[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

THE PREPARATION OF METHYLCOPPER AND SOME OBSERVATIONS ON THE DECOMPOSITION OF ORGANOCOPPER COMPOUNDS[1]

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Received June 11, 1952

Incidental to the study of the reactions of alkyl Grignard reagents and organolithium compounds with some heavy metal salts[4] a more or less stable methylcopper compound was obtained. Methyllithium, dimethylmagnesium, or methylmagnesium chloride reacted with cupric chloride to give first cuprous chloride and ethane. The cuprous chloride then reacted with more of the Grignard reagent or organolithium compound to give a bright yellow, ether-insoluble methylcopper compound. The same compound was formed when cuprous iodide or cuprous thiocyanate was used in place of the cuprous chloride. The product

$$2\ CH_3Li + 2\ CuCl_2 \rightarrow C_2H_6 + Cu_2Cl_2 + 2\ LiCl$$
$$2\ CH_3Li + Cu_2Cl_2 \rightarrow 2[CH_3Cu] + 2\ LiCl$$

appeared to be stable in a nitrogen atmosphere at temperatures below 0°. At room temperature, however, it decomposed with the evolution of gas (ethane and methane) and the formation of metallic copper. Samples of the methylcopper compound exploded violently when allowed to dry in the air at room temperature. In all of the preparations the ether-insoluble, yellow methylcopper compound contained considerable quantities of halogen. Unreacted cuprous halides may be an explanation for the presence of halogen. On the other hand, the formation of a complex of the methylcopper with lithium halides may account for the halogen-containing product. It is apparent that methylcopper lends itself to complex formation. When one equivalent of cuprous iodide was treated with one equivalent of methyllithium the yellow, ether-insoluble product was formed. Both the precipitate and the ether solution gave a negative color test with Michler ketone (1). However, when one equivalent of cuprous iodide was treated with two equivalents of methyllithium a clear, practically colorless ether solution was formed. This ether solution gave a strong color test. The same observations were made in the reaction of methyllithium with cuprous thiocyanate. That the methylcopper behaves as expected has been shown in the reaction with benzoyl chloride (2), acetophenone being produced.

If ethylcopper was formed in the reaction of ethylmagnesium bromide with cuprous iodide it was much less stable than methylcopper, for even at tempera-

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[1] Paper LXXI in the series: "Relative Reactivities of Organometallic Compounds." The preceding paper is, Gilman and Beel, *J. Am. Chem. Soc.*, **73**, 2880 (1951).

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tures below zero, the only products obtained were metallic copper, ethane, and ethylene.[4] Ethylmagnesium bromide is not decomposed catalytically by cupric chloride, for we have found that a four-fold excess of ethylmagnesium bromide gave only the theoretical yields of ethane and ethylene on the basis of reaction [I]. However, there is a catalytic effect when a mixture of ethylmagnesium bromide and ethyl bromide is treated with a small quantity of cupric chloride, and the following reactions may account for the products.

$$2\ C_2H_5MgBr + CuCl_2 \rightarrow Cu + C_2H_6 + C_2H_4 + 2\ MgBrCl \qquad [I]$$

$$2\ Cu + 2\ C_2H_5Br \rightarrow 2[C_2H_5CuBr] \rightarrow C_2H_6 + C_2H_4 + Cu_2Br_2 \qquad [II]$$

$$Cu_2Br_2 + 2\ C_2H_5MgBr \rightarrow 2\ MgBr_2 + 2[C_2H_5Cu] \rightarrow C_2H_6 + C_2H_4 + 2\ Cu \qquad [III]$$

When a mixture of methyl iodide and dimethylmagnesium was treated with a catalytic quantity of cuprous iodide, ethane and a small amount of methane were produced, probably according to reactions [II] and [III].

Ethylmagnesium bromide reacted with bromobenzene in the presence of a catalytic amount of cupric chloride to give a practically quantitative yield of ethane and ethylene, but no diphenyl. This observation is in contrast to the lack of catalytic action of copper halides on a mixture of an aryl Grignard reagent and an aryl halide. On the other hand, it has been shown that phenyllithium reacts with ethyl bromide in the presence of cobaltous bromide to give biphenyl, ethane, and ethylene (3).

Metallic copper, without directly taking part, may be capable of initiating coupling reactions. Methyl iodide did not react with metallic copper when refluxed for a long period of time. However, when the above mixture was treated with methyllithium a vigorous reaction began which resulted in refluxing and a rapid evolution of gas (ethane and methane). The earlier observation that the yields of some alkylmagnesium halides were markedly lowered when magnesium-copper alloys were used to initiate the formation of some RMgX compounds (4) also indicates that metallic copper catalyzes the reaction between alkyl halides and alkylmagnesium halides.

