In conclusion the author wishes to thank Messrs. W. Lamb and G. Greenwood for revising the literature on phosphorus and iron respectively.

MANCHESTER, ENGLAND.

AROMATIC MERCURI-ORGANIC DERIVATIVES. THE HOFMANN REARRANGEMENT AND THE NATURE OF VALENCES OF MERCURY IN MERCURI-ORGANIC DERIVATIVES.
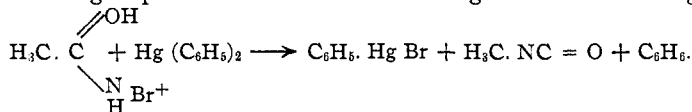
BY MORRIS S. KHARASCH.[1]

The effect of the halogens on mercury diphenyl has been studied by Otto[2] who found that bromine (one molecule) in water solution or in anhydrous media, gave rise to phenyl mercury bromide, and phenyl bromide. When, however, an excess of bromine was used, the resulting products were mercuric bromide and phenyl bromide. The behavior of mercury diphenyl with bromine is representative of the behavior with any other halogen. With the halogen acids the result was similar but, of course, instead of the phenyl halide, benzene was the other product. It was, therefore, of interest to find out just what the effect of positive halogen[3] alone on mercury diphenyl would be.

It was with this idea in mind that the effect of N-bromo-acetamide in sodium-dried benzene upon mercury diphenyl, dissolved in the same solvent, was tried. After the solution was warmed for about 10 minutes on the water-bath, a solid separated which was identified as phenyl mercury bromide.[4]

The reaction when studied in greater detail, and also, with other N-bromo-amides revealed the fact that mercury diphenyl played the same part in this reaction as sodium hydroxide in aqueous solution and sodium ethylate in absolute alcohol,[5] and that it also led to a rearrangement in which the group attached to the carbon migrated to the nitrogen.

$$H_3C.\ C\overset{\displaystyle /\!\!/OH}{\underset{\displaystyle \overset{N}{\underset{H}{\diagdown}}Br^+}{}} + Hg\ (C_6H_5)_2 \longrightarrow C_6H_5.\ Hg\ Br + H_3C.\ NC = O + C_6H_6.$$

[1] National Research Fellow in Organic Chemistry.

[2] Otto, *J. prakt. Chem.*, [2] **1**, 182 (1870).

[3] Seliwanow, *Ber.*, **25**, 3617 (1892); Lengfeld and Stieglitz, *Am. Chem. J.*, **15**, 215, 504 (1893); W. A. Noyes, THIS JOURNAL, **23**, 450 (1901); J. Stieglitz, *ibid.*, **23**, 796 (1901), etc.

[4] The same reaction takes place also in bright sunlight in the course of a few minutes, without any heating whatsoever.

[5] Lengfeld and Stieglitz, *Am. Chem. J.*, **15**, 215, 504 (1893).

Furthermore, we find that just as sodium hydroxide or sodium ethylate fails to effect a rearrangement in the case of the N-substituted alkyl or aryl bromo-and chloro-acetamides,[6] so mercury diphenyl seems not to be acted upon by the latter reagent. Even after prolonged boiling (12 to 14 hours), no action occurs, although N-chloro-acetanilide is a chlorinating agent in anhydrous media. Thus, when the latter was treated with aniline in dry benzene, 2,4-dichloro-aniline and acetanilide were formed. Also dimethyl aniline, diphenylamine, and m-dimethylamino-acetyl phenol gave acetanilide and chlorinated products, while triphenylamine and m-nitro-dimethylaniline were not acted upon at all.

Thus, the reaction of mercury diphenyl and the N-bromo amides affords an excellent illustration of the basicity of mercury diaryl compounds. Of course, we must distinguish bases derived from hydrides which acquire their basicity through two additional valences, one positive and one negative, forming

