[Contribution from the Chemistry Laboratory of the University of Michigan]

THE REDUCING ACTION OF A MIXTURE OF MAGNESIUM IODIDE (OR BROMIDE) AND MAGNESIUM ON AROMATIC KETONES. PROBABLE FORMATION OF MAGNESIUM SUBIODIDE (OR SUBBROMIDE)

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The alkaline-earth metals have been reduced from normal to lower valence either by fusion at 800–1200° of the mixture of the halide salt and metal, or by electrolysis of the anhydrous salt at elevated temperatures.[2] Although the reaction is reversible, $MeX_2 + Me \rightleftharpoons 2MeX$, nevertheless some of these unstable subhalides have been actually isolated in sufficient purity for analysis. It was also reported[3] that anomalous suboxides result when oxalates of cadmium and of other metals are reduced at the low temperature of 200° to 300°, and it has been further maintained[4] that subsalts result when *aqueous* solutions of salts of cadmium, lead, bismuth, etc., are warmed with the corresponding metals.

Spectroscopic results, too, indicate that the alkaline-earth elements, including magnesium, in the production of their spark spectra, are stripped of one valence electron and that they function then as ion-atoms Me^+.[5] Moreover, the formation of neutral, uncharged molecules of MeX is inferred from the nature of the electronic band spectra which are emitted when the halide salts MeX_2 of the alkaline earths, or MgF_2 and BeF_2, are fed into the Bunsen flame.[6] Of similar significance is the evidence in regard to the existence of the compound MgH.[7]

Theoretical considerations, as well, do not preclude—rather presage—the existence of subsalts in this group. Thus, the formation of barium subchloride at 600° is an exothermic process: $BaCl_2 + Ba = 2BaCl + 34.6$ Cal.[8] The probable stability of the MeX salts, in general, has been calculated, taking into account the possible energy changes in each of the

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[1] The material here presented is from a dissertation submitted by W. E. Bachmann to the Faculty of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy, **1926**.

[2] Wöhler and Rodewald, *Z. anorg. Chem.*, **61**, 54 (1909). This article contains a full bibliography.

[3] Tanatar, *ibid.*, **27**, 432 (1901). Glaser, *ibid.*, **36**, 1 (1903). Brislee, *J. Chem. Soc.*, **93**, 162 (1908). Denham, *ibid.*, **111**, 29 (1917).

[4] Denham, *ibid.*, **93**, 424, 833 (1908).

[5] Fowler, Supplement to *Nature*, **1924**, p. 217; Saunders and Russell, *Astrophys. J.*, **62**, 1 (1925).

[6] Mulliken, *Phys. Rev.*, **26**, 1, 561 (1925).

[7] Watson and Rudnick, *Astrophys. J.*, **63**, 31 (1926).

[8] Haber and Tolloczko, *Z. anorg. Chem.*, **41**, 426 (1904).

several stages of the reaction Me (solid) + $\frac{1}{2}$ $X_2 \longrightarrow Me^{+}X^{-}$ (solid).[9] The figures indicate that with the exception of magnesium iodide, for which the heat of formation is —5 Cal., all other MeX halide salts of the alkaline-earth elements are exothermic, and generally with a fair margin to insure their stability as such. The reason that these compounds are so seldom met is to be ascribed to the fact that the subsequent reaction, $2MeX \underset{\text{endotherm.}}{\overset{\text{exotherm.}}{\rightleftharpoons}} MeX_2 + Me$, would naturally tend to result in the conversion of the subhalide into the normal halide. It should, however, prove feasible to determine the conditions which will delay the ensuance of the second reaction, at least for a period long enough to make it possible to prove the actual presence of the subhalide in the metastable system.

Yet, notwithstanding the fairly preponderating evidence in favor of the existence of MeX salts, it can hardly be said that the doctrine of the possible univalence of second group elements, outside of mercury, has been generally accepted.[10] The opinion is prevalent that "MeX molecules do not appear in ordinary chemistry" (Mulliken). The reluctance to concede the non-fixity of valence in these elements must be due to our lack of simple, ordinary chemical reactions by means of which the presence of subsalts could be revealed, especially when they are present in only very small quantities. Obviously, diagnostic reactions in non-aqueous media are much to be preferred. Such a reaction is described in this paper.[11] It applies to what should be one of the least promising cases in the alkaline-earth group, as $\frac{1}{2}MgI_2 + \frac{1}{2}Mg = MgI - 55$ Cal. (Grimm and Herzfeld). We have taken advantage of the fact that many magnesium salts are soluble in organic solvents. We have obtained, we believe, evidence that the reaction $MgI_2 + Mg \longrightarrow 2MgI$ actually occurs at ordinary room temperature. Our proof depends upon the reactivity of the MgX, sodium-like in nature, to form *addition* compounds with organic substances which contain the unsaturated group C:O—such as ketones, aldehydes, esters, etc.

Outline of the Reaction

In the course of two different experiments in "grignarding" benzophenone by heating the mixture of metallic magnesium, the aryl halide and the ketone together, we observed, upon hydrolyzing the reaction mixture, that the benzophenone was reduced to benzopinacol.[12] A closer investigation

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[9] Grimm and Herzfeld, *Z. Physik*, **19,** 141 (1923). Hildebrand. *Chem. Rev*.. **2.** 413 (1926).

[10] Lewis, "Valence," The Chemical Catalog Co., **1923,** p. 61. Lowry, "Inorganic Chemistry," Macmillan and Co., **1922,** pp. 612, 723.

[11] Preliminary notice, Gomberg, *Chem. Rev.*, **2**, 309 (1925).

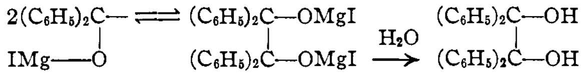
[12] Schmidlin, *Ber.*, **39**, 4202 (1906).

revealed that the reduction in our experiments was in no way connected with the Grignard reagent itself,[13] but that it was occasioned by the binary system, magnesium and magnesium iodide, the latter substance owing its presence to the iodine which had been added in order to activate the magnesium for the intended Grignard reagent. Further experiments established definitely that neither magnesium iodide alone nor, contrary to statements of others,[14] metallic magnesium alone can accomplish the reduction of the ketone to pinacol. *The simultaneous action of the two is demanded.*

The potency of the combination of magnesium and magnesium iodide in contrast to the impuissance of either substance alone, is explained on the naturally following assumption that the active reducing agent is generated by the interaction of magnesium and magnesium iodide. No other unsaturated substance that will function like metallic sodium could be formed in this reaction unless it be MgI (Equation 1), and this is just the group we find attached now to the ketone molecule. The one still unpaired valence electron in the magnesium atom of the subiodide would correspond to the one valence electron in metallic sodium. Like the latter, the magnesium subiodide, strongly electropositive, will tend to add itself to the unsaturated oxygen atom of the C:O group, and as a consequence of this the carbon atom becomes temporarily tervalent (Equation 2). This free radical may be called a halomagnesium ketyl, in analogy to Schlenk's sodium ketyls, $R_2\overset{\diagup}{C}\text{—ONa}$. As with all free radicals, the unimolecular modification of our ketyl is in equilibrium with the bimolecular form (Equation 3), and this equilibrium seems to be very much in favor of the latter, since hydrolysis yields almost quantitatively pinacol.

$$\text{Mg} + \text{MgI}_2 \rightleftharpoons 2\text{MgI} \qquad (1)$$

$$(C_6H_5)_2C{=}O + \text{MgI} = (C_6H_5)_2\overset{\diagup}{C}\text{—OMgI} \qquad (2)$$



$$2\begin{array}{l}(C_6H_5)_2C\text{—}\\ \qquad|\\ \text{IMg——O}\end{array} \rightleftharpoons \begin{array}{l}(C_6H_5)_2C\text{—OMgI}\\ \qquad\quad|\\ (C_6H_5)_2C\text{—OMgI}\end{array} \xrightarrow{H_2O} \begin{array}{l}(C_6H_5)_2C\text{—OH}\\ \qquad\quad|\\ (C_6H_5)_2C\text{—OH}\end{array} \qquad (3)$$

Undoubtedly the equilibrium which exists as indicated in Equation 1 is almost entirely in favor of the left-hand side in view of the endothermic nature of the reaction, and the existence of more than a minute amount of magnesium subiodide at one time could hardly be expected. In fact, an analysis indicated that no weighable amount of the subiodide was present. However, the speed of the reaction in Equation 2 need not depend upon the actual quantity of magnesium subiodide present at any one time, but upon the rate at which the equilibrium of the reducing system is restored when the magnesium subiodide is being removed. This res-

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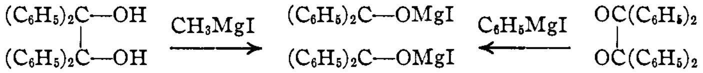
[13] Meisenheimer, *Ann.*, **442**, 180 (1925). Marshall, *J. Chem. Soc.*, **127**, 2184 (1925).

