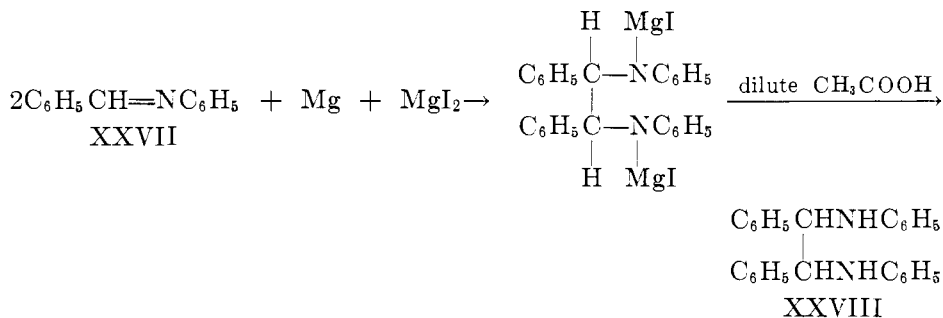
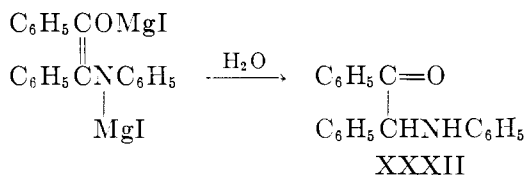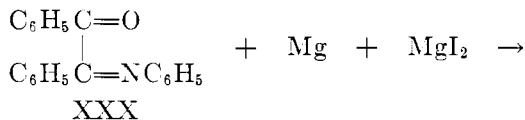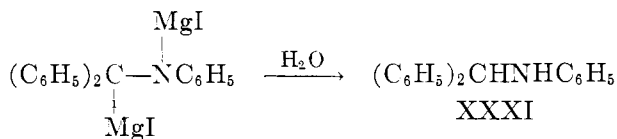### E. Reduction of miscellaneous compounds

Isolated examples of the reduction of a wide variety of functional groups not falling in any of the categories previously noted have also been described. A number of such reductions are cited below.

Aromatic thioketones are transformed by the magnesium–magnesium iodide mixture into the corresponding ethylene sulfides. For example, di-p-anisylthioketone (XXV) yields tetra-p-anisylethylene sulfide (XXVI) (60).

$$(p\text{-}CH_3OC_6H_4)_2C=S \qquad (p\text{-}CH_3OC_6H_4)_2C\text{——}C(C_6H_4OCH_3\text{-}p)_2$$
$$\underset{\displaystyle S}{\diagdown\diagup}$$

$$\text{XXV} \qquad\qquad\qquad\qquad \text{XXVI}$$

Since magnesium–magnesium iodide adds to the azo and carbonyl groups, it is of interest to compare the behavior of the azomethine group toward this mixture. Two different effects have been observed. Whereas benzalaniline (XXVII) gives, after hydrolysis, α,α'-dianilinobibenzyl (XXVIII), benzophenone anil (XXIX) and benzil monoanil (XXX) give N-phenylbenzohydrylamine (XXXI) and α-anilino-α-phenylacetophenone (XXXII), respectively (5).

$$2C_6H_5CH=NC_6H_5 \; + \; Mg \; + \; MgI_2 \rightarrow$$

XXVII

$$\begin{array}{c} H \quad MgI \\ | \quad\;\; | \\ C_6H_5C\text{—}NC_6H_5 \\ | \\ C_6H_5C\text{—}NC_6H_5 \\ | \quad\;\; | \\ H \quad MgI \end{array} \xrightarrow{\text{dilute } CH_3COOH}$$

$$\begin{array}{c} C_6H_5CHNHC_6H_5 \\ | \\ C_6H_5CHNHC_6H_5 \end{array}$$

XXVIII

$(C_6H_5)_2C{=}NC_6H_5 \quad + \quad Mg \quad + \quad MgI_2 \quad \rightarrow$
XXIX

$$
(C_6H_5)_2\overset{\displaystyle MgI}{\underset{\displaystyle MgI}{C}}{-}NC_6H_5 \quad \xrightarrow{\ H_2O\ } \quad (C_6H_5)_2CHNHC_6H_5
$$
XXXI

$$
\begin{array}{l} C_6H_5C{=}O \\ \mid \\ C_6H_5C{=}NC_6H_5 \end{array} \quad + \quad Mg \quad + \quad MgI_2 \quad \rightarrow
$$
XXX

$$
\begin{array}{l} C_6H_5COMgI \\ \parallel \\ C_6H_5\overset{\ }{\underset{\displaystyle MgI}{C}}NC_6H_5 \end{array} \quad \xrightarrow{\ H_2O\ } \quad \begin{array}{l} C_6H_5C{=}O \\ \mid \\ C_6H_5CHNHC_6H_5 \end{array}
$$
XXXII

In contrast to the behavior of benzophenone anil (XXIX) toward the binary mixture, attempted reduction of the ethylenic analog, 1,1-diphenylethylene, was unsuccessful (37). Only two other attempts have been made to effect reaction of magnesium–magnesium iodide with hydrocarbons. No evidence of reduction was found with triphenylmethane, but a very small quantity of 1,1,2,2-tetraphenylethane was obtained from diphenylmethane (39).

