155. *Reaction between Mercuric Acetate, Ethylene, and Amines.*

By Georg Sachs.

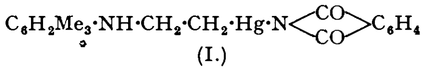
The formation of organic mercury compounds from mercuric acetate and ethylene in the presence of amines has been studied. From the reaction with mesidine, N-(2-*phthalimidomercuriethyl*)*mesidine* and NN-*bis*-(2-*phthalimidomercuriethyl*)*mesidine* were isolated. Their structures were established by analogy and by the action of acetyl chloride upon the first substance, which afforded *aceto*-(2-*chloromercuriethyl*)*mesidide*. With pyridine, salts of a bivalent kation $[Hg{\cdot}C_2H_4{\cdot}C_5H_5N]^{++}$ were obtained. The *mercuribromide, mercuri-iodide,* and the unstable *thiocyanate* are described.

When mercuric salts such as the acetate are added to olefinic substances in the presence of water (see, *e.g.*, Hofmann and Sand, *Ber.*, 1900, **33**, 1340, 1353; Biilman, *ibid.*, p. 1647) or to an organic hydroxylic compound such as alcohol (*e.g.*, Schoeller, Schrauth, and Essers, *Ber.*, 1913, **46**, 2864), one of the acid radicals is displaced by the less electronegative group OR(R = H or alkyl). The resulting substances contain the grouping $\cdot\overset{|}{C}(HgX)\cdot\overset{|}{C}(OR)\cdot$ (X = acid radical).

The work now described was undertaken in order to determine whether amines could play a part analogous to that of hydroxyl compounds. Daskais (U.S.P., 2,329,883, 2,369,339; *Chem. Abs.*, 1944, **38**, 1604; 1945, **39**, 3618) effected replacement of the alkoxyl radical in the β-position with regard to mercury in the above compounds by an acylimido-radical, so preparing compounds with a nitrogen atom in that position. While this work was in progress, Freĭdlina and Kochetkova (*ibid.*, 1946, **40**, 3450) reported the preparation of a compound $C_5H_{10}N{\cdot}CH_2{\cdot}CH_2{\cdot}HgCl$ from mercuric acetate, ethylene, and piperidine, and Kochetkova, Freĭdlina, and Nesmeyanov (*ibid.*, 1948, **42**, 1572) have prepared the corresponding diethylamine compound.

In the present work an aromatic amine and pyridine were employed. Mesidine, as aromatic amine, was preferred to aniline which, owing to the easy replacement of *o*- and *p*-hydrogen by HgX, gave, in preliminary experiments, a variety of impure substances. Mesidine, on the other hand, is not mercurated noticeably under the experimental conditions.

The organic mercury compounds formed when ethylene is absorbed by a mixture of mercuric acetate and excess of mesidine were precipitated in the form of the phthalimides, as the more common anions, except the chlorate ion, did not give well-crystallised precipitates. The purified main product had the composition of N-(2-*phthalimidomercuriethyl*)*mesidine* (I). Since both



$C_6H_2Me_3{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}Hg{\cdot}N{<}{}^{CO}_{CO}{>}C_6H_4$

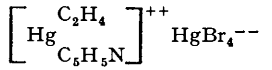
(I.)

$C_6H_2Me_3{\cdot}N[CH_2{\cdot}CH_2{\cdot}N{<}(CO)_2{>}C_6H_4]_2$ (II.)

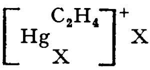
$C_6H_2Me_3{\cdot}NAc{\cdot}CH_2{\cdot}CH_2{\cdot}HgCl$ (III.)

hydrogen atoms in the amino-group of mesidine are reactive, the *bis-compound* (II) was obtained as by-product as in the case of water in which also one or both hydrogen atoms may be exchanged for radicals derived from olefins and mercuric salts (Hofmann and Sand, *Ber.*, 1900, **33**, 1340, 2692). The adoption of a structure corresponding to that of the piperidine compound was justified by the action of acetyl chloride on (I), which leads to formation of phthalimide and *aceto*-(2-*chloromercuriethyl*)*mesidide* (III). Substance (III) yields acetomesidide when boiled with concentrated hydrochloric acid; otherwise it is surprisingly stable against reagents which usually split the mercury–carbon linkage. The stabilising effect of acylation has also been observed in the dibenzoylation of 2 : 3-dihydroxypropylmercury iodide (Sand, *Ber.*, 1901, **34**, 1393).

