[CONTRIBUTION FROM THE DEPARTMENT OF PHYSIOLOGICAL CHEMISTRY, THE JOHNS HOPKINS UNIVERSITY]

THE BEHAVIOR OF ALIPHATIC DIAZO COMPOUNDS WITH DERIVATIVES OF METALS. I. MERCURI-ORGANIC DERIVATIVES AND MERCURIC SALTS WITH DIAZOMETHANE. (NOTE ON THE REACTION OF MERCURIC CHLORIDE WITH DIPHENYLDIAZOMETHANE)[1]

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Some years ago we were investigating the methylation with diazomethane of certain hydroxylated aromatic mercury derivatives,[2] as an aid to the elucidation of their structures. There was encountered, in the course of those studies, an interesting new reaction which seemed to involve essentially a transformation of the type represented by the equation

$$RHgX + CH_2N_2 \longrightarrow RHgCH_2X + N_2 \qquad (1)$$

The investigation of this reaction has recently been resumed by us and has included observations of the action of diazomethane and its derivatives upon a variety of simple mercuri-organic compounds and mercuric salts. Some of the results of the studies are recorded in this paper and certain theoretical implications set forth.

When *p*-tolylmercuric chloride, suspended in ether, is suitably treated with a molecular equivalent of diazomethane[3] a gas (nitrogen) is evolved and slightly soluble mercury di-*p*-tolyl remains suspended in the ether and may be separated from the latter by filtration; upon evaporation of the ether, there is obtained a third product, the hitherto unknown substance, bis-chloromethyl mercury.

$$2CH_3C_6H_4HgCl + 2CH_2N_2 \longrightarrow 2N_2 + (2CH_3C_6H_4HgCH_2Cl \longrightarrow)$$
$$CH_3C_6H_4HgC_6H_4CH_3 + ClCH_2HgCH_2Cl \qquad (2)$$

Thus diazomethane plays here the role of a peculiar type of "bridging" reagent which, itself, participates in the establishment of a new carbon-to-mercury bond. Its behavior, in this instance, bears a striking resemblance to its reactions[4] and those of some of its derivatives[5] with certain acid chlorides. Reference will be made to this further on. The assumption, implied in equation (2), that the unsymmetrical substance, chloromethyl *p*-tolyl mercury, is first formed and that this disproportionates to yield two

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[1] This paper was presented before the Division of Organic Chemistry at the Buffalo Meeting of the American Chemical Society, September, 1930.

[2] Hellerman and Newman, unpublished work; Minette D. Newman, Doctorate Dissertation, The University of Chicago, 1930.

[3] See the Experimental Part for details.

[4] For references see Malkin and Nierenstein, THIS JOURNAL, **52**, 1504 (1930); Bradley and Robinson, *ibid.*, **52**, 1558 (1930).

[5] Staudinger and co-workers, *Ber.*, **49**, 1940, 1959, 1976 (1916).

symmetrical mercuri-bis compounds is supported by the work presently to be described. That this unsymmetrical derivative, if formed first, would very readily undergo disproportionation, seems to us entirely likely in view of the relatively great disparity in the apparent electron affinities of the groups carried by the mercury atom, that of the *p*-tolyl group presumably being high with respect to that of the chloromethyl group.[6]

From the interaction of phenylmercuric chloride and diazomethane there was obtained a liquid product ($C_6H_5HgCH_2Cl$?). After some time the product began slowly to deposit crystals of mercury diphenyl. This behavior suggested disproportionation, a change that would again be accompanied by the formation of bis-chloromethyl mercury.[7] The residual oil, separated from the precipitated mercury diphenyl, yielded, when treated with hot alcoholic hydrogen chloride, the beautifully crystalline new substance, chloromethylmercuric chloride, $ClCH_2HgCl$.

$$C_6H_5HgCH_2Cl + HCl \longrightarrow C_6H_6 + ClHgCH_2Cl \qquad (3)$$

$$ClCH_2HgCH_2Cl + HCl \longrightarrow CH_3Cl + ClHgCH_2Cl \qquad (4)$$

This was also obtained when bis-chloromethyl mercury, one of the products from the interaction of diazomethane and *p*-tolylmercuric chloride or mercuric chloride (equation 8), was similarly treated.[8]

These results encouraged us to attempt, by means of the interaction of diazomethane and a suitable mercury compound, the direct preparation of a relatively stable unsymmetrical derivative, disproportionation of which would take place but slowly. For this purpose, benzylmercuric chloride was selected, on the supposition that the desired stability in the product might be attained if the chloromethyl group were "balanced" against a group which, like itself, appears to possess relatively low electron affinity.[9]

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[6] A large number of unsymmetrical mercury compounds, RHgR′, were prepared by Kharasch and Marker, THIS JOURNAL, **48**, 3130 (1926), by the use of the classical method whereby an organomagnesium halide is treated with an appropriate organomercuric halide. Careful control of the experimental conditions was found by them to be essential because of the tendency of these substances to undergo disproportionation. The results obtained from the decomposition of the unsymmetrical derivatives with alcoholic hydrogen chloride were used by these investigators in the construction of a table of organic groups in the order of their increasing "relative electronegativities" (apparent degrees of "affinity" or "attraction" of the organic groups for their assumed bonding electron pairs).

