

2. The values found for this constant are 7.0×10^{-10} at 25° , and 10.1×10^{-10} at 40° .

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REACTIONS OF MERCURY DIPHENYL WITH SOME ACYL HALIDES

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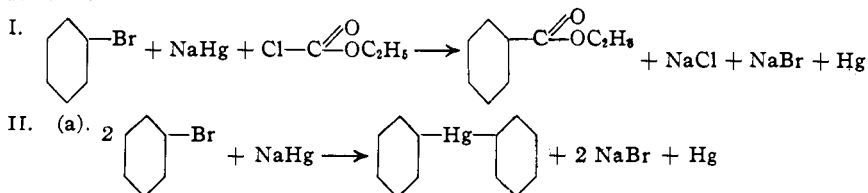
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In the preparation of ethyl benzoate from bromobenzene, ethyl chloroformate and sodium amalgam,¹ Wurtz obtained some mercury diphenyl. It has been suggested that mercury diphenyl is an intermediate product in the formation of the ethyl benzoate. Since the action of ethyl chloroformate with mercury diphenyl has not been studied it was decided to investigate it in order to learn more about the mechanism of the reaction observed by Wurtz. In general, unsatisfactory results have been obtained by several investigators who have studied the reactions of acid halides and organic mercury compounds.²

Whitmore and Thurman³ have published the first of a series of papers in which they are studying in some detail the action of several organic halides on mercury *p*-ditolyl. They have chosen this particular mercury compound because of the ease of preparation and because of the fact that it differs in a number of its reactions from mercury diphenyl⁴. The first definite results they obtained were with *p*-toluene-sulfonyl iodide. It has been found to give a good yield of *p*-ditolyl-sulfone, tolylmercuric iodide and mercuric iodide. Whitmore and Thurman discuss the previous work in this general field and show that sulfonyl chlorides have been more thoroughly investigated than ordinary acyl halides.

Several mechanisms may be suggested for the action of bromobenzene, ethyl chloroformate and sodium amalgam. These may be illustrated as follows.

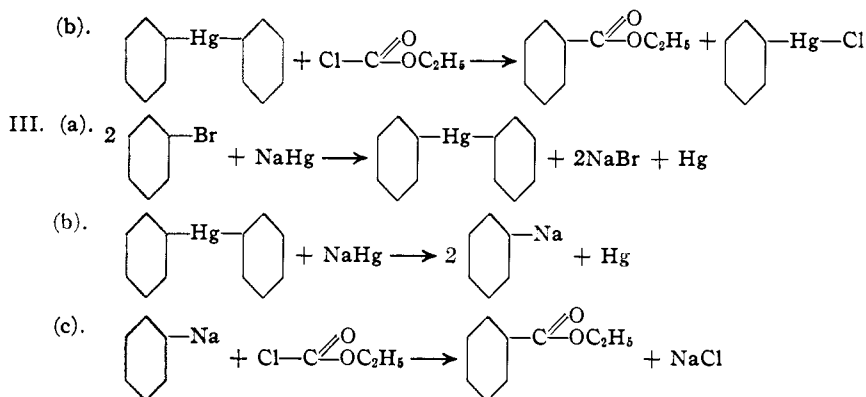


¹ Wurtz, *Compt. rend.*, **68**, 1298 (1869).

² Steinkopf and Bauermeister, *Ann.*, **403**, 59 (1914). Otto, *Ber.*, **3**, 197 (1870); **18**, 246 (1885). Paterno, *Ber.*, **10**, 1749 (1877).

³ Whitmore and Thurman, *THIS JOURNAL*, **45**, 1068 (1923).

⁴ Whitmore, private communication.



If Reaction I is correct, the mercury diphenyl is formed as a by-product by IIa. If II is the correct mechanism, mercury diphenyl and ethyl chloroformate should react to give ethyl benzoate. If III is correct, sodium amalgam is necessary to form sodium phenyl by IIIb and then ethyl benzoate by IIIc. The action of these substances was studied under various conditions. It was found that they react to form phenylmercuric chloride but do not form enough ethyl benzoate for identification. The presence of sodium amalgam did not affect the results. Furthermore, the phenylmercuric chloride formed did not react with the ethyl chloroformate. Thus, Mechanism I is probably correct, both because mercury diphenyl does not form ethyl benzoate with ethyl chloroformate either in the presence or absence of sodium amalgam and because Wurtz obtained no phenylmercuric chloride.

While studying the reaction of ethyl chloroformate and mercury diphenyl two other representative acyl halides were studied. These were acetyl chloride and benzoyl chloride. Like ethyl chloroformate they react to give phenylmercuric chloride. They also give acetophenone and benzophenone, respectively, in large enough amounts to be identified completely. In each case a low-melting solid was obtained which was probably diphenyl. In the present investigation it was of interest that the work of Dreher and Otto⁵ was verified with reference to the solubility of phenylmercuric chloride in alkali.

Experimental Part

Preparation of Mercury Diphenyl.—A mixture of 900 g. of 3% sodium amalgam, 180 g. of bromobenzene, 200 cc. of toluene and 10 cc. of ethyl acetate was refluxed for 12 hours on an oil-bath, the temperature of which was kept at 130°. It was transferred while still hot to a large funnel, leaving behind as much mercury as possible. It was extracted by the method of Clarke and Kirner.⁶ The extraction was complete after

⁵ Dreher and Otto, *Ann.*, **154**, 126 (1870).

