[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF IOWA STATE COLLEGE]

THE REACTION BETWEEN ORGANOMAGNESIUM HALIDES AND CUPRIC CHLORIDE

BY HENRY GILMAN AND HAROLD H. PARKER[1]

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In connection with studies concerned with the mechanism of reaction and the proof of structure, it was necessary to find some so-called reliable reagent which will replace the —MgX group[2] by another in order to get a compound that lends itself to ready identification. Diethyl sulfate was recommended[3] as a reagent satisfying these conditions. However, it was subsequently[4] shown to be virtually without value when the —MgX is attached to oxygen, although it appears to be quite satisfactory when the same group is attached to carbon, nitrogen and sulfur.

Because cupric chloride appears to react smoothly with many Grignard reagents in accordance with the following reaction, $2C_6H_5MgBr + 2CuCl_2 = C_6H_5.C_6H_5 + Cu_2Cl_2 + 2MgBrCl$, its behavior towards a wider variety of organomagnesium halides has been studied. It has been shown that the same type of coupling, or oxidation-reduction reaction, occurs when the —MgX group is attached to an ethylenic carbon atom, to nitrogen and to sulfur, but not to oxygen. The reaction, therefore, is essentially without value, for good yields are only obtained when the —MgX group is attached to sulfur. The disulfides so formed are more conveniently synthesized by other reactions and for determining structure, the—SMgX grouping is better characterized by diethyl sulfate.[5]

Very extensive studies have been made of the reaction between organometallic compounds and metallic halides. In recent years considerable work has been done on the reaction between RMgX compounds and metallic halides with a view to the synthesis of new classes of organometallic compounds. In this connection, Bennett and Turner[6] attempted to prepare organochromium compounds from chromic chloride and the Grignard reagent. Although their primary object was not realized,[7] they discovered,

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[1] This paper is an abstract of a part of a thesis presented by Harold H. Parker in fulfilment of the requirements for the degree of Master of Science in Chemistry at Iowa State College.

[2] The —MgX group is that ordinarily present when the Grignard reagent (RMgX) adds to a molecule. This group may be attached to a rather wide variety of elements, but generally it is found with carbon, oxygen, nitrogen and sulfur.

[3] Gilman and Hoyle, THIS JOURNAL, **44,** 2621 (1922).

[4] Gilman and Kinney, *ibid.*, **46,** 493 (1924).

[5] Studies in this Laboratory indicate that isocyanates are even better suited generally than diethyl sulfate for identifying an —MgX group.

[6] Bennett and Turner, *J. Chem. Soc.*, **105,** 1057 (1914).

[7] Organochromium compounds were later prepared with the same reagents when special precautions (particularly low temperatures) were observed. The most recent paper is by Hein and Spaete, *Ber.*, **57,** 899 (1924).

when phenylmagnesium bromide was used, that the chromic chloride was reduced to chromous chloride and that excellent yields of diphenyl were obtained. This suggested the use of other metallic halides and Krizewsky and Turner[8] found that cupric chloride was perhaps the best reagent to effect this coupling reaction.

These studies by Turner and co-workers on cupric chloride, in particular, have been unavoidably overlooked by some later investigators. However, a wider variety of inorganic salts has been used for the same purpose by others.[9] Also, the coupling reaction accompanied by reduction of the metallic halide has been noted quite incidentally in attempts to prepare new organometallic compounds. Turner,[10] after unsuccessful attempts to prepare organotungsten compounds, defined some limitations to the formation of organometallic compounds. Another and earlier generalization was made by Zeltner.[11] It is probable that all metals are capable of forming organometallic compounds and generally by the use of other organometallic compounds. This is so despite some very recent[12] unsuccessful studies, which are pertinent because they involve the coupling reaction noted. It has received unusual confirmation by the excellent work of Job and Reich.[13]