[7] Compare equation (2).

[8] Two reactions resulted when bis-chloromethyl mercury was treated with mercuric chloride: (1) the anticipated cleavage reaction in which the substance was converted to chloromethylmercuric chloride; and (2) an oxidation-reduction resulting in the formation of much *calomel.* For a discussion of the reactions of mercuri-bis compounds with mercuric halides consult Whitmore, "Organic Compounds of Mercury," The Chemical Catalog Company, New York, 1921, p. 65.

[9] "Groups" that have *marked attractions* for their bonding doublet pairs (for example, C_6H_5 or Cl) often appear to induce a lowering of the *apparent* electron affinity of methyl carbon atoms upon which they are substituted. This principle cannot be

$$C_6H_5CH_2HgCl + CH_2N_2 \longrightarrow N_2 + C_6H_5CH_2HgCH_2Cl \qquad (5)$$

As a matter of fact, benzyl chloromethyl mercury, the liquid product (obtained in practically quantitative yield) from the action of diazomethane upon benzylmercuric chloride, showed little apparent tendency to disproportionate while standing for a period of several weeks. The identity of the product was demonstrated by means of (a) analysis, (b) evidence of homogeneity after an attempted fractionation with ether, and (c) its behavior during decomposition with hydrogen chloride on the one hand and mercuric chloride on the other.

It seems worthy of emphasis that a completely unsymmetrical breakdown in benzyl chloromethyl mercury resulted from the action upon it of alcoholic hydrogen chloride. The only mercury compound produced as a result of this process was chloromethylmercuric chloride. This was obtained directly in a high state of purity and in good yield. In the reaction mixtures from several independent experiments benzylmercuric chloride was sought but could not be detected. The change may, therefore, be represented by the following equation.[10]

$$C_6H_5CH_2HgCH_2Cl + HCl \longrightarrow C_6H_5CH_3 + ClHgCH_2Cl \qquad (6)$$

Of especial interest in connection with the foregoing are the reactions of mercuric salts with aliphatic diazo compounds. It had already been incidentally observed[11] that diazomethane *reduces* mercuric chloride. However, employment of the experimental procedure developed in this work has demonstrated that the course of the reaction may be very different. From mercuric chloride with one molecular equivalent of diazomethane, there was obtained in high yield chloromethylmercuric chloride.

$$ClHgCl + CH_2N_2 \longrightarrow N_2 + ClCH_2HgCl \qquad (7)$$

The same salt with two equivalents of the diazo compound yielded the expected symmetrical derivative, bis-chloromethyl mercury.

$$ClHgCl + 2CH_2N_2 \longrightarrow 2N_2 + ClCH_2HgCH_2Cl \qquad (8)$$

It has already been stated that chloromethylmercuric chloride is obtained as a product when bis-chloromethyl mercury is decomposed by either hydrogen chloride or mercuric chloride. Both compounds are physiologically active; for example, in minute quantities they act upon the skin causing a "dermatitis." This may be severe in the case of individuals who are very susceptible to the action of mercurials. The di-chloromethyl compound is a powerful vesicating agent and causes painful blisters.

elaborated here. It is illustrated by certain aspects of the chemical behavior of such compounds as benzyl-, benzohydryl- and triphenylmethylmagnesium halides, highly phenylated hydrocarbons, phenylated or halogenated acetic acids, etc.

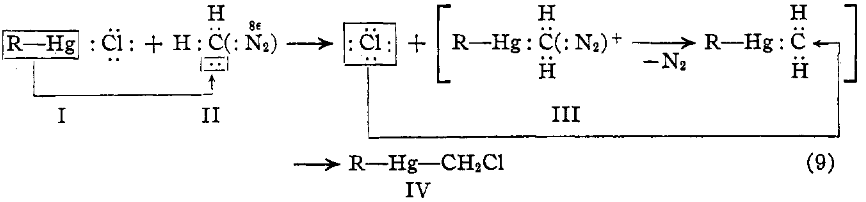
[10] When mercuric chloride was substituted for hydrogen chloride in this reaction, there was produced the expected *mixture* of chlorides. On the basis of the result of the hydrogen chloride reaction it would be concluded, following Kharasch's reasoning (see Ref. 6), that the group, $ClCH_2$—, is less "electronegative" than the benzyl group.

