

hot 95% ethyl alcohol. It was purified by recrystallization from hot 60–70° petroleum ether; white crystals, m. p. 167.5–168.5°.

Anal. Calcd. for $C_{12}H_6Cl_6N_2$ (Parr Bomb): Cl, 54.50. Found: Cl, 54.88.

2,4,6,2',4',6'-Hexachloro-3,3'-chloroacetaminodiphenyl.—A mixture of 2 g. of the hexachlorodiaminodiphenyl and an excess of chloroacetyl chloride was refluxed for several hours on a steam cone. The mixture was then cooled and the excess of chloroacetyl chloride was decomposed with cracked ice. The product was recrystallized from 70–80° petroleum ether as white crystals, m. p. 125–126°.

Anal. Calcd. for $C_{16}H_8Cl_6N_2O_2$ (Parr Bomb): Cl, 52.2. Found: Cl, 52.3.

Attempts to condense hexachlorodiaminodiphenyl with *d*-camphorsulfonic acid and oxymethylenecamphor, respectively, proved unsuccessful.

Summary

1. 2,4,6,2',4',6'-Hexachloro-3,3'-dicarboxydiphenyl was prepared by the condensation of 1-iodo-2,4,6-trichloro-3-methylbenzene with copper and oxidation of the product.

2. The product was resolved through the brucine salt. The active forms were stable to ordinary methods of racemization.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

THE ACTION OF MERCURY ON ORGANIC IODIDES. I. THE FORMATION OF METHYLMERCURIC IODIDE AND BENZYL MERCURIC IODIDE¹

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Introduction

For over eighty years it has been known that when mercury is allowed to stand in the sunlight with methyl or ethyl iodide, reactions occur with the formation of organomercuric iodides, $RHgI$, and certain gaseous products.² In addition to the instances cited, the direct action of mercury with organic iodides has been noted only in the cases of allyl iodide,³ methylene iodide and iodoform,⁴ and propargyl iodide.⁵ With the higher saturated alkyl iodides it is possible that a very slow reaction with mercury takes place, but no accurate data are available.⁶ Up to the present time,

¹ A part of this material has been presented in a thesis submitted to the University of Minnesota.

² Frankland, *J. Chem. Soc.*, **3**, 322 (1851); *Ann.*, **111**, 59 (1859); Strecker, *ibid.*, **92**, 76 (1854).

³ Zinin, *ibid.*, **96**, 363 (1855).

⁴ Sakurai, *J. Chem. Soc.*, **37**, 658 (1880); **39**, 485 (1881); **41**, 360 (1882).

⁵ Henry, *Ber.*, **17**, 1132 (1884).

⁶ Whitmore, "Organic Compounds of Mercury," A. C. S. Monograph Series, The Chemical Catalog Co., New York, 1921, p. 26.

no other halogen alkyls or any aryl halides have been found to react with mercury to give organomercuric halides.

Preliminary Observations.—The preparation of a large quantity of methylmercuric iodide, CH_3HgI , was carried out by the action of mercury on methyl iodide in the sunlight. During the course of this work it was noted that in each batch there was a lag of from three to ten hours before the presence of methylmercuric iodide could be detected in the reaction mixture. The first observable mercury compound to be formed was invariably found to be mercurous iodide, its presence being detected by the appearance of green specks on the surface of the layer of mercury. The formation of this compound resulted from the action of an excess of mercury on iodine liberated photochemically from methyl iodide. After a lapse of time of a few minutes, methylmercuric iodide in steadily increasing concentration was found in solution in the methyl iodide. A reason was sought for the failure of the organomercuric iodide to appear until after the formation of mercurous iodide.

Discussion and Further Observations.—From the observed behavior of a mixture of mercury and methyl iodide it was concluded that mercurous iodide facilitated the formation of methylmercuric iodide.⁷ Acceptance of this conclusion demanded that there be no lag in the formation of methylmercuric iodide on exposure of a mixture of mercury, mercurous iodide and methyl iodide to the sunlight. This proved to be the case, for, after a few minutes of exposure of such a mixture, methylmercuric iodide was found to be present. Since the mixture did not react in the dark, and since pure mercurous iodide alone reacted with methyl iodide in the light in the absence of an excess of mercury, it was decided that the mercury necessary for the reaction in either case was produced by the photochemical decomposition of mercurous iodide. Thus: $\text{Hg}_2\text{I}_2 \rightarrow \text{Hg} + \text{HgI}_2$. The metal formed in this manner was in a finely divided condition.

