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THE PREPARATION OF DIALKYL MERCURY COMPOUNDS
FROM THE GRIGNARD REAGENT.

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Although many of the metal alkyls have been prepared by the action of the Grignard reagent on the anhydrous metal halide, this method has not been generally applied to the preparation of the dialkyl mercury compounds. Diphenyl mercury,¹ dicyclohexyl mercury² and dibenzyl mercury³ have already been prepared from the Grignard reagent and mercuric chloride, but only in poor yields. This method, however, may be applied to the preparation in good yields, of various dialkyl mercury compounds. The present paper contains a description of some of these preparations and points out the precautions that must be observed to obtain good results.

Many reactions have so far been used in the preparation of dialkyl mercury compounds, but all give poor results and none is of wide application. The method which has been most commonly and successfully employed is the treatment of an alkyl halide with dilute sodium amalgam in the presence of a catalyst such as ethyl acetate.⁴ Even this reaction, however, is limited to primary alkyl halides. As a consequence the mercury compounds with secondary alkyl groups are almost unknown. Di-*sec*-butyl mercury has been prepared by the electrolytic reduction of methyl-ethyl ketone using a mercury cathode,⁵ but no simple method has previously been available for preparing this type of mercury compound.

When an excess of the Grignard reagent reacts with a mercuric halide, there is formed first an alkyl mercury halide, which is then converted to the dialkyl mercury compound. The first reaction goes very easily but a large excess of Grignard reagent and long heating are necessary to bring about the second. Either mercuric chloride or iodide may be used without changing the yield of dialkyl mercury compound. Mercurous chloride may also be used, but the yields are always lower than those obtained from the mercuric salts. It is quite necessary to remove any unchanged magnesium from the Grignard reagent before treating it with the mercuric

¹ *Ber.*, **37**, 1127 (1904).

² *Ibid.*, **47**, 1655 (1914).

³ *J. Chem. Soc.*, **101**, 735 (1912); *Ber.* **46**, 64 (1913); **48**, 907 (1915); **THIS JOURNAL**, **40**, 1266 (1918).

⁴ *J. Chem. Soc.*, **16**, 416, 418, 420 (1863); **19**, 150 (1866). *Ann.*, **130**, 105, 109, 110 (1864); **139**, 128 (1866); **154**, 199 footnote (1870). *Compt. rend.*, **76**, 134 (1873); **77**, 1405 (1873). *Jahresber.*, **1873**, 517. *J. prakt. Chem.*, [2] **8**, 397 (1873). *Ber.*, **12**, 1880 (1879); **21**, 2037 (1888). **THIS JOURNAL**, **33**, 1561 (1911); **40**, 1269-71 (1918). *Zentr.*, **1921**, III, 26.

⁵ *Ber.*, **39**, 3628 (1906).

halide, or reduction to the mercurous salt occurs and the yields are lowered. When these precautions are observed, dimethyl mercury is formed to the extent of 61–66% of the calculated amount; di-ethyl, 60–63%; di-*n*-propyl, 45–51%; di-*isopropyl*, 60%; di-*n*-butyl, 47%. From these results it can readily be seen that the reaction of the Grignard reagent with mercuric halides to form dialkyl mercury compounds is quite general and is not limited in its application as are the older methods.

An attempt was made to obtain the intermediate alkyl mercury compound which is first formed when the Grignard reagent reacts with mercuric chloride. Methyl-magnesium iodide and an excess of mercuric chloride give methyl mercury iodide in 85–88% yields. However, if an alkyl magnesium bromide reacts with mercuric chloride, a mixture of alkyl mercury chloride and bromide is produced. For example, *n*-butyl-magnesium bromide reacts with an excess of mercuric chloride to give a product melting at 125.5–126°. The melting point is not changed by several crystallizations from alcohol or ligroin. However, the product contains both chlorine and bromine, and a quantitative analysis for carbon showed that it was a mixture of approximately equal parts of *n*-butyl-mercury chloride and *n*-butyl-mercury bromide. The pure chloride (from di-*n*-butyl mercury and hydrochloric acid) melts at 125° and the pure bromide (from di-*n*-butyl mercury and hydrobromic acid) melts at 129°. A mixture containing approximately equal parts of these two substances melts at 125–126° and might easily be mistaken for a pure substance. Similar results were obtained using propyl and *isopropyl* magnesium bromides with mercuric chloride. There is no doubt that pure substances could be obtained in good yields if the halogen of the alkyl halide were the same as that in the mercuric salt.

In a recent report⁶ it has been stated that an excess of *n*-butyl-magnesium bromide reacts with mercuric chloride to give *n*-butyl-mercury bromide, mercurous chloride and only small amounts of di-*n*-butyl mercury. In the same article it is claimed that *n*-butyl-magnesium bromide reacts with an excess of mercuric chloride to give *n*-butyl-mercury bromide. In view of the results which have been given above, it is apparent that the statements in the article referred to are based on results obtained without using the proper precautions.

The analyses given in this paper were made by the Parr total carbon method.⁷ This method is much more satisfactory for mercury compounds than is an ordinary combustion.

Experimental.