[11] Meerwein and Burneleit, *Ber.*, **61B**, 1843 (1928).

In contrast to the chloride, mercuric iodide does not react "smoothly" with diazomethane. With either one or two molecular equivalents of the diazo compound, mercuric iodide yields but a small amount of a pure crystalline product that is probably bis-iodomethyl mercury, $(ICH_2)_2Hg$. A large proportion of gummy material, that has not yet been carefully examined, is formed at the same time. This difference in behavior may be related to the fact that the tendency toward the formation of complex salts seems to be more pronounced in the case of mercuric iodide than mercuric chloride. Under the experimental conditions diazomethane may in effect be acting upon the simple salt, HgI_2, in the presence of "complexes," $(HgI_2)_n$.[12]

Diazomethane reacts also with mercuric acetate and with "bases" such as phenylmercuric hydroxide.[13] These reactions involve some novel features and require further study. Toward mercury diphenyl,[14] mercury di-*p*-tolyl and mercuric cyanide the diazo compound is not active under the experimental conditions used. The aliphatic diazo compounds react with certain salts and organic derivatives of metals other than mercury. This general behavior is now under investigation in this Laboratory, since it appears to hold a considerable interest from the theoretical as well as the synthetic point of view.

It has been found useful to interpret the reaction type described in this paper in terms of an "electronic" formula for diazomethane and its derivatives. The mechanism is schematically represented as follows.



$$\boxed{R{-}Hg}\ :\underset{\cdot\cdot}{\ddot{Cl}}: + H:\overset{H}{\underset{\boxed{\cdot\cdot}}{\ddot{C}}}(\overset{8\epsilon}{:}N_2) \longrightarrow \boxed{:\underset{\cdot\cdot}{\ddot{Cl}}:} + \left[R{-}Hg:\overset{H}{\underset{H}{\ddot{C}}}(:N_2)^+ \xrightarrow[-N_2]{} R{-}Hg:\overset{H}{\underset{H}{\ddot{C}}}\leftarrow\right]$$

I II III

$$\longrightarrow R{-}Hg{-}CH_2Cl \qquad (9)$$

IV

The formula (II) is essentially that proposed by Professor W. A. Noyes for diazomethane, except that eight valence electrons (8ϵ) are assigned to the diazo group as a whole since their exact distribution is not certain.[15] The "driving force" of the reaction is considered to be related to the ultimate "sharing" of an electron pair of the diazo carbon atom with the relatively oxidized mercuric atom. The diazonium ion (III) might thus transi-

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[12] Compare Sakurai, *J. Chem. Soc.*, **37**, 658 (1880); *ibid.*, **39**, 485 (1881).

[13] Compare Buchner, *Ber.*, **28**, 218 (1895).

[14] Mercury diphenyl, after treatment with diazomethane in ether solution, was recovered unchanged.

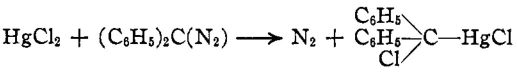
[15] This formula is used here as a *convenience* to depict a potentially reactive form of diazomethane. The enclosed electron pair ($\boxed{\cdot\cdot}$) is considered to be only potentially "exposed" as represented. The matter will be more fully discussed in a forthcoming communication by the senior author and R. L. Garner. See also Hellerman, Cohn and Hoen, THIS JOURNAL, **50**, 1722 (1928), footnote 25.

torily exist; but the concomitant destruction of the electrical neutrality of the diazo molecule would cause the diazo group to be "lost" together with the electron pair with which it is bound to the carbon atom (*i. e.*, as N_2) and the latter would again complete its octet by attracting Cl^- with the elaboration of the final product (IV).

An analogous interpretation for the reactions of acid chlorides[4,5] with diazo compounds should be of service. Here the carboxyl carbon atom is the *relatively* oxidized atom that would "share" an electron pair with the diazo carbon atom in the first stage of the reaction. Such reactions seem to be closely allied to the changes involved in the decomposition of diazo compounds with acids, in which hydrogen ions presumably share the "exposed" doublet pairs.

Staudinger has demonstrated that chloro-ketonic derivatives may be formed when certain acid chlorides react with aliphatic diazo compounds in which the diazo carbon atoms are *fully substituted* (*i. e.*, carry no hydrogen atoms). In the following section preliminary results are presented that indicate that a diazo compound of that type may also react with mercuric chloride. The applicability of the concept of "electron-sharing" as tentatively suggested in the foregoing is thus strengthened.