[14] Schlenk and Thal, *Ber.*, **46**, 2847 (1913).

toration of the equilibrium is apparently very rapid, for in a short time the ketone is completely changed to the pinacolate. That in our reaction the precursor of pinacol is actually the halomagnesium compound of the formula given above in Equation 3 was established beyond doubt by proving the identity of the substance in all its characteristic reactions, with the compound definitely known to have that constitution and which had been prepared directly from pinacol, and also from benzil.

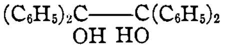
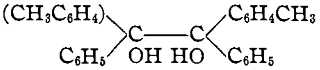
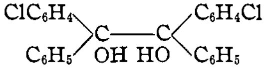
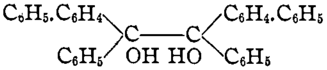
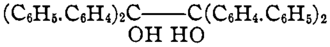
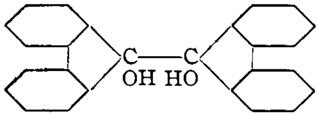
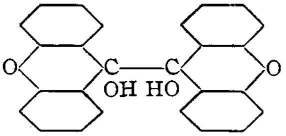
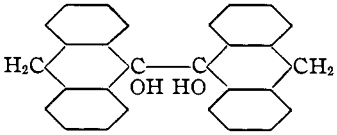
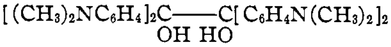


$$\begin{matrix}(C_6H_5)_2C-OH\\ |\\ (C_6H_5)_2C-OH\end{matrix} \xrightarrow{CH_3MgI} \begin{matrix}(C_6H_5)_2C-OMgI\\ \\ (C_6H_5)_2C-OMgI\end{matrix} \xleftarrow{C_6H_5MgI} \begin{matrix}OC(C_6H_5)_2\\ |\\ OC(C_6H_5)_2\end{matrix} \qquad (4)$$

Our investigation thus assumed two somewhat distinct aspects. First, we wished to obtain evidence of the formation of MgX, and for this purpose we studied, on a group of selected ketones, how readily and completely the pinacolates are formed. Of special interest here were those ketones (5, 6, 7, 8, in Table I) which by methods other than ours had failed to yield pinacols—although in some cases particular efforts were made by various

TABLE I

LIST OF KETONES REDUCED AND PINACOLS OBTAINED

No.	Ketone, R_2CO	Pinacol, $R_2C(OH).(HO)CR_2$	Yield, %
1	Benzophenone	 $(C_6H_5)_2\underset{OH}{C}-\underset{HO}{C}(C_6H_5)_2$	99.6
2	4-Methyl-benzophenone		98
3	4,4′-Dimethyl-benzophenone	 $(CH_3C_6H_4)_2\underset{OH}{C}-\underset{HO}{C}(C_6H_4CH_3)_2$	94
4	4-Chlorobenzophenone		94
5	4-Phenyl-benzophenone		97
6	4,4′-Diphenyl-benzophenone	 $(C_6H_5.C_6H_4)_2\underset{OH}{C}-\underset{HO}{C}(C_6H_4.C_6H_5)_2$	95
7	Fluorenone		99
8	Xanthone		92
9	Anthrone		83
10	Michler's ketone	 $[(CH_3)_2NC_6H_4]_2\underset{OH}{C}-\underset{HO}{C}[C_6H_4N(CH_3)_2]_2$	53

workers to obtain the corresponding pinacols. The constitution of the individual pinacols was definitely established by their rearrangement into β-pinacolins, and these were then hydrolyzed according to the well-known reaction $R_2C(OH).(HO)CR_2 \xrightarrow{-H_2O} R_3C.CO.R \xrightarrow{KOH} R_3CH + KOCOR$.

The second aspect of our problem is concerned with the study of the free radicals, $R_2C—OMgI$, which result from the slight, but unmistakable dissociation of the pinacolates. These radicals contain only two aryl groups.

In Table I are listed the ketones studied and the yields of the pinacol obtained.

Reduction of Ketones to Pinacols

Reduction of Benzophenone

Ether or benzene may be used as the solvent, but for our purposes a mixture of one volume of ether to two volumes of benzene served exceedingly well, and represents the mixture used most frequently throughout this work. The benzene employed was obtained by distilling the ordinary benzene over sodium hydroxide; the distilled product was then kept over metallic sodium. The ether was the commercial anhydrous ether, "containing 0.3% of alcohol and 0.1% of water;" it was likewise kept over sodium. Magnesium was used in the form of magnesium powder; magnesium ribbon and turnings may be employed, but the rate of the reaction is slower. The iodine was carefully dried over sulfuric acid.

Apparently concentration plays but a small role in the reaction. It was observed that even when the amount of solvent was insufficient to dissolve the entire amount of ketone, the reaction nevertheless went to completion because the pinacolate, as it is formed, is quite soluble, and it was thus possible to have at the end of the reaction a clear solution containing no precipitate. When the solution is too concentrated, however, the solid pinacolate crystallizes, although only some time after the ketone has been completely reduced.

The ether does not take part in the reduction of benzophenone to the pinacol, as it does when a mixture of zinc chloride and ether reduces triphenylcarbinol to triphenylmethane.[15] All doubt on this score was set aside by running the reaction in pure benzene, with no ether present. Magnesium powder was boiled with iodine in benzene but we found, as others have,[16] that magnesium does not react with iodine under these conditions. Very little ether suffices, however, to promote this reaction; 1 cc. of ether in 100 cc. of benzene does it; but with no ether present, not even after the mixture was boiled for 24 hours was there any appearance

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[15] Gomberg, THIS JOURNAL, **35**, 204 (1913).

[16] Zelinsky, *J. Russ. Phys.-Chem. Soc.*, **35**, 399 (1903). Parsons, THIS JOURNAL, **47**, 1833 (1925).

of a reaction having occurred. However, curiously enough, as soon as benzophenone was added, reaction ensued, the iodine disappeared in a short time, and after the iodine was gone the pure red color, characteristic of the reduction product, appeared in the solution. Hydrolysis of the red solution yielded benzopinacol, which showed conclusively that the reduction does not depend upon the presence of ether.

Addition Complex of Ketone and Magnesium Iodide.—When a solution of magnesium iodide in benzene or in ether is added to a solution of benzophenone, a complex is formed which is very little soluble in either of the two solvents mentioned. It has the composition, three molecules of ketone to one of magnesium iodide and is readily decomposed by water into its components. One may consider it to be $[((C_6H_5)_2CO)_3MgI]I$, with the coördination number for magnesium of 4. With other ketones, one molecule of the ketone is replaced by a molecule of ether still leaving the same coördination number for the metal.