Dimethyl Mercury.—The Grignard reagent was prepared from 180 g. of methyl iodide and 30 g. of magnesium in 500 cc. of dry ether. After filtering the solution

⁶ *Science*, **54**, No. 1384, p. 37 (1921).

⁷ *THIS JOURNAL*, **26**, 296 (1904).

through glass wool to remove the unreacted magnesium, it was heated to boiling under a reflux condenser of wide bore. One hundred g. of powdered mercuric chloride was added through the condenser in 5 to 10g. lots over a period of about 45 minutes. The reaction proceeded very vigorously and the mercuric chloride could not be added more rapidly without danger of losing some material through the condenser. Some of the mercuric chloride stuck to the wall of the condenser and had to be pushed down occasionally by means of a glass rod. After all of the mercuric chloride had been added, the reaction mixture was refluxed for 10 to 12 hours to complete the reaction. The solution was then cooled in ice and the excess of Grignard reagent was destroyed by adding through the condenser about 250 cc. of water. The water was added very slowly to keep the reaction from becoming too vigorous. After the water had been added, the ether layer was separated and the water layer extracted once with 100 cc. of ether. The combined ether extract was washed with about 15 to 20 cc. of water, dried over calcium chloride and carefully distilled using a good column. When most of the ether had been removed, the residue was transferred to a smaller flask and the distillation was completed. All of the ether was again distilled in order to obtain the best yields of dimethyl mercury. The average yield was 51 to 56 g. (61-66% of the calculated amount) boiling at 89-92°. In several runs yields of 65 g. (75% of the calculated amount) were obtained. There is always a small amount of methyl mercury iodide left in the distilling flask. The boiling point of dimethyl mercury is given in the literature as 91-92°,⁸ 93-96°⁹ and 95°.¹⁰ A sample of dimethyl mercury, after careful purification was found to boil at 92° (cor.) under 740 mm. pressure.

The large excess of Grignard reagent and long heating seem to be necessary in order to obtain good yields. Unless the ether was redistilled, the yield was 10-15% lower than the amounts given above. In one run the mercuric chloride was added to the Grignard reagent in the cold. A hard cake separated in the bottom of the flask and a very poor yield of dimethyl mercury was obtained. When the unreacted magnesium in the solution of the Grignard reagent was not removed before adding the mercuric chloride, the yields were lowered.

In one run, using 180 g. of methyl iodide and 30 g. of magnesium, 170 g. of mercuric iodide was substituted for the mercuric chloride. Fifty-two g. of dimethyl mercury was obtained. With the same amount of Grignard reagent, 137 g. of mercurous chloride gave only 27 g. of dimethyl mercury.

Di-ethyl Mercury.—This preparation was carried out in essentially the same manner as described for dimethyl mercury, except that mechanical stirring was used. The Grignard reagent from 125 g. of ethyl bromide and 25 g. of magnesium in 500 cc. of anhydrous ether was treated with 97 g. of mercuric chloride. No difficulty was experienced in separating the ether from the di-ethyl mercury. It was found best to distill the product under reduced pressure to avoid decomposition. The yield of di-ethyl mercury boiling at 97-99° under 125 mm. pressure was 55 to 59 g. (60-63% of the calculated amount). The boiling point of di-ethyl mercury is given in the literature as 159° at atmospheric pressure.¹¹

When an equivalent amount of mercuric iodide was used in place of the chloride, the yield was not changed.

Di-*n*-propyl Mercury.—The Grignard reagent from 21 g. of magnesium and 108 g. of *n*-propyl bromide in 500 cc. of dry ether was treated with 98 g. of mercuric chloride and the reaction mixture worked up as described for the di-ethyl mercury. Forty-seven

⁸ *J. Chem. Soc.*, **105**, 668 (1914).

⁹ *Ann.*, **108**, 104 (1858).

¹⁰ *THIS JOURNAL*, **40**, 1271 (1918).

¹¹ *Ann.*, **130**, 109 (1864).

to 53 g. (45–51% of the calculated amount) of di-*n*-propyl mercury boiling at 81–84° at 19 mm. was obtained. The boiling point of di-*n*-propyl mercury is given in the literature as 189–191° at atmospheric pressure.¹²

Di-isopropyl Mercury.—The Grignard reagent prepared from 24.5 g. of magnesium and 130 g. of isopropyl bromide was treated with 80 g. of mercuric chloride. The yield of di-*iso*-propyl mercury was 50–51 g. (60% of the calculated amount) boiling at 119–121° at 125 mm.

Analysis. Subs., 0.4693: 258.2 cc. of CO₂ (28° and 741.4 mm.). Calc. for C₆H₁₄Hg: Hg: C, 25.17. Found: 25.07.

This compound has already been obtained in small quantities by the electrolytic reduction of acetone, using a mercury cathode,¹³ but no constants have been recorded.

