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Diazonium Borofluorides. IV. The Preparation of Arylcopper Compounds

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The use of metallic copper or its salts to promote the formation of diaryls and dialkyls by coupling Grignard reagents with halides is well known.[1] In extending this principle to diazonium compounds, an attempt was made to synthesize 4-methyldiphenyl by coupling phenyldiazonium borofluoride with toluene in the presence of copper. There resulted a toluene solution which decomposed on filtering in air, the copper precipitating as cuprous oxide and hydroxide. This substantial evidence for the formation of an organocopper compound prompted the following investigation.

Early endeavors to prepare ethylcopper from cuprous chloride and diethylzinc were unavailing.[2] Later the Grignard reagent was successfully employed in the production of organocopper compounds,[3] and excellent yields from this method were reported in one article.[4] The highly unstable methylcopper has recently been shown to be an intermediate in the reaction between tetramethyllead and cupric nitrate,[5] though its existence must have been truly evanescent in the presence of alcohol and the water of crystallization of cupric nitrate.

Diazonium borofluorides have been used in the preparation of aromatic mercurials[6] and arsonic acids.[7] Complexes of diazonium chlorides with metallic salts have been used to prepare organometallic compounds of bismuth,[8] tin and lead.[9] Thermal decomposition of diazonium chlorides, suspended with various elements in acetone, produced aromatic compounds of mercury, tin, arsenic, antimony, sulfur, selenium and tellurium, but not of gold, thallium, germanium, lead, bismuth, magnesium or copper.[10] Another attempt to produce an organobismuth compound by decomposition of a diazonium borofluoride in the presence of bismuth and copper resulted in failure.[8] Diazo compounds may be involved in the formation of organometallic compounds from phenylhydrazine and mercuric acetate or arsenic acid, which are oxidizing agents.[11]

Arylcopper compounds were prepared by heating copper powder and the diazonium borofluorides suspended in dry benzene or toluene. The reaction may be represented by the specific example

$$C_6H_5N_2BF_4 + 2Cu \longrightarrow C_6H_5Cu + N_2 + CuF + BF_3$$

The insoluble material remaining after the reaction was shown to contain cuprous copper. The solution contained the organocopper compound and also the corresponding diphenyl derivative, indicating partial metathetical decomposition of the copper compound. The relative stabilities of the copper compounds are indicated by the amounts present in a definite volume of solvent as shown by determination of the copper content. On this basis under the conditions used, phenylcopper was found to the extent of only 4–8%, while *p*-nitrophenylcopper was obtained in 30–35% yield. *o*-Nitrophenylcopper and *p*-tolylcopper were also prepared but their yields were not determined. Though a solution of phenylcopper in toluene or benzene reacted readily with butyl bromide, no reaction was observed with *p*-nitrophenylcopper. Neither reacted with Michler ketone.

The arylcopper compounds hydrolyzed immediately and completely on addition of a trace of water. They were not detected unless all reacting materials were completely anhydrous. By pouring the solution of the copper compound onto carbon dioxide snow, the copper compound was precipitated from the solvent as an amorphous solid which reacted at once with the air. However, all reactions of the organometallic compounds were carried out immediately in solution without attempt at isolation. They were precipitated from solution by dioxane and ether, probably as complexes. Addition of pyridine to a solution of the copper compound resulted in precipitation of a blue pyridinium compound,

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[1] Job, Reich and Dubien, *Bull. soc. chim.*, [4] **37**, 976 (1925); Danehy, Killian and Nieuwland, THIS JOURNAL, **58**, 611 (1936); Kharasch and Fields, *ibid.*, **63**, 2316 (1941).

[2] Buckton, *Ann.*, **109**, 225 (1859); Wanklyn and Carius, **120**, 70 (1861).

[3] Reich, *Compt. rend.*, **177**, 322 (1923).

[4] Gilman and Straley, *Rec. trav. chim.*, **55**, 821 (1936).

[5] Gilman and Woods, THIS JOURNAL, **65**, 435 (1943).

[6] Dunker, Starkey and Jenkins, *ibid.*, **58**, 2308 (1936).

[7] Previous paper of this series, Ruddy, Starkey and Hartung, *ibid.*, **64**, 828 (1942).

[8] Gilman and Yablunky, *ibid.*, **63**, 949 (1941).

[9] Nesmeyanov, Kocheshkov, Klimova and Gipp, *Ber.*, **68B**, 1877 (1935).

[10] Waters, *J. Chem. Soc.*, 864 (1939).