Mercuric Chloride with Diphenyldiazomethane.—When mercuric chloride is treated with diphenyldiazomethane (I), under the conditions used, nitrogen is evolved and there is obtained, as the main product, a white amorphous solid which is not appreciably soluble in dry ether. This solid has the mercury content calculated for chlorodiphenylmethylmercuric chloride (II).



$$HgCl_2 + (C_6H_5)_2C(N_2) \longrightarrow N_2 + \begin{matrix}C_6H_5\\C_6H_5\\Cl\end{matrix}\!\!>\!C\text{—}HgCl \qquad (10)$$

I II

Upon exposure to moist air, it is converted chiefly to benzophenone and calomel. Hydrogen chloride is also formed. Of preëminent interest is its behavior when shaken with moist ether. Calomel is produced *quantitatively* and, at the same time, organic material dissolves in the ether, which is abruptly colored yellow. This indicates cleavage at the carbon-to-mercury bond, a property to be anticipated for a substance of the type assumed.[16] From the ethereal solution, after spontaneous evaporation of the solvent (during which the yellow color vanishes), there is obtained chiefly a white crystalline substance. The properties of the latter indicate that it is 1,2-dichlorotetraphenylethane. The following equation depicts the assumed course of the decomposition.

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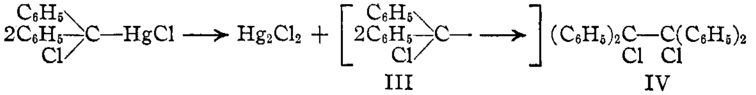
[16] Triphenylmethylmercuric bromide, $(C_6H_5)_3CHgBr$, would be a similar substance of much theoretical interest. It is not produced when triphenylmethylmagnesium bromide is treated with mercuric bromide. Instead, the mercuric salt is reduced; triphenylmethyl bromide is a product of the reaction (unpublished results of the authors).



$$2(C_6H_5)_2ClC{-}HgCl \longrightarrow Hg_2Cl_2 + \left[\underset{\text{III}}{2(C_6H_5)_2ClC{-}} \longrightarrow\right] \underset{\text{IV}}{(C_6H_5)_2CCl{-}CCl(C_6H_5)_2} \qquad (11)$$

Work is being continued upon the preparation and properties of unstable metallic derivatives of this type (II) and upon the probable elaboration from them of free radicals (III). Enough has been accomplished here to indicate that the new reaction type considered in this paper is applicable also to *derivatives* of diazomethane and that the mechanism suggested [equation (9)] for the course of such reactions is not inconsistent with the experimental results.

Experimental Part

For the addition of diazomethane to the various mercury compounds treated, a simple standard type of apparatus was found useful. The reaction vessel, set up in a good hood, was a three-necked flask of convenient volume fitted with (a) a short return condenser ("closed" with a calcium chloride tube), (b) a mercury-sealed stirrer and (c) the delivery end of a condenser which in turn was sealed to the outlet tube of a suitable distilling flask to be used for the generation of diazomethane. The distilling flask was equipped with a dropping funnel.

The Interaction of Mercuric Chloride and Diazomethane in Equimolecular Proportions: Chloromethylmercuric Chloride, $ClCH_2HgCl$.—Pure mercuric chloride, 13.6 g. (0.05 mole), and 200 cc. of ether (c. p.) were mixed in the reaction flask which was placed in an ice-bath. The mixture was well stirred mechanically. In the distilling flask a molecular equivalent (2.1 g.) of diazomethane[17] was prepared in the usual manner by the slow addition of 12.0 cc. of nitrosomethylurethan to a mixture of 60 cc. of ether and 18 cc. of a 25% solution of potassium hydroxide in methyl alcohol. The ethereal diazomethane was distilled during its preparation directly into the reaction vessel at such a rate that the mercuric chloride was always in excess and the reaction mixture remained colorless. The reaction took place rapidly with the evolution of nitrogen. At the end of the operation the product had crystallized partially. It was obtained in almost pure form and in practically quantitative yield after the solvent had been allowed to evaporate spontaneously. Recrystallization of the product from 95% ethanol yielded micaceous scales of the pure substance; m. p. 131° (corr.). The substance is slightly soluble in water. It is appreciably hydrolyzed in its aqueous solution. It is decomposed in the presence of concentrated sodium hydroxide with the formation of metallic mercury.

Anal. Subs., 0.2776 g.: required 16.25 cc. of NH_4CNS (1.00 cc. = 0.01196 g. Hg). Calcd. for CH_2Cl_2Hg: Hg, 70.3. Found: Hg, 70.0. Subs., 0.4287, 0.4945 g.: AgCl, 0.4384, 0.4976. Calcd. for CH_2Cl_2Hg: Cl, 24.8. Found: Cl, 25.3, 24.9.