Preparation of Benzopinacol.—To 15 g. of powdered magnesium (0.62 g. atom), 100 cc. of ether and 150 cc. of benzene contained in a 500cc. flask attached to a condenser, is added 42 g. of iodine (0.33 g. atom) in portions of several grams each at such intervals as to keep the solution boiling quite vigorously. The practically colorless solution of the magnesium salt is cooled and to it is added a solution of 54.6 g. of benzophenone (0.3 mole) in 50 cc. of warm benzene. The heavy, white precipitate of the ketone plus magnesium iodide addition complex fills the flask. The flask is stoppered and shaken for 15 minutes; during this time the precipitate disappears and a deep red solution results. The complete disappearance of the precipitate indicates that the reduction is practically at an end; when the flask is shaken for too long a time the iodomagnesium pinacolate precipitates upon the metallic magnesium, making subsequent separation rather troublesome. After the magnesium has been allowed to settle, the solution is filtered or simply decanted from the excess of metal; the magnesium remaining is extracted with a mixture of ether and benzene and this solution filtered and added to the main portion. Water is added to the solution of the pinacolate; the magnesium hydroxide formed on hydrolysis is dissolved by the addition of dil. sulfuric or hydrochloric acid. A pinch of sodium bisulfite serves to remove what little free iodine may have been liberated. By shaking the mixture, the pinacolate is completely decomposed in a short time, the liberated benzopinacol precipitating in large quantities. At this point one may filter off the solid benzopinacol from the ether-benzene and aqueous solutions, or the pinacol may be brought into solution entirely by adding a sufficient amount of benzene. The benzene solution, after separation from the aqueous layer, is washed with water, dried over anhydrous sodium sulfate, and the solvent evaporated. The crude pinacol is digested with 100 cc. of petroleum ether (40–60°), which takes out traces of benzophenone and other material; yield of pinacol, 54.7 g., or 99.6%. Benzopinacol crystallizes from a mixture of alcohol and chloroform in large, colorless prisms.

It is quite possible to prepare the pinacol by adding the iodine to the mixture of magnesium and ketone in ether-benzene, but this procedure has practical drawbacks, and we recommend that the magnesium iodide be prepared prior to the addition of the ketone.

Widely different values are given in the literature for the melting point of benzopinacol, the values ranging from 168° to 189°, the one most frequently reported being 186°. Benzopinacol decomposes near its melting point, so that what is measured is not the true melting point but rather the temperature at which decomposition occurs. The presence of small amounts of impurities and a relatively slow heating cause a considerable lowering in this decomposition point. We find that pure benzopinacol generally melts at 192–194°, and if not to much time is taken in heating the substance, the pinacol does not melt until 195–196°.

Use of "Wet" Solvents.—We also tried using ether which had been dried only over calcium chloride, and benzene which had not been fractionated. The magnesium reacted very readily with iodine in such solvents; it appeared, however, to be coated with some substance formed because of the moisture present. This did not prevent the magnesium from reacting; after an hour of shaking, a 95% yield of benzopinacol was obtained. In small amounts the effect of moisture is merely to use up some of the anhydrous magnesium iodide by forming a hydrate of the salt. Too much water must not be present; otherwise, reaction will not take place, the coating of hydrate on the metal finally becoming thick enough to keep the magnesium from reacting.

Speed of Reaction.—The reaction proceeds even at 0°. In one experiment, one-quarter of the benzophenone used was reduced in half an hour, and complete reduction required three hours. At room temperature, however, the speed becomes so great that the difference between it and the rate at the boiling point of the solution, about 60°, is indistinguishable, and the ketone is completely reduced in a few minutes. The speed of the reduction at 25° is truly astonishing. An experiment in which 55 g. of benzophenone was used disclosed that the addition complex which had precipitated was entirely used up in five minutes; after shaking for a few minutes longer a yield of 99.5% of benzopinacol was obtained.

A further idea of the speed of this reduction may be gained from a comparison with the speed with which a Grignard reagent acts on the ketone. Equivalent amounts of phenylmagnesium iodide and of our binary system were allowed to compete for the same benzophenone, and the relative rates of the two reactions were ascertained by determining the relative amounts of triphenylcarbinol and benzopinacol produced. The quantity of the former indicated the quantity of benzophenone usurped by the Grignard reagent, while the benzophenone claimed by the magnesium subiodide was revealed by the benzopinacol produced. The relative amounts of pinacol and carbinol showed that 50% of the benzophenone was won by the magnesium subiodide and 40% was annexed by the phenylmagnesium iodide, the remaining 10% of the ketone having gone to form undetermined products.

Effect of Varying the Amounts of Magnesium and Magnesium Io-

dide.—According to our postulations, one gram atom of magnesium and one gram atom of iodine are required to convert one gram molecule of ketone to the iodomagnesium pinacolate.

$$2R_2C{=}O + 2Mg + I_2 = R_2C(OMgI).(IMgO)CR_2 \qquad (5)$$

An experiment was run in which just one gram atom of magnesium was used for one gram molecule of benzophenone, one-half of this magnesium having been converted into magnesium iodide prior to the addition of the ketone. At the end of the reaction no trace of magnesium remained; a clear red solution was obtained which, with water, gave an amount of benzopinacol corresponding to 93% of that calculated according to the equation.

With regard to iodine, however, the situation is different. When the amount of iodine employed is that required by the equation, the yield of pinacol is practically quantitative. When fractions of the theoretical quantity of iodine are used, the results will depend upon the temperature at which the reaction is allowed to proceed. The addition of a solution of benzophenone to a colorless solution of magnesium iodide in ether-benzene at 25° results in the formation of the complex, $[(C_6H_5)_2CO]_3.MgI_2$. Consequently for each gram molecule of ketone, there is needed one-third of a gram molecule of magnesium iodide, or, what amounts to the same thing, two-thirds of a gram atom of iodine. In the cold, the molecular compound is stable and nearly insoluble. Since *free* magnesic iodide is required, in solution, to furnish magnesous iodide, it would be predicted, *ex hypothesi*, that if the amount of magnesium iodide used is not above that needed for the complex, no reaction would take place. Experiment completely and very strikingly verified this. If less than two-thirds of a gram atom of iodine is employed for a mole of benzophenone, no matter how large the amount of metallic magnesium may be, no reaction occurs. In one experiment, with 0.65 gram atom of iodine no pinacol was produced in 18 days. Ever so slight an excess over the two-thirds limit induces the reaction, and the latter can now proceed to the end slowly but surely, even when there is present, instead of the theoretical 1.0, only 0.70 of a gram atom of iodine. We assume, therefore, that iodomagnesium pinacolate is spontaneously converted partially into magnesium pinacolate by splitting off a molecule of magnesium iodide; the latter can thus react further with magnesium and supply more magnesous iodide for the reduction of more ketone.

$$\begin{array}{l} R_2C{-}OMgI \\ \,| \\ R_2C{-}OMgI \end{array} \longrightarrow \begin{array}{l} R_2C{-}O \\ \,| \\ R_2C{-}O \end{array}\!\!\Big\rangle Mg + MgI_2 \qquad (6)$$

Again, when instead of at 25°, the reaction is carried on at a temperature near the boiling point of the solvent, even smaller fractions of the calculated amount of magnesic iodide than in the former case may suffice for the purpose of initiating and completing the reduction of the ketone. No precipitation of the complex $MgI_2.(R_2CO)_3$ occurs; apparently it is decomposed at 60° largely into its components, and the magnesic iodide becomes at once available for the reaction with the metallic magnesium. Moreover, at this high temperature, the reaction in Equation 6 will undoubtedly proceed faster than at room temperature. Indeed, even with only 0.1 g. atom of iodine, appreciable reduction of the ketone occurs, 30% in 15 hours; with 0.5 g. atom of iodine, the reduction was 62% in 23 hours.

Analysis of the Iodomagnesium Pinacolate.—The extent to which the secondary reaction takes place whereby some of the iodomagnesium pinacolate is converted to the magnesium pinacolate through loss of magnesium iodide (Equation 6) was determined by an analysis of the product as it is obtained from ether-benzene. A mixture of the two pinacolates was isolated from a relatively concentrated solution, made by reducing 20 g. of benzophenone in 35 cc. of ether and 25 cc. of benzene by 5 g. of magnesium and 16 g. of magnesium iodide. The thick red solution of the reaction mixture, filtered from the metallic magnesium, was shaken until crystallization seemed complete. By filtration and repeated washing with cold solvent, the pinacolate mixture was obtained as a pure, white, crystalline product. All operations were carried out in a stream of nitrogen.