Mercuric acetate, when wetted with pyridine, absorbs ethylene slowly. For preparative purposes the materials were dissolved in acetic acid. The *mercuribromide* of a *mercury–ethylene–pyridine complex* (IV) and a corresponding *mercuri-iodide* could be isolated.

(IV.) 

$$\left[\mathrm{Hg}\begin{matrix}\mathrm{C_2H_4}\\ \\ \mathrm{C_5H_5N}\end{matrix}\right]^{++}\mathrm{HgBr_4}^{--}$$

 (V.)

$$\left[\mathrm{Hg}\begin{matrix}\mathrm{C_2H_4}\\ \\ \mathrm{X}\end{matrix}\right]^{+}\mathrm{X}^{-}$$

In accordance with the formulation (IV), only one of the two mercury atoms gives the normal reactions with ammonia and with ammonium sulphide The use of the complex formula enables these substances to be contrasted with the addition compounds of mercuric salts and ethylene only, to which the discoverers (Hugel and Hibou, *Chim. et Ind.*, 1929, Special Number, p. 296) attributed a similar formula, such as (V; X = acid radical). This explains why in these two types of substance one or two acid valencies respectively are exchangeable in ionic reactions.

Although the complex formula adequately explains the properties so far described, this mode of representation is out of date. It has, however, been revived, in a certain respect, by Nesmeyanov who, with his co-workers (*Chem. Abstr.*, 1946, **40**, 2122, 4659, 4686, 6567), had found that the properties of the addition compounds between mercuric chloride and acetylene may be represented partly by, *e.g.*, $\mathrm{CH{\vdots}CH,HgCl_2}$ and partly by $\mathrm{Cl{\cdot}CH{:}CH{\cdot}HgCl}$. He suggested that resonance occurs between the two formulæ, in one of which the parts of the molecule are not held together by covalencies, describing such compounds as " quasi-complex ", and adducing evidence that all substances formed from mercuric salts and unsaturated compounds may be of this character (*Bull. Soc. chim.*, 1946, [v], **13**, 569). According to this conception, the complex indicated above should resonate with a structure such as $[\mathrm{C_5H_5N^{+}{\cdot}CH_2{\cdot}CH_2{\cdot}Hg^{+}}]\mathrm{X_2}^{-}$, though this formula still remains to be confirmed.

Roughly one molecule of ethylene is absorbed per atom of mercury in the preparation of these substances. The *thiocyanate* precipitate approaches closely the composition corresponding to formula [IV, with $(\mathrm{SCN})_2$ in place of $\mathrm{HgBr_4}$] if allowance is made for its instability. It does not contain ionogenic mercury. Attempts to obtain halides of the analogous simple formula failed.

EXPERIMENTAL.

N-2-(*Phthalimidomercuriethyl*)*mesidine*.—The yellow paste formed from mesidine (6 g.) and mercuric acetate (5 g.) was shaken with ethylene under slight pressure. The rate of absorption increased, and the mixture gradually turned into a viscous liquid, reaction being complete in 2 days, and about 1 mol. per mol. of mercury salt being absorbed. The mixture was diluted with acetone (20 c.c.), separated from a little grey deposit, and precipitated with a solution of sodium phthalimide, prepared by dissolving phthalimide in an equivalent quantity of a N-solution of sodium hydroxide in 90% alcohol. (Use of absolute alcohol led to precipitation of sodium phthalimide.) Crystallisation was favoured by inoculation and stirring. The *substance* was recrystallised from ethyl acetate in which 20% of it remained undissolved; the yellowish crystals (Found : N, 5·5; Hg, 39·7; $\mathrm{C_2H_4}$, 5·6. $\mathrm{C_{19}H_{20}O_2N_2Hg}$ requires N, 5·5; Hg, 39·4; $\mathrm{C_2H_4}$, 5·5%) had m. p. 188—190° (yield, 40%). Hydrogen sulphide water, added to the solution in pyridine (Kharasch and Chalkley, *J. Amer. Chem. Soc.*, 1924, **46**, 1211), gives a white precipitate which darkens after a short time with the formation of gas bubbles; ethylene is evolved by boiling with moderately dilute hydrochloric acid.