$$H_n X + H_2O \rightleftharpoons H_n X \diagdown \begin{matrix} OH \\ H \end{matrix}$$
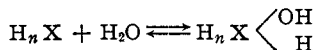
where X is negative, such as ammonium, sulfonium, oxonium, iodonium and similar bases, and those derived from metal hydroxides, $M(OH)_x$, where M is positive, e. g., the derivatives of zinc, magnesium, mercury, etc. Mercury compounds of the type R-Hg-R and R-Hg-OH could well be, and probably are, derived from mercuric hydroxide $Hg(OH)_2$ giving them the structure R-Hg-R and R-Hg-OH respectively. In the case of the latter compounds, which are strong bases, the substitution could easily bring out the high ionizing tendency of a univalent base, comparable with silver hydroxide. Mercury diaryl compounds in benzene solution are then quite comparable to calcium hydroxide in aqueous solution,[7] which may be considered as the metal hydroxide or salt of the very weak acid water. Mercury diphenyl Hg (R)₂ is therefore a base of the benzene system, as sodium amide NaNH₂ is a base of the ammonium system, sodium hydroxide of the aqueous system, etc.

A different view point as to the electronic structure of mercury dialkyl and diaryl compounds is held by Jones and Werner.[8] These authors assume that in these substances one of the valences of mercury functions positively and the other negatively, i. e., to give a compound of the type

[6] Stieglitz and Slosson, Ber., 28, 3266; 34, 1613 (1901); Slosson, Am. Chem. J., 29, 289 (1903).

[7] The same view point has been maintained by Stieglitz for some years for the zinc methyl derivatives. Stieglitz, "Qualitative Chemical Analyses," 1, 177 (1911). See also Jones, THIS JOURNAL, 40, 1250 (1918).

[8] Jones and Werner, ibid., 40, 1257 (1918).

$\overset{-}{}+\overset{-}{}+$

R-Hg-R. The experimental evidence for this assumption is confined to the study of the behavior of mercury diethyl, di-*iso*-amyl and dibenzyl. At high temperatures, these decompose to give metallic mercury and a
$+-$
hydrocarbon R-R. Upon hydrolysis with glacial acetic acid, again at high temperatures, these give, for instance, in the case of mercury dibenzyl, metallic mercury, benzyl acetate, toluene and dibenzyl.

Jones and Werner, therefore, infer that if a compound upon hydrolysis gives metallic mercury, an alcohol, and a hydrocarbon, its electronic struc-
$\overset{-}{}+\overset{-}{}+$
ture must be R-Hg-R. While the validity of such reasoning is unquestioned it can be shown very readily that Jones and Werner's experimental data do not necessitate such a conclusion—one that is quite in disagreement with the position of mercury in the periodic system—and that direct experimental evidence that the valences of mercury function in any way but positively in all mercuri-organic derivatives is still lacking.

In the first place, we know that mercury in all inorganic compounds functions positively, and we should expect, therefore, that a bond between negatively charged mercury and a positive radical would be less stable than one between a positive mercury and a negative radical. This is in direct contradiction to Jones and Werner's formula which requires that the more stable union be ruptured first, when compounds of the type
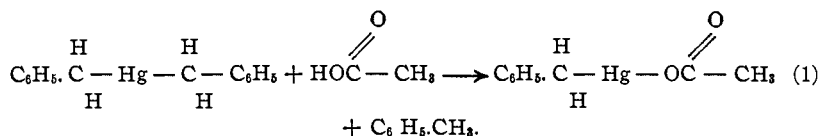$\overset{-}{}+\overset{-}{}+$
R-Hg-R are treated with acids, the following taking place, according to Jones and Werner.

$$\overset{-}{R}\ \overset{+-}{Hg}\ \overset{+}{R} + \overset{+}{H}\ \overset{-}{X} \longrightarrow \overset{-}{X}\ \overset{+-}{Hg}\ \overset{+}{R} + \overset{-}{R}\ \overset{+}{H}.$$
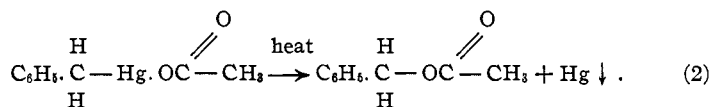
Furthermore, Jones and Werner seem to ignore entirely the fact that mercuric ion is an oxidizing agent, the oxidizing power of which increases with the temperature. Thus stannous ion is oxidized by mercuric ion to the stannic ion, even at ordinary temperatures. Again, a good many organic compounds more or less sensitive to oxidation are oxidized by mercuric ion; dimethyl-*p*-phenylene-diamine is first oxidized to Wurster's red by a solution of mercuric acetate, and at a somewhat higher temperature metallic mercury is thrown out. The same is true of hydroquinone. In view of these facts one must always be on the lookout for the oxidizing tendency of the mercuric ion especially when working with mercury compounds at high temperatures.