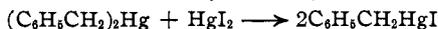
The conclusion reached was supported by further experimental evidence. It must be noted at this point that the course of the reactions between mercury and methyl iodide was the same whether the source of light was the sun, a mercury vapor lamp or a carbon arc. In this study the arc was selected as the most convenient source of illumination. Light from this source brought about the liberation of iodine from methyl iodide, and, with an excess of massive mercury present, the formation of mercurous iodide took place. This was followed shortly by the formation of methylmercuric iodide. If, however, the photochemical decomposition of the methyl iodide was prevented by passing the light through a screen of cod liver oil, neither mercurous iodide nor methylmercuric iodide was formed during an exposure of seventy-two hours. It was found also that the photochemical decomposition of methyl iodide was not necessary for the

⁷ Cf. Maynard and Howard, *J. Chem. Soc.*, **123**, 963 (1923).

reaction between mercury and the alkyl iodide, because a mixture of the latter with mercurous iodide reacted behind a screen of cod liver oil to form the organomercuric iodide. Mercurous iodide was photochemically decomposed in the shielded system.

Conclusions.—Thus it has been shown that, while the reaction between massive mercury and methyl iodide must be extremely slow, the finely divided metal reacted readily with the alkyl iodide. This was further demonstrated by the fact that finely divided mercury prepared by the action of ammonium hydroxide on mercurous chloride reacted with methyl iodide protected by a screen of cod liver oil. From this experiment it seemed logical to conclude that mercurous iodide functioned solely as a source of supply of finely divided mercury in the reactions previously noted.

The Action of Mercury on Benzyl Iodide.—With a convenient source of finely divided mercury at hand, it has seemed of interest to attempt to broaden the scope of this action between the metal and an organic iodide by its application to other iodides. Benzyl iodide was the first to be selected for this study, and it was found to react readily and completely with finely divided mercury to form benzylmercuric iodide. The latter compound has been prepared previously in a pure condition only by the action of mercuric iodide on mercury dibenzyl.⁸

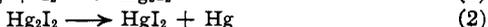


This organomercuric iodide has proved to be interesting because work now in progress shows that it reacts with acid chlorides, a reaction not previously noted with a compound of the type RHgI . Studies of the action of mercury with other organic iodides are also being made.

Experimental Part

Reaction between Mercury and Methyl Iodide in the Sunlight.—A stoppered Pyrex test-tube containing 10 g. of mercury and 20 g. of methyl iodide was exposed to direct sunlight at a temperature of 30°. Frequent tests over a period of three hours showed an absence of methylmercuric iodide. At the end of this time the first speck of mercurous iodide had appeared on the surface of the mercury. Ten minutes later, evaporation to dryness of the methyl iodide left a small quantity of a slightly yellowish crystalline solid. This was recrystallized from a small volume of alcohol, and was identified as methylmercuric iodide by its melting point of 144°. The experiment was repeated five times, and although the period of lag varied considerably because of the obscuring of the sun by clouds during parts of the exposure, in no case was the presence of methylmercuric iodide detected previous to the appearance of mercurous iodide.

The use of larger quantities of reactants, 45 g. of mercury and 80 g. of methyl iodide, yielded 30.9 g. of methylmercuric iodide after an exposure of one week in a sealed Carius tube. This represented a yield of 80.7% of that calculated for 45 g. of mercury reacting in the following way



⁸ Wolff, *Ber.*, **46**, 64 (1913).

The iodine appearing in reaction (1) was formed by the photochemical decomposition of methyl iodide. It can be seen that when the mercurous iodide reacted as shown in equation (2) it was regenerated from the mercuric iodide and the excess of massive mercury present. The methylmercuric iodide was obtained from the reaction product by extraction with boiling benzene.

The Action of a Mixture of Mercury, Mercurous Iodide and Methyl Iodide in the Sunlight.—To a solution of 1 g. of iodine in 10 ml. of methyl iodide contained in a Pyrex test-tube there was added 13 g. of mercury. The mixture was shaken vigorously to effect the formation of mercurous iodide, and was then exposed to the sunlight at a temperature of 31°. A sample taken after a five-minute exposure showed methylmercuric iodide to be present in solution in the methyl iodide. The organomercuric iodide was identified by its melting point of 144°.

The Action of Mercurous Iodide on Methyl Iodide in the Sunlight.—A mixture of 5 g. of pure yellow mercurous iodide⁹ and 10 ml. of methyl iodide was exposed to direct sunlight at 28° in a stoppered Pyrex test-tube. After a ten-minute exposure methylmercuric iodide was found in solution in the methyl iodide.

