considerable interest because of their bearing on the hypothesis which assigns to cobaltous subhalide the function of a chain carrier. If the function of the alkyl halide is to regenerate the cobaltous halide, then it must at the same time form a free alkyl radical. The behavior of these free alkyl radicals is of general interest because of the light it throws on reactions involving free radicals in solution. Our experiments with the ethyl, propyl and *n*-butyl halides indicate that the corresponding radicals do not dimerize to any appreciable extent (if at all), but disproportionate to the alkanes and alkenes. The slight deviations from the one to one ratio of these substances are probably due to the experimental error (±5%) inherent in our analytical method. The *t*-butyl free radical probably decomposes similarly to alkane and alkene, but the isobutylene, thus formed, probably polymerizes considerably. The composition of the collected gas (80% isobutane and 20% isobutylene) is thus explained. That isobutylene polymerizes more readily than the straight chain alkenes has been well established.

The composition of the gas formed in the reactions involving the methyl radical (60% methane, 20% ethane, 20% ethylene) is best explained by assuming two distinct reactions. The faster one is the capture by the methyl radical of a hydrogen atom from the solvent. Methane is thus formed. The slower one is the attack of the methyl radical on the oxygen atom of the ether molecule. This reaction leads to the formation of methyl ethyl ether and ethyl radicals; the latter disproportionate to ethylene and ethane. The formation of equal quantities of these two gases supports the assumption of their common origin.

Experimental Part

In all experiments here recorded, 0.3 mole of the organic halide dissolved in anhydrous ether solution was added during ten minutes to 0.3 mole of phenylmagnesium bromide (kept at 0°). In the cobaltous chloride catalyzed experiments, 0.015 mole of this halide was added to the Grignard reagent (kept at 0°) before the addition of the organic halide. The evolved gases were collected and analyzed. The reaction mixtures were allowed to come to room temperature after one hour, and were decomposed with water and acetic acid at the end of twenty hours. Ethylene was determined as ethylene dibromide (b. p. 131°, $n^{20}\text{D}$ 1.538); propylene, as 1,2-dibromopropane (b. p. 140°, $n^{20}\text{D}$ 1.520); butene-1, as *s*-butyl bromide (b. p. 91°, $n^{20}\text{D}$ 1.434); isobutylene, as *t*-butyl bromide (b. p. 74°, $n^{20}\text{D}$ 1.428).

Summary

1. The gases formed by the reaction of phenylmagnesium bromide on alkyl halides in the presence of cobaltous chloride have been analyzed.

2. A chain mechanism to explain the formation of these gases is suggested.

3. The methyl radical differs from the other alkyl radicals studied in that it attacks the solvent (ethyl ether) in two ways. One of these leads to the formation of methane, the other to the formation of ethane, ethylene and (probably) methyl ethyl ether.

CHICAGO, ILLINOIS RECEIVED JULY 31, 1942

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

Factors Determining the Course and Mechanisms of Grignard Reactions. VIII. The Effect of Metallic Halides on the Reaction of Grignard Reagents with Aromatic Acyl Halides

BY M. S. KHARASCH, WALTER NUDENBERG AND S. ARCHER

Introduction

Recent publications from this Laboratory have described the effect of small amounts of certain metallic halides on the course of Grignard reaction.[1] The results were explained on the basis of a chain reaction involving free radicals and a metallic subhalide as the chain carrier. In view of the novelty of these results, it was of interest to investigate the reactions of aromatic acid chlorides with phenylmagnesium bromide in the presence of cobaltous halides.

Previous Studies

Treatment of benzoyl chloride with sodium in dry ether is reported to give an excellent yield of ethyl benzoate.[2] The substitution of sodium amalgam for metallic sodium causes the reaction

---

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

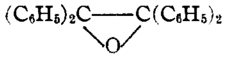
[2] Pearl, Evans and Dehn, *ibid.*, 60, 2479 (1938).

to take a more complicated course.[3] Benzoic acid, benzyl alcohol, benzyl benzoate, benzil, isobenzil and hydrobenzoin dibenzoate have been identified among the products. Sodium vapor reacts with benzoyl chloride to give benzil.[4] The products formed in these sodium reactions can best be explained by a radical mechanism involving the free benzoyl radical as an intermediate.