⁶ Clarke and Kirner in "Organic Syntheses," John Wiley and Sons, vol. II, 1922, p. 48.

ten hours. The solution containing the mercury diphenyl was distilled under a pressure of 20 mm. on an oil-bath, the temperature of which was raised to 110° near the end of the distillation. The solid residue, formed after removal of the toluene and benzene, was removed and washed with cold alcohol until it was white; yield, 96 g., or 47%; m. p., 122–123°.

Action of Ethyl Chloroformate with Mercury Diphenyl

In Benzene Solution on a Water-Bath.—Seven g. of mercury diphenyl, 21.8 g. of ethyl chloroformate and 100 cc. of benzene were heated on a water-bath for 60 hours cooled in an ice box overnight and then in a freezing mixture for one hour and filtered. The precipitate of phenylmercuric chloride melted sharply at 251°; yield, 1 g. The filtrate was evaporated under 50 mm. pressure on a water-bath. The solid residue contained no ethyl benzoate. It was mercury diphenyl; m. p., 120–121°.

Without a Solvent on a Water-Bath.—Seven g. of mercury diphenyl and 87.2 g. of ethyl chloroformate were heated at 95° for 80 hours on a water-bath. The mercury diphenyl was converted completely to phenylmercuric chloride. After filtering and boiling the filtrate with 10% sodium hydroxide solution it gave no benzoic acid when acidified with hydrochloric acid. An organic mercury compound was obtained instead. There was no evidence of reaction of ethyl chloroformate and phenylmercuric chloride.

In the Presence of Sodium Amalgam.—Seven g. of mercury diphenyl, 87 g. of ethyl chloroformate and 100 g. of 3% sodium amalgam were heated for three days on a steam-bath and the same results were obtained as described above.

Without a Solvent on an Electric Hot-Plate.—The temperature of the hot-plate was about 400°. The same quantities were used as in the experiment described above and, after heating for 60 hours, the results were the same as those obtained on a water-bath.

Without a Solvent at Room Temperature.—The same molecular proportions were used as above and allowed to stand at room temperature for three days. After removal of the ethyl chloroformate the mercury diphenyl was recovered unchanged.

Reactions of Acetyl Chloride and Mercury Diphenyl

In Benzene Solution on a Water-bath.—Seven g. of mercury diphenyl, 31.6 g. of acetyl chloride and 100 cc. of benzene were refluxed for 80 hours on a water-bath. After cooling and filtering 5.6 g. of phenylmercuric chloride was obtained; m. p., 251°. The filtrate was evaporated under reduced pressure. The residue was taken up in alcohol and diluted with water. The brown oil which separated was converted to the oxime and phenylhydrazone melting at 54–55° and 104–105°, respectively, which correspond to the acetophenone derivatives.

Without a Solvent on a Water-Bath.—After heating had been continued for 60 hours the same results were obtained.

Without a Solvent on an Electric Hot-Plate.—After heating on an electric hot-plate, the temperature of which was about 400°, for 75 hours no organic mercury compounds were recovered. A low-melting solid (68–69°) was obtained which was probably diphenyl.

Without a Solvent at Room Temperature.—After standing for three days the reaction gave phenylmercuric chloride and acetophenone.

Reactions of Benzoyl Chloride and Mercury Diphenyl

In Benzene Solution on a Water-Bath.—Seven g. of mercury diphenyl, 56.4 g. of benzoyl chloride and 100 cc. of benzene were heated on a water-bath for 80 hours. After the mixture had been cooled and filtered it gave 2 g. of phenylmercuric chloride. After removal of the benzene the filtrate was decomposed with 20% ammonium

hydroxide, filtered and the precipitate washed with hot water. The brown oil which separated was converted to the oxime, m. p. 138°, which corresponds to the benzophenone derivative.

Without a Solvent on a Water-Bath.—The same results were obtained as above; 2 g. of mercury diphenyl was recovered.

Without a Solvent on an Electric Hot-Plate.—The temperature of the hot-plate was about 400°. No mercury diphenyl was recovered. Phenylmercuric chloride and mercuric chloride were identified. Benzophenone was identified and probably diphenyl as in the case above.

Without a Solvent at Room Temperature.—The mercury diphenyl was recovered almost quantitatively.

Solubility of Phenylmercuric Chloride in Sodium Hydroxide.—Phenylmercuric chloride was found to be soluble in sodium hydroxide to the extent of about 1 g. per 100 cc. of 10% sodium hydroxide.

Summary

1. It has been found that ethyl chloroformate, acetyl chloride and benzoyl chloride all react with mercury diphenyl to give phenylmercuric chloride. Acetyl chloride gives acetophenone while benzoyl chloride gives benzophenone and both possibly give diphenyl.

2. Ethyl chloroformate did not give ethyl benzoate in large enough quantities to be identified.

3. From this work it has been shown that mercury diphenyl is probably not an intermediate product in the formation of ethyl benzoate from bromobenzene, ethyl chloroformate and sodium amalgam but is a by-product in that reaction.

4. It has also been shown that acetyl chloride is the most reactive of the three halides towards mercury diphenyl.

5. The statement that phenylmercuric chloride is soluble in alkali has been confirmed.

6. An improvement in the yield of mercury diphenyl was obtained by the use of a stronger amalgam, a longer period of heating and an improved method of extraction.

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