g. of phenyl *o*-tolyl ketone was collected. This material represents a yield of 33% based on the *o*-toluyl chloride used. The distillation pressure was then reduced to 2 mm. and two fractions were collected: (a) b. p. 180–220° (6.1 g.); (b) 220–240° (2.1 g.). Neither fraction crystallized from either methanol or ligroin.

Fraction (a) was redistilled. The portion distilling below 150° at 1 mm., when diluted with ligroin, deposited a few milligrams of crystals. These proved to be *o*-toluic acid. The portion boiling above 150° at 1 mm. was dissolved in ligroin and cooled to −70°. One gram of a yellow crystalline solid separated. It was collected on a filter and crystallized several times from methanol to which small quantities of Norit had been added. The yellow needles melted sharply at 92°. The color and analysis of the compound indicate that it is 2,2′-dimethylbenzoin.

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.73; H, 5.75.

Fraction (b) boiling above 220° at 2 mm. was saponified with methanolic potassium hydroxide (10%). The purple solution was refluxed for twelve hours and then poured into water. The oily matter was removed with ether. The aqueous layer, when acidified, gave 0.7 g. of *o*-toluic acid (m. p. 104–105°). The acid obtained represents a 7% yield of the di-*o*-toluate of 2,2′-dimethylstilbenediol.

Identification of Tetraphenylethylene Oxide (II).—This product was identified by its melting point, which was not depressed by admixture of a sample with an authentic sample of (II) prepared by known methods. Portions of the material were converted into β-benzopinacolin by (a) treatment with thionyl chloride and (b) reaction with Clar's mixture. The substances thus obtained had the correct melting point and composition.

Saponification of (III).—Substance (III) (0.4 g.) was refluxed with potassium hydroxide (10%) in methanol. The purple solution yielded 0.25 g. of benzoin (m. p. 132–133°) and 40 mg. of benzoic acid.

Identification of (I).—Compound (I) (0.3 g.), when refluxed with methanol potassium hydroxide (10%), yielded 60 mg. of benzoic acid and 170 mg. of benzohydrol. There was no depression of the melting point when this material was mixed with an authentic sample of benzohydrol.

Phenylbenzoin, prepared by Acree's procedure,[6] did not depress the melting point of (I).

Summary

1. The reaction between phenylmagnesium bromide and benzoyl chloride in the presence of 2 mole per cent. of cobaltous chloride yields benzoic acid, ethyl benzoate, biphenyl, benzophenone, phenylbenzoin, tetraphenylethylene oxide and stilbene dibenzoate. When 5 mole per cent. of cobaltous bromide is used as the catalyst, phenylbenzoin and tetraphenylethylene oxide are not found in the reaction mixture.

2. A mechanism to account for the various products has been suggested. It involves a cobaltous subhalide as the chain carrier in a series of reactions which produces free benzoyl (or aroyl) radicals. The isolation of *o*-tolil from reaction of phenylmagnesium bromide and *o*-toluyl chloride lends strong support to this hypothesis.

CHICAGO, ILLINOIS RECEIVED JULY 31, 1942

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, THE UNIVERSITY OF CHICAGO]

Factors Determining the Course and Mechanisms of Grignard Reactions. IX. The Effect of Metallic Halides on the Reaction of Organolithium Compounds with Organic Halides

BY M. S. KHARASCH, DANIEL W. LEWIS AND W. B. REYNOLDS

It has been shown in previous papers from this Laboratory that small quantities of metallic halides, particularly those of iron, nickel and cobalt, affect the reaction between Grignard reagents and organic halogen compounds.[1] Thus, although *p*-tolylmagnesium bromide does not react with bromobenzene at ordinary temperatures, these reagents upon addition of 2–5 mole per cent. of cobaltous chloride react vigorously and quantitatively to give *p*,*p*′-bitolyl (high yield), biphenyl (trace), and polyphenyls. In the presence of cobaltous halide, ethylmagnesium bromide and bromobenzene (which ordinarily do not react with one another) react rapidly to give ethane, ethylene, biphenyl (trace) and polyphenyls.

The present investigation of reactions of organolithium compounds with alkyl and aryl halides was undertaken to determine whether, in the presence of metallic halides, normal coupling occurs, or whether metallic halides produce effects similar to those just described. This paper extends considerably the scope of the findings previously reported in a Communication to the Editor.[2]

The products formed by various organolithium compounds when they react with organic halides

---

(1) For previous references, see Kharasch and Fields, THIS JOURNAL, 63, 2316 (1941).