It was also of interest to determine how phenylcopper (5) would add, if at all, to a conjugated system like benzalacetophenone. This organometallic compound gave 1,4-addition showing that it is of moderate reactivity (6). Since phenyllithium, which gives principally 1,2-addition, was used in the preparation, the formation of a good yield of the 1,4-addition product other than through the phenylcopper is excluded.

EXPERIMENTAL

Preparation and decomposition of the methylcopper compound in ether. The yellow solid formed by stirring, for three hours, 0.03 mole of dimethylmagnesium with an ether suspension of 0.050 mole of cuprous iodide cooled to −15°, was washed with anhydrous ether until the washings no longer gave tests for magnesium or iodine. The yellow product was heated in ether until decomposition appeared to be complete. The evolved gas contained 0.0137 mole of ethane and 0.0057 mole of methane.

From two additional experiments, carried out as above but using 0.015 mole of dimethylmagnesium and 0.025 mole of cuprous iodide, the yields of ethane were 0.0084 and 0.0081 mole and the yields of methane were 0.0017 and 0.0021 mole, respectively. The residue remaining in the flask after the decomposition of the methylcopper compound consisted of a mixture of metallic copper and cuprous iodide.

When the methylcopper compound was dried and exposed to the air it exploded violently. It would probably be dangerous to isolate more than small quantities of the material.

Reaction of methyllithium on cuprous thiocyanate. A solution of 0.028 mole of methyllithium (prepared from methyl chloride) in 22 cc. of ether was added, during a period of 1½ hours, to a stirred suspension of 3.04 g. (0.025 mole) of cuprous thiocyanate in 50 cc. of ether cooled to −15°. The suspended material was then a bright yellow. However, after stirring the mixture for three hours at 0° the yellow color had changed to a reddish-brown color. The color change was probably due to a slight amount of decomposition; very little gas was evolved. The mixture was allowed to come to room temperature, and gas was rapidly evolved. Sufficient heat was generated to promote gentle refluxing. The reaction subsided after one hour. The yields of gases were 0.011 mole (87.0%) of ethane and 0.003 mole (12.0%) of methane.

Reaction of two equivalents of methyllithium with one equivalent of cuprous salts. A solution of 0.050 mole of methyllithium in 40 cc. of ether was added, during one hour, to a stirred suspension of 4.77 g. (0.025 mole) of cuprous iodide in 50 cc. of ether cooled to −15°. The addition of the first equivalent of methyllithium resulted in a yellow suspension, which gave a negative color test with Michler ketone. The addition of the second equivalent produced a clear, practically colorless solution, which gave a strong color test.

In another experiment slightly less than two equivalents of methyllithium were used, and although stirred for four hours at −15°, the last portion of flocculent yellow precipitate did not disappear. The addition of the remainder of the methyllithium caused the precipitate to dissolve giving a clear solution.

The same conditions and the same relative proportions of methyllithium and cuprous thiocyanate in place of cuprous iodide were employed in another experiment. The results were identical.

Reaction of ethylmagnesium bromide with ethyl bromide in the presence of copper and copper salts. A solution of 0.070 mole of ethylmagnesium bromide in 45 cc. of ether was added, during one-half hour, to a suspension of 0.675 g. (0.005 mole, 7 mole-%) of cupric chloride in 25 cc. of ether containing 7.63 g. (0.070 mole) of ethyl bromide. The mixture immediately assumed a dark blue color and gas was rapidly evolved as the Grignard reagent was added. The gas was collected over water and an analysis showed 0.0590 mole (84.5%) of ethane and 0.0589 mole (84.3%) of ethylene. The yields are based on reactions [II] and [III].

A solution of 15.7 g. (0.144 mole) of ethyl bromide in 25 cc. of ether was added, during 15 minutes, to a stirred suspension of 1.00 g. of magnesium-copper alloy (12.75% Cu) in 25 cc. of ether. This quantity of alloy contains 0.036 g.-atom of magnesium and 0.0002 g.-atom of copper. After all of the ethyl bromide had been added, the mixture was refluxed for one-half hour. The gases were collected over water, and an analysis showed 0.0312 mole of ethane and 0.0262 mole of ethylene. On the basis of equations [II] and [III] the yields are: ethane, 87%, and ethylene, 73%. The reaction mixture now contained 0.072 mole of ethyl bromide. To this mixture was added, with stirring, 0.072 mole of ethylmagnesium bromide in 50 cc. of ether. Gas was evolved quite rapidly. After refluxing the mixture for six hours the evolved gases were analyzed and found to contain 0.0770 mole (97.3% yield) of ethane and 0.0665 mole (92.3% yield) of ethylene. Yields are based on reactions [II] and [III].