Mercury and Methyl Iodide in a Shielded System.—A stoppered clear quartz test-tube containing a mixture of 5 g. of mercury and 10 ml. of methyl iodide was suspended in cod liver oil contained in a square, clear quartz container. This system was then exposed to light from a carbon arc placed 25 cm. from the outer quartz container. The light passed through a 3-mm. layer of cod liver oil and at the end of a seventy-two hour exposure the contents of the test-tube remained unchanged. The temperature was 34°.

Mercurous Iodide and Methyl Iodide in a Shielded System.—A mixture of 10 g. of mercurous iodide and 15 ml. of methyl iodide was placed in a stoppered quartz test-tube shielded by a 3-mm. layer of cod liver oil. At the end of a fifteen-minute exposure to light from the arc, methylmercuric iodide was found in solution in the methyl iodide. The temperature was 34°.

Finely Divided Mercury from Mercurous Chloride.—Mercurous chloride was prepared by precipitating it from a 0.1 *N* solution of mercurous nitrate with dilute hydrochloric acid. The precipitate was washed repeatedly with water, and then added in small portions to a concentrated solution of ammonium hydroxide. Mechanical stirring maintained a fine state of division of the product. The black insoluble material was filtered off, washed with water and then dried at room temperature.

Reaction of the Black Precipitate with Methyl Iodide.—A mixture of 10 g. of the black precipitate prepared in the preceding experiment and 15 ml. of methyl iodide was exposed in the shielded system to light from the arc at a temperature of 34°. At the end of a ten-minute exposure enough methylmercuric iodide was obtained for a melting point determination.

The Preparation of Benzylmercuric Iodide.—To 5 g. of iodine dissolved in 10 ml. of alcohol there was added 30 g. of mercury. The mixture was thoroughly shaken until a dark green product was obtained. This was sucked free from alcohol on a Büchner funnel, and then sealed up with 15 g. of benzyl iodide in a short length of Carius tubing. The tube was exposed to light from the arc for three hours at a temperature of 50°. The reaction product was found to be free from benzyl iodide, for no lachrymatory action was noted on opening the tube. The benzylmercuric iodide was extracted with boiling alcohol. The yield of pure product, melting at 117°, was 26 g. or 94.5% of that calculated for 15 g. of benzyl iodide.

⁹ Prepared according to directions given in Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., London, 1923, Vol. IV, p. 896.

The author wishes to acknowledge with appreciation the kindly advice and criticism given by Dr. William H. Hunter during the course of this investigation.

Summary

1. Methylmercuric iodide is not formed from methyl iodide and mercury on exposure to light until after the appearance of mercurous iodide in the reaction mixture.

2. Finely divided mercury produced by the photochemical decomposition of mercurous iodide enters into reaction readily with methyl iodide to form methylmercuric iodide.

3. The action of mercury with organic iodides to form organomercuric iodides has been extended to benzyl iodide.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

THE PINACOL-PINACOLIN REARRANGEMENT. THE REARRANGEMENT OF UNSYMMETRICAL AROMATIC PINACOLS

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The rearrangement of symmetrical mixed pinacols of the type $RR'(OH)CC(OH)RR'$ has received considerable attention because the reaction offers an excellent method for determining the relative migration aptitudes of groups. The groups R and R' are in structurally identical positions, and the mode of water elimination from the molecule is therefore immaterial; the principal factor determining the course of the rearrangement is the relative migration aptitudes of the groups. Moreover, it has been shown that in such pinacols each group may be assigned a definite numerical value which represents the migration aptitudes of that group relative to some other group. The most recent series¹ showing the migration aptitudes of a number of groups with respect to the phenyl group taken as unity is the following: anisyl, 70 or more; *p*-tolyl, 15; *p*-biphenyl, 11.5; *p*-isopropylphenyl, 9; *p*-ethylphenyl, 5; *m*-tolyl, 1.95; *p*-fluorophenyl, 1.85; *p*-iodophenyl, 1; phenyl, 1; *p*-bromophenyl, 0.7; *p*-chlorophenyl, 0.66; *m*-methoxyphenyl, 0.2; *o*-tolyl, *o*-bromophenyl and *o*-chlorophenyl, very small. It has further been demonstrated that by means of these values it is possible to calculate the course of rearrangement of a symmetrical pinacol containing two of these groups.

We have now undertaken an investigation to determine whether the same series holds in the rearrangement of unsymmetrical pinacols of the type $RR(OH)CC(OH)R'R'$. Various investigators have pointed out that in pinacols of this type the nature of the rearrangement depends practi-

¹ Bachmann and Moser, *THIS JOURNAL*, **54**, 1124 (1932).