of methanol. The catalyst was quite stable and may be used continually for months.

At least in the case of molybdenum oxide there is evidence that the reaction between methanol and oxygen takes place when both reactants are on the surface of the catalyst.

Evidence has been presented which indicates that the catalyst surface of these oxide catalysts is continually renewed during use; therefore the relationship between an effective catalyst and the reactants must not only be such that the former brings about the reaction of the latter, but the reactants must maintain the catalyst in the state of oxidation which is favorable to the desired reaction.

MADISON, WISCONSIN

THE EFFECT OF COPPER UPON THE YIELDS OF GRIGNARD REAGENTS

BY GEORGE JOHNSON AND HOMER ADKINS

It is well known that the reaction of alkyl halides and magnesium results in the formation of Grignard reagents and of hydrocarbons, as indicated in equations I and II.

$$RX + Mg = RMgX \qquad \qquad (I)$$
$$2RX + Mg = R_2 + MgX_2 \qquad \qquad (II)$$
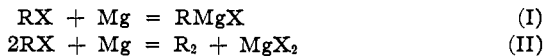
There has been in progress for some time in this Laboratory a study of the factors which determine the ratio of these two competitive reactions. During the course of this investigation some observations have been made in regard to the effect of copper upon the ratio of the reaction products which are of such practical importance that it seems desirable to publish them in advance of a more comprehensive paper, especially in view of the results of Gilman, Peterson, Schultz and Heck,[1] who reported that magnesium in certain copper–magnesium alloys reacted more rapidly with alkyl halides than did pure magnesium. Upon the basis of these findings it seemed that the use of the alloy might be advantageous in the preparation of Grignard reagents and this practice has been followed by a number of investigators.

The determination of the effect of various experimental conditions upon the ratio of the Grignard and Wurtz reactions was made in the following manner. The apparatus used was essentially of the type and size described and used by Gilman and Meyers for the preparation of ethyl-

[1] Gilman, Peterson and Schulze, *Rec. trav. chim.*, 47, 22 (1928); Gilman and Heck, *Bull. soc. chim.*, 45, 250 (1929).

magnesium iodide,[2] except that a detachable side-arm buret was connected to the outer end of the siphon tube passing through the wall of the flask. The desired quantity of magnesium was introduced into the reaction flask and the apparatus assembled. The flask and attached condenser were then swept out with dry hydrogen while the sample of alkyl halide was being weighed. After discontinuing the flow of hydrogen, from 10 to 15 ml. of anhydrous ether was introduced from the attached 60-ml. separatory funnel. The alkyl halide, contained in a 50-ml. glass-stoppered flask, was diluted with about 20 ml. of anhydrous ether, quickly transferred to the dropping funnel, after which approximately 15 ml. of ether, in two or three portions, was used to wash out any remaining sample from the bottle, and all washings rapidly transferred to the dropping funnel. This diluted the sample to a volume of 35 to 40 ml. The contents of the flask were then stirred and the alkyl halide introduced dropwise over a period of thirty-five to forty minutes. A reaction, evidenced by the boiling of the solution, usually set in after one to three minutes. After the halide was all introduced, stirring was continued for five minutes, or longer if boiling continued, and a further quantity of about 50 ml. of dry ether was then introduced through the dropping funnel, over a period of ten to fifteen minutes, so as to bring the total volume up to approximately 105 ml. Dry hydrogen gas was then bubbled through the reaction mixture for two or three minutes, after which the stirring was stopped, all openings to the reaction flask corked to exclude air, and the reaction mixture allowed to stand undisturbed for one-half hour, or until all solid matter had settled. Making due allowance for the stirring rod and any other residual solid matter, the total volume of the reaction mixture was then obtained from the graduated scale on the neck of the flask, and three aliquots of approximately 20 ml. each were forced out under hydrogen pressure through the siphon tube into the buret.

The acid titration method, as recommended by Gilman, Wilkinson, Fishel and Meyers,[3] was used for the estimation of the Grignard reagent produced. Each 20-ml. aliquot was drained from the buret into 50 ml. of water, an excess of 0.2 N sulfuric acid added and the product heated on the steam-bath to accelerate hydrolysis and to expel the ether. The resulting solution was then cooled, and the sample titrated with 0.1 N sodium hydroxide, using phenolphthalein as an indicator. From these data the amount of Mg(OH)X present in the mixture was calculated and hence the yield of RMgX.

The magnesium (88%) copper (12%) alloy used in this investigation was in the form of turnings and was supplied by the Dow Chemical Company. Powdered copper alloy from the Eastman Kodak Company was

[2] Gilman and Meyers, THIS JOURNAL, **45**, 159–165 (1923).

