

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

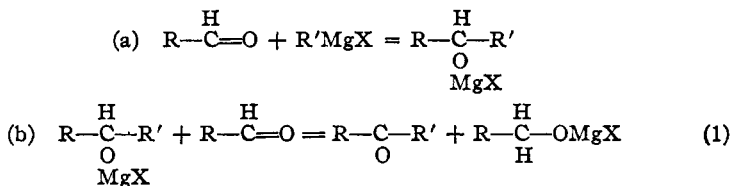
THE REDUCING ACTION OF COMPOUNDS CONTAINING THE GROUP $>\text{CHOMgI}^1$

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Aliphatic Grignard reagents have long been known to be capable of exerting a reducing action on aldehydes and ketones, the carbonyl group being reduced to a carbinol group while from the Grignard reagent saturated or unsaturated hydrocarbons, or both, were formed. In some of the cases, however, the by-product is neither saturated nor unsaturated hydrocarbon, and this is particularly so when aromatic Grignard reagents are employed. Instead, the oxidation product is a ketone, namely, that ketone which corresponds to the secondary alcohol which would be the result of the normal addition product of the aldehyde and Grignard reagent. Although several complicated theories have been proposed to account for the formation of these anomalous products, the mechanism of the reaction is, no doubt, relatively simple. In these cases, as was first shown by Marshall,² and as has been concurred in, finally, by Meisenheimer,³ the reductions cannot be ascribed to the Grignard reagent itself, but rather to the primary normal addition product of that reagent with the aldehyde, according to the equation



The oxidation and reduction reaction involves thus merely the transfer of H and MgX from one molecule to another, although the exact mechanism of this transfer still remains uncertain.

We converted secondary aromatic alcohols to their iodomagnesium derivatives and the latter were then treated with aldehydes. We found, in agreement with Meisenheimer's experiment on phenylethylcarbinol,⁴ that the aldehydes were reduced to primary alcoholates, while the secondary alcoholates were oxidized to ketones.

The reducing action upon aldehydes, and also upon certain other compounds containing the carbonyl group, is not limited, however, to secondary

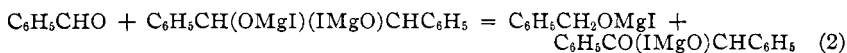
¹ From a dissertation submitted by R. V. Shankland, holder of the du Pont Fellowship 1929-1930, to the Faculty of the University of Michigan in partial fulfillment of the requirements for the degree of Doctor of Science, 1930.

² Marshall, *J. Chem. Soc.*, **105**, 527 (1914); **107**, 509 (1915); **127**, 2184 (1925).

³ Meisenheimer, *Ann.*, **446**, 76 (1926).

⁴ Ref. 3, p. 84.

alcohols; primary alcohols act more slowly, while dihydroxy secondary alcohols, glycols, are even more effective than monohydroxy secondary alcohols. Gomberg and Bachmann⁵ found that the iodomagnesium derivative of hydrobenzoin reduces benzaldehyde to benzyl alcohol very rapidly, itself becoming oxidized to benzoin



In other words, hydrobenzoin, although a di-secondary alcohol, functions in this reaction only through one of its two alcohol groups, just as if it were a monohydroxy alcohol. The ketone which results here, benzoin, can be isolated readily and the amount of it accurately established. This fact offered an opportunity to determine by means of hydrobenzoin on various aldehydes the extent of the possible occurrence of step (b) in Equation 1. Further quantitative evidence could thus be supplied in regard to Marshall's explanation concerning the apparently anomalous results in the Grignard reaction with aldehydes, especially when the aldehyde is employed in excess.

Experimental

Reduction of Benzaldehyde by Iodomagnesium Hydrobenzoinate.—The reduction of benzaldehyde by iodomagnesium hydrobenzoinate is very rapid. The rapidity of the reaction can be judged from the following set of experiments. Hydrobenzoin, prepared in 60% yield according to the procedure described by Danilov,⁶ was converted into the iodomagnesium salt by adding 10.7 g. (0.05 mole) of the glycol to a standardized solution of ethylmagnesium iodide containing 0.1 mole of the Grignard reagent. To each sample was added a solution of 4.85 g. of benzaldehyde in benzene, and at the end of predetermined periods the reaction products were hydrolyzed and the components determined as described by Gomberg and Bachmann. The measure of oxidation-reduction that has occurred is based on the yield of benzoin. The results are given in Table I.

TABLE I
REDUCTION OF BENZALDEHYDE BY IODOMAGNESIUM HYDROBENZOINATE

Time	Temperature	Yield of benzoin		%
		Calcd., g.	Found, g.	
5 Min.	Refluxing	9.70	7.10	73.2
15 Min.	Refluxing		9.2	95.3
30 Min.	Refluxing		8.95	92.3
5 Min.	Room temp.		5.82	60.0
30 Min.	Room temp.		8.40	86.6
4 Hrs.	Room temp.		8.45	87.1
42 Hrs.	Room temp.		9.05	93.3

Reduction of Various Aldehydes and of Ketones by Hydrobenzoin.—The reduction of aldehydes by iodomagnesium hydrobenzoinate proved to be a general method for the preparation of primary alcohols. The method might prove particularly useful in the preparation of primary unsaturated alcohols, since the ethylene bond remains unaffected

⁵ Gomberg and Bachmann, *THIS JOURNAL*, **52**, 4967 (1930).

⁶ Danilov, *Ber.*, **60**, 2393 (1927).

by the hydrobenzoinate salt. Although ketones, in general, proved unsuited for reduction by the glycolate, cyclohexanone and benzil were quantitatively reduced. The reduction of benzil by the glycolate is of especial interest as the oxidation product and reduction product are both iodomagnesium benzoinate. When acetophenone was treated with the glycolate a fair yield of benzoin was obtained but no α -phenylethyl alcohol could be detected. Attempts to reduce *p*-dimethylaminobenzaldehyde by this method were unsuccessful. Other methods of reduction are known to have failed in the case of that aldehyde; in fact, there is still some uncertainty as to the properties of *p*-dimethylaminobenzyl alcohol.⁷ Iodomagnesium benzoate was not affected by the glycolate.

A summary of the results obtained appears in Table II. The solvent used in all experiments consisted of a mixture of one part absolute ether and two parts anhydrous benzene, and a total of 225 cc. of the solvent was used when 0.1 mole of the aldehyde was employed for the experiment, which amount was generally used except in Experiment 20, when 0.05 mole of each reactant was taken. In Experiment 7 hydrolysis was accomplished by means of ammonium acetate solution, while in Experiments 16, 17 and 18, water alone, followed by steam distillation, hydrolyzed the reaction product; in all other cases a mixture of ice and a slight excess of hydrochloric acid was used.

In Experiments 11 and 12, due to the relatively high boiling points of the alcohols formed, practically all of the benzoin was directly precipitated by adding petroleum

TABLE II
REDUCTION OF ALDEHYDES AND KETONES BY IODOMAGNESIUM HYDROBENZINOATE

Carbonyl compound used		Yield of benzoin, g. %		Yield of alcohol, g. %	
Aldehydes					
1	Benzaldehyde	20.2	95.3	8.9	82.5
2	<i>o</i> -Tolualdehyde	19.0	89.6	10.0	81.9
3	<i>p</i> -Tolualdehyde	19.1	90.1	9.8	80.3
4	<i>o</i> -Anisaldehyde	18.3	86.3	9.6	69.6
5	<i>p</i> -Anisaldehyde	16.4	77.4	9.6	69.6
6	Piperonal	19.5	92.0
7	Salicylic aldehyde methoxymethyl ether	15.1	71.2	10.2	60.7
8	<i>o</i> -Chlorobenzaldehyde	18.8	88.7	12.5	88.7
9	<i>p</i> -Chlorobenzaldehyde	19.1	90.1	12.0	84.2
10	<i>p</i> -Bromobenzaldehyde	19.5	92.0	15.2	81.3
11	α -Naphthaldehyde	20.3	95.7	13.1	82.2
12	β -Naphthaldehyde	19.8	93.4	14.3	90.4
13	Phenylacetaldehyde	15.3	72.2	7.1	58.2
14	Cinnamic aldehyde	17.6	82.9	9.7	72.4
15	<i>n</i> -Heptaldehyde	16.5	77.8	7.6	65.5
16	Citronellal	16.6	78.3	10.7	68.6
17	Citral	15.8	74.5	10.1	65.6
18	Furfural	15.1	71.3	5.8	59.2
Ketones					
19	Cyclohexanone	17.7	83.5	7.9	79.0
20	Benzil	20.5	96.7
21	Acetophenone	9.8	46.2

⁷ Clems and Smith, *J. Chem. Soc.*, 2423 (1928); Carothers and Adams, *THIS JOURNAL*, 46, 1675 (1924).

ether to the freshly hydrolyzed reaction product. After filtration, the solvents were removed by distillation and the residue was fractionated, yielding the alcohol. In Experiments 16 and 17 steam distillation separated the alcohol from the benzoin; the distillate was extracted with ether and benzene and the alcohol obtained from these by fractionation of the dried solution. In Experiment 18, after the ether and benzene were removed by steam distillation, the residue in the distilling flask was filtered from the water, the solid was washed with warm water and the aqueous filtrate extracted with ether and benzene. The furfuryl alcohol was obtained by distillation of the ether-benzene extract. In Experiment 6, although good yields of benzoin were obtained, none of the pure alcohol to correspond to piperonal could be isolated. Apart from these exceptions, all experimental details were similar to those described under the reduction of benzaldehyde, and the alcohols formed were separated from the benzoin by distillation under highly diminished pressure. The alcohols were identified by their boiling points, mixed melting points if solid and by their naphthylurethans.

Reductions by Substituted Hydrobenzoins.—A summary of these reductions is given in Table III. Equimolecular quantities of oxidizing agent and reducing agent were used in each experiment. Since *p*-toluoin, unlike benzoin, is very soluble in ether and benzene, none precipitated on hydrolysis of the reaction mixture. The ether-benzene solution, after hydrolysis, was fractionated under reduced pressure; after the alcohol had distilled the *p*-toluoin came over at 210° under a pressure of 1 mm., and was finally purified by crystallization from alcohol. Dichlorobenzoin is also quite soluble in all ordinary solvents. After the alcohol had been distilled, the residue was dissolved in boiling benzene; on cooling the solution, 0.35 g. of the 4,4'-dichlorobenzil, m. p. 195°, separated, due to the ready oxidation of the benzoin by air. The benzene was removed by distillation and the residue was dissolved in boiling aqueous alcohol, an atmosphere of nitrogen being maintained over the surface of the liquid. On cooling, the dichlorobenzoin crystallized in the form of fine needles. In the experiment with methylhydrobenzoin, the reaction product was hydrolyzed as usual and the ether-benzene solution was extracted with a saturated solution of sodium bisulfite, after which the organic solvents were allowed to evaporate spontaneously. The residual mass was digested with cold water until partial solidification took place. The mixture was filtered through a sintered glass filter. From the solid, recrystallized, the methylbenzoin, melting at 65.6°,⁸ was obtained; the liquid yielded the corresponding benzyl alcohol. Under similar conditions of experiment, phenylhydrobenzoin, as well as tetraphenylerythritol, did not reduce aldehydes.

TABLE III

REDUCTION OF ALDEHYDES BY SUBSTITUTED HYDROBENZOINS

Hydrobenzoin used	Benzaldehyde reduced	Benzoin obtained	Yield, %	Yield of alcohol obtained, %
4,4'-Dimethyl-	4-Methyl-	4,4'-Dimethyl-	84.6	81.8
4,4'-Dimethyl-	2-Chloro-	4,4'-Dimethyl-	83.3	84.8
4,4'-Dimethyl-	4-Chloro-	4,4'-Dimethyl-	82.5	81.2
4,4'-Dichloro-	2-Chloro-	4,4'-Dichloro-	85.8	82.5
α -Methyl	Benzald	α -Methyl-	64.2	51.5

Reductions by Iodomagnesium Derivatives of Secondary Alcohols.—A summary of the results obtained with benzhydrol as the reducing agent appears in Table IV. Besides reducing aldehydes, this alcohol was found capable of reducing benzil also, to iodomagnesium benzoinate. The oxidation product was in all cases benzophenone; that the ketone was formed directly as such was proved by the fact that when the still

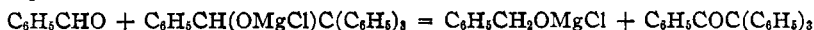
⁸ Roger, *J. Chem. Soc.*, 127, 518 (1925).

unhydrolyzed reaction product was subjected to the action of the binary system $\text{MgI}_2 + \text{Mg}$, good yields of benzopinacol were obtained.⁹ Since the pinacol is quite insoluble in alcohol and could therefore be separated readily from other products of the reaction, the treatment with the binary system afforded a better method of estimating the yield of ketone formed than isolation of benzophenone itself. In the case of the reduction of benzil by the iodomagnesium derivative of benzhydrol, since the binary system would attack both benzil and iodomagnesium benzoinate, that method of estimating the yield of benzophenone was not used. One-tenth mole of each reactant was used except in Experiment 6, in which case 0.05 mole of each reactant was taken.

TABLE IV
REDUCTION BY BENZHYDROL

	Carbonyl compound reduced	Yields	
		Benzophenone, %	Alcohol, %
1	Benzaldehyde	83.7	71.7
2	<i>p</i> -Tolualdehyde	80.8	72.2
3	<i>o</i> -Chlorobenzaldehyde	71.7	73.0
4	<i>p</i> -Chlorobenzaldehyde	79.7	75.8
5	<i>p</i> -Bromobenzaldehyde	77.5	72.7
6	Benzil	82.4	79.2 (benzoin)

Table V contains the yields of the products obtained when the iodomagnesium derivatives of two other secondary alcohols were used as reducing agents. The reaction of the iodomagnesium derivative of benzopinacolin alcohol with benzaldehyde was of especial interest, as it furnished the explanation why Schmidlin¹⁰ and Chichibabin¹¹ failed to obtain benzopinacolin alcohol (unsym.-tetraphenyl alcohol) by the action of triphenylmethylmagnesium halides on benzaldehyde, the explanation being that the excess of aldehyde oxidized the alcohol so formed to the corresponding ketone, *i. e.*, the pinacolin

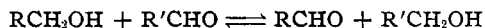


Our low yields of acetone, obtained when iodomagnesium isopropylate was used, were due to the occurrence of condensations of aldehyde with the acetone formed in the reaction; in fact, styryl methyl ketone, 7 g., was isolated in the experiment with benzaldehyde. The amounts of the reducing alcohols used were 0.05 mole.

TABLE V
REDUCTION BY VARIOUS SECONDARY ALCOHOLS

Secondary alcohol	Aldehyde	Oxidation product	Yield, %	Reduction product, alcohol	Yield, %
Benzopinacolin	Benz-	Benzopinacolin	80.0	Benzyl	78.0
Benzopinacolin	<i>o</i> -Chlorobenz-	Benzopinacolin	77.3	<i>o</i> -Chlorobenzyl	75.0
Isopropyl	Benz-	Acetone	30.0	Benzyl	52.0
Isopropyl	<i>o</i> -Chlorobenz-	Acetone	20.4	<i>o</i> -Chlorobenzyl	71.0

Reductions by Iodomagnesium Derivatives of Primary Alcohols.—Primary alcohols, in the presence of a small amount of aluminum, or halogenomagnesium, alcoholate salt as catalyst, are known to be capable of reducing aldehydes and some other carbonyl compounds¹²



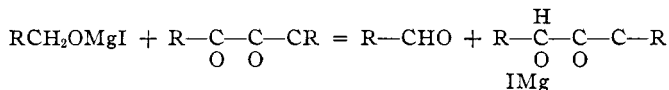
⁹ Gomberg and Bachmann, *THIS JOURNAL*, **49**, 2361 (1927).

¹⁰ Schmidlin, *Ber.*, **39**, 4183 (1906).

¹¹ Chichibabin, *ibid.*, **42**, 3469 (1909).

¹² Meerwein and Schmidt, *Ann.*, **444**, 221 (1925).

This reaction is reversible, but if, for instance, iodomagnesium benzylate be treated with a susceptible carbonyl compound whose reduction product is not affected by benzaldehyde, then the reaction should go to completion. Benzils are such compounds



In two experiments of this nature, using benzyl and chlorobenzyl alcohol, respectively, and benzil as the oxidizing compound, we obtained an 85% yield of the corresponding aldehydes and 90% of benzoin.

Summary

To a still greater extent than the iodomagnesium salts of monohydroxy alcohols, the similar salts of hydrobenzoin and of substituted hydrobenzoins have been found effective in reducing saturated and unsaturated, aromatic and aliphatic aldehydes to their corresponding primary alcohols. Only one of the two alcohol groups in the hydrobenzoins is involved in this reaction, the hydrobenzoins becoming oxidized by the aldehydes to benzoins, just as secondary alcohols become oxidized to ketones.

The mechanism of this oxidation-reduction reaction consists in the transfer of an H and MgI from the group $>\text{CHOMgI}$ in the alcohol to the carbonyl group of the aldehyde.

The results of this investigation supply further evidence in favor of Marshall's explanation in regard to the apparently anomalous formation of primary alcohols and ketones in the course of the Grignard reaction on aldehydes: namely, the normally produced addition product, $\text{RR}'\text{CHO-MgI}$, is liable to become oxidized by the excess of aldehyde to the ketone RCOR' , and the aldehyde reduced to RCH_2OMgI .

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THE PYROLYSIS OF PROPYLENE¹

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That hydrocarbons of different types differ quite widely from each other in their behavior on pyrolysis has been demonstrated in earlier papers of this series. Normal and isobutane⁴ both undergo primary changes into

¹ This paper contains results obtained in an investigation on "The Pyrolysis of Pure Hydrocarbons," listed as Project No. 18 of American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by the Universal Oil Products Company. This fund is being administered by the Institute with the cooperation of the Central Petroleum Committee of the National Research Council.

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³ American Petroleum Institute Junior Research Fellow.

⁴ Hurd and Spence, *THIS JOURNAL*, **51**, 3353 (1929).