Analytical Methods. (1) Mercury.—The convenient thiocyanate method gave excellent results when used in conjunction with the treatment (somewhat modified) recommended by Kharasch and Flenner (cited by Hillebrand and Lundell)[18] for mercury compounds containing halogens.

(2) **Halogens.**—In a long-necked flask fitted with a condenser (preferably with a ground-glass seal) the substance, suspended in anhydrous ethanol, is decomposed by

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[17] The directions given in Houben–Weyl, "Die Methoden der organischen Chemie," Georg Thieme, Leipzig, 1923, Vol. III, p. 124, were found reliable; it was considered that 1 cc. of ethyl-N-methyl-N-nitrosocarbamate (nitrosomethylurethan) produced 0.18 g. of diazomethane.

[18] Hillebrand and Lundell, "Applied Inorganic Analysis," Wiley, New York, 1929.

the addition of pieces of pure sodium. Water is then added and the alcohol removed by distillation. The residual solution is filtered and neutralized with nitric acid. Halogen is determined in the usual manner.

Mercuric Chloride with Diazomethane in Excess: Bis-Chloromethyl Mercury, $(ClCH_2)_2Hg$.—In the standard apparatus and under conditions of temperature, stirring, etc., identical with those set forth in the preceding section, mercuric chloride in ethereal solution and suspension was treated with two molecular equivalents and a 10% excess of diazomethane. At the end of the operation, the solution of the product was colored yellow (excess diazomethane). It was filtered from a trace of calomel and the filtrate evaporated as completely as possible in a rapid stream of calcium chloride-dried air. A slightly colored oil remained; its weight was that expected, assuming that bis-chloromethyl mercury had been formed quantitatively. The crude product was assayed (calcd.: Hg, 67.0. Found: Hg, 63.6, 63.4). After several days the oil crystallized, when manipulated; the crystals consisted of rods and plates. Although they were quite soluble in various organic solvents, it was found possible to effect the purification of a quantity sufficient for analysis by means of recrystallization from ether. A second recrystallization from isopropyl ether yielded material with the same melting point. The latter property was evidently materially affected by the presence of small amounts of impurities; m. p. 37–40° (rather indefinite). The molten substance re-solidified upon cooling. The physiological properties are touched upon in the first part of the paper.

Anal. Calcd. for $C_2H_4Cl_2Hg$: Hg, 66.98. Found: Hg, 66.83, 66.97.

Bis-Chloromethyl Mercury with Mercuric Chloride.—Of the bridged compound, 2 g. was heated with a mixture of 15 cc. of ethanol and 2 g. of mercuric chloride just below the boiling point of the solvent for one-half hour. The compound dissolved; a solid product precipitated. The mixture was filtered while hot. The residue consisted of 0.91 g. of calomel, which was identified by its physical and chemical properties. When the filtrate was cooled there were obtained characteristic spangles of chloromethylmercuric chloride. The product was pure; it melted at 128° (uncorr.) and did not depress the melting point of known chloromethylmercuric chloride.

Bis-Chloromethyl Mercury with Hydrogen Chloride.—Some of the substance was heated for ten minutes with a freshly prepared, concentrated solution of hydrogen chloride in ethanol at the boiling point of the solvent. Crystals did not appear until the reaction mixture had been permitted to stand at room temperature for a week. After most of the solvent had evaporated spontaneously, the characteristic scales that had been formed were collected and washed with alcohol. They were in all respects identical with chloromethylmercuric chloride; m. p. 129° and "mixed m. p." 129°. This was the only mercury compound that could be isolated from the reaction mixture.

$$ClCH_2HgCH_2Cl + HCl \longrightarrow CH_3Cl + ClCH_2HgCl \qquad (12)$$

The Interaction of Diazomethane and *p*-Tolylmercuric Chloride.—*p*-Tolylmercuric chloride, 16.4 g. (0.05 mole), suspended in 100 cc. of pure ether, was treated at 0° with 2.4 g. of diazomethane (0.055 mole) in a manner entirely similar to that described in the foregoing except that the ethereal diazomethane was added rather rapidly. There was no difficulty in controlling the action, which was slow but increased in rate when the temperature was raised somewhat. After the evolution of nitrogen had entirely ceased (two hours) the suspended solid was collected on a filter and washed *well* with ether. The product contained no chlorine; it was identified as mercury di-*p*-tolyl (7.1 g.) by its solubility behavior and its melting point (233–236°). It depressed the melting point of a sample of *p*-tolylmercuric chloride and did not depress that of authentic mercury di-*p*-tolyl ("mixed m. p." 236°).