The literature on the coupling reaction when cupric chloride is treated with RMgX compounds is somewhat confusing. It is generally admitted that excellent yields of symmetrical diaryls are obtained when arylmagnesium halides are treated with cupric chloride. Apparently the reaction takes place to a decidedly limited extent when attempts are made to prepare unsymmetrical compounds from a mixture of RMgX compounds having unlike R groups.[14] There are contradictions concerning the applicability of the reaction with alkyl magnesium halides. Also, the function of the metallic halide is variously interpreted. Experiments by some indicate the action to be catalytic; others show it to be non-catalytic.[15]

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[8] (a) Krizewsky and Turner, *J. Chem. Soc.*, **115**, 559 (1919). Also, (b) Turner, *J. Proc. Royal Soc. N. S. Wales*, **54**, 37 (1920). Also, (c) Sakellarios and Kyrimis, *Ber.*, **57**, 322 (1924).

[9] (a) Konduirov and Fomin, *J. Russ. Phys.-Chem. Soc.*, **47**, 190 (1915). (b) Michailenko and Sassypkina, *ibid.*, **53**, 343 (1921). (c) Michailenko and Protassowa, *ibid.*, **53**, 347 (1921).

[10] Turner, *Proc. Chem. Soc. London*, **30**, 4 (1914).

[11] Zeltner, *J. prakt. Chem.*, **77**, 393–402 (1908).

[12] Challenger and Jinks [*J. Chem. Soc.*, **125**, 864 (1924)] were unsuccessful in attempted preparations of organotitanium compounds from titanium tetrachloride. Also, Marie Farnsworth with one of us has tried to prepare organo-uranium compounds in connection with some studies on radio-activity.

[13] Job and Reich, *Compt. rend.*, **174**, 1358 (1922). They have apparently succeeded in making an unusual number of new organometallic compounds by the use of organozinc halides. Reich has just reported [*ibid.*, **177**, 322 (1923)] the preparation of copper phenyl and silver phenyl. These compounds, prepared by means of the Grignard reagent and the metallic halides, are extremely unstable and decompose completely at low temperatures into the metal and diphenyl.

Kraus and Wendt [*Ber.*, **56**, 2064 (1923)] have made the same observations with silver phenyl.

[14] The unsuccessful attempts of some others to prepare unsymmetrical compounds were confirmed in part by C. C. Vernon in this Laboratory. He obtained no 4-methoxydiphenyl when a mixture of *p*-anisylmagnesium bromide and phenylmagnesium bromide was treated with cupric chloride.

[15] In this connection studies are being made in this Laboratory with a variety of inorganic compounds.

It has been shown that cupric chloride and *p*-thiocresylmagnesium bromide, prepared from *p*-thiocresol and ethylmagnesium bromide, give a 67% yield of *p*-tolyl disulfide. The experiment was carried out in an atmosphere of dry hydrogen to preclude the possibility of oxidation by air to disulfide.

In sharp contrast is the behavior of —OMgX compounds. Bromomagnesium benzoate ($C_6H_5CO_2MgBr$) and bromomagnesium triphenylmethylate ($(C_6H_5)_3COMgBr$) gave no benzoyl peroxide and triphenylmethyl peroxide, the respective compounds which should have resulted with a coupling reaction. This confirms studies now in progress of some essential differences between —OMgX and —SMgX groups.[16] However, it appears that an —MgX group attached to hexavalent sulfur is also comparatively inactive towards cupric chloride and diethyl sulfate. The results in this case are not too conclusive, for the work so far has concerned compounds of the bromomagnesium sulfinate type (RSO_2MgBr) where tautomerism involving oxygen and sulfur is probable.

Some coupling occurs with —NMgX compounds, but the extent is virtually negligible. Bromomagnesium aniline ($C_6H_5NHMgBr$) when treated with either cupric chloride or chromic chloride gave very small amounts of azobenzene. It is probable that hydrazobenzene is formed first by a coupling reaction and then undergoes the known easy oxidation to azobenzene. With mercuric chloride, again, most of the aniline was recovered and a small quantity of an unidentified compound was obtained. This compound contains mercury and chlorine and melts at 191–192°. From the reaction between bromomagnesium methylaniline [$(C_6H_5N(CH_3)MgBr)$] and cupric chloride, no dimethyl-azobenzene was isolated.