Reduction of N,N-diphenylhydroxylamine yields diphenylamine (38).

Reaction of the binary mixture with o- and p-quinones has been studied (17). The products are the expected quinols.

5,12-Diphenylnaphthacene is obtained by the action of magnesium–magnesium bromide mixture on 5,12-dihydro-5,12-diphenyl-5,12-naphthacenediol (1).

F. Summary of reductions with the magnesium–magnesium iodide mixture

The numerous reductions effected by means of the binary mixture magnesium–magnesium iodide are listed in table 2. The solvent employed in each case, unless otherwise noted, was a mixture of ether and benzene. In many of the reductions cited the products can exist in two or more stereoisomeric forms. Appropriate notation has been made when isomers have been identified by the authors of the original articles.

VI. REFERENCES

(1) ALLEN, C. F. H., AND BELL, A.: J. Am. Chem. Soc. 62, 2408 (1940).
(2) AOYAMA SCIENTIFIC RESEARCH INSTITUTE, INC.: Japanese patent 162,577 (March 7, 1944); Chem. Abstracts 42, 4200 (1948).
(3) BABOROVSKY, G.: Z. Elektrochem. 11, 465 (1905).
(4) BACHMANN, W. E.: J. Am. Chem. Soc. 53, 1524 (1931).

 (5) BACHMANN, W. E.: J. Am. Chem. Soc. **53**, 2672 (1931).
 (6) BACHMANN, W. E.: J. Am. Chem. Soc. **54**, 1969 (1932).
 (7) BACHMANN, W. E.: J. Am. Chem. Soc. **56**, 449 (1934).
(7a) BACHMANN, W. E., AND FERGUSON, J. W.: J. Am. Chem. Soc. **56**, 2081 (1934).
 (8) BACHMANN, W. E., AND MOSER, F. H.: J. Am. Chem. Soc. **54**, 1124 (1932).
 (9) BACHMANN, W. E., AND SHANKLAND, R. V.: J. Am. Chem. Soc. **51**, 306 (1929).
(10) BACHMANN, W. E., AND WISELOGLE, F. Y.: J. Am. Chem. Soc. **56**, 1559 (1934).
(11) BAILAR, J. C., JR.: J. Am. Chem. Soc. **52**, 3596 (1930).
(12) BARTLETT, P. D., AND BROWN, R. F.: J. Am. Chem. Soc. **62**, 2927 (1940).
(13) BEETZ, W.: Phil. Mag. [4] **32**, 269 (1866).
(14) BENNETT, W. E., DAVIDSON, A. W., AND KLEINBERG, J.: J. Am. Chem. Soc. **74**, 732 (1952).
(15) DAVIDSON, A. W., AND JIRIK, F.: J. Am. Chem. Soc. **72**, 1700 (1950).
(16) ELSASSER, E.: Ber. **9**, 1818 (1876); **11**, 587 (1878).
(17) FIESER, L. F.: J. Am. Chem. Soc. **50**, 464 (1928).
(18) FUSON, R. C.: Record Chem. Prog. (Kresge-Hooker Sci. Lib.) **12**, 1 (1951).
(19) FUSON, R. C., AND ARMSTRONG, M. D.: J. Am. Chem. Soc. **63**, 2650 (1941).
(20) FUSON, R. C., BYERS, D. J., AND RACHLIN, A. I.: J. Am. Chem. Soc. **64**, 2891 (1942).
(21) FUSON, R. C., AND CORSE, J.: J. Am. Chem. Soc. **61**, 975 (1939).
(22) FUSON, R. C., CORSE, J., AND McKEEVER, C. H.: J. Am. Chem. Soc. **61**, 2010 (1939).
(23) FUSON, R. C., CORSE, J., AND WELLDON, P. B.: J. Am. Chem. Soc. **63**, 2645 (1941).
(24) FUSON, R. C., AND HEITMILLER, R. F.: J. Am. Chem. Soc. **75**, 1494 (1953).
(25) FUSON, R. C., AND HEITMILLER, R. F.: J. Am. Chem. Soc. **77**, 174 (1955).
(26) FUSON, R. C., AND HORNBERGER, C., JR.: J. Org. Chem. **16**, 631 (1951).
(27) FUSON, R. C., AND HORNBERGER, C., JR.: J. Org. Chem. **16**, 637 (1951).