The ether filtrate from the solid product was evaporated in a stream of dry air. A slightly colored viscous oil remained which resembled in appearance and properties crude *bis*-chloromethyl mercury. Possibly some chloromethyl *p*-tolyl mercury was present. The oil was treated with concentrated alcoholic hydrogen chloride according to the directions of the preceding section. The results of this experiment were analogous to those noted for the corresponding decomposition of known bis-chloromethyl mercury. But one substance containing mercury was isolated. The product, obtained in excellent yield, was identical in all respects with samples of chloromethylmercuric chloride which had been prepared during the course of this investigation from other sources. It melted at 131° (corr.). For analysis it was recrystallized from ethanol and dried over phosphoric anhydride and paraffin.

Anal. Calcd. for CH_2Cl_2Hg: Hg, 70.3. Found: Hg, 69.7, 70.2.

The Interaction of Diazomethane and Phenylmercuric Chloride.—Phenylmercuric chloride was treated with diazomethane according to the general procedure. During the action, the evolution of gas proceeded evenly and the mercurial gradually "dissolved"; the action ceased abruptly and the reaction mixture became yellow immediately after one molecular equivalent of the diazo compound had been added. The solution thus obtained was cooled (5°) and concentrated in a stream of dry air. A colorless oil remained. Upon standing some needle-like crystals were deposited from the oil and the amount soon became very appreciable. Those were collected and washed with ether; they were found to be slightly impure mercury diphenyl. They were identified (a) by means of comparison with authentic mercury diphenyl and (b) by the observation that their decomposition in the presence of alcoholic mercuric chloride yielded only pure phenylmercuric chloride (m. p. 252°, "mixed m. p." 252°).

The residual oil (filtrate from the mercury diphenyl) was mixed with alcoholic hydrogen chloride and the mixture heated for fifteen minutes. When the mixture was cooled there crystallized pure chloromethylmercuric chloride, identified by comparison with authentic material (see above).

The Interaction of Diazomethane and Benzylmercuric Chloride: Benzyl Chloromethyl Mercury, $C_6H_5CH_2HgCH_2Cl$.—Benzylmercuric chloride, 8.18 g., was suspended in 200 cc. of ether (c. P.). To the mixture, cooled to 0° and stirred well, was added 1.05 g. of diazomethane (a 5% excess) in ether solution. The general procedure, as described in preceding experiments, was employed. The reaction proceeded slowly with the evolution of nitrogen; the gas ceased to be evolved after one equivalent of the diazo compound had been added and at this stage all of the suspended solid had "dissolved." Ether and excess diazomethane were next removed in a blast of clean, dry air and an oil, colored faintly yellow, remained. Crystallization of the product could not be effected. The initial unpleasant odor of the product vanished after the oil had been brought to constant weight (at room temperature) in a vacuum desiccator (over chipped paraffin and phosphoric anhydride). The yield of the product was quantitative. Its analysis indicated that it was either an equimolecular mixture of mercury dibenzyl and mercury di-chloromethyl or the unsymmetrical compound, benzyl chloromethyl mercury. That the latter alternative is correct was rather convincingly demonstrated by the experiments to be described.

Anal. Calcd. for C_8H_9ClHg: Hg, 58.8. Found: Hg, 58.4, 58.8.

Decomposition with Hydrogen Chloride.—Benzyl chloromethyl mercury, 22.4 g., was treated with 125 cc. of alcoholic hydrogen chloride on a water-bath for fifteen minutes. The odor of toluene became evident almost at once. To the solution, which had been freed from a suspended trace of mercury by means of filtration, was added water; a large amount of solid was precipitated. The solid was collected and directly (without being washed) dried in a vacuum desiccator over paraffin and phosphoric anhydride. It consisted of 14.8 g. of practically pure chloromethylmercuric chloride (m. p. 129–131°; m. p. of a mixture with authentic material, 129–131°). The filtrate contained more of the same substance. The product was recrystallized from ethanol; m. p., unchanged. No other mercury compound could be isolated from the reaction mixture. The decomposition of benzyl chloromethyl mercury by hydrogen chloride took thus the course depicted by equation (6).

Decomposition with Mercuric Chloride.—The decomposition of benzyl chloromethyl mercury with hot alcoholic mercuric chloride resulted in the production of a substantial amount of calomel together with a mixture of benzylmercuric chloride and chloromethylmercuric chloride. The nature of the mixture was indicated by its melting point behavior before and after a partial fractionation with alcohol; the products were compared with the pure individual chlorides.