Reaction of dimethylmagnesium and methyl iodide in the presence of cuprous iodide. A solution of 0.055 equivalent of dimethylmagnesium in 50 cc. of ether was added to a suspension of 0.50 g. (0.0026 mole, 4.7 mole-%) of cuprous iodide in 25 cc. of ether containing 7.9 g. (0.055 mole) of methyl iodide. The mixture was refluxed, but gas was only slowly evolved, and the yellow methylcopper compound, which quickly formed, maintained its yellow color even after several hours at 35°. The gas which had collected after 16 hours of refluxing was analyzed and found to contain 0.0265 mole (48%) of ethane and 0.0057 mole (10%) of methane.

Catalytic action of metallic copper on the coupling of methyl iodide with methyllithium. The metallic copper obtained from the reaction of methyllithium with 3.04 g. (0.025 mole) of cuprous thiocyanate (see above) was washed well with ether, then suspended in 25 cc. of ether containing 7.75 g. (0.054 mole) of methyl iodide. The mixture was refluxed for 24 hours, but no gas was evolved and no reaction appeared to take place. Then, a solution of 0.054 mole of methyllithium in 45 cc. of ether was added during 45 minutes. Gas was rapidly evolved. The yields were 0.052 mole (96.3%) of ethane and 0.005 mole (4.6%) of methane.

Reaction of ethylmagnesium bromide with bromobenzene in the presence of cupric chloride. A solution of 0.089 mole of ethylmagnesium bromide in 50 cc. of ether was added to a suspension of 1.2 g. (0.0089 mole, 10 mole-%) of cupric chloride in a mixture of 15 cc. of ether and 11.0 g. (0.070 mole) of bromobenzene. The mixture was refluxed for three hours. Analysis of the evolved gas showed the presence of 0.0336 mole (37.8%) of ethane and 0.0533 mole (60.0%) of ethylene. If any biphenyl was formed it could not be separated from the tar-like reaction product.

Another reaction was carried out exactly like the one just described except that in place of the cupric chloride, 1.13 g. (0.0089 mole, 10 mole-%) of anhydrous ferrous chloride was used. The reaction proceeded so rapidly that it was necessary to add the ethylmagnesium bromide slowly. The yields of ethane and ethylene were 0.0420 mole (47.0%) and 0.0520 mole (58.0%), respectively. No biphenyl or other products could be identified from the oily reaction product.

Reaction of phenylcopper with benzalacetophenone. A solution of 0.055 mole of phenyllithium in 70 cc. of ether was added, during 25 minutes, to a stirred suspension of 9.5 g. (0.05 mole) of cuprous iodide in 75 cc. of ether cooled to −12°. The mixture was then stirred for ten minutes at −5°. One cc. of suspension gave a negative color test. Then, over a period of 25 minutes, a solution of 20.7 g. (0.1 mole) of benzalacetophenone in 75 cc. of ether was added to the mixture, at −5°.[5] After stirring for one-half hour at −5° and allowing to stand for one hour at room temperature, the mixture was hydrolyzed by an aqueous solution of ammonium chloride. The hydrolysis mixture was filtered and the residue dried and extracted with 100 cc. of boiling benzene. The ether and benzene solutions were combined and the solvent distilled until about 10 cc. of benzene remained. Then 40 cc. of ether was added and a precipitate formed. The mixture was cooled on an ice-salt bath. The β-phenyl-γ-benzoyl-γ-benzhydrylbutyrophenone was filtered off and washed with 40 cc. of cold ether. The product amounted to 17.5 g. (69.3%) and melted at 178.5–180.5°. It was identified by mixture melting point.

SUMMARY

The reaction of cuprous salts with one equivalent of methylmagnesium halide or methyllithium gave a yellow, solid methylcopper compound. This product was soluble in an ether solution of methyllithium. The yellow solid was unstable and decomposed to form copper metal and ethane. When dried in the air it exploded violently. Metallic copper and copper salts were found to catalyze reactions between organic halides and Grignard reagents or organo-

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[5] The two equivalents of benzalacetophenone were added in order to insure complete formation of β-phenyl-γ-benzoyl-γ-benzhydrylbutyrophenone. See Kohler and Peterson, *J. Am. Chem. Soc.*, **55**, 1073 (1933).

lithium compounds. Phenylcopper was found to react with benzalacetophenone by 1,4-addition yielding β-phenyl-γ-benzoyl-γ-benzhydrylbutyrophenone.

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