[3] Gilman, Wilkinson, Fishel and Meyers, *ibid.*, **45**, 150 (1923).

also used, as was pure magnesium turnings plus copper powder ("Natur Kupfer C"). The results obtained with the powder were not greatly different from those obtained with magnesium turnings. Copper powder reduced the yield of Grignard reagent but not so markedly as when the metal was alloyed with the magnesium. In the case of four of the halides only a small excess of magnesium was used over that necessary for the formation of the Grignard reagent. In the case of cyclohexyl bromide and allyl bromide a considerable excess of magnesium was used because Gilman and McGlumphy[4] reported that the yield of Grignard reagent from allyl bromide was higher when a large excess of magnesium was used. Ethyl iodide was used both with a small and large excess of magnesium.

TABLE I

THE EFFECT OF COPPER UPON THE YIELD OF GRIGNARD REAGENTS[a]

| Alkyl halide | | Magnesium, | % yield of RMgX | |
Name	Moles	g. atoms	From Mg	From Cu–Mg
n-Butyl bromide	0.056	0.062	92.5	78.7 ± 2 (3)
Sec.-butyl bromide	.059	.062	73.8	49.6
n-Butyl iodide	.057	.058	82.4	64.2
Ethyl iodide	.059	.062	83.4	76.1
Ethyl iodide	.058	.250	90.8	80.7
Benzyl chloride	.059	.065	94.1 ± 0 (2)	80.2 ± 2 (8)
Cyclohexyl bromide	.059	.165	82.5 ± 2 (3)	64.7 ± 1 (3)
Allyl bromide	.058	.272	72.1 ± 4 (10)	6.0 ± 4 (6)
Phenyl bromide	.059	.063	90.8 ± 0.5 (3)	89.1 ± 2 (3)

[a] Three analyses were made on each reaction mixture. When more than one reaction mixture was made up the numbers as well as the variation in yields are indicated in the table.

There are given in Table I the yields of Grignard reagents obtained for eight halides through their reactions with magnesium and the copper magnesium alloy. It is apparent from the data so reported that copper lowers the yield of Grignard reagent. The halides in the order of their increasing susceptibility to the effect of copper were phenyl bromide, ethyl iodide, benzyl chloride, n-butyl bromide, n-butyl iodide, cyclohexyl bromide, sec.-butyl bromide and allyl bromide. The formation of the Grignard reagent from the first of these was little affected by copper, while in the case of allyl bromide the yield of the reagent was lowered to 10% of the value obtained with pure magnesium.

Meisenheimer[5] ascertained the ratio of reactions I and II by comparing the amount of Grignard reagent with the total amount of halogen in the ether solution which was precipitable as silver halide. If no Wurtz reaction had occurred, the ratio of precipitable halogen to the Grignard reagent would be 1 to 1. If the Wurtz reaction had occurred, then the

[4] Gilman and McGlumphy, Bull. soc. chim., 43, 1322 (1928).

[5] Meisenheimer, Ber., 61, 708 (1928).

ratio of halogen to Grignard reagent would be greater than 1 to 1 by a corresponding amount. For example, if the two reactions had occurred to an equal extent, the ratio would be 2 to 1.

There is given below after the name of each halide the amount of pre-cipitable halogen, for one part of Grignard reagent, which was found for pure magnesium and for magnesium–copper alloy: benzyl chloride, 1.02 (Mg); 1.20 (Mg–Cu); cyclohexyl bromide 1.20 (Mg), 1.52 (Mg–Cu); n-butyl bromide 1.08 (Mg), 1.26 (Mg–Cu); sec.-butyl bromide 1.33 (Mg), 1.98 (Mg–Cu); n-butyl iodide 1.21 (Mg), 1.54 (Mg–Cu); ethyl iodide 1.20 (Mg) 1.27 (Mg–Cu), phenyl bromide 1.1 (Mg), 1.1 (Mg–Cu); and allyl bromide 1.35 (Mg). These figures show very definitely that copper promotes the Wurtz reaction. The ratio is without significance in the case of magnesium–copper alloy and allyl bromide because so much mag-nesium bromide was formed that the solubility of its etherate was exceeded,[6] and so was not found upon analysis of the ether solution.

The completeness of reaction of each alkyl halide with magnesium may also be determined from the amount of halogen in the ether solution which was precipitable as silver halide. Upon this basis from 98 to 100% of the phenyl, n-butyl, sec.-butyl and cyclohexyl bromide and n-butyl and ethyl iodide and from 94 to 98% of the benzyl chloride underwent reaction over both pure magnesium and the alloy. In the case of allyl bromide, from 96 to 98% of the halide underwent reaction with pure magnesium, while with magnesium–copper alloy so much magnesium bromide was formed that the solubility of its etherate was exceeded, as noted above.

No attempt has been made during this investigation to determine accurately the rates of reaction of the alkyl halide; however, there has been no evidence that the halides reacted more rapidly with the alloy than with pure magnesium. In fact, in some cases the reaction started more slowly with the alloy than with the pure magnesium.

Summary

The yields of Grignard reagents obtained by reacting eight alkyl halides with magnesium and with an alloy of magnesium and copper have been determined. The yields of the Grignard reagent were very considerably lowered, except from phenyl bromide, by the presence of the copper, which promoted the competitive Wurtz reaction.

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[6] Cf. Evans and Rowley, THIS JOURNAL, 52, 3523 (1930).