An Attempt at Fractionation.—Some benzyl chloromethyl mercury (about 8 g.) was well agitated with a little ether until about one-third had dissolved. The extract was separated from residual oil (R) by decantation and the two fractions freed from ether and brought to constant weight in the manner already described. The two fractions were found to be identical in their chemical behavior (decomposition reactions, etc.); their mercury contents were identical.

Anal. Calcd. for C_8H_9ClHg: Hg, 58.8. Found: (first fraction, R) Hg, 58.6; (second fraction) Hg, 58.6.

It had been observed that occasionally freshly prepared benzyl chloromethyl mercury contained in suspension a trace of mercury, from which it could be separated by filtration. As the unsymmetrical compound stood the formation of mercury continued; heat or exposure to light accelerated the process. The nature of this oxidation–reduction change was not studied in detail; such behavior is not unusual for compounds of this type. The fractions described above were permitted to stand for several weeks, after which they were separated from precipitated mercury. They were then assayed for chlorine and, as was expected, the chlorine contents were somewhat high.

Anal. Calcd. for C_8H_9ClHg: Cl, 10.4. Found: (first fraction, R) Cl, 11.0; (second fraction) Cl, 10.8.

Diazomethane and Mercuric Iodide: Bis-iodomethyl Mercury, $(ICH_2)_2Hg$(?).—Of red mercuric iodide (c. p.), one-twentieth mole was treated with one-tenth mole of diazomethane, the procedure being entirely similar to the general method already described. A vigorous action ensued and nitrogen was evolved. However, much solid remained undissolved. Some of it was probably yellow mercuric iodide. When the action had ceased, the ether solution was still deeply colored (yellow diazomethane). The solution was separated from undissolved yellowish material (S) and the removal of ether and diazomethane effected as usual. During the evaporation, some well-formed long needles crystallized; m. p. 80–84°. The solid (S) possessed a disagreeable odor; when heated with various alcohols or ethers it became gummy and but little dissolved in the solvents. Nevertheless, some indefinite crystalline matter precipitated when methyl alcohol, ether or isopropyl ether extracts were cooled. After repeated recrystallizations of this from isopropyl ether, there was obtained a pure substance as fine, white, silky plates; m. p. 82–84°. The total yield amounted to but a few grams. In another preparation in which mercuric iodide was treated with one molecular equivalent of diazomethane, diazomethane again remained in excess and the final results were similar to those described, except that less of the pure product was obtained.

Anal. Calcd. for $C_2H_4I_2Hg$: Hg, 41.6. Found: Hg, 41.6, 41.7.

Diazomethane with Mercuric Cyanide.—Of powdered mercuric cyanide, 6.32 g. (one-fortieth mole) suspended in ether was treated with diazomethane (one-fortieth mole). No action took place, although the mixture was finally boiled (refluxed) for some time. There was recovered 6.20 g. of the mercuric salt.

Diphenyldiazomethane and Mercuric Chloride.—To pure, dry mercuric chloride, one-twentieth mole, in 150 cc. of anhydrous ether, cooled to 0° and stirred mechanically, was added during one hour a molecular equivalent of diphenyldiazomethane[19] (dissolved in a little ether). Care was taken to exclude moisture. The pink color of the diazo compound vanished, a gas was evolved and a pale yellow product, insoluble in the ether, appeared. The product was rapidly brought upon a Buchner funnel, washed thoroughly with anhydrous ether and dried at room temperature for twelve hours in a vacuum over phosphoric anhydride and chipped paraffin. When the preparation was carried out as described, the ether filtrates contained but little dissolved material. An analysis indicated that the product might be chlorodiphenylmethylmercuric chloride, $Cl(C_6H_5)_2C \cdot HgCl$.

Anal. Calcd. for $C_{13}H_{10}HgCl_2$: Hg, 46.9. Found: Hg, 47.5.

When some of the product was exposed to moist air, it was hydrolyzed and decomposed rather rapidly with the evolution of hydrogen chloride. All of the mercury in the initial compound was recovered as *calomel*, insoluble in ether, when the decomposed material was extracted with that solvent. When the ether was allowed to evaporate spontaneously there remained a colorless oil that crystallized in prismatic plates when "seeded" with benzophenone. That the material was chiefly benzophenone was indicated by its melting point and conversion to benzophenone oxime. Air oxidation was probably a factor here; further data are required for an accurate description of the nature of the change. Calomel is also one of the products when the compound is decomposed thermally in the presence of xylene.