If we bear this fundamental property of mercury in mind, the reactions of aryl and alkyl mercury compounds studied by Jones and Werner do not then necessitate the assumptions made by those writers. Thus, they started with 15 g. of mercury dibenzyl and after heating it for 7 hours at 200° isolated the following products in the quantities given: mercury 7.776 g.; toluene, 1.756 g.; benzyl acetate, 2.267 g.; dibenzyl,

3.05 g. These results show convincingly that two reactions took place simultaneously. In the first place, part of the mercury dibenzyl, namely 7.9 g., was transformed into metallic mercury and dibenzyl,[9] and the rest (7.1 g.) into mercury, toluene and benzyl acetate. In the latter case, the reaction undoubtedly takes place in the following stages.

$$
\underset{\overset{|}{H}}{\overset{\overset{|}{H}}{C_6H_5.\,C}} - Hg - \underset{\overset{|}{H}}{\overset{\overset{|}{H}}{C}} - C_6H_5 + HOC\overset{O}{\overset{\diagup\!\diagup}{{}}} - CH_3 \longrightarrow \underset{\overset{|}{H}}{\overset{\overset{|}{H}}{C_6H_5.\,C}} - Hg - OC\overset{O}{\overset{\diagup\!\diagup}{{}}} - CH_3 \quad (1)
$$
$$
+ C_6H_5.CH_3.
$$

In the benzyl mercuric acetate thus formed, *at the high temperature used*, the doubly positive mercury atom oxidizes the carbon and we get benzyl acetate and mercury, *i. e.*,

$$
\underset{\overset{|}{H}}{\overset{\overset{|}{H}}{C_6H_5.\,C}} - Hg.\,OC\overset{O}{\overset{\diagup\!\diagup}{{}}} - CH_3 \overset{heat}{\longrightarrow} \underset{\overset{|}{H}}{\overset{\overset{|}{H}}{C_6H_5.\,C}} - OC\overset{O}{\overset{\diagup\!\diagup}{{}}} - CH_3 + Hg\downarrow. \quad (2)
$$

There is, therefore, nothing unusual about all the reactions mentioned by Jones and Werner. The reaction is simply a case of intramolecular oxidation and reduction and quite comparable with the molecular rearrangements which take place due to intramolecular oxidation and reduction.[10] Again, the decomposition of mercury compounds by chlorine, bromine and iodine, taken in connection with the decomposition by acids,[11] lends more weight to the well accepted fact that mercury always functions positively in all mercuri-organic compounds.

We might add also that at no time do results obtained by the use of high temperatures prove anything as to the electronic structure of the starting product. As yet, we are quite ignorant of the changes which take place at high temperatures. Thus, the formation of diphenyl alone, at a high temperature, from benzene would be a very poor argument that, in benzene, we have two tautomeric electromers in equilibrium:
$\overset{+}{C_6} + \overset{+}{H_5} - \overset{-}{H} \rightleftharpoons \overset{-}{C_6H_5} - \overset{+}{H}$; and Jones and Werner carried out the hydrolysis of mercury dialkyl and diaryl compounds at temperatures ranging from 170° to 220°.

[9] This observation was made by Wolff [*Ber.*, **46**, 64 (1913)] who states that when mercury dibenzyl is heated above its melting point, 111°, it is decomposed into metallic mercury and dibenzyl.

[10] L. W. Jones, *Am. Chem. J.*, **48**, 1 (1912); **50**, 440 (1913). J. Stieglitz, *Ber.*, **43**, 782 (1910); THIS JOURNAL, **36**, 287 (1914); *Ber.*, **46**, 2149 (1913).

[11] Jones and Werner have to assume the existence of two tautomeric electromers in equilibrium, $R - \overset{-++-}{Hg} - R \rightleftharpoons R - \overset{-+-+}{Hg} - R$, to explain the decomposition of mercury dialkyl and diaryl compounds by conc. hydrochloric acid, *i. e.*, mercuricchloride and a hydrocarbon being the products.

Summing up, we might say that from experimental work described in this paper, and the behavior of mercury diaryl compounds, in general, the structure R-Hg-R is the most appropriate one: it explains the reactions of mercury diaryl and dialkyl compounds without any additional postulates and is in perfect agreement with the chemistry of the element.

$$- ++ -$$
$$\text{R-Hg-R}$$

Experimental.