Di-*n*-butyl Mercury.¹⁴—The Grignard reagent prepared from 21 g. of magnesium and 134 g. of *n*-butyl bromide was heated with 98 g. of mercuric chloride. It was necessary to distil the product a second time to remove all of the *n*-butyl-mercury halide that was carried over in the first distillation. The yield of di-*n*-butyl mercury was 55 to 56 g. (47% of the calculated amount) boiling at 120–123° at 23 mm. About 42 g. of a mixture of mercury butyl halides was left in the distilling flask. The di-*n*-butyl mercury was pure after a second distillation, as is shown by the analysis.

Analyses. Subs. 0.3862, 0.3314; CO₂, 265.7 cc. (32° and 739.4 mm.), 229.5 cc. (34° and 745.2 mm.). Calc. for C₈H₁₈Hg: C, 30.57. Found: 30.54, 30.60.

The boiling point of di-*n*-butyl mercury is given in the literature as 117–118° at 10 mm.¹⁵

A few cc. of di-*n*-butyl mercury was dissolved in alcohol and a little hydrochloric acid added. After standing overnight, *n*-butyl-mercury chloride had crystallized from the solution. This was filtered with suction and recrystallized from alcohol. Pearly white crystals with a melting point of 125° were obtained. The melting point given in the literature is 125.5°.¹⁵

Analysis. Subs., 0.6000: CO₂, 226.2 cc. (37° and 741.5 mm.). Calc. for C₄H₉HgCl: C, 16.41. Found: 16.24.

In a similar manner *n*-butyl-mercury bromide was prepared and purified. The melting point is 129°; that given in the literature is 128°.¹⁵

Analysis. Subs., 0.6000: CO₂, 190 cc. (34.5° and 742.2 mm.). Calc. for C₄H₉HgBr: C, 14.24. Found: 13.96.

Methyl-mercury Iodide.—The Grignard reagent was prepared from 2.4 g. of magnesium and 15 g. of methyl iodide in 50 cc. of anhydrous ether. The ether solution of methyl-magnesium iodide was filtered through a little glass wool to remove any unreacted magnesium. In a flask fitted with a stopper carrying a reflux condenser, dropping funnel and a stirrer running in a mercury seal were placed 30 g. of mercuric chloride and 150 cc. of dry ether. The stirrer was started and the solution of Grignard reagent was added from the dropping funnel at such a rate that the ether refluxed gently. The reaction mixture was refluxed for 1 hour after all of the Grignard reagent had been added. A little water was then added and the ether removed by distillation. About 200 cc. of water and 5 to 10 cc. of conc. hydrochloric acid were added to the residue to dissolve the excess of mercuric chloride and the magnesium compounds formed during the

¹² *Jahresber.*, 1873, 517.

¹³ Ref. 5, p. 3626.

¹⁴ While this paper was being written, an abstract of an article describing di-*n*-butyl mercury, *n*-butyl-mercury chloride and *n*-butyl-mercury bromide appeared in *Zentr.*, 1921, III, 26. As the original article was not available for comparison, analyses have been given in order to prove that these compounds were pure.

¹⁵ Cf. Ref. 14.

reaction. The methyl-mercury iodide was filtered with suction and recrystallized from boiling alcohol. The yield was 29 to 30 g. (85–88%). The product was light yellow in color and had a melting point of 142–143°. The melting point given in the literature is 143°.¹⁶

Action of *n*-Butyl-magnesium Bromide on an Excess of Mercuric Chloride.—The Grignard reagent was prepared from 15 g. of *n*-butyl bromide and 2.4 g. of magnesium in 50 cc. of dry ether. This was added to a suspension of 30 g. of mercuric chloride in 150 cc. of dry ether and worked up as described in the preceding experiment. Twenty-five to 26 g. of product melting at 125.5–126° was obtained after recrystallization from alcohol. It may be recrystallized from either alcohol or ligroin without changing the melting point. Qualitative tests show the presence of chlorine and bromine. The quantitative analysis for carbon shows that this product is a mixture of almost equal parts of *n*-butyl-mercury chloride and *n*-butyl-mercury bromide.

Analyses. Subs., 0.6000, 0.600: CO₂, 206 cc. (32.5° and 744.2 mm.), 208 cc. (33.5° and 744.0 mm.). Calc. for C₄H₉HgCl: C, 16.41; calc. for C₄H₉HgBr: C, 14.25. Found: 15.29, 15.34.

A mixture containing approximately equal parts of pure *n*-butyl-mercury chloride and *n*-butyl-mercury bromide was prepared and the melting point was found to be 125–126°.

n-Propyl-magnesium bromide and *isopropyl*-magnesium bromide give similar mixtures when allowed to react with an excess of mercuric chloride.

Summary.

1. The reaction between an excess of the Grignard reagent and a mercuric halide has been shown to furnish a very satisfactory method for the preparation of di-alkyl mercury compounds, provided the proper precautions are observed.

2. Mercury compounds containing primary and secondary alkyl groups can be prepared by this reaction. Compounds with tertiary alkyl groups could undoubtedly be prepared by the same method.

3. An alkyl magnesium bromide reacts with excess of mercuric chloride to give a mixture of alkyl mercury chloride and bromide. To obtain these compounds pure, the halogen of the alkyl halide must be the same as the halogen of the mercuric salt.

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¹⁶ *Ann.*, **85**, 363 (1853).