

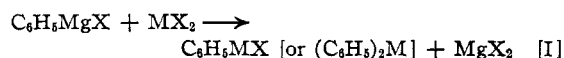
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

## Relative Reactivities of Organometallic Compounds. XXV. Coupling Reaction with Halides of Group VIII Metals\*

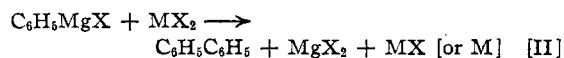
BY HENRY GILMAN AND MYRL LICHTENWALTER

## Introduction

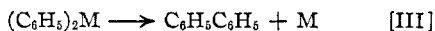
In general, metallic halides react with Grignard reagents to give organometallic compounds which are less reactive than the  $\text{RMgX}$  compounds.



However, there are some metallic halides which react with Grignard reagents to give only a coupling product.



A third, and intermediate, class of metallic halides reacts with  $\text{RMgX}$  compounds to give highly thermally unstable organometallic compounds which decompose readily to the coupling product and metal.



The coupling reaction was first examined by Bennett and Turner,<sup>1</sup> who obtained an almost quantitative yield of biphenyl from interaction of phenylmagnesium bromide and chromic chloride, incidental to an attempt to prepare organochromium compounds. It is now known that, in some cases, organometallic compounds are intermediates in the coupling reaction. This is well established in reactions of phenylmagnesium halides with silver salts.<sup>2</sup> The phenylsilver formed in such reactions decomposes completely at room temperatures<sup>3</sup> to give biphenyl and silver. Metallic halides of copper, gold and iron have been employed for the preparation of coupling products. When arylmagnesium halides are used, the unstable arylcopper compounds can be isolated,<sup>3,4</sup> the more unstable arylgold compounds ( $\alpha$ -naphthylgold) have been observed but not isolated,<sup>5</sup> and the aryliron compounds have appar-

ently neither been observed nor isolated. Evidence for the existence of organoiron compounds is conflicting, and there is at this time no unequivocal support for a true organoiron compound.<sup>6,11</sup>

However, it is reasonable to conclude that where a coupling reaction (II) takes place, an RM compound is formed intermediately (I) and this compound then breaks down to the coupling product and metal (or its equivalent) (III). Originally, only coupling was observed with chromic chloride,<sup>1</sup> but subsequently the relatively unstable organochromium compounds were isolated.<sup>7</sup> The same is true with organomanganese compounds.<sup>8</sup>

In connection with studies of organometallic compounds of Group VIII metals, we have examined the reactions of halides of these metals with phenylmagnesium iodide. It should be stated that on the basis of previously published results, the only definitely established organometallic compounds of Group VIII metals are those of platinum.<sup>9</sup> The present results lend support to the idea that the extent of the coupling reaction is a rough measure of the stability of new organometallic compounds. We have found that the halides of iron, cobalt, nickel, ruthenium, rhodium and palladium give practically quantitative yields of biphenyl; osmium trichloride gives a 53% yield; iridium trichloride a 28% yield; and platinic chloride only a few per cent. yield of biphenyl. If coupling is preceded by the formation of new organometallic compounds, then all the metals of Group VIII may be said to have

(6) (a) Bennett and Turner, *J. Chem. Soc.*, **105**, 1062 (1914); *J. Proc. Roy. Soc. N. S. Wales*, **53**, 100 (1919); [*C. A.*, **14**, 414 (1920)]; (b) Oddo, *Gazz. chim. ital.*, **44**, II, 268 (1914); (c) Job and Champetier, *Compt. rend.*, **89**, 1089 (1929); (d) Michailenko and Sasy-pinka, *J. Russ. Phys.-Chem. Soc.*, **53**, 343 (1921); (e) Kondyrew and Fomin, *ibid.*, **47**, 190 (1915); (f) Champetier, *Bull. soc. chim.*, **[4]** **47**, 113 (1930); (g) Weichselfelder and Thiede, *Ann.*, **447**, 64 (1926). A subsequent report will discuss a miscellany of methods tried by us for the isolation of organoiron compounds.

(7) Hein and co-workers, *Ber.*, **54**, 1916, 1936, 2710, 2727 (1921), and later papers.

(8) Gilman and Barnett, *J. Org. Chem.*, **2**, 84 (1937), see p. 87.

(9) (a) Pope and Peachey, *Proc. Chem. Soc.*, **23**, 86 (1907); (b) *J. Chem. Soc.*, **95**, 571 (1909); (c) Krause and v. Grosse, "Die Chemie der metall-organischen Verbindungen," Gebrüder Borntraeger, Berlin, 1937, p. 788; (d) Gilman and Lichtenwalter, *THIS JOURNAL*, **60**, 3085 (1938).