Action of Mercury Diphenyl on N-Bromo-amides. N-Bromo-acetamide.— Of this 0.6 g. was dissolved in dried benzene,[12] and then treated with 1.3 g. of mercury diphenyl dissolved in 40 cc. of benzene. The solution was then boiled for 20 minutes at the end of which time no active bromine could be detected in it. A white crystalline compound separated, and the solution had a pungent, irritating odor very characteristic of an isocyanate. The precipitate was collected on a filter, care being taken not to allow any atmospheric moisture to come in contact with the filtrate. The precipitate thus obtained (0.7 g.) melted at 276°. After a single crystallization it melted at 291°. When the compound was mixed with some known phenyl mercuric bromide the melting point of the latter was not lowered.

The filtrate from the phenyl mercury bromide contained some phenyl mercury bromide, a little unchanged mercury diphenyl and methyl isocyanate. To separate the latter from other compounds, dry aniline was added[13] to the filtrate to form methylphenyl urea. The mixture was warmed for 3 minutes at 60°, cooled and ligroin added until the solution became turbid. Beautiful white needles were thus obtained, m. p. 152° to 153°. The melting point of α,β-phenyl-methyl urea given in the literature is 150°.

The urea thus obtained exhibits the reactions given in the literature for phenylmethyl urea (α, β), $i. e.$, when a minute quantity of it was dissolved in conc. sulfuric acid and a little powdered potassium dichromate added to it, an intense maroon color was imparted to the solution.

The same arrangement is also effected if the solution of N-bromo-acetamide and mercury diphenyl is allowed to stand in bright sunlight for 3 to 4 minutes. In the dark however, the reaction takes place very slowly as indicated by the fact that after a lapse of two weeks there was still a considerable quantity of unchanged N-bromo-acetamide in the solution.

N-Bromobenzamide.—2 g. of this substance was dissolved in 100 cc. of hot benzene and 3.4 g. of mercury diphenyl dropped into the solution. It was then put out in the sunlight. After 20 minutes a considerable quantity of phenyl mercury bromide separated. The reaction, however, did not go to completion, as indicated by the presence of active bromine in the solution. To complete the reaction the solution was boiled on the water-bath for one hour longer. The precipitate (2.5 g.) was collected on a filter paper and identified as phenyl mercury bromide. To the filtrate aniline was added, and after 3 to 4 minutes a precipitate began to separate. It was allowed to stand for 20 minutes and the precipitate (0.8 g.) then collected on a filter paper, m. p. 231°. The melting point of symmetrical diphenyl urea given in the literature is 230°, mixed m. p. 230°.

---

[12] Throughout this investigation, only sodium-dried benzene was used.

[13] Since only small amounts of material were used throughout this investigation, it was thought advisable to solate the urea derivatives by treating the isocyanates in solution with aniline rather than the free isocyanates.

By working up the filtrate from symmetrical diphenyl urea some more phenyl mercury bromide, a little unchanged mercury diphenyl and also an appreciable quantity of the symmetrical diphenyl urea were obtained.

m-**Nitro-N-Bromobenzamide.**—To 0.7 g. of *m*-nitro-N-bromobenzamide dissolved in 180 cc. of benzene 1 g. of mercury diphenyl was added. After 1 hour it still gave a positive test for active bromine, and the reaction was only complete after 2 $^3/_4$ hours' boiling. The precipitate (0.4 g.) that separated was identified as phenyl mercury bromide. From the filtrate after the addition of aniline and then ligroin a yellow crystalline compound (0.3 g.) was obtained which was identified as *m*-nitro-carbanilide, m. p. 197°. This melting point is not lowered by mixing the compound with known *m*-nitro-carbanilide.

The filtrate from the urea when evaporated to dryness and then worked up yielded some more phenyl mercury bromide and also *m*-nitro-carbanilide.

o- And *p*-nitro-N-bromobenzamides were treated in the same way as the *meta* isomer. The time of heating was from 2 to 3 hours. When worked up like the *meta* compound they yielded phenyl mercury bromide and the corresponding nitro-carbanilides which were identified by their melting points.

Action of N-Chloro-acetanilide on Various Compounds.