(2) Kharasch and Reynolds, *ibid.*, 63, 3239 (1941).

TABLE I

PRODUCT ISOLATION AND HALIDE RECOVERY FROM REACTIONS OF ORGANOMETALLIC COMPOUNDS WITH ORGANIC HALIDES[a]

	Bromobenzene reacting with						Butyl bromide reacting with			
	C_6H_5Li		n-C_4H_9Li		n-C_4H_9MgBr		C_6H_5Li		C_6H_5MgBr	
Mole % $CoCl_2$ present	0.0	5.0	0.0	5.0	0.0	5.0	0.0	5.0	0.0	5.0
% Reaction	10	62	68	76	5	88	68	79	14	77
In (X) hours	(24)	(24)	(44)	(44)	(48)	(48)	(43)	(43)	(20)	(20)
Benzene	60	23	4	10	0	44	3	4	67	19
Biphenyl	10	47	0	50	0	3	4	67	4	44
Polyphenyls	0	9	0	3	0	11	0	2	2	8
Butylbenzene[b]	..	..	52	4	0	3	55	5	6	9
C_4H_{10} and C_4H_8	..	..	0	35	0	83	0	8	0	25
Octane[c]	..	..	0	27	0	0	0	40	0	0
Bromobenzene	86	20	11	20	87	12	..	..	..	..
Butyl bromide	..	..	17	0	..	..	25	13	75	14

[a] In all reactions, equimolecular equivalents of organometallic compounds and organic halides were used. Per cent. reaction is calculated on basis of titratable halide ion. Product isolations are expressed in per cent. of the theoretical yield, based on the amount of halide reacting. Halide recoveries are expressed in per cent. of halide (or organolithium compound) originally present. [b] Identified by its boiling point (180°) and index of refraction ($n^{20}\text{D}$ 1.4978) and specific gravity (0.862). [c] Identified by its boiling point (124–126°), index of refraction ($n^{20}\text{D}$ 1.4013) and specific gravity (0.71).

in the presence and absence of cobaltous chloride are recorded in Table I. The per cent. reaction (indicated in the column headings) denotes the amount of organic halide entering into the reaction, as measured by the increase of halide ion in the reaction mixture. The yields and recoveries are based on the amount of halide originally present.

The striking similarity between the control experiments with phenyllithium and butyl bromide and those with butyllithium and bromobenzene is probably due to a metathetical exchange. The isolation of butyl bromide from the mixture of butyllithium and bromobenzene supports this assumption. This metathetical change probably does not go to completion in the cobalt-catalyzed experiments because the catalyzed reaction is too rapid. Such metathetical changes are known to occur readily with lithium compounds,[3] but do not seem to take place with Grignard reagents. The Grignard experiments are therefore included for comparison.

The tabulation shows that the reaction products of organolithium compounds with organic halides depend markedly on the presence or absence of cobaltous chloride. The coupling reaction, which predominates in the uncatalyzed reactions, is almost completely suppressed by small quantities of cobaltous chloride. The reaction products of phenyllithium with butyl bromide in the presence of cobaltous chloride may be readily accounted for by a chain mechanism in which a cobalt subhalide acts as the chain carrier.

$$C_6H_5Li + C_4H_7Br \rightleftarrows C_6H_5Br + C_4H_9Li$$

$$\text{(A)}\quad C_6H_5Li + CoCl_2 \longrightarrow C_6H_5CoCl^{4} + LiCl$$

$$\text{(B)}\quad 2C_6H_5CoCl \longrightarrow C_6H_5\text{—}C_6H_5 + 2(CoCl)$$

$$\text{(C)}\quad C_4H_9Br + \cdot CoCl \longrightarrow CoClBr + C_4H_9\cdot$$

$$\text{(D)}\quad 2C_4H_9\cdot \longrightarrow C_4H_{10} + C_4H_8$$

An oxidation of the organometallic compound by the organic halide is thus brought about through the agency of the cobaltous halide.