The Effect of Cobaltous Chloride on the Reaction of Phenylmagnesium Bromide with Benzoyl Chloride.—When phenylmagnesium bromide is added to an ethereal solution of benzoyl chloride, the normal reaction products are benzophenone and triphenylcarbinol.[5] When benzoyl chloride is treated with phenylmagnesium bromide in the presence of two mole per cent. of cobaltous chloride, ethyl benzoate, biphenyl, benzophenone and benzoic acid may be readily obtained by distillation of the reaction product. By suitable treatment of the residue three crystalline products may be obtained. These (as will be shown later) are phenylbenzoin (I), tetraphenylethylene oxide (II) and stilbene dibenzoate (III).

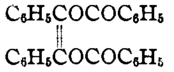
$(C_6H_5)_2COHCOC_6H_5$

I



$(C_6H_5)_2C\overset{O}{—}C(C_6H_5)_2$

II

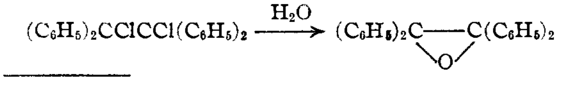


$$\begin{array}{c} C_6H_5COCOC_6H_5 \\ \| \\ C_6H_5COCOC_6H_5 \end{array}$$

III

When 5 mole per cent. of cobaltous bromide was used, the only product isolated from the residue was the ester (III). In other experiments, (II) was obtained unaccompanied by (I) or (III). All three products appeared only when two mole per cent. of the halide was used.

Compound (I) was proved to be phenylbenzoin by hydrolyzing the substance to benzohydrol and benzoic acid. Moreover, there was no depression of the melting point when (I) was mixed with an authentic sample of phenylbenzoin.[6] Reduction with zinc dust (Clar's method[7]) or treatment with thionyl chloride converted compound (II) to β-benzopinacolin. Tetraphenylene oxide was prepared by the reaction



$$(C_6H_5)_2CClCCl(C_6H_5)_2 \xrightarrow{H_2O} (C_6H_5)_2C\overset{O}{—}C(C_6H_5)_2$$

When this material was mixed with (II), there was no depression of the melting point. Compound (III) was hydrolyzed to benzoin and benzoic acid. It was further found to be identical with stilbene dibenzoate prepared by the method of Gomberg and Bachmann.[8]

When o-toluyl chloride was treated with phenylmagnesium bromide in the presence of 5 mole per cent. of cobaltous bromide, over 90% of the phenyl radical present was isolated either as diphenyl or as phenyl o-tolyl ketone. The viscous high boiling residue yielded a small quantity of a yellow crystalline solid which melted at 92°. The carbon and hydrogen content of this substance agreed excellently with that calculated for 2,2′-dimethylbenzil. There was also obtained a sirup which dissolved in a methanol solution of potassium hydroxide. When the red solution thus formed was heated for twelve hours, o-toluic acid was obtained. The behavior of the sirup is thus similar to that of stilbene dibenzoate; probably it contained some of the homologous orthotoluene esters.

Discussion

The findings are best elucidated by assuming, for the catalyzed reaction, a mechanism in which a cobaltous subhalide is the chain carrier. Considerable evidence (as yet unpublished) is now available to substantiate the following scheme.

$$\begin{array}{lll} (1) & C_6H_5MgBr + CoCl_2 & \longrightarrow C_6H_5CoCl + MgBrCl \\ (2) & 2C_6H_5CoCl & \longrightarrow C_6H_5 \cdot C_6H_5 + \cdot CoCl \\ (3) & C_6H_5CoCl + \cdot CoCl & \longrightarrow C_6H_5CO\cdot + CoCl_2 \end{array}$$

These three steps constitute the chain whereby free benzoyl radicals are formed. The reaction of these free radicals with the molecules in solution readily accounts for the products found.