Mercury Diphenyl.—N-chloro-acetanilide (0.84 g.) was dissolved in 80 cc. of sodium-dried benzene and then 1.7 g. of mercury diphenyl added to it. The solution was then boiled for 14 hours, but even at the end of that time it still gave a strong test for active chlorine, and the mercury diphenyl was recovered by distilling the benzene *in vacuo*, and extracting the N-chloro-acetanilide with ligroin.

Aniline.—N-chloro-acetanilide (2 g.) was dissolved in 60 cc. of sodium-dried benzene and 0.6 g. of aniline added to it. The resulting solution was perfectly colorless, but turned dark after boiling it for 4 minutes. The reaction was complete in 20 minutes as indicated by the fact that the test for positive chlorine failed. Upon cooling a crystalline compound separated, (0.8 g.), which, after crystallization, melted at 114°. Its melting point was not lowered by mixing it with pure acetanilide.

To the filtrate from the acetanilide was added acetyl chloride to convert the dichloro-aniline into its acetyl derivative, and the mixture was warmed 10 minutes. The benzene solution was washed three times with water to destroy the excess of acetyl chloride, dried with sodium sulfate, and the benzene distilled. Crystals were thus obtained which upon crystallization melted at 146°. The melting point of 2,4-dichloro-aniline given in the literature is 147°; mixed m. p. 147°.

When dimethylaniline was used in place of aniline, acetanilide was also obtained and an oil, which was probably 2,4-dichloro-dimethylaniline. The latter compound is described in the literature as an oil.

Summary.

1. It has been shown that the Hofmann Rearrangement takes place when various acyl halogen amides, in sodium-dried benzene, are treated with mercury diphenyl.

2. It has been demonstrated that mercury diphenyl acts as a base in benzene solution.

3. A convenient method for the preparation of isocyanates is described.

4. It has been pointed out that the structure, R-Hg-R, for mercury

diaryl compounds has no sound theoretical or experimental basis, and the structure R-Hg-R is supported.

$$\overset{-\ ++\ -}{\text{R-Hg-R}}$$

5. It has been shown that N-chloro-acetanilide has no effect on mercury diphenyl, although it is a good chlorinating agent.

CHICAGO, ILL.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO AND THE OTHO S. A. SPRAGUE MEMORIAL INSTITUTE.]

MERCURI-ORGANIC DERIVATIVES. THE MERCURIZATION OF AROMATIC AMINES AND ITS RELATION TO THE THEORY OF SUBSTITUTION.

BY MORRIS S. KHARASCH[1] AND ISADORE M. JACOBSOHN.[2]

Received February 15, 1921.

The principles underlying the mercurization of aromatic compounds have occupied the attention of one of us (Kh.) for the past two years. The important fact that, in a mono-substituted benzene derivative, the mercury enters *para* or *ortho* to the group already present in the molecule, was pointed out early by Dimroth,[3] and has been substantiated by the vast amount of experimental work done by others. This fact of *ortho* and *para* substitution is particularly striking when one attempts to apply the theories of substitution to mercurization since mercury never enters *meta* to the group already present in the molecule. Even where the usual rules of substitution require that a *meta* derivative be formed, *e. g.*, with benzoic acid, benzophenone, and nitrobenzene, only *ortho* substituted mercury compounds have been isolated.

The phenomenon of mercurization was considered by Dimroth to be similar to that of nitration, sulfonation, etc., in the sense that the position taken by the entering mercury in compounds containing groups now considered electro-negative, *e. g.*, amino or hydroxyl groups, was quite in agreement with the rule of Crum Brown and Gibson. He considered the exceptional behavior of nitrobenzene, benzoic acid, and benzophenone as anomalous reactions which needed to be accounted for. However, until recently, no effort has been made to explain the orientation of mercury in the benzene molecule.[4] The rule of Crum Brown and Gibson, being purely empirical, offers no suggestion as to the mechanism of the

---

[1] National Research Fellow in Organic Chemistry.

[2] The material presented here is used by I. Jacobsohn in his dissertation presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Chicago.

[3] Dimroth, *Ber.*, **35**, 2853 (1902).

[4] Schoeller, Schrauth, and Liese (*Ber.*, **52B**, 1777 (1919)) apply the theory of Armstrong for substitution in aromatic amines to mercurization, the limitations of which theory will be pointed out later.