A definite weight of the mixture was decomposed with acidulated water, and the relative amounts of pinacol, magnesium and iodine were determined. With other weighed portions, the magnesium hydroxide, formed after hydrolysis with water alone, was titrated with standard acid. The iodine found was calculated as being entirely in the form of iodomagnesium pinacolate, the remaining pinacol and magnesium being considered as magnesium pinacolate, $(C_6H_5)_2C(OMgO)C(C_6H_5)_2$. Calculated in this way, the crystalline mixture consisted, after being washed with ether-benzene, of 63% of the iodomagnesium pinacolate and 37% of the magnesium pinacolate. Of course, prior to crystallization, and prior to the crystals being washed, these two components might have been in a somewhat different ratio.

Reduction of Benzophenone by the Binary System, $Mg + MgBr_2$.—The combination, $MgBr_2 + Mg$, reduces benzophenone with the production of pinacol. With Q_f $MgBr_2 = 129$, and Q_f MgBr calculated (Grimm and Herzfeld) as 10 Cal., the reaction is $\frac{1}{2}MgBr_2 + \frac{1}{2}Mg = MgBr - 55$ Cal. Consequently, the tendency to form subbromide is equal to that in the formation of the subiodide. The ketones are reduced equally by either subhalide, but the speed of reduction is greater with the subiodide, and this may be accounted for by the lesser stability of magnesic iodide as compared with magnesic bromide.

The reaction was carried out in two ways: (1) by first forming magnesium bromide from bromine and magnesium in ether-benzene and then adding the benzophenone; and (2) by adding bromine drop by drop to the boiling solution containing the benzophenone and magnesium. Both methods gave practically the same results, and the benzophenone was reduced to the pinacol to the extent of 84 to 92%. The use of bromine, however, gave rise to a less pure product than the use of iodine. This is accounted for by the fact that the bromine reacts to some extent with the benzene used as solvent; the bromobenzene thus produced is then acted upon by the magnesium, forming phenylmagnesium bromide which in turn reacts with some of the benzophenone to give triphenylcarbinol. If anhydrous magnesium bromide could be made in some suitable solvent not attacked by bromine, the latter could readily be used in place of iodine in this reduction of ketones. Powdered magnesium and liquid bromine, with no solvent present, are very unreactive toward each other, even on heating.

Magnesium bromide was then made without recourse to free bromine, by permitting magnesium to react with a hot solution of anhydrous mercuric bromide in a mixture of ether and benzene. The solution of magnesium bromide was filtered from the magnesium amalgam; a test showed the complete absence of mercury salt in the solution. Using this magnesium bromide in the binary system, yields of 90 to 95% of benzopinacol could be obtained in one hour. One need not even filter the solution from the magnesium amalgam formed in the reaction of magnesium upon mercuric bromide; a mixture of benzophenone, mercuric bromide and an excess of magnesium yields benzopinacol. Zinc bromide and cadmium bromide were also used to furnish magnesic bromide; in like manner, magnesic iodide was prepared from the action of magnesium on zinc, cadmium and aluminum iodides.

Attempts were made to prepare solutions of magnesium chloride from magnesium and mercuric chloride in ether-benzene, but no reaction took place between the two substances; magnesium was unable to displace the mercury from the chloride, as it had done from the bromide and iodide. Here, too,[17] the fact that magnesium chloride is insoluble in ether-benzene may account for the lack of reaction. Anhydrous magnesium chloride, prepared from the hexahydrate by dehydration in a stream of hydrogen chloride, was found to have no action, with magnesium, upon benzophenone.

The Binary System, $BeI_2 + Be$.—Preliminary experiments with this system indicate that yields of pinacol up to 50% of the calculated amounts can be obtained. The less favorable reaction than with magnesium is due, in a measure, to the lesser solubility of the beryllium iodide in our solvent. Further work with this system is being done.

Attempts to Employ Other Binary Systems.—The action of the following systems was tried on benzophenone in the usual mixture of ether and

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[17] Ref. 16. Raynoud, *Bull. soc. chim.*, **39**, 195 (1926).

benzene: $Zn–ZnI_2$; $Zn–ZnBr_2$; $Zn–ZnCl_2$; $Cd–CdI_2$; $Cd–CdBr_2$; $Al–AlI_3$; and the mixed systems $Ag–MgI_2$; $Zn–HgI_2$; $Zn–MgBr_2$; $Zn–HgCl_2$; $Zn–MgI_2$. In each case negative results were obtained; perhaps other solvents than ether-benzene mixture are required with these combinations.

Magnesium Amalgam Does Not Reduce Benzophenone.—It was stated above that magnesium amalgam was one of the products of the reaction between magnesium and mercuric bromide. This amalgam decomposed water with great violence, but it was unable to reduce benzophenone in a solution of ether and benzene to magnesium pinacolate. Magnesium amalgam, prepared directly from magnesium and mercury, after considerable heating with the ketone did give a blue color to the solution, which gradually changed to red. However, even after 40 hours' boiling, no benzopinacol could be found; practically all of the benzophenone was recovered unchanged. The introduction of magnesium iodide into a mixture of amalgam and ketone brought about complete reduction of the latter. Our results thus do not confirm the statement[18] that magnesium amalgam reacts with aromatic ketones similarly to sodium. The sodium ketyl of benzophenone is known to give pinacol and hydrol on hydrolysis, while magnesium amalgam does not affect benzophenone in this manner. Our results are, however, not inconsistent with the fact that in 80% alcohol the aromatic ketones are reduced by the amalgams of magnesium, zinc and aluminum, and give a mixture of pinacol and hydrol.[19]

Rearrangement to β-Benzopinacolin.—The methods given in the literature for converting benzopinacol to β-benzopinacolin are, for the most part, rather drastic in their treatment. We found a very simple method which depends upon the catalytic effect of iodine.

Five g. of benzopinacol was heated with 25 cc. of glacial acetic acid containing 0.01 g. of iodine. In a few minutes a clear solution was obtained, as the pinacolin formed is soluble in that quantity of acid. On cooling, 4.5 g. of benzopinacolin crystallized in fluffy masses; m. p., 179–180°.

This method is of very general application. In some instances an unsuspected trace of iodine in the crude pinacol suffices for the conversion of the latter into the corresponding pinacolin (see p. 249).

Dissociation of Iodomagnesium Pinacolates

The intense colors of the reaction mixtures engendered by the action of our binary systems on aromatic ketones are ascribed to the presence of the ketyl radicals, $R_2\overset{/}{C}\text{—OMgI}$. These colors varied from the deep fuchsine red with concd. benzophenone solutions to the intense indigo blue of the solution obtained from dibiphenyl ketone. The admission of a small amount of air to the filtered solution was sufficient to discharge

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[18] Schlenk and Thal, *Ber.*, **46**, 2847 (1913).

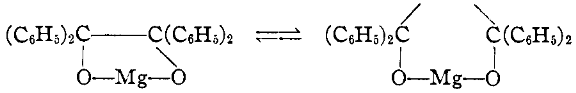
[19] (a) Böeseken and Cohen, *Verslag Akad. Wetenschappen Amsterdam*, **22**, 52, 98 (1913). (b) Cohen, *Rec. trav. chim.*, **38**, 72, 113 (1919). (c) Prins, *ibid.*, **44**, 1093 (1925).

the color, but the color reappeared when the air was prevented from entering. The phenomenon of decolorization and renaissance of the color is analogous to what occurs with the triarylmethyls.

On adding iodine to a red pinacolate solution, the color of the solution as well as of the iodine is discharged. Very shortly after all of the iodine has disappeared the original color of the reaction mixture returns. This again is in complete harmony with the demeanor of a solution of triphenylmethyl toward iodine.

The analogy with the triarylmethyls goes still further. In the solid state, hexa-arylethanes are colorless; when dissolved, dissociation into free radicals with the consequent production of color, results. Such is the case with halomagnesium pinacolates.

An equilibrium thus exists between the iodomagnesium pinacolate and the iodomagnesium ketyl as given in Equation 3. The magnesium pinacolate may dissociate in much the same manner, except that here dissociation would occur within the molecule:



That we are actually dealing here with a phenomenon involving dissociation of an ethane derivative into free radicals, was definitely proved in the following manner. Pure benzopinacol was treated, in an atmosphere of nitrogen, with methylmagnesium iodide, and this reaction could give no other product than methane and iodomagnesium pinacolate: $R_2C(OH).(HO)CR_2 + 2CH_3MgI = R_2C(OMgI).(IMgO)CR_2 + 2CH_4$.

Each addition of the pinacol solution to the Grignard reagent resulted in the formation of a red color in the mixture and was accompanied by a vigorous evolution of methane. The red color persisted in the solution and at the end of the addition of pinacol looked like the color of the usual reaction mixture obtained from benzophenone, magnesium and magnesium iodide. The net volume of methane produced amounted to that calculated for the reaction with the two hydroxyl groups in the pinacol. The red solution of this iodomagnesium pinacolate was found by comparison to be identical in its behavior toward iodine and oxygen with the pinacolate solution obtained from benzophenone. The identical iodo magnesium pinacolate was obtained from benzil[20] and phenylmagnesium iodide (see Equation 4). The behavior of the other pinacols (Table I) gave in every instance with methylmagnesium iodide the iodomagnesium pinacolate, which proved to be similar in color and in every other respect to the pinacolate obtained directly from the corresponding ketone by reduction with magnesous iodide.

The dissociation of benzopinacol derivatives is not without precedent.

[20] Acree, *Ber.*, **37**, 2753 (1904).

According to Wieland,[21] the diphenyl ether of benzopinacol shows on heating a very slight dissociation. Löwenbein and Gagarin,[22] as well as Blicke,[23] have reported instances of apparent dissociation of dicyano-tetra-arylethanes in naphthalene. It may be added that the reduction of benzophenone to benzopinacol by nascent hydrogen is formulated on the basis of intermediate radical formation.[24] By the addition of a hydrogen atom to benzophenone, there is generated diphenyl-hydroxymethyl, $(C_6H_5)_2\overset{/}{C}$—OH, a free radical containing a tervalent carbon atom. The association of two such "molecules" gives benzopinacol.

Absorption of Iodine.—By the action of iodine the pinacolate is completely broken down to the original ketone. The free radical apparently plays an important part in this reaction; even after 80% of the total amount of iodine had been absorbed, the colorless solution, on standing, gradually assumed the red color characteristic of the radical. The following formulation best expresses the nature and course of the reaction with iodine: $(C_6H_5)_2\overset{/}{C}(OMgI) + I = (C_6H_5)_2C(OMgI).I = (C_6H_5)_2CO + MgI_2$. Although there may be only a slight dissociation of the pinacolate into the free radicals, yet the reaction goes to completion even in the cold; as the ketyl is removed by the iodine, more of the pinacolate must dissociate to restore the equilibrium, whereby more of the active radical is produced for further reaction.

Titration of the solution of pinacolate with a solution of iodine, as is done with the triarylmethyls, was not so successful, because the absorption of iodine slowed down very markedly after about 25% of the calculated quantity had been added. Because of this retardation, which made working with ethereal solutions of iodine inconvenient, the iodine was introduced in the solid form.

Nine g. of benzophenone was reduced by the mixture of magnesium and magnesium iodide. The red solution was filtered from the excess of magnesium, and the solution was divided into two approximately equal parts. One aliquot portion was immediately decomposed with water and the amount of benzopinacol determined; it indicated a yield of 85%. To the other portion was added the calculated quantity of powdered iodine in amounts of 0.25–0.30 g. The first 25% of the total iodine added in the course of the experiment was taken up in 20 minutes, the next 25% in ten hours, the next 25% in 35 days, and the last 25% in 65 days. After ten hours, when 50% of the iodine had been added, crystals of the addition complex, $MgI_2.3R_2CO$, began to appear and the quantity increased as the reaction proceeded. On hydrolysis of the resulting mixture no magnesium hydroxide was formed, indicating that no more pinacolate remained, and the product was found to be pure benzophenone. The reaction, though proceeding rather slowly at room temperature, is nevertheless practically complete. When, how

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[21] Wieland, *Ber.*, **44**, 2551 (1911).

[22] Löwenbein and Gagarin, *Ber.*, **58**, 2643 (1925).

[23] Blicke, This Journal, **47**, 1477 (1925).

[24] Ref. 19 b, p. 129. Ref. 19 c.

ever, the pinacolate solution is warmed with the iodine, the absorption is complete in a much shorter time, apparently in a few hours. Pinacol itself is not affected by iodine in ether or benzene.

Absorption of Oxygen.—Oxygen, like iodine, converts the pinacolate-ketyl system into benzophenone: $2(C_6H_5)_2COMgI + O = 2(C_6H_5)_2CO + IMgOMgI$. By passing oxygen through a cold, filtered solution of the pinacolate for three hours a yield of benzophenone was obtained corresponding to 17% of the total amount of pinacolate originally present. With a warm solution, the oxidation is much faster, and quantitative yields of ketone have been obtained.

Reduction of 4-Methyl-benzophenone

4,4'-Dimethyl-benzopinacol.—To the colorless reaction product from 15 g. of iodine and 5 g. of magnesium, in 120 cc. of solvent, was added a solution of 19.6 g. of 4-methyl-benzophenone in benzene. The flask was corked and the contents were shaken. In a minute or two the olive-green mixture (no precipitate of the ketone magnesium iodide complex had formed) changed suddenly to a red color, which increased in intensity as the reaction progressed. After 15 minutes of shaking, the solution was hydrolyzed with water and the pinacol isolated in the manner described for benzopinacol. Unchanged ketone was removed by digestion of the crude pinacol with hot petroleum ether; yield of dimethyl-benzopinacol, 19.3 g., which was 98% of the amount possible. The pinacol crystallizes very well from a mixture of chloroform (3 parts) and alcohol (1 part); m. p., 173–175°; that reported in the literature is 163–165°. When heated rather slowly, the pinacol melts, or rather decomposes, at a temperature somewhat lower than 173°.

On recrystallization from acetic acid containing a trace of iodine, the dimethyl-benzopinacol gave crystals which were no longer pinacol; the product melted at 114–116° and was probably a pinacolin, or a mixture of the two structurally possible pinacolins.

Absorption of Iodine and Oxygen by the Ketyl.—The solution of the pinacolate, prepared from ethylmagnesium iodide and dimethyl-benzopinacol, like the solution of the pinacolate prepared from *p*-methyl-benzophenone, was red. The color was discharged by iodine, but reappeared after the iodine had been used up. Warming the solution for two hours with iodine in excess converted 90% of the iodomagnesium pinacolate to 4-methyl-benzophenone.

Dry oxygen was passed through a solution of the pinacolate in the manner already described, the mixture being heated gently on the steam-bath. The red solution was decolorized by the oxygen, and in five hours 95% of the pinacolate was converted to the ketone.

Reduction of 4,4'-Dimethyl-benzophenone

4,4',4",4"'-Tetramethyl-benzopinacol.—A mixture of 17 g. of magnesium iodide, 4 g. of magnesium, 21 g. of the ketone and 150 cc. of solvent had been shaken for only a minute when a deep red color made its appearance, and in five minutes the heavy white precipitate of the addition complex, $[(C_7H_7)_2CO]_2.MgI_2.(C_2H_5)_2O$, which initially had filled the flask, entirely disappeared. The shaking was continued for only five minutes more; when the reaction is allowed to proceed longer a precipitate of the pinacolate forms in the solution. The decanted solution was decomposed with water and worked up in the usual manner. The yield of pinacol amounted to 19.8 g., or 94%, and from the petroleum ether solution 1.3 g. of unchanged ketone was recovered, so no product other than pinacol was formed. The pinacol was obtained from chloroform in large, colorless prisms, and melted at 183–184°, higher than reported. When heated slowly, it decomposed at 175–177°.

The iodomagnesium pinacolate absorbs iodine and oxygen, and is oxidized back to the ketone.

4,4′,4″,4‴-Tetramethyl-benzopinacolin.—Tetramethyl-benzopinacol which had been recrystallized from chloroform is unaffected by hot glacial acetic acid. When, however, to the solution of the pure pinacol in hot acetic acid a crystal of iodine is added, the product that crystallizes on cooling is the pinacolin; m. p., 137–138°.

Anal. Calcd. for $C_{30}H_{28}O$: C, 89.06; H, 6.98. Found: C, 88.64; H, 6.93.

The pinacolin, when heated with alcoholic potassium hydroxide, gave 4,4′,4″-tritolylmethane[25] and 4-methylbenzoic acid.

Reduction of 4-Chlorobenzophenone

4,4′-Dichlorobenzopinacol.—The reaction materials were 9 g. of iodine for magnesium iodide, 2.5 g. of magnesium, 30 cc. of ether, 100 cc. of benzene and 10.82 g. (0.05 mole) of 4-chlorobenzophenone. No precipitate of an addition complex was formed; on shaking the green solution, the color changed to red and heat was evolved. After an hour the deep red solution of the pinacolate was hydrolyzed. The pinacol, after digestion with 30 cc. of hot petroleum ether, weighed 10.31 g., which represents a yield of 94%. After recrystallization from alcohol, the pinacol melted at 172–178°.[26]

Iodine converted the iodomagnesium pinacolate quantitatively to *p*-chlorobenzophenone. The reaction of the pinacolate with oxygen proceeded in the same fashion, and gave the ketone.

Reduction of Phenyl-biphenyl Ketone

Preparation of Biphenyl.—In a previous paper,[27] a general procedure has been described for synthesizing biaryl compounds by means of the diazo reaction: $R—N_2Cl + R'H + NaOH = R—R' + N_2 + NaCl + H_2O$. In adding sodium hydroxide to the mixture of phenyl-diazonium chloride solution and benzene, it is difficult to avoid the formation of tarry products, especially toward the end of the reaction. When, however, magnesium sulfate has first been added in order to convert the incoming sodium hydroxide into magnesium hydroxide, thereby acting as a buffer, the coupling reaction is milder, and a clear, golden-yellow solution is obtained, entirely free from solid tarry particles. By this modification, we obtained from 93 g. of aniline and 100 g. of magnesium sulfate heptahydrate, 54 g. of biphenyl; the yield was thus increased from 22 to 35%.

4,4′-Diphenyl-benzopinacol.—A mixture of 15.48 g. of phenyl-biphenyl ketone (0.06 mole), 220 cc. of ether-benzene, 4 g. of magnesium and 9 g. of iodine was used. No precipitate of the addition complex formed when the ketone and magnesium iodide solutions were mixed, probably because the solution was rather hot. The reaction was started by heating the mixture for a few minutes; the flask was then closed and shaken

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[25] Gomberg, *Ber.*, **35**, 2399 (1902).

[26] (a) Montagne, *Rec. trav. chim.*, **26**, 264, (1907). (b) Ref. 19b.

[27] Gomberg and Bachmann, THIS JOURNAL, **46**, 2339 (1924).

for half an hour at room temperature. The green color which was initially present soon changed, and finally the color was deep greenish-blue. The product obtained on hydrolysis was digested with 50 cc. of hot alcohol to remove any unchanged ketone; in this alcoholic solution was found 0.5 g. of ketone, but no hydrol; yield of pinacol, 15.1 g., or 97%. Whereas other methods[28] have failed to give appreciable yields of this pinacol, our procedure produces it in quantitative yield.

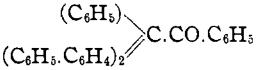
The 4,4′-diphenyl-benzopinacol is practically insoluble in cold alcohol, not very soluble in hot alcohol, nor in cold or hot benzene. It is moderately soluble in hot chloroform and in hot xylene, from which it may be recrystallized; m. p., 198–199°.

Anal. Calcd. for $C_{38}H_{30}O_2$: C, 87.99; H, 5.83. Found: C, 87.75; H, 5.91.

The molecular weight of the pinacol was determined in boiling benzene by means of Menzies' apparatus. Calcd.: 518. Found: 524.

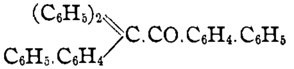
Rearrangement to the Pinacolin. Relative Wandering Tendencies of the Phenyl and Biphenyl Groups.—On dehydration and rearrangement of diphenyl-benzopinacol, two pinacolins are possible.

(A)



$$\left.\begin{matrix}(C_6H_5)\\(C_6H_5.C_6H_4)_2\end{matrix}\right>C.CO.C_6H_5$$

(B)



$$\left.\begin{matrix}(C_6H_5)_2\\C_6H_5.C_6H_4\end{matrix}\right>C.CO.C_6H_4.C_6H_5$$

The two are actually produced, but A is formed in ever so much larger proportion than B. The relative amount of the second pinacolin was found by determining the quantity of *p*-phenylbenzoic acid which a given weight of the mixture of the pinacolins yielded on treatment with alcoholic potassium hydroxide. This acid, in distinction to benzoic, is almost completely insoluble in water. The results indicated that 8% of the rearrangement had occurred with a wandering of the phenyl group, while the biphenyl group had migrated to the extent of 92%. It is interesting to note that the biphenyl group, in wandering from one carbon atom to the other, attaches itself to the second carbon atom in the *para* position, the same position in which it was originally attached to the first carbon atom. This result is in harmony with the observations of others on substituted phenyl groups.[26a]

Four g. of 4,4′-diphenyl-benzopinacol, 40 cc. of acetyl chloride, 20 cc. of acetic acid and 100 cc. of benzene were gently boiled on the steam-bath for 12 hours. The solution was evaporated to dryness and the residue was recrystallized by adding petroleum ether to a concentrated benzene solution, whereupon 2.1 g. of the benzoyl-4,4′-diphenyl-triphenylmethane (A) was obtained; m. p., 198°.

Anal. Calcd. for $C_{38}H_{28}O$: C, 91.16; H, 5.64. Found: C, 90.75; H, 5.75.

Two g. of this pinacolin, heated with alcoholic potassium hydroxide for 12 hours, gave 1.61 g. of 4,4′-diphenyl-triphenylmethane,[29] m. p. 165°, and 0.4 g. of benzoic acid.

Absorption of Iodine and of Oxygen by the Ketyl.—The deep blue solution of the iodomagnesium pinacolate absorbed iodine with discharge of the color and the formation of the original ketone. At room temperature the pinacolate was completely converted into the ketone in 24 days,

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[28] Böeseken and Cohen, *Chem. Centr.*, **1915**, I, 1375. Schlenk and others, *Ber.*, **47**, 473 (1914).

[29] Schlenk and Herzenstein, *Ann.*, **372**, 19 (1910).

while 15 hours sufficed to yield the same result at higher temperature. Oxygen acted upon the solution in a similar manner.

Reduction of Dibiphenyl Ketone

4,4′,4″,4‴-Tetraphenyl-benzopinacol.—The dibiphenyl ketone was recrystallized from chlorobenzene and from a mixture of acetone and benzene. There were taken for the reaction 2 g. of iodine for magnesium iodide, 2 g. of magnesium, 50 cc. of ether-benzene and 2 g. of dibiphenyl ketone. No reaction was apparent in 20 minutes; this delay must have been caused by the fact that the magnesium was coated with the insoluble addition complex that had precipitated, and not by any lack of free magnesium iodide. About 0.2 g. of fresh magnesium was, therefore, introduced, whereupon reaction ensued in a few minutes. The dark green color of the solution changed to a deep indigo blue and within an hour all precipitate had vanished. After 18 hours the color was purplish-blue. Decomposition with water precipitated the pinacol. The solid pinacol, which was suspended in the benzene layer, was filtered off; weight, 1.63 g. From the benzene solution was obtained an amount of pinacol that increased the yield to 95%. The pinacol is extremely insoluble in most solvents; it may be recrystallized from chlorobenzene and is obtained in pure white crystals. A definite melting point can hardly be given because the compound decomposes very readily on heating. The melting point of the pinacol, observed on inserting melting-point tubes into baths at various temperatures, was 200–203°. Attempts to prepare this pinacol by other methods have not been successful.[30]

Anal. Calcd. for $C_{50}H_{38}O_2$: C, 89.52; H, 5.71. Found: C, 88.91; H, 5.74.