Thus, the benzoyl radical may react with the solvent (ether) to give ethyl benzoate.

$$C_6H_5CO\cdot + C_2H_5OC_2H_5 \longrightarrow C_6H_5COOEt + C_2H_5\cdot$$
$$2C_2H_5\cdot \longrightarrow C_2H_4 + C_2H_6$$

The other products found arise from the combination of two benzoyl radicals to form benzil.

In view of the high reactivity of benzil, it is not surprising that only reaction products of this substance were isolated. (A small quantity of 2,2′-dimethylbenzil was isolated after the reaction of o-toluyl chloride with phenylmagnesium bromide in the presence of cobaltous chloride.) The presence of benzil as an intermediate readily accounts for the reaction products (I),

---

[3] Brigl, *Ann.*, **135**, 17 (1865); Klinger, *Ber.*, **16**, 994 (1883); **24**, 1264 (1891).

[4] V. Hartel, *Trans. Faraday Soc.*, **30**, 187 (1934).

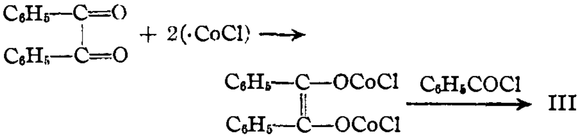
[5] Gilman and Mayhue, *Rec. trav. chim.*, **51**, 47 (1932).

[6] Acree, *Ber.*, **37**, 2758 (1904).

[7] Clar, *ibid.*, **72**, 1645 (1939).

[8] Gomberg and Bachmann, THIS JOURNAL, **49**, 2584 (1927).

(II) and (III). Thus, condensation of benzil with phenylmagnesium bromide should yield phenylbenzoin (I). The following reaction probably accounts for the stilbene dibenzoate (III).



$$\begin{array}{l} C_6H_5\text{—}C\text{=}O \\ \quad\;\;| \\ C_6H_5\text{—}C\text{=}O \end{array} + 2(\cdot CoCl) \longrightarrow \begin{array}{l} C_6H_5\text{—}C\text{—}OCoCl \\ \quad\;\;\| \\ C_6H_5\text{—}C\text{—}OCoCl \end{array} \xrightarrow{C_6H_5COCl} \text{III}$$

This suggested scheme agrees well with the observation of Bachmann[9] that triphenylmethylmagnesium bromide converts benzil to benzoin.

Experimental

Materials Used.—The Grignard reagent was prepared from freshly distilled bromobenzene and Mallinckrodt magnesium. It was filtered under nitrogen into a brown storage bottle and titrated before use. Freshly distilled Merck benzoyl chloride was used. *o*-Toluyl chloride (b. p. 83° at 8 mm.) was prepared in 92% yield from the acid and pure thionyl chloride. The cobaltous halides were prepared as previously described.[1]

The Reaction of Benzoyl Chloride with Phenylmagnesium Bromide in the Presence of 2 Mole Per Cent. of Cobaltous Chloride.—In the usual Grignard apparatus, was placed 0.8 g. (2 mole per cent.) of cobaltous chloride, and a solution 44 g. (0.31 mole) of benzoyl chloride in 100 cc. of dry ether. To this mixture 190 cc. (0.35 mole) of 1.85 *N* phenylmagnesium bromide was added at a rate sufficient to keep the ether refluxing gently. The time required was two hours. The brown reaction mixture was refluxed for one hour more, after which time dilute sulfuric acid was added. The two liquid layers were separated, and the aqueous layer was extracted with ether. The ethereal layers were combined and washed thoroughly with dilute sodium hydroxide. The alkaline extract upon acidification yielded 1.5 g. of benzoic acid. The combined ether extracts were heated on the steam-bath to remove the ether. The residue was then steam distilled. The steam distillate was extracted with ether. After evaporation of the ether, distillation of the residue at atmospheric pressure yielded 1.5 g. (3%) ethyl benzoate and 15.5 g. (56%) of biphenyl. The residue from the steam distillation was dissolved in ether and washed with alkali. Upon acidification of the alkaline extract, an additional 2.2 g. of benzoic acid was obtained. The total yield of benzoic acid was 3.7 g. (10%).