(28) FUSON, R. C., AND HORNING, E. C.: J. Am. Chem. Soc. **62**, 2962 (1940).
(29) FUSON, R. C., HORNING, E. C., WARD, M. L., ROWLAND, S. P., AND MARSH, J. L.: J. Am. Chem. Soc. **64**, 30 (1942).
(30) FUSON, R. C., AND KELTON, S. C., JR.: J. Am. Chem. Soc. **63**, 1500 (1941).
(31) FUSON, R. C., AND KERR, R. O.: J. Org. Chem. **19**, 373 (1954).
(32) FUSON, R. C., McKEEVER, C. H., AND BEHR, L. C.: J. Am. Chem. Soc. **63**, 2648 (1941).
(33) FUSON, R. C., McKEEVER, C. H., AND CORSE, J.: J. Am. Chem. Soc. **62**, 600 (1940).
(34) FUSON, R. C., AND PARSHALL, G. W.: J. Am. Chem. Soc. **76**, 5561 (1951).
(35) FUSON, R. C., SCOTT, S. L., AND LINDSEY, R. V.: J. Am. Chem. Soc. **63**, 1679 (1941).
(36) FUSON, R. C., AND WARD, M. L.: J. Am. Chem. Soc. **68**, 521 (1946).
(37) GILMAN, H., AND HARRIS, S. A.: Rec. trav. chim. **49**, 762 (1930).
(38) GILMAN, H., AND HECK, L. L.: Rec. trav. chim. **50**, 522 (1931).
(39) GILMAN, H., AND LEERMAKERS, J. A.: Rec. trav. chim. **49**, 532 (1930).
(40) GOMBERG, M., AND BACHMANN, W. E.: J. Am. Chem. Soc. **49**, 236 (1927).
(41) GOMBERG, M., AND BACHMANN, W. E.: J. Am. Chem. Soc. **49**, 2584 (1927).
(42) GOMBERG, M., AND BACHMANN, W. E.: J. Am. Chem. Soc. **50**, 2762 (1928).
(43) GOMBERG, M., AND BACHMANN, W. E.: J. Am. Chem. Soc. **52**, 4967 (1930).
(44) GOMBERG, M., AND BAILAR, J. C., JR.: J. Am. Chem. Soc. **51**, 2229 (1929).
(45) GOMBERG, M., AND VAN NATTA, F. J.: J. Am. Chem. Soc. **51**, 2238 (1929).
(46) HATT, H. H.: J. Chem. Soc. **1929**, 1623.
(47) INHOFFEN, H. H., POMMER, H., AND BOHLMANN, F.: Ber. **81**, 507 (1948).
(48) KLEINBERG, J., McEWEN, W. E., BURDICK, D. L., HOFFMAN, W. D., SANTORO, A. V., AND YANG, J. Y.: Unpublished observations.
(49) KOHLER, E. P., AND BALTZLY, R.: J. Am. Chem. Soc. **54**, 4015 (1932).
(50) LAUGHLIN, B. D., KLEINBERG, J., AND DAVIDSON, A. W.: J. Am. Chem. Soc. **78**, 559 (1956).
(51) McEWEN, W. E., KLEINBERG, J., BURDICK, D. L., HOFFMAN, W. D., AND YANG, J. Y.: J. Am. Chem. Soc. **78**, 4587 (1956).
(52) OLDHAM, J. W. H., AND UBBELOHDE, A. R.: J. Chem. Soc. **1938**, 201.

(53) PETTY, R. L., DAVIDSON, A. W., AND KLEINBERG, J.: J. Am. Chem. Soc. **76**, 363 (1954).

(54) RAIJOLA, E., AND DAVIDSON, A. W.: J. Am. Chem. Soc. **78**, 556 (1956).

(55) RAUSCH, M. D., MCEWEN, W. E., AND KLEINBERG, J.: J. Am. Chem. Soc. **76**, 3622 (1954).

(56) RAUSCH, M. D., MCEWEN, W. E., AND KLEINBERG, J.: J. Am. Chem. Soc. **77**, 2093 (1955).

(57) RAUSCH, M. D., POPP, F. D., MCEWEN, W. E., AND KLEINBERG, J.: J. Org. Chem. **21**, 212 (1956).

(58) ROYER, D. J., DAVIDSON, A. W., AND KLEINBERG, J.: J. Inorg. and Nucl. Chem., in press.

(59) SCHÖNBERG, A., AND MOUBASHER, R.: J. Chem. Soc. **1949**, 212.

(60) SCHÖNBERG, A., AND SCHÜTZ, O.: Ber. **60**, 2351 (1927).

(61) TURRENTINE, J. W.: J. Phys. Chem. **12**, 448 (1908).

(62) YANG, J. Y.: Unpublished observations.

(63) ZWOLINSKI, B. J., MARCUS, R. J., AND EYRING, H.: Chem. Revs. **55**, 157 (1955).