When the concentration of hydrochloric acid was varied from 1.95 *N* to 7.84 *N*, the velocity in the hydrogen cyanide hydrolysis increased about 1000 times. It is pointed out that this increase in velocity corresponds to the increase in activity for corresponding concentrations of the undissociated hydrogen chloride molecule as measured by electromotive force methods, and it is suggested that this increase in velocity is due to an increase in the concentration of activated hydrogen chloride molecules.

A 4 *N* hydrochloric acid solution is more than 6 times as effective in hydrolyzing hydrogen cyanide as a corresponding hydrobromic acid solution.

A tentative mechanism for the hydrolysis of hydrogen cyanide is proposed.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF WEST VIRGINIA UNIVERSITY AND THE JOHNS HOPKINS UNIVERSITY]

A METHOD OF COUPLING ORGANIC RADICALS BY MEANS OF THE GRIGNARD REAGENT[1]

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The coupling of organic radicals by the action of heavy metal salts on organomagnesium compounds has been studied by a number of investigators.[2] However, the use of silver halides for this purpose has not been investigated, although Gilman and Kirby studied the action of certain Grignard reagents on silver cyanide. They observed the coupling of the organic radicals, the cyanide radical reacting as a halogen.[3]

We have investigated the application of the reaction of Grignard reagents with silver bromide to the preparation of symmetrical biaryls and bialkyls. A few preliminary experiments with cuprous chloride failed to give promising results. The bromide was selected in place of the chloride, as dry silver bromide is so little sensitive to light that it may be used in a fairly well lighted room.

The advantage of silver bromide over other heavy metal salts lies in the fact that it is easily prepared pure and dry. Its cost is compensated for by the fact that it can be recovered readily and almost completely. We have found the laboratory accumulation of silver residues a cheap and satisfactory source of silver bromide.[4]

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[1] The major part of this work was done while one of us (G.) was a National Research Fellow in Chemistry.

[2] Gilman and Parker, THIS JOURNAL, **46**, 2823 (1924), give a very complete review of the literature; see also Moyer and Adams, *ibid.*, **51**, 630 (1929).

[3] Gilman and Kirby, *Rec. trav. chim.*, **48**, 155 (1929).

[4] We are indebted to Mr. C. F. Brown of West Virginia University for the working up of silver residues into the bromide used in the early part of this work.

The procedure for the preparation of biaryls consists in adding the arylmagnesium halide to a well-stirred suspension of silver bromide in dry ether, adding benzene and decomposing the silver aryl first formed by heating to boiling for a short time. In the case of the alkylmagnesium halides, the silver alkyl which is probably first formed decomposes immediately with the formation of silver and bialkyl.

It has been found possible to prepare biphenyl and 4,4′-dimethoxybiphenyl in quite satisfactory yield by this method. Bi-*p*-tolyl was obtained in good yield and purity in a small run (0.05 mole), but on increasing the amount of the bromide to 0.35 mole the yield was reduced to 25%. Among the aliphatic and alicyclic compounds, *n*-octane, bibenzyl and bicyclohexyl were obtained in fair yield and satisfactory purity. In reacting silver bromide with the Grignard reagents prepared from *iso*- and *sec*-butyl bromides, no pure compounds could be isolated, the products distilling over a considerable range with no detectable break in the distillation curves. Whether this was due to side reactions during the formation of the Grignard reagents or during the reaction with silver bromide cannot at present be stated. This will be further investigated.

We believe that this procedure can be used to couple aryl and alkyl radicals whenever the Grignard reagents can be prepared without excessive side reactions. Obviously, if by-products resulting from intramolecular rearrangements during the formation of the Grignard reagent or the reaction with silver bromide are produced in too great amounts, it will be impossible to obtain a uniform product by this method.[5] It does, however, permit the preparation of symmetrical biaryls and certain bialkyls without the complicated side reactions encountered in the use of the Wurtz–Fittig reaction.[6]

Experimental

General Procedure.—The appropriate Grignard reagent was added, with stirring, to a suspension of the equivalent quantity of dry silver bromide in dry ether. The mixture was stirred for a half hour and then boiled under a reflux for an hour. In the case of the Grignard reagents derived from *p*-bromotoluene and *p*-bromo-anisole, a volume of benzene equal to that of the ether was added to raise the boiling point before refluxing. If the product was solid, the ether and the benzene if present were distilled off and the residue was treated with very dilute hydrochloric acid. After cooling, the mixture was filtered and the residue air dried. The product was extracted from the residue with hot alcohol and purified by distillation or by recrystallization from alcohol.

When the product was a liquid, dilute hydrochloric acid was added to the mixture after refluxing, the solvent and product were distilled off, dried over calcium chloride and distilled. The results are given in Table I.

The absence of the formation of any definite product from *iso*- and *sec*-butyl bromides may be due to intramolecular rearrangement on the

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[5] Compare Gilman and Fothergill, THIS JOURNAL, **50**, 3334 (1928); Gilman and Kirby, *ibid.*, **51**, 1571 (1929).

[6] Compare Bachmann and Clarke, *ibid.*, **49**, 2089 (1927).

Table I

Results of Experiments

Halide	Amount, mole	Product	Yield		M. p. or b. p., °C.
			G.	%	
Bromobenzene	1.0	Biphenyl	51	66	68.5 (m.) 250–254 (b.)
p-Bromotoluene	0.05	Bi-*p*-tolyl	3.3	72	117–119 (m.)
	.35		8	25	117–119 (m.)
p-Bromo-anisole	.35	Bi-*p*-anisyl	17.5	48	171–172 (m.)
Benzyl chloride	1.0	Bibenzyl	65	71	51 (m) 278 (b.)
Cyclohexyl bromide	1.0	Bi-cyclohexyl	25	40	232–234 (b.)
n-Butyl bromide	1.0	*n*-Octane	24	42	121–123 (b.)
*Iso*butyl bromide	1.0	......	..	..	89.5–110.5 (b.)
Sec.-butyl bromide	1.0	......	..	..	89–120.5 (b.)

part of free radicals formed by the interaction of the Grignard reagents with silver bromide, assuming the reaction to take place according to the equations

$$\mathrm{RMgX + AgBr = R + Ag + MgXBr}$$
$$\mathrm{2R = R{-}R}$$

This is to be further investigated.

Preparation of Silver Bromide.—The silver bromide was precipitated from a warm solution of silver nitrate with sodium bromide, washed with water and with acetone and dried in an oven at a temperature not exceeding 80°. It is important that it be dried at a low temperature as a higher temperature, even 90°, results in larger particles and a less effective product.

Recovery of Silver Bromide.—The silver residues were reduced in the usual way with zinc and sulfuric acid to metallic silver which was converted into silver nitrate.

Summary

Biphenyl, bi-*p*-tolyl, bi-*p*-anisyl, bibenzyl, bi-cyclohexyl and *n*-octane have been prepared by the action of the appropriate Grignard reagent on silver bromide.

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