The course of the reaction with most aromatic radicals is schematically represented by equations (A) and (B). However, as can be seen from Table I, the reaction does not always follow this scheme. Alkylcobaltous halides do not dimerize (as in B) but break down into free alkyl radicals and cobalt subhalides

$$C_4H_9MgBr + CoCl_2 \longrightarrow C_4H_9CoCl + MgBrCl$$

$$C_4H_9CoCl \longrightarrow C_4H_9\cdot + \cdot CoCl$$

The free radical disproportionates to the alkane and alkene. The cobalt subhalide is oxidized by the organic halide (*e. g.*, bromobenzene) to cobaltous halide, thus re-establishing the chain. This mechanism accounts for the large yield of butane and butylene (83%) obtained when butylmagnesium bromide is treated with bromobenzene in the presence of cobaltous chloride; it also accounts for the formation of the same gases in the experiments with butyllithium and with butyl bromide. The same hypothesis also accounts satisfactorily for the catalytic effects of some metallic halides on the decomposition of aliphatic Grignard reagents. Thus, it has

---

(3) Gilman and Moore, THIS JOURNAL, **62**, 1843 (1940).

(4) Other molecular species, such as $C_6H_5CoC_6H_5$, $C_6H_5CoC_4H_9$, etc., are undoubtedly present in solution. In order not to confuse the points here at issue, they are omitted in the present discussion and will be treated more fully in a later publication.

been found that traces of iron, copper, nickel and cobalt halides quantitatively decompose a mixture of cyclohexylmagnesium bromide and ethyl bromide to cyclohexane and cyclohexene with the simultaneous formation of gases (presumably ethane and ethylene).[5]

The differences between the final products recorded in the lithium experiments and those found in the corresponding experiments where magnesium was substituted for lithium are readily accounted for by the metathetical equilibrium which has been observed in the case of the lithium compounds.[3] However, there is one outstanding fact which as yet is not readily explained. *In the lithium experiments cited above, octane is formed in the presence of cobaltous chloride, whereas no octane is produced in the corresponding experiments where magnesium is used in place of lithium.* It is hoped to elucidate this effect of cobaltous chloride in a subsequent publication.

Experimental Part

Preparation of Organolithium Compounds.—Lithium metal was first pounded into thin sheets and then bathed in dry ether to free it from the kerosene in which it had been kept. An excess (10%) of the required amount of lithium was cut into shreds which were allowed to fall into a three-necked reaction flask containing one-third of the dry ether to be used. To minimize the oxidation of the freshly cut metal, a stream of dry nitrogen was passed into one of the side-necks, and out via the neck through which the metal was dropped into the flask. The appropriate organic halide, dissolved in the remaining two-thirds of the ether, was added from a dropping funnel at a rate sufficient to cause gentle boiling. The dropping funnel was equipped with an adapter through which nitrogen was admitted so that the reaction took place in an inert atmosphere. The mole ratio of ether to organic halide was 6 to 1. A mercury-sealed stirrer provided constant agitation during the addition and for one to two hours after all the organic halide had been added. The reaction mixture was then refluxed for one-half hour on a steam-bath. The organolithium solution was filtered through glass wool in a nitrogen atmosphere and stored under nitrogen in a brown bottle. Titration of this solution with standard acid gave the concentration of the organolithium compound; Volhard titration with silver nitrate gave the concentration of halide ion.

Reaction with Organic Halides.—When anhydrous cobaltous chloride is added to some organometallic compounds at room temperature, a vigorous reaction takes place. To moderate this reaction, the flask containing the organometallic compound was chilled in an ice-bath during the addition of both the metallic halide catalyst and the organic halide. The time for removing the ice-bath was determined by the rate of reflux and the rate of gas evolution. The reaction mixture was stirred for approximately two hours after both these evidences of reaction had ceased, and was finally heated for one-half hour longer. For purposes of comparison, this same procedure was followed in all experiments, even when some of the precautions (such as the initial cooling and final refluxing) were known to be unnecessary. Equimolecular amounts of organic halide and organometallic compound were used in all experiments.

Summary

1. Organolithium compounds, when treated with organic halides in the presence of small quantities of cobaltous chloride, give products other than those formed in similar reactions where no catalyst is used.

2. Octane is formed by the interaction of phenyl- (or butyl-) lithium and butyl bromide or bromobenzene in the presence of cobaltous chloride.

3. A chain mechanism to account for the effect of cobaltous chloride in these reactions is suggested.

Chicago, Illinois Received September 25, 1942

---

[5] Kharasch and Martin, unpublished work.