On melting, decomposition occurs usually into dibiphenyl ketone and dibiphenyl carbinol in equivalent amounts; the carbinol is easily soluble in alcohol, the ketone is insoluble: $(C_{12}H_9)_2C(OH).(HO)C(C_{12}H_9)_2 \xrightarrow{\text{heat}} (C_{12}H_9)_2CO + (C_{12}H_9)_2CH(OH)$.

4,4′,4″,4‴-Tetraphenyl-benzopinacolin.—A mixture of 1 g. of tetraphenyl-benzopinacol, 10 cc. of acetyl chloride, 5 cc. of acetic acid and 20 cc. of benzene was boiled gently for six hours; during this time the white, pasty suspension gave way to a clear solution. By recrystallization of the precipitated product from acetic acid, 0.35 g. of tetraphenyl-benzopinacolin was obtained in the form of white, granular crystals; m. p., 204–207°. With the pinacolin was found about 0.1 g. of tetrabiphenylethylene.

Alcoholic potassium hydroxide split the tetraphenyl-benzopinacolin into tribiphenylmethane, m. p. 233°,[31] and *p*-phenylbenzoic acid.

Reduction of Fluorenone

Fluorenopinacol.—This pinacol has not been made heretofore, all attempts having yielded only the corresponding pinacolin.[32]

From 18 g. of fluorenone (0.1 mole), 4 g. of magnesium and 17 g. of magnesium iodide in 50 cc. of ether and 150 cc. of benzene, we obtained 17.84 g. of fluorenopinacol, which represents a yield of 98.6%. The ketone must be added to the magnesium iodide solution in small portions, and the mixture shaken after each addition, since considerable heat is developed in the formation of the addition complex. An evanescent, deep blue precipitate was visible for but a moment. The reaction was allowed to proceed at

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[30] Schlenk and Weickel, *Ber.*, **44**, 1187 (1911).

[31] Schmidlin, *Ber.*, **45**, 3178 (1912).

[32] Graebe and Stindt, *Ann.*, **291**, 5 (1896). Klinger and Lonnes, *Ber.*, **29**, 2154 (1896). Meerwein, *Ann.*, **396**, 205 (1913). Ref. 19 b, p. 119.

room temperature for ten hours. Almost all of the pinacol precipitated in the benzene-ether layer on the addition of water to the reaction mixture. The crude pinacol was digested with 15 cc. of hot alcohol, in which the ketone is very soluble and the pinacol is not. From chloroform, fluorenopinacol crystallizes in colorless needles; from acetone and alcohol it may be obtained in the form of large prisms. The pinacol melts at 190–192° to a yellow liquid, the color being occasioned by the fluorenone which undoubtedly results as one of the decomposition products of the pinacol.

Anal. Calcd. for $C_{26}H_{18}O_2$: C, 86.24; H, 5.06. Found: C, 86.10; H, 5.01.
Mol. wt. in benzene. Calcd.: 362. Found: 360.

Warming the orange-yellow solution of the iodomagnesium pinacolate with iodine overnight gave a conversion to the fluorenone to the extent of 80%. Oxygen behaves towards the ketyl in a manner similar to iodine. The pinacolate-ketyl system, which had been made from the pinacol and ethylmagnesium iodide, was identical with that from the fluorenone.

When warmed for some hours with a mixture of 70% sulfuric acid and acetic acid, the pinacol is rearranged to the corresponding pinacolin, 9-diphenylene-phenanthrone; the melting point of our product is 255°, while Klinger and Lonnes give 258°.

Fluorenopinacol forms a molecular complex with the ketone, fluorenone. When a mixture of colorless pinacol and yellow ketone is dissolved in a small amount of hot alcohol and the solution allowed to cool, large tan-colored crystals of the double compound crystallize from the solution; m. p., 123–124°. This compound is analogous to the addition compound formed between fluorenone and biphenyl-fluorenyl carbinol[33] and, as with that complex, it is extremely difficult to separate our compound directly into its two ingredients. By treatment of the complex with sulfuric acid the pinacol part of the complex was transformed into the pinacolin, the ketone remaining unchanged by this procedure. By means of hot alcohol the fluorenone was easily separated from the rather insoluble pinacolin. The complex was thus found to contain one molecule of pinacol to one molecule of ketone.

Reduction of Xanthone

Xanthopinacol.—To the colorless reaction mixture of 4 g. of magnesium and 15 g. of iodine in 100 cc. of ether-benzene was added a solution of 19.6 g. of xanthone (0.1 mole) in 100 cc. of hot benzene. To aid in keeping the magnesium from becoming coated by the insoluble complex, $(C_{13}H_8O_2)_2.MgI_2.(C_2H_5)_2O$, which began to deposit, the mixture was heated on the steam-bath until reaction began; the flask was then shaken at room temperature for twelve hours. If the magnesium does become so coated as to prevent it from reacting, the addition of a small amount of fresh metal induces reaction in a short time.

When the yellow pinacolate solution was decomposed with water, the greater part of the xanthopinacol precipitated in the layer of organic solvents; this was filtered off. From the benzene solution additional pinacol was obtained. After having been freed from unreduced xanthone by digestion with hot benzene, the pinacol weighed 18.1 g., which represents a yield of 92%. Xanthopinacol is not very soluble in alcohol or benzene. From toluene it crystallizes in shining white needles, that are highly refracting.

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[33] Schlenk and Herzenstein, *Ann.*, **372**, 27 (1910).

In the solid state the pinacol assumes a lilac fluorescence. Xanthopinacol melts at 185–187° with decomposition to a clear, colorless liqiud.

Anal. Calcd. for $C_{26}H_{18}O_4$: C, 79.16; H, 4.60. Found: C, 79.02; H, 4.84.

Mol. wt. in benzene. Calcd.: 394. Found: 394.

Two g. of solid xanthopinacol was added to a solution of ethylmagnesium iodide; the pinacol reacted readily with the Grignard reagent, going into solution with development of a yellow color as the iodomagnesium pinacolate, with evolution of ethane. Both iodine and oxygen converted the ketyl quantitatively into xanthone.

On treatment with a mixture of 70% sulfuric acid and acetic acid at 100° for four hours, the xanthopinacol gave, not the corresponding pinacolin, but dixanthylene, $O:(C_6H_4)_2C:C(C_6H_4)_2:O$; m. p., 312–313°. Gurgenjanz and Kostanecki[34] found that zinc dust and acetic acid reduced xanthone not to the pinacol but to dixanthylene.

Reduction of Anthrone

Anthrapinacol.—Schulze[35] observed that this substance is one of the products when anthraquinone is reduced by means of zinc and ammonium hydroxide. As a starting product, we used anthrone.[36] The anthrone was reduced by a mixture of magnesium and magnesium iodide in the usual manner; at first the solution was red but later became green and contained a precipitate. After hydrolysis, hot alcohol was used to take out any ketone mixed with the pinacol; yield of pinacol, 83%. Schulze gives 182° for the melting point of the pinacol; our product melted at 184–185°, although it decomposed at a lower temperature when heated slowly.

Reduction of Michler's Ketone

4,4′,4″,4‴-Octamethyl-tetra-aminobenzopinacol.—The pinacol has been described previously.[37] We find that Michler's ketone is also reduced by our method to the same pinacol. The addition of the ketone to a solution of magnesium iodide resulted in the formation of a complex which in this case is an oil, but on boiling the mixture with magnesium this oil disappeared, yielding a red solution. After half an hour of reaction, the solution was decomposed with an aqueous solution of ammonium chloride. Unchanged ketone was extracted from the reaction product by means of hot alcohol; yield of pinacol, 53%. The recrystallized pinacol melted at 196–197°. On melting, the pinacol decomposed and often the products of decomposition after solidification did not remelt below 240°. This may account for the variation in the values reported for the melting point of this pinacol, from 193° to 211°.