[11] Seide, Scherlin and Bras, *J. prakt. Chem.*, **138**, 55, 225 (1933).

which could be purified by precipitation from alcohol with ether. The compound in each case was soluble in water and stable in air, even at 110°. Analysis showed it to be R-Cu$(C_5H_5N)_3$. This shows the maximum coördination number of cuprous copper to be four. *p*-Nitrophenylpyridinium-copper was soluble in cold water, but on boiling the solution metallic copper precipitated. Analyses have shown that restricting the amount of pyridine caused the precipitation of complexes with less than three pyridine molecules. Previously, the solubility of phenylcopper had been determined in pyridine,[4] but no complex was isolated in pure form. Phenylcopper and *o*-nitrophenylcopper reacted with chloroacetyl chloride to yield phenacyl chloride and *o*-nitrophenacyl chloride, respectively, the latter being obtained in good yield.

Attempts to apply this reaction to the formation of organosilver compounds gave negative results, probably due to the thermolability of the silver aryls.[12]

Discussion

The production of arylcopper compounds by the thermal decomposition of diazonim borofluorides in the presence of metallic copper is of some theoretical importance. It suggests a basis for the explanation of the Sandmeyer and Gattermann reactions, the use of cuprous chloride in a modification of the Bart synthesis,[7] and the use of copper bronze to catalyze the decomposition of aryldiazonium chloride–bismuth chloride complexes,[8] as well as complexes of tin and lead salts.[9] It perhaps also explains the use of copper powder in the replacement of a diazo group by hydrogen,[13] a reaction which would not proceed in absence of a metal.

The reaction with ethers indicates that the formation of copper alkyls and aryls from Grignard reagents in ether produces the oxonium complex and not the simple organometallic compound. The use of the diazonium compounds offers a route to organometallic compounds having substituents which would forbid the use of the Grignard reagent.

Work is continuing on the arylcopper compounds, and further attempts will be made to extend the reaction to the formation of other organometallic derivatives in the same manner.

Experimental

The diazonium borofluorides used were prepared in the usual way.[14]

Phenylcopper.—On heating a mixture of 19.2 g. of phenyldiazonium borofluoride, 8 g. of finely divided (precipitated) copper, and 250 cc. of dry benzene or toluene in a three-neck flask equipped with thermometer, mercury-sealed stirrer, and a reflux condenser leading to a gas-absorption trap, decomposition started at 80°, and continued smoothly at 70°. After one-half hour, when evolution of boron trifluoride ceased, the solution was filtered out of contact with air and used directly for the desired reactions. Analysis was accomplished by hydrolyzing the organometallic compound and determining copper gravimetrically as cupric oxide.

***p*-Nitrophenylcopper.**—By the same procedure, the decomposition of *p*-nitrophenyldiazonium borofluoride began after heating for one hour in boiling toluene, and required two hours more for completion.

***o*-Nitrophenylcopper.**—*o*-Nitrophenyldiazonium borofluoride required three hours for decomposition, without liberation of boron trifluoride, however.

***p*-Tolylcopper.**—*p*-Tolyldiazonium borofluoride began to decompose on reaching 85°, continued at 80° with completion in three-quarters of an hour.

Phenylpyridinium-copper.—Pyridine was added to a solution of phenylcopper in toluene to complete precipitation. The pyridinium complex was dissolved in hot alcohol, filtered, cooled, and precipitated with ether. The compound was dried in an oven at 110°.

Anal. Calcd. for $C_{21}H_{20}N_3Cu$ (378): Cu, 16.8. Found: Cu, 15.2.

***p*-Nitrophenylpyridinium-copper.**—This complex was prepared in the same way as phenylpyridinium-copper, and possessed the same properties.

Anal. Calcd. for $C_{21}H_{19}N_4O_2Cu$ (423): Cu, 15.1. Found: Cu, 15.2.

Summary

The preparation of arylcopper compounds from diazonium borofluorides is described. Phenylcopper, *p*-nitrophenylcopper, *o*-nitrophenylcopper, and *p*-tolylcopper have been prepared. Proof is given of the existence of the copper compounds, and several preliminary reactions are included. The stable pyridinium complexes have been prepared and analyzed. Organosilver compounds could not be prepared from diazonium borofluorides.

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[12] *Cf.* Semerano and Riccoboni, ***Chem. Abs.***, **37**, 71 (1943).

[13] Hodgson and Marsden, *J. Chem. Soc.*, 207 (1940).

[14] Starkey, *Org. Syntheses*, Vol. XIX, p. 40.