Some of the supposed chlorodiphenylmethylmercuric chloride was covered with anhydrous ether. When a drop of water was added and the mixture shaken, the ether became *pronouncedly yellow* and a white solid remained undissolved. That the latter was calomel was proved by its properties (ammonia test, etc.) and an assay of its mercury content. The formation of calomel was shown to be quantitative. Samples were decomposed as described; the residues of calomel were collected in Gooch crucibles, washed well with ether, alcohol and water and dried to constant weight over phosphorus pentoxide.

Anal. Subs., 0.2994, 0.2978: Hg_2Cl_2, 0.1656, 0.1635. Calcd. for $C_{13}H_{10}Cl(HgCl)$: (HgCl), 55.2. Found: (HgCl), 55.3, 54.9.

From the yellow ether filtrates (from the calomel) the solvent was permitted to evaporate spontaneously. The residue consisted of a portion very soluble in ether and a less soluble part. The former portion contained benzophenone. The less ether-soluble material consisted of large, white, thick, rhomboidal plates. These were purified by means of crystallization and recrystallization from a mixture of benzene and isopropyl ether (1:3). They melted and decomposed at 183° with the evolution of hydrogen chloride. The physical and chemical properties of this product and its analysis indicated that it was 1,2-dichlorotetraphenylethane.[20]

Anal. Subs., 0.2449: CO_2, 0.6943; H_2O, 0.1092. Calcd. for $C_{26}H_{20}Cl_2$: C, 77.4; H, 4.96. Found: C, 77.3; H, 4.98.

Summary

1. It is shown that, under appropriate conditions, diazomethane reacts with a variety of mercuric salts and mercuri-organic derivatives with the formation of interesting new products. For example, from mercuric chloride, mercuric iodide and benzylmercuric chloride there are obtained, respectively, bis-chloromethyl mercury (and chloromethylmercuric chlo-

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[19] Staudinger, Anthes and Pfenninger, *Ber.*, **49**, 1932 (1916).

[20] Schmidlin and Escher, *ibid.*, **43**, 1153 (1910).

ride), bis-iodomethyl mercury and benzyl chloromethyl mercury. The primary product of the interaction of diazomethane and *p*-tolylmercuric chloride undergoes disproportionation, yielding mercury di-*p*-tolyl and bis-chloromethyl mercury; that from phenylmercuric chloride behaves analogously.

2. There are described the reactions with alcoholic hydrogen chloride and those with mercuric chloride of bridged mercury compounds prepared in this work. With the former reagent benzyl chloromethyl mercury yields toluene and chloromethylmercuric chloride and no benzylmercuric chloride.

3. Aliphatic diazo compounds react also with some other types of mercury compounds and with certain salts and organic derivatives of metals other than mercury. Mercuric chloride and *diphenyldiazomethane* interact forming, apparently, diphenylchloromethylmercuric chloride. The latter displays interesting decomposition reactions.

4. Certain theoretical implications of the results of the investigation are discussed.

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

AN OPTICAL METHOD FOR THE STUDY OF REVERSIBLE ORGANIC OXIDATION-REDUCTION SYSTEMS.
I. PARA-BENZOQUINONES[1]

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Introduction

Extensive studies have been made on the reduction potentials of reversible organic oxidation-reduction systems.[2] In one of these investigations, Conant and Fieser[2h,k] determined the oxidation-reduction potentials of a number of systems composed of a quinone and its hydroquinone referred to the solid, dissolved and gaseous states.

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[1] (a) The work described in this paper constituted part of a thesis submitted to the Graduate Faculty of the University of Minnesota by Donovan E. Kvalnes in partial fulfilment of the requirements for the degree of Doctor of Philosophy, July, 1931. This paper was prepared by the junior author after the death of Dr. W. H. Hunter.—L. I. Smith. (b) Presented at the spring meeting of the American Chemical Society, New Orleans, 1932.

[2] (a) Granger and Nelson, THIS JOURNAL, **43**, 1401 (1921); (b) Clark, *J. Wash. Acad. Sci.*, **10**, 225 (1920); (c) Clark, *Science*, **54**, 557 (1921); (d) Biilmann, *Ann. chim.*, **15**, 109 (1921); (e) Conant, Kohn, Fieser and Kurtz, THIS JOURNAL, **44**, 1382 (1922); (f) La Mer and Baker, *ibid.*, **44**, 1954 (1922); (g) Conant and Fieser, *ibid.*, **44**, 2480 (1922); (h) Conant and Fieser, *ibid.*, **45**, 2194 (1923); (i) Biilmann, *Trans. Faraday Soc.*, 676 (1923); (j) Conant and Fieser, THIS JOURNAL, **46**, 1858 (1924); (k) Conant, *ibid.*, **49**, 293 (1927); (l) Fieser, *ibid.*, **51**, 3101 (1929).