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[34] Gurgenjanz and Kostanecki, *Ber.*, **28**, 2310 (1895).

[35] Schulze, *Ber.*, **18**, 3034 (1885).

[36] Kurt Meyer, *Ann.*, **379**, 55 (1910).

[37] Fischl, *Monatsh.*, **34**, 337 (1913). Escherich and Moest, *Z. Electrochem.*, **8**, 849 (1902). Ref. 19b, p. 121.

Does Activation of Magnesium for the Grignard Reagent Depend upon the Formation of Magnesium Subiodide

No satisfactory explanation has yet been advanced to account for the effect of iodine in activating magnesium in the Grignard reaction. The customary view is to consider that the metal is "etched" by its reaction with iodine, an active surface being created by this process. Zelinsky[16] has observed that in addition to iodine, magnesium iodide, hydrogen iodide, methylmagnesium iodide, etc., are able to catalyze the reaction. Ehrlich and Sachs[38] activate the magnesium by allowing it to react first with a small amount of an alkyl halide, and decant the "largest part" of the solution; the magnesium remaining is then able to react with the aryl halide. Baeyer's[39] method, which furnishes highly active magnesium, consists in heating together magnesium and iodine just below the sintering point. Baeyer observed that this activated magnesium loses to a large extent its activity when washed with ether, and he attributes the activation to something more than mere etching, preferring to speak of a vague "loosening" effect in connection with the magnesium.

We find that the addition of a small amount of magnesium iodide solution activates the metal just as well as does free iodine, so the doctrine of "etching" is untenable. In this manner, we found it possible to bring about activation in some of the most resistant cases, such as *p*-bromobiphenyl,[40] *m*-bromobiphenyl, and apparently even with *p*-iodo-dimethylaniline, the example used by Baeyer, this mode of activation was successful. We are inclined to ascribe the influence of the magnesium iodide to the reaction of the latter with metallic magnesium, and it is magnesium subiodide which thus becomes the active agent in the formation of the Grignard reagent. Indeed, Tingle[41] was led to the idea that the activity of Baeyer's magnesium was occasioned by the presence of "IMg-MgI," and he formulated a scheme of reaction on the basis of that assumption. Reychler[42] expresses the opinion that the chemical function of the activator is unknown, but is inclined to assume that the Grignard reagent itself is produced through the intermediate formation, perhaps, of the MgX "group." Grignard,[43] on the other hand, believes that the formation of RMgX proper is invariably preceded by the production of ever so little MgX_2, and he formulates, for the subsequent progression of the reaction, a mechanism which is based upon the continuous utilization and regeneration of the magnesium iodide as an etherate complex. With Grignard, we are of

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[38] Ehrlich and Sachs, *Ber.*, **36**, 4296 (1903).

[39] Baeyer, *Ber.*, **38**, 2759 (1905).

[40] Schmidlin, *Ber.*, **45**, 3172 (1912).

[41] Tingle, *Am. Chem. J.*, **35**, 95 (1906); **37**, 489 (1907).

[42] Reychler, *Bull. soc. chim.*, **35**, 803 (1906).

[43] Grignard, *ibid.*, **41**, 260 (1907).

the opinion that in absence of all catalyst, the first step in the reaction between magnesium and the halide is: $2RX + Mg = R{-}R + MgX_2$. With alkyl halides and with aryl iodides, this ensues spontaneously; but whenever, in virtue of the stability of the particular RX, this important initial step is delayed, or fails entirely to materialize, then addition of some activator which does produce MgX_2, or the addition of some MgX_2 as such, becomes desirable or even essential. As regards the function of this catalyst, however, we differ in our opinion from Grignard. We consider that the magnesium first reacts with the magnesic iodide and gives magnesous iodide; then the latter, being soluble and much more reactive than the metal, is able to remove the halogen from the aryl halide; the aryl groups then partly double up, but largely unite with the MgX groups in the solution: $RX + MgI = XMgI + R{-}$; $XMgI + Mg = XMg + MgI$; $R{-} + MgX = RMgX$.

The magnesous iodide is thus regenerated and consequently a very small amount of it suffices to convert a large amount of magnesium and aryl halide into RMgX. The fact that magnesium, activated according to Baeyer's procedure, not infrequently proves more efficient in initiating the reaction than when activated in the usual manner is readily explained on the assumption that it contains a comparatively larger proportion of the desired subiodide. Heating the solid ingredients, metal and iodine, to a high temperature and conserving thereafter the product in the solid phase are the very conditions that generally favor the retention of the MeX state.

It is worth noticing in this connection that the MgX hypothesis offers also a plausible explanation in regard to the paralyzing function which certain agents exert on the formation of RMgX. Chloroform, acetone, ethyl acetate are, according to Reychler, agents of that type. On the other hand, these are all substances that would react with, or unite with, magnesium subhalide.

The MgX hypothesis may also prove of service in the interpretation of many other reactions, where activation of the metal has been empirically found to be desirable. The removal of halogen by magnesium from two adjoining carbon atoms in the same molecule,[44] the action of magnesium in presence of iodine upon alcohols,[45] especially those higher than methyl alcohol;[46] Hollemann's method of reducing acetone to pinacol by $Mg + HgCl_2$; the method patented recently for reducing[47] unsaturated aromatic aldehydes to alcohols with magnesium activated by means of iodine, are but a few reactions that may be mentioned in this connection.

[44] Braun and Lemke, *Ber.*, **56**, 1562 (1923), and previous publications.

[45] Zelinsky, *J. Russ. Phys.-Chem. Soc.*, **35**, 402 (1903).

[46] Bjerrum and Zechmeister, *Ber.*, **56**, 894 (1923).

[47] *Badische Anilin-und Soda-Fabr.*, Ger. pat. 384,351 (1923).

Summary

1. A brief statement is given of the existing evidence that the alkaline-earth elements can function as univalent. A simple chemical reaction is then outlined that purports to furnish new evidence in this regard with the element magnesium and, in a preliminary way, with beryllium.[48]

2. The reducing action of the binary system, $MgX_2 + Mg$, on aromatic ketones in ether and benzene has been investigated. The intermediate formation of an active reducing agent, magnesium subiodide, is postulated: $MgI_2 + Mg \rightleftharpoons 2MgI$; this subiodide reacts with the C:O group of the ketone in the manner of the alkali metals, and gives a free radical of the ketyl type, which associates to the iodomagnesium pinacolate, $2R_2C{-}OMgI \rightleftharpoons R_2C(OMgI).(IMgO)CR_2$; the latter, on hydrolysis, forms pinacol. The actual existence of the system, ketyl $\rightleftharpoons$ pinacolate, has been definitely proved, in that the identical system is obtained whether we start, synthetically, from the ketone or from the pinacol. The nature of these ketyls as free radicals has been shown by their capacity to give colored solutions, and to absorb oxygen and iodine.

3. An explanation has been suggested to account for the hitherto baffling effect of iodine in inducing activation of magnesium for the preparation of the Grignard reagent. The intermediate formation of magnesium subiodide is postulated.

In conclusion, we may mention that preliminary experiments with aldehydes and esters indicate that here the action of magnesium subiodide is more complex, but fundamentally similar to that on ketones. Thus, in one experiment, 43 g. of benzaldehyde yielded 10 g. of benzyl alcohol, and 15 g. of benzoin.[49] Similarly, benzil was readily reduced, the main product being benzoin. Work is now in progress on the action of this reducing agent upon various classes of compounds.

ANN ARBOR, MICHIGAN

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[48] Sven Bodforss, from his study of the electropotential of beryllium in beryllium salt solutions in water [*Z. physik. Chem.*, **124**, 66 (1926)], has arrived, provisionally, at the conclusion that "the metal sends into solution not the bivalent, but univalent ions, Be^{+}"; the same is, presumably, true of magnesium. The *Zeitschrift* containing Bodforss' paper arrived at the time of our proof-reading of this article.

[49] Kling and Roy, *Bull. soc. chim.*, **1**, 696 (1907).