NN-*Bis*-(2-*phthalimidomercuriethyl*)*mesidine* (II).—The portion insoluble in ethyl acetate, recrystallised from amyl alcohol, gave sand-glass-shaped off-white crystals which charred at about 200° (Found : N, 4·7; Hg, 45·2; $\mathrm{C_2H_4}$, 7·0. $\mathrm{C_{29}H_{27}O_4N_3Hg_2}$ requires N, 4·8; Hg, 45·5; $\mathrm{C_2H_4}$, 6·4%). The *substance* dissolves in pyridine only after boiling, but is not reprecipitated on cooling. The solution gives with hydrogen sulphide water a white precipitate which turns dark after a short time and evolves gas bubbles. The substance darkens in sunlight, but seems indefinitely stable in the dark.

Aceto-(2-*chloromercuriethyl*)*mesidide* (III).—Substance (I) (5 g.) was refluxed with ethyl acetate in a quantity (40 c.c.) insufficient to dissolve it completely. A solution of acetyl chloride (0·7 g., 1 mol.) in ethyl acetate (15 c.c.) was added dropwise within 15 minutes. The remaining solid went into solution, and after half of the solvent had been distilled off, the remaining liquid deposited on cooling crystals of impure phthalimide, which were quickly filtered off. In the filtrate a precipitate of the impure organic mercury compound was slowly formed. Both fractions were boiled with chloroform, in which only the mercury compound dissolved. Phthalimide (1 g., 70%) was identified, after recrystallisation from benzene, by analysis and mixed m. p. (Found : C, 65·6; H, 3·3. Calc. for $\mathrm{C_8H_5O_2N}$: C, 65·3; H, 3·4%). The mercury *compound* (III) (50%) was purified by fractional precipitation from benzene with light petroleum (b. p. 50—60°); m. p. 161—165° (Found : N, 3·4; Cl, 8·1; Hg, 45·8. $\mathrm{C_{13}H_{18}ONClHg}$ requires N, 3·2; Cl, 8·1; Hg, 45·5%). The pyridine solution gives with hydrogen sulphide water a stable white precipitate. The solution in chloroform is not attacked by bromine at room temperature, and no mercury ion is split off by boiling with 6N-hydrochloric acid.

The substance (0·25 g.) and concentrated hydrochloric acid (5 c.c.) were placed in a small flask fitted with a reflux condenser carrying a bent glass tube dipping into mercury, and heated on a water-bath. A gas was evolved, and mercury ions were liberated. On addition of water, a white substance was precipitated (0·1 g.) which, after recrystallisation from benzene, was found, by mixed m. p. and analysis, to be acetomesidide (Found : N, 7·6. Calc. for $\mathrm{C_{11}H_{15}ON}$: N, 7·9%).

Reaction between Mercuric Acetate, Ethylene, and Pyridine.—The slightly turbid liquid, obtained by introducing mercuric acetate (3·2 g.) into a mixture of pyridine (0·9 g.) and acetic acid (2·5 g.), absorbed, when shaken with ethylene under slight pressure, a little more than 1 mol. per mol. of mercuric acetate within about 8 hours. The resulting liquid, when tested with ammonium hydroxide and ammonium sulphide, gave a dirty-white precipitate which soon turned black. The mixture was diluted with a 50% acetic acid solution. Cooling with ice water was applied for the following precipitations, as generally the crystals formed decomposed easily in the mother-liquor with evolution of a gas. Addition of sodium chloride solution removed, together with a part of the organic mercury compound, mercurous ions which had been formed during the preparation. The filtrate, after renewed dilution with 50% acetic acid solution, was used for further precipitations.

Mercuribromide (IV). On addition of sodium bromide solution, needle-shaped crystals were precipitated which contained more mercury and halogen than required by a simple halide (so also did the sodium chloride precipitate, mentioned above, even after repeated precipitation from pyridine with water or alcohol which did not lead to a compound of constant m. p.). No chlorine was present in the bromide precipitate. When the bromide was boiled with methyl cyanide, a part of it was extracted by the solvent while the crