On evaporation of the ether, a dark reddish brown tar resulted. This tar reacted with bromine in carbon tetrachloride with formation of hydrogen bromide. On sublimation, no phenol could be separated. The infrared was determined on a film placed on a salt plate by painting the salt plate warmed on a hot plate with an acetone or ether solution of the tar.

Search for benzophenone. Pilot runs were conducted with synthetic mixtures of triphenylcarbinol and benzophenone. Chromatography using petroleum ether (b.p. 60–68°) as solvent and alumina as a support was not satisfactory. An infrared extinction coefficient was determined for a carbon tetrachloride solution of benzophenone by drawing an arbitrary base line connecting the start and end of the ketone peak. When the neutral fraction was analyzed in the same way, there was found to be no more than 0.0136 g. of benzophenone. Because of the method of drawing the base line, this is an upper limit rather than an indication of the presence of benzophenone.

Thiosulfate titration of iodine solutions. An iodine–potassium iodide solution was prepared to approximately $0.1N$. An approximately $0.1N$ solution of sodium thiosulfate was prepared and standardized against potassium iodate. The iodine-iodide was then determined by the standard thiosulfate solution. A solution of approximately $1N$ sodium hydroxide was prepared and standardized against potassium acid phthalate. Solutions of sulfuric acid ranging from $1N$ to $18N$ were prepared and determined by the standard base. The acidic iodine solutions were then prepared on the most part by mixing a precooled 25-ml. aliquot of the iodine-iodide and a precooled 25-ml. aliquot of the acid. The amount of the acid aliquot was changed slightly for several of the runs in order to obtain a range of acidities. The acidic iodine solution was then titrated in the usual manner with thiosulfate.

Caro's acid reaction with triphenylcarbinol. Caro's acid was prepared by dissolving 5 g. of potassium peroxydisulfate in 20 ml. of concd. sulfuric acid and allowing to stand for 1 hr. Five grams of triphenylcarbinol was dissolved in 25 ml. of concd. sulfuric acid and poured into the Caro's acid. After an appropriate period of time the reaction was quenched by pouring on ice. The quench mixture was then extracted in a separatory funnel by a number of portions of ether until the ether no longer became colored. At this point there was still a distinct brown color in the aqueous layer. The combined ether extract was then extracted several times with $3N$ sodium hydroxide. The color was extracted by the base leaving a clear ether solution. This ether solution after evaporation produced triphenylcarbinol contaminated by a slight amount of a light tan impurity. The base portions on acidification with $6N$ sulfuric acid turned from a dark brown color to a light brown color. On extraction of the acidified portions with ether, a colored ether layer resulted. The combined ether extracts on evaporation gave rise to a reddish brown tar. In some runs, the ether extract of the acidified base extract was extracted further with a 5% sodium bicarbonate solution.

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Some Facets of the Grignard Reagent–Cobaltous Halide Reaction

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The reactions of several Grignard reagents with stoichiometric equivalents or an excess of cobaltous bromide have been examined. Arylmagnesium halides react principally to give coupling products, while alkylmagnesium halides give disproportionation or hydrogen abstraction products. When mixtures of alkyl and aryl Grignard reagents are treated with cobaltous bromide very little cross coupling occurs. Changes in the ratios of unsaturated to saturated products in these mixed reactions indicate some modification of the course of the reaction compared to the reactions of the individual reagents.

The reactions of Grignard reagents with cobaltous halides and other metallic halides have for many years been a subject of considerable interest.[1] In most of the "abnormal" reactions of Grignard reagents the cobalt salt was used in small over-all amount, and the reaction proceeded in the presence of some third compound such as an aryl or alkyl halide. Surprisingly, there seem to be only a few cases available where the Grignard reagents alone were treated with anything approaching the required stoichiometric amount of cobalt salt.

Gilman and Lichtenwalter[2] have reported that the treatment of a cold ether solution of 0.03 mole of phenylmagnesium iodide with 0.01 mole of cobaltous chloride produced a 98% yield of biphenyl, while Kharasch and Fields[3] reported that the phenylmagnesium bromide (0.11 moles)–cobaltous chloride (0.03 mole) reaction gave only a 64% yield of biphenyl. Smith[4] has reported that treatment of *n*-butyl bromide with magnesium and cobaltous bromide in ether produced a quantitative yield of mixed butanes and butenes. It has been observed also that the treatment of 1-bromo-2-phenylethane with magnesium and cobaltous bromide gives a 44% yield of ethylbenzene and

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[1] M. S. Kharasch and O. Reinmuth, *Grignard Reactions of Nonmetallic Substances*, Prentice-Hall, New York, 1954, Chap. V.

[2] H. Gilman and M. Lichtenwalter, *J. Am. Chem. Soc.*, **61**, 957 (1939).

[3] M. S. Kharasch and E. K. Fields, *J. Am. Chem. Soc.*, **63**, 2316 (1941).

[4] W. B. Smith, *J. Org. Chem.*, **23**, 509 (1958).

styrene.[5] The ratio of saturated to unsaturated hydrocarbon was *ca.* 0.7.

It is now generally accepted that the reaction of a Grignard reagent with a cobalt salt proceeds to give organocobalt compounds though the exact nature of these substances has not been agreed upon[1,2,6-8] The complexity of the problem is indicated by the multiplicity of products which Polya and co-workers isolated when the naphthyl Grignard reagents were allowed to react with various cobalt salts, *i.e.* $ArCoX_3$, Ar_2CoX_2, Ar_3CoX, and $Ar_3Co_2X_5$.[7] Recently, Tsutsui[8] has isolated dimesitylcobalt from the reaction of mesitylmagnesium bromide with cobaltous bromide.

In view of the difficulties experienced by earlier workers in isolating any organocobalt intermediates, it has been accepted generally that most of these compounds are very unstable.[1,2,6,7a] Cotton,[6] in his review article, has classified the thermal decomposition reactions of organometallic compounds according to three general pathways as follows: (1) a bimolecular process leading to the coupling of organic groups; (2) a bimolecular disproportionation reaction; and (3) dissociation into free radicals. The first process is particularly prone to occur with arylmetallic compounds. Alkylmetallic compounds react preferentially by paths (2) and (3). The free radicals produced *via* (3) may: (a) couple; (b) disproportionate; or (c) abstract hydrogen from the solvent if one is used. It will be observed in the subsequent data that all these types of behavior are observed when Grignard reagents are allowed to react with cobaltous bromide in refluxing ether.

In order to clarify further the reactions between Grignard reagents and cobaltous halides, a study was initiated of the decomposition products formed with stoichiometric quantities of the halide. In these experiments a known amount of the Grignard reagent in ether was refluxed, and cobaltous bromide was slowly added. The evolution of gaseous products was carefully followed. Upon completion of the reaction, the mixture was treated with water, and the products in the ether layer were determined by vapor phase chromatography. The gaseous reaction products were also determined by vapor phase chromatography. In this fashion, it was possible to obtain material balances of 85% to 104% based on the starting amount of Grignard reagent.

The reaction of methylmagnesium bromide was carried out by the slow addition of cobaltous bromide to the refluxing mixture. Gas evolution was closely connected with the rate of addition of the halide. The theoretical volume of gas was obtained with a 3:1 molar ratio of Grignard reagent to halide. The further addition of cobaltous bromide failed to produce any more gas. The analysis of the gas is given in Table I. Since the major product of the reaction was methane, it is clear that reaction in the sense of path (3c) above is the dominant mode of decomposition.[9]

Ethylmagnesium bromide and butylmagnesium bromide both react largely by disproportionation. The results in Table I show a preponderance of ethylene over ethane in the reaction of the ethyl Grignard reagent. The reason for this is not clear. However, ethyl free radicals prepared by treating phenylmagnesium bromide with cobaltous chloride in the presence of ethyl bromide show the same behavior.[10] The coupling reaction here is slight. With the butyl Grignard reagent, coupling is more significant.

TABLE I

REACTIONS OF ALKYL GRIGNARD REAGENTS (0.05 MOLE) WITH COBALTOUS BROMIDE

RMgX	$CoBr_2$, Mole	Composition of Gaseous Products[a]
Methyl	0.017	94% Methane, 2.7% ethane, 3.3% ethylene
Ethyl	0.025	37% Ethane, 63% ethylene, 0.7% butane
Butyl	0.025	50% Butane, 23% 1-butene, 19% *trans*-2-butene, 6% *cis*-2-butene, 2% octane in the ether layer

[a] The volume of gas produced in each case corresponded with the volume produced upon simple hydrolysis of the Grignard reagents—*i.e.*, *ca.* 1.2 l. of gas collected over brine at room temperature and pressure from 0.05 mole of Grignard reagent.

In a similar fashion, phenylmagnesium bromide and *p*-tolylmagnesium bromide were each treated with cobaltous bromide (Table II). In keeping with Cotton's observations,[6] the coupling reaction was found here to play a major role. The hydrolyzed products, however, showed large amounts of benzene and toluene in each case. These did not arise solely by the hydrolysis of some organocobalt intermediate since direct examination of the reaction mixture before hydrolysis indicated the presence of appreciable amounts of benzene when phenylmagnesium bromide was used. Furthermore, a small amount of gas was given off during the course of this reaction. Examination indicated the presence of ethylene, presumably from the ether.

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[5] W. B. Smith and J. D. Anderson, *J. Am. Chem. Soc.*, **82**, 656 (1950).

[6] F. A. Cotton, *Chem. Revs.*, **55**, 551 (1955).

[7] (a) D. L. Ingles and J. B. Polya, *J. Chem. Soc.*, 2280 (1949); (b) D. A. E. Briggs and J. B. Polya, *J. Chem. Soc.*, 1615 (1951).

[8] M. Tsutsui, Abstracts, 139th Meeting of the American Chemical Society, March, 1961, St. Louis, Mo.

[9] The question of what happens to those ether molecules which have undergone attack by methyl radicals has not yet been answered. Some information on the matter is available: see M. S. Kharasch and W. H. Urry, *J. Org. Chem.*, **13**, 101 (1948).

[10] M. S. Kharasch, D. W. Lewis, and W. B. Reynolds, *J. Am. Chem. Soc.*, **65**, 495 (1943).

TABLE II

REACTIONS OF TWO ARYL GRIGNARD REAGENTS (0.05 MOLE) WITH COBALTOUS BROMIDE

ArMgX	$CoBr_2$, Moles	Product Yields
Phenyl	0.05	42% Benzene, 45% biphenyl
Phenyl	0.025	43% Benzene, 56% biphenyl[a]
p-Tolyl	0.025	55% Toluene, 33% bi-*p*-tolyl

[a] Approximately 80 ml. of gas was produced during this reaction. Discounting the argon and ether peaks, the only reaction product in the gas was ethylene. In addition, vapor phase chromatography of the ether layer also showed a very small band, less than 1 wt. %, which corresponded in retention time exactly with ethylbenzene. A similar band at a slightly longer time was found in the reaction of *p*-tolylmagnesium bromide. No attempt was made to collect the gas in the two other cases.

These findings support the view that path (3c) can also operate with arylmagnesium halides and cobaltous bromide.

A comparison of the data in Table III with that in Tables I and II brings out several points of interest. First, it is quite evident that there is no interaction of significance when the mixed system methylmagnesium bromide–phenylmagnesium bromide is treated with cobaltous bromide. No detectable amount of cross coupling to form toluene was observed. It seems reasonable to ascribe path (3c) as the major reaction sequence for the methylmagnesium bromide. Bimolecular processes involving this reagent are apparently insignificant.

However, when phenylmagnesium bromide is mixed with either the ethyl or butyl Grignard reagent and then treated with cobaltous bromide a decided alteration in the reactions paths is noted. The coupling reaction of the aryl groups (path 1) is greatly reduced. An examination of the distribution of saturated and unsaturated hydrocarbons in the gaseous product indicates that this effect is the result of the introduction of a new disproportionation reaction in which the alkyl group gives up a hydrogen to the aryl group. It seems reasonable that this is a bimolecular process. In keeping with this observation is the discovery of a small amount of cross coupling which occurs, producing alkylbenzenes.

TABLE III

REACTION OF PHENYLMAGNESIUM BROMIDE (0.05 MOLE) WHEN MIXED WITH ONE OF SEVERAL OTHER GRIGNARD REAGENTS (0.05 mole) AND COBALTOUS BROMIDE (0.025 MOLE)

Other Grignard		Product and Yields[a]
Methyl	Gas	96% Methane, 2.1% ethane, 1.5% ethylene
	Ether	60% Benzene, no toluene, 44% biphenyl
Ethyl	Gas	52% Ethane, 47% ethylene, 1% butane
	Ether	81% Benzene, 5% ethylbenzene, 16% biphenyl
Butyl	Gas	31% Butane, 49% 1-butene, 15% *trans*-2-butene, 5% *cis*-2-butene
	Ether	73% Benzene, 2% butylbenzene, 10% biphenyl
p-Tolyl	Ether	53% Benzene, 55% toluene, 30% biphenyl
		15% *p*-Methylbiphenyl, 18% bi-*p*-tolyl

[a] The gas yields are expressed as wt. % of the gas collected. The yields of material in the ether layer are calculated on the basis of 0.05 mole of Grignard reagent. In the last entry above yields are based on both phenylmagnesium bromide and *p*-tolylmagnesium bromide.

Table III records the results of treating a mixture of phenylmagnesium bromide and *p*-tolylmagnesium bromide with cobaltous bromide. It will be noted here that no change is effected in the yields of simple aromatic hydrocarbons produced. However, cross coupling between the reagents does occur. As phenyl groups seem to show a stronger tendency to couple than do *p*-tolyl groups there is not a statistical distribution of coupling products.

Finally, while various free metals have been reported as products of the thermal decomposition of organometallic compounds,[2] there seems to be no reported identification of cobalt from the Grignard–cobaltous halide reaction. In each of the experiments discussed above,the magnetic stirring bar used in the reaction vessel emerged heavily coated with a black sludge. This material was strongly held to the magnet. When treated with acid, the sludge evolved hydrogen suggesting that metallic cobalt was present.

EXPERIMENTAL

All Grignard reagents were prepared according to the usual procedures using Grignard grade magnesium and anhydrous ether in all-glass systems which were carefully flushed with argon before use. In each case a slight excess of magnesium was used. The organic halide was dissolved in something less than the amount of ether required to make a 1*M* solution of the halide. Following the initial spontaneous reaction, each reaction was refluxed for several hours. The solutions were stored in glass bottles, and enough ether was added to each to make the reagent *ca.* 1*M* based on starting organic halide. In this fashion stock solutions of methylmagnesium bromide, ethylmagnesium bromide, *n*-butylmagnesium bromide, phenylmagnesium bromide, and *p*-tolylmagnesium bromide were prepared.

The Grignard reagents were analyzed in a crude fashion by hydrolyzing an aliquot of refluxing reagent. In the case of each of the alkyl Grignard reagents the volume of gas produced was close to that calculated for the theoretical amount (± 10%). For the purposes of these experiments, it was assumed that these were 1*M* in alkylmagnesium bromide. The two arylmagnesium bromides were hydrolyzed in the same fashion. The ether layers were then examined by means of vapor phase chromatography in the fashion described below. The yields from the hydrolysis of phenylmagnesium bromide were: 90% benzene, 2% bromobenzene, and 9% biphenyl. The hydrolysis of *p*-tolylmagnesium bromide gave 82% toluene, 5% *p*-bromotoluene, and 6% bi-*p*-tolyl.

General procedure. All reactions were carried out in a 500-ml., three-neck flask equipped with a pressure-equalizing dropping funnel, an ice water-cooled Friedrich condenser, an air tight solids addition tube, and a magnetic stirrer. The exit port on the condenser was attached through a calcium chloride drying tube to a gas collection bottle filled with brine.

The system was first flushed thoroughly with argon, and then the Grignard reagent was introduced. In cases where two Grignard reagents were to be used, one was introduced into the flask while the second was stored in the dropping funnel. A second flush with argon was then carried out. It was found that if the two Grignard reagents were not kept separate until after this second flush, appreciable quantities of phenols, due to reaction with oxygen in the air were formed. Using this procedure no phenols were ever detected. Following the second argon flush, the system was rapidly brought to reflux. Where two reagents were used, mixture was allowed to occur after the Grignard in the flask was boiling briskly. The ether vapor in the system thus kept air out. After equilibrium was reached, the gas collection bottle was attached to the system.

The appropriate amount of anhydrous cobaltous bromide was now added over a 30–60 min. period. Gas evolution closely paralleled the rate of addition in those cases involving alkyl Grignard reagents. Following the addition of the cobalt salt, the reaction was refluxed for 30–60 min. The gas volume was then recorded, and the collection bottle replaced by a new one. The rapidly stirred mixture was chilled in an ice bath, and 50 ml. of water was slowly added. A vigorous reaction occurred at this point, but no gas was evolved.

The ether layer was separated from the water layer. The flask and the water layer were each washed with several small portions of fresh ether, and the combined ether portions were dried over magnesium sulfate. In order successfully to carry out the analysis of the material in the ether layer, it was necessary to reduce the amount of ether by slow distillation through a Widmer column. The total weight of the ether residue, containing any non-gaseous reactions products, was then recorded. The ether residue was then qualitatively and quantitatively analyzed by vapor phase chromatography as described below. The various combinations of reagents are recorded in Tables I, II, and III.

In one experiment with phenylmagnesium bromide, a sample of the reaction mixture was withdrawn from the reaction flask before hydrolysis and injected directly into the chromatographic instrument. An Apiezon L column at 100° was used. While no quantitative calculations could be made from this sample, it was evident from the size of the benzene peak that an appreciable amount of benzene was present.

In two experiments with phenylmagnesium bromide the reaction mixture was carbonated immediately after the addition of the cobaltous bromide. No benzoic acid could be isolated in either case.

In each of the above experiments, it was found that the magnetic stirring bar was coated with a black sludge following the work up of the reaction mixture. This material was clearly magnetic. Treatment of the sludge with dilute sulfuric acid produced a gas which was tentatively identified as hydrogen by the usual ignition test.

Analytical procedure. All gaseous reaction products were analyzed by vapor phase chromatography over a 12-ft. column of hexadecane supported on firebrick operated at room temperature using helium as the eluting gas. Under these conditions the separation of all gaseous components was clear cut. Consequently, the comparison of retention times with those of known samples was assumed to be valid. The area under each peak was carefully determined with a planimeter, and the per cent composition calculated in the usual fashion. The results for the various reactions are included in the Tables.

The material in the ether layer was also determined by vapor phase chromatography. In this case, a 12-ft. column of Apiezon L on firebrick was used at 295°. With 12 p.s.i. of helium applied to the column, all components from ether through biphenyl were cleanly separated.

Several synthetic mixtures made up from possible reaction products were run under these conditions to determine the quantitative validity of this method. The best agreement with the known composition was given when the results were expressed as weight per cent rather than as mole per cent. Some typical results are as follows (where the figure in parentheses is the experimental value): 30% (31%) ether; 23% (25%) benzene; 14% (15%) *sec*-butylbenzene; 28% (25%) *n*-butylbenzene; and 5% (5%) biphenyl.

Using the above methods it was possible to calculate per cent yields leading to a material balance of 85% to 104% for all reactions contained in Tables I, II, and III.

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