Bromomagnesium diphenylamine [$(C_6H_5)_2NMgBr$] and cupric chloride gave a small amount of *sym*-diphenyl-benzidine ($C_6H_5NHC_6H_4C_6H_4NHC_6H_5$). Again, it is probable that the coupling reaction took place first to give tetraphenyl hydrazine [$(C_6H_5)_2NN(C_6H_5)_2$]. This compound may then have been rearranged by the dil. hydrochloric acid used in the hydrolysis reaction, to give the *sym*-diphenyl-benzidine. Concentrated acids are known to effect such a rearrangement, and it is possible that the magnesium compounds may be a contributing factor.

Styrylmagnesium bromide ($C_6H_5CH{=}CHMgBr$) and cupric chloride gave a 17.6% yield of 1,4-diphenylbutadiene.[17] At best, all that can be said is that some reaction occurred, because a parallel experiment showed

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[16] Work of Mr. W. B. King.

[17] Sakellarios and Kyrimis (Ref. 8c) in a paper published after this work was completed, report a 40.5% yield of 1,4-diphenylbutadiene. This yield, however, is based on the weight of magnesium actually used. Their work confirms and extends that of Turner[8] on the action of cupric chloride.

a 10% formation of the butadiene in the preparation of the Grignard reagent.

Experimental Part

***p*-Thiocresylmagnesium Bromide and Cupric Chloride.**—Nineteen-hundredths mole or 23.7 g. of *p*-thiocresol in ether was added to 0.4 mole of ethylmagnesium bromide in an atmosphere of dry hydrogen. After the slow addition of 0.37 mole of anhydrous cupric chloride (the commercial variety, kept in a desiccator before use), the mixture was refluxed for one hour. It was then hydrolyzed with iced dil. hydrochloric acid, and the product extracted with ether, after which the ether layer was separated and washed several times with 10% sodium hydroxide solution to remove unchanged thiocresol. From the dried ether solution there was obtained 15.7 g. or a 67.2% yield of *p*-tolyl disulfide.

Bromomagnesium Benzoate and Cupric Chloride.—Fifty g. or 0.41 mole of benzoic acid in ether was added slowly to a cold ether solution containing about 0.45 mole of ethylmagnesium bromide; 60 g. or 0.44 mole of cupric chloride was then added and after the mixture had been stirred in the cold for one hour the reaction product was carefully worked up in a standard manner. No benzoyl peroxide was isolated. In another run, the reaction mixture was refluxed and stirred for one hour before hydrolysis, but no benzoyl peroxide was obtained.

Bromomagnesium Triphenylmethylate.—In these experiments the bromomagnesium triphenylmethylate was prepared in approximately 0.2 *M* quantities from ethyl benzoate and phenylmagnesium bromide; 28 g. or 0.2 mole of cupric chloride was added in the cold, and then the mixture was refluxed with stirring for two hours. After hydrolysis with dil. acid, the solid was extracted with ether to remove triphenyl carbinol. No triphenylmethyl peroxide was obtained.

In a second experiment, the reaction mixture was refluxed and stirred for 16 hours, and in a third experiment, benzene was substituted for ether and the mixture refluxed and stirred for 24 hours. No triphenylmethyl peroxide was obtained from either of these runs.

Bromomagnesium Aniline and Cupric Chloride, Chromium Chloride and Mercuric Chloride.—Thirty-six g. or 0.38 mole of freshly distilled aniline in an equal volume of ether was added to a cold ether solution containing about 0.45 mole of ethylmagnesium bromide; 0.45 mole of cupric chloride was then added. The mixture was refluxed for 30 minutes and then hydrolyzed with cold dil. hydrochloric acid. The only compound identified other than a large quantity of aniline was 0.2 g. of azobenzene.

In a similar experiment, dry chromic chloride was added. Again, a small quantity of azobenzene was obtained. An unsuccessful search was made for benzidine, the rearrangement compound of hydrazobenzene which was probably an intermediate.

Dry mercuric chloride was added in another experiment. Most of the aniline was recovered. In addition, there was obtained a small amount of compound melting at 191–192°. It is soluble in ether, alcohol, hot sodium hydroxide and insoluble in hydrochloric acid. A qualitative analysis showed the presence of mercury and chlorine.

Bromomagnesium Diphenylamine and Cupric Chloride.—Sixty-four g. or 0.37 mole of diphenylamine was added to about 0.45 mole of ethylmagnesium bromide. The slow addition of 0.33 mole of cupric chloride was accompanied by a considerable evolution of heat and a color change from blue to brown. After the product had been refluxed for one hour it was hydrolyzed and worked up as in the preceding experiments. No compound other than diphenylamine was isolated.

In a similar experiment, 0.5 g. of a solid was obtained which when crystallized from chloroform melted at 243°. A mixed-melting-point determination with some *sym*-diphenyl benzidine prepared according to the method of Kadiera[18] showed no depression.

Styrylmagnesium Bromide and Cupric Chloride.—Styrylmagnesium bromide, prepared from β-bromostyrene, when treated with an equivalent amount of cupric chloride gave a 17.6% yield of *sym*-diphenylbutadiene. The apparently ready polymerization of the butadiene makes it difficult to separate this compound from the tarry substances generally present. A check experiment showed 10% of this compound to be formed in the preparation of the Grignard reagent.

In another experiment the ether was replaced by benzene. The vigor of reaction appeared to increase with this solvent; however, the product was a tar from which the butadiene was obtained with difficulty and in a scarcely appreciable quantity.

Summary

A study has been made of the reaction between RSMgX, ROMgX, R_2NMgX and RCH=CHMgX compounds and cupric chloride. Coupling, in varying yields, takes place with all types other than ROMgX. This gave no compound of the type ROOR.

AMES, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS]

2-PHENYL SEMICARBAZIDE[1]

BY R. C. GOODWIN AND J. R. BAILEY

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Arnold[2] found that the hydrochloride of acetone phenylhydrazone reacts with potassium cyanate with the formation of acetone-2-phenyl semicarbazone.

$$C_6H_5NHN{=}C(CH_3)_2.HCl + KCNO \longrightarrow C_6H_5N(CONH_2)N{=}C(CH_3)_2 + KCl$$

Arnold states that "on boiling with water the compound passes to 'Phenylhydrazinsemicarbazid' with the elimination of acetone." From the text it is not clear whether "Phenylhydrazinsemicarbazid" means 2- or 1-phenyl semicarbazide, since the properties of the compound are not reported. On repetition of Arnold's work we find that neutral hydrolysis of acetone-2-phenyl semicarbazone gives 1-phenyl semicarbazide, C_6H_5-$NHNHCONH_2$. That 2-phenyl semicarbazide is not an intermediary product in the hydrolysis and that the transformation of the carbamyl group from one nitrogen to the other is coupled in some way that remains to be explained with the elimination of acetone from the semicarbazone, is indicated by the fact that 2-phenyl semicarbazide itself on steam distillation is not changed to 1-phenyl semicarbazide.

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[18] Kadiera, *Ber.*, **38,** 3575 (1905).

[1] This name is in accordance with the system of numbering given in Beilstein-Prager-Jacobsen, Handbuch "Handbuch der Organischen Chemie," 4th ed., J. Springer, **1921,** vol. 3, p. 98, for semicarbazide, $NH_2NHCONH_2$.

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[2] Arnold, *Ber.*, **30,** 1016 (1897).