(\*) Paper XXIV, *THIS JOURNAL*, **61**, 743 (1939).

(1) Bennett and Turner, *J. Chem. Soc.*, **105**, 1057 (1914).

(2) (a) Reich, *Compt. rend.*, **177**, 322 (1922); (b) Krause and Wendt, *Ber.*, **56**, 2064 (1923); (c) Gilman and Kirby, *Rec. trav. chim.*, **48**, 155 (1929); (d) Danehy and Nieuwland, *THIS JOURNAL*, **58**, 1609 (1936); (e) Gardner and co-workers, *ibid.*, **51**, 3375 (1929) and **59**, 2583 (1937). The latter article describes the particularly interesting coupling of dissimilar radicals.

(3) Gilman and Straley, *Rec. trav. chim.*, **55**, 821 (1936).

(4) Reich, *Compt. rend.*, **177**, 322 (1923); Krizewsky and Turner, *J. Chem. Soc.*, **115**, 559 (1919).

(5) Kharasch and Isbell, *THIS JOURNAL*, **52**, 2919 (1930).

formed organometallic compounds, those of platinum being most stable. The reaction products from experiments with halides of osmium, iridium and platinum showed that organometallic compounds of these metals were formed, and these will be reported later. The selection of appropriate R groups<sup>5</sup> and particular experimental conditions may also make available the other RM compounds in this series.

Pope and Peachey<sup>9a</sup> reported that the chlorides of each of the Group VIII metals reacted vigorously with methylmagnesium iodide, but the only products described by them were trimethylplatinum iodide and its derivatives. Organopalladium compounds have been postulated as intermediates in the catalytic hydrogenation of aryl halides.<sup>10</sup> Grignard reagents have been treated with halides of iron,<sup>6</sup> cobalt,<sup>11</sup> and nickel.<sup>12</sup>

The Experimental Part describes reactions of cobalt bromide with 2,4,6-trimethylphenylmagnesium bromide, and nickel cyanide with phenylmagnesium bromide.

### Experimental Part

Phenylmagnesium iodide was first prepared in ether; benzene was then added; and the resulting solution was filtered, and then standardized by the acid-titration method of analysis. All operations were carried out in an atmosphere of nitrogen.

The Grignard solution was cooled by means of an ice-salt bath until a small amount of benzene had frozen around the edge of the flask. To this well-stirred mixture was added slowly the anhydrous metal halide by flushing from a dropping funnel with an ether-benzene solution.

An outline of one reaction follows, and the general results are contained in Table I. To a solution of 0.03 mole of phenylmagnesium iodide was added 1.27 g. (0.01 mole) of anhydrous ferrous chloride. The solution turned black, and a black solid deposited. The color test<sup>13</sup> was positive after stirring the cold mixture for one hour. The solution was hydrolyzed by filtration through a sintered glass plate into an iced solution of ammonium chloride. The products of hydrolysis were worked up by customary procedures to give 1.51 g. or a 98% yield of biphenyl. No other organic material could be isolated. The reaction was repeated with the same results.

**Cobalt Bromide and 2,4,6-Trimethylphenylmagnesium Bromide.**—To 0.05 mole of 2,4,6-trimethylphenylmagnesium bromide in an ether-benzene solution (2 parts of ether to 1 part of benzene), cooled in an acetone-dry-ice bath, was added 0.05 mole of anhydrous cobaltous bromide. There was no apparent reaction at this low tem-

TABLE I

| REACTION OF METALLIC HALIDES WITH $C_6H_5MgI$ |        |                  |                                |
|-----------------------------------------------|--------|------------------|--------------------------------|
| Metallic halide                               | Mole   | Mole $C_6H_5MgI$ | % yield, biphenyl <sup>a</sup> |
| $FeCl_2$                                      | 0.01   | 0.03             | 98 <sup>b</sup>                |
| $CoBr_2^c$                                    | .01    | .03              | 98 <sup>b</sup>                |
| $NiBr_2^c$                                    | .03    | .095             | 100 <sup>b</sup>               |
| $RuCl_3$                                      | .0036  | .0108            | 99 <sup>d</sup>                |
| $RhCl_3^e$                                    | .0036  | .013             | 97.5                           |
| $PdCl_2^f$                                    | .00566 | .0163            | 98                             |
| $OsCl_4$                                      | .00275 | .007             | 53 <sup>g</sup>                |
| $IrCl_3$                                      | .003   | .01              | 28 <sup>h</sup>                |
| $PtCl_4$                                      | .006   | .06              | <sup>i</sup>                   |

<sup>a</sup> No correction was made for the biphenyl contained in the Grignard solution. <sup>b</sup> This yield was checked.

<sup>c</sup> A black solution resulted, on addition to the Grignard reagent, and a black deposit formed. The color test remained positive. No organic product other than biphenyl was isolated. <sup>d</sup> Metallic ruthenium was also a reaction product. <sup>e</sup> The reaction mixture was allowed to stand overnight after having been stirred for six hours in an ice-salt bath. The color test was positive, as usual. Metallic rhodium was also a reaction product. <sup>f</sup> The reaction mixture was stirred for three hours in an ice-salt bath and then allowed to stand overnight. Metallic palladium was formed. <sup>g</sup> A small amount of tarry organic material containing osmium remained after removal of the biphenyl. Metallic osmium was also a reaction product.

<sup>h</sup> Partly because of the high insolubility of iridium chloride, no reaction was evident when the reactants were mixed. After stirring for two hours in an ice-salt bath, the mixture was stirred for three weeks at room temperature. At the end of this time there was no color test. In addition to biphenyl, there was formed a small quantity of brown amorphous solid, resembling that obtained from the reaction of platonic chloride with phenylmagnesium iodide. This solid burned, leaving a residue of metallic iridium; and it was difficultly soluble in benzene, alcohol, acetone and ether, but readily soluble in dioxane. It appeared to be a mixture as it was only partially soluble in some solvents. <sup>i</sup> Anhydrous platonic chloride was prepared in accordance with the directions of Kharasch and Ashford, *THIS JOURNAL*, **58**, 1733 (1936). Ten equivalents of phenylmagnesium iodide were required for a permanent color test. The phenylplatonic compounds, to be described later, dissolved in hot concd. nitric acid to give 4,4'-dinitrobiphenyl. Biphenyl was found to nitrate to 4,4'-dinitrobiphenyl under the same conditions. However, the phenylplatonic compounds were extracted with benzene (prior to treatment with nitric acid), and any free biphenyl would have been removed by this solvent. The yield of coupling product or biphenyl was 6%.

perature. When the mixture was allowed to warm up to  $-20^\circ$  in an ice-salt bath, an immediate reaction set in, the solution turned black and the color test soon became negative. Subsequent to hydrolysis, there was obtained a 20% yield of the coupling product, bimesityl.

**Nickel Cyanide and Phenylmagnesium Bromide.**—To a solution of 0.05 mole of phenylmagnesium bromide in 100 cc. of ether was added 5.5 g. (0.05 mole) of anhydrous nickel cyanide. A very slow reaction set in with darkening of the reaction mixture. The reaction was stirred for

(10) Busch and Weber, *J. prakt. Chem.*, **146**, 1 (1936).

(11) Sims and Mardles, *Trans. Faraday Soc.*, **22**, 368 (1926); see, also ref. 6e.

(12) Schlenk and Weichselfelder, *Ber.*, **56**, 2230 (1923); Job and Reich, *Compt. rend.*, **177**, 1439 (1923), **179**, 330 (1924); see also refs. 6e and 6g.

(13) Gilman and Schulze, *THIS JOURNAL*, **47**, 2002 (1925).

three weeks, at the end of which time there was a strong color test. The yield of biphenyl was 27%. In a check experiment the yield of biphenyl was 30%.

The trace of biphenyl reported earlier<sup>2c</sup> indicates that the nickel cyanide used then was not completely anhydrous. This conclusion is reasonable when one recalls that in the former experiments a more vigorous reaction was reported.

### Summary

In reactions of phenylmagnesium iodide with anhydrous halides of Group VIII metals, practically quantitative yields of biphenyl were ob-

tained with the halides of iron, cobalt, nickel, ruthenium, rhodium and palladium; and markedly reduced yields with the chlorides of osmium, iridium and platinum. The latter three halides also formed the corresponding organometallic compounds. The extent of the coupling reaction is suggested as a rough measure of the thermal instability of the intermediately formed organometallic compounds.

AMES, IOWA

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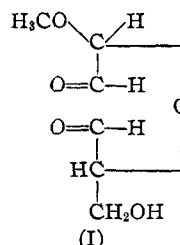
[CONTRIBUTION FROM THE NATIONAL INSTITUTE OF HEALTH, U. S. PUBLIC HEALTH SERVICE]

## The Periodic Acid Oxidation of Beta-Methyl-D-mannopyranoside<sup>1</sup>

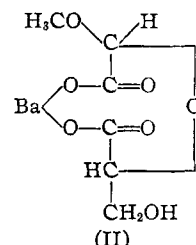
BY ERNEST L. JACKSON AND C. S. HUDSON

The oxidation of  $\beta$ -methyl-D-glucopyranoside by periodic acid and subsequent oxidation of the product, L'-methoxy-D-hydroxymethyl-diglycolic aldehyde (I), with bromine water kept neutral with barium carbonate has been shown by us<sup>2</sup> to produce the crystalline barium salt, barium L'-methoxy-D-hydroxymethyl-diglycolate (II). This crystalline barium salt has now been obtained by the application of these oxidation reactions to  $\beta$ -methyl-D-mannopyranoside and also to  $\beta$ -methyl-D-galactopyranoside, which previously has been oxidized by periodic acid to the dialdehyde<sup>2</sup> (I). The identity of the dialdehyde, the dibasic acid and the barium salt from the three  $\beta$ -methyl-D-aldohexosides is evident from the agreement of the rotations of corresponding compounds recorded in Table I. These methylglycosides, therefore, have the same configuration for carbon atom 1 and they possess the pyranoside ring

structure that is now generally accepted from the results of other methods of study,<sup>3</sup> particularly methylation.



L'-Methoxy-D-hydroxymethyl-diglycolic aldehyde



Barium L'-methoxy-D-hydroxymethyl-diglycolate

TABLE I

ROTATIONS OF THE OXIDATION PRODUCTS OF THE  $\beta$ -METHYL-D-ALDOHEXOPYRANOSIDES

| Substance                                      | Methyl glyco-<br>side<br>[ $\alpha$ ] <sub>20</sub> <sup>D</sup> | Dial-<br>dehyde <sup>a</sup><br>[ $\alpha$ ] <sub>20</sub> <sup>D</sup> | Di-<br>basic<br>acid <sup>b</sup><br>[ $\alpha$ ] <sub>20</sub> <sup>D</sup> | Barium<br>salt <sup>c</sup><br>[ $\alpha$ ] <sub>20</sub> <sup>D</sup> |
|------------------------------------------------|------------------------------------------------------------------|-------------------------------------------------------------------------|------------------------------------------------------------------------------|------------------------------------------------------------------------|
| $\beta$ -Methyl-D-galactopyranoside            | + 1                                                              | -148.1 <sup>2</sup>                                                     | +45.0                                                                        | +36.2                                                                  |
| $\beta$ -Methyl-D-glucopyranoside <sup>2</sup> | -34                                                              | -150.6                                                                  | +45.0                                                                        | +35.9                                                                  |
| $\beta$ -Methyl-D-mannopyranoside              | -69                                                              | -149.7                                                                  | +45.4                                                                        | +36.1                                                                  |

<sup>a</sup> L'-Methoxy-D-hydroxymethyl-diglycolic aldehyde. Specific rotations calculated from the final [M]<sub>D</sub> values of the oxidation solutions. <sup>b</sup> Determined by liberating the acid (*c*, 1.5) from its barium salt with an equivalent of hydrochloric acid. <sup>c</sup> *C*, 3.4.

(1) Publication authorized by the Surgeon General, U. S. Public Health Service.

(2) Jackson and Hudson, *THIS JOURNAL*, **59**, 994 (1937).

The data that have now been obtained for the alpha and beta methyl-pyranosides of glucose, galactose and mannose and the alpha methyl-pyranoside of gulose not only show the ring type of these substances and their alpha or beta classification, but also prove that these substances are homogeneous, no one of them being a molecular compound of an alpha and beta form, such as are known in the case of a certain xyloside<sup>4</sup> (7  $\alpha$ -methyl-D-xylopyranoside:2  $\beta$ -methyl-D-xylopyranoside) and a certain crystalline form of lactose<sup>4</sup> (5  $\alpha$ -lactose:3  $\beta$ -lactose). This conclusion follows from the fact that the solutions of the four  $\alpha$ -methyl-hexopyranosides<sup>2</sup> show closely the same end rotation when they are oxidized by periodic acid to the dialdehyde, and likewise the three  $\beta$ -methyl-hexopyranosides when they are converted to their common dialdehyde. In il-

(3) Bott, Haworth and Hirst, *J. Chem. Soc.*, 2653 (1930); Pryde, *ibid.*, 1808 (1923); Haworth, Hirst and Jones, *ibid.*, 2428 (1927); Schlubach and Moog, *Ber.*, **56**, 1962 (1923); Müller, *ibid.*, **64**, 1820 (1931).

(4) Hockett and Hudson, *THIS JOURNAL*, **53**, 4454, 4455 (1931).