The ether solution was dried and concentrated, and the residue was distilled at reduced pressure. Slightly impure benzophenone (16.5 g.) was first collected. When the pressure was further reduced (to 2 mm.), two fractions were collected: (a) b. p. 205–220° (7.1 g.), (b) 220–270° (4.3 g.). Fraction (a) yielded, on standing, 0.5 g. (1%) of tetraphenylethylene oxide which melted at 204–205° after crystallization from a mixture of ethanol and ethyl acetate.

Anal. Calcd. for $C_{26}H_{20}O$: C, 89.66; H, 5.75. Found: C, 90.09, 90.73, 90.54; H, 6.33, 6.30, 6.64.

The sirup remaining after removal of the tetraphenylethylene oxide gave 4.5 g. (11%) of phenylbenzoin. This substance, after crystallization from a mixture of benzene and ligroin, melted at 83–85°.

Anal. Calcd. for $C_{20}H_{10}O_2$: C, 83.3; H, 5.6. Found: C, 84.1; H, 6.0.

Fraction (b) deposited 1 g. (3%) of stilbene dibenzoate. This material, after crystallization from methanol, melted at 158–160°.

Anal. Calcd. for $C_{26}H_{20}O_4$: C, 80.0; H, 4.8. Found: C, 80.6; H, 5.0.

The Reaction of Benzoyl Chloride with Phenylmagnesium Bromide in the Presence of 5 mole per cent. of Cobaltous Bromide.—To 0.31 mole of benzoyl chloride in 200 cc. of ether containing 5 mole per cent. of cobaltous bromide, was added, over a period of six hours, 178 cc. of 1.98 *N* (0.35 mole) of phenylmagnesium bromide. The mixture was kept at 0° during the addition and was then refluxed for two hours. After hydrolysis, the reaction mixture was worked up in the manner previously described. The alkaline layers, upon acidification, gave 4.8 g. of benzoic acid. The ether extract was treated as follows. The ether was removed on the steam-bath and the residue submitted to steam distillation. The distillate was taken up in ether. The ether solution was made up to 500 cc. volume. An aliquot (100 cc.) was evaporated to constant weight (steam-bath) and the residue saponified. In this way it was determined that 4.1 g. of ethyl benzoate (10%) and 12 g. (44%) of biphenyl were present.

The sirupy residue from the steam distillation was allowed to stand in a desiccator for seven days. By the end of that time 1 g. of impure stilbene dibenzoate (III) had crystallized. This substance, upon crystallization from methanol, melted at 158–160°. The remainder of the sirupy residue, upon distillation, gave 20.3 g. of benzophenone (41% yield based on the benzoyl chloride used). The residue from the distillation, upon trituration with methanol, yielded 2.2 g. (6%) additional stilbene dibenzoate (III). The mother liquors, after removal of the methanol did not crystallize after standing for several months. No phenylbenzoin (I) or tetraphenylethylene oxide (II) could be isolated.

The Reaction of *o*-Toluyl Chloride with Phenylmagnesium Bromide in the Presence of 5 Mole Per Cent. of Cobaltous Bromide.—Over a period of one and one-quarter hours, 150 cc. of 1.35 *N* phenylmagnesium bromide (0.2 mole) was added to a mixture of 2.2 g. (5 mole per cent.) of cobaltous bromide and 24.1 g. (0.155 mole) of *o*-toluyl chloride in 150 cc. of dry ether. The mixture was kept at zero degrees until all the reagent had been added, and was then refluxed for an hour before it was hydrolyzed with dilute sulfuric acid. The mixture was treated as in the previous experiment. The alkaline extracts yielded 2.3 g. (15%) of toluic acid. The melting point of this substance, after crystallization from water, was 104–105°.

The steam distillate was taken up in ether. The ether extract was dried and the solvent removed. The residue was distilled at atmospheric pressure. There was obtained 10.8 g. of biphenyl boiling at 240–260°. This amount represents 70% of the calculated yield. No ethyl *o*-toluate was found. The material non-volatile in steam was taken up in ether, dried and distilled. At 6 mm., 10.1

---

(9) Bachmann, THIS JOURNAL, 53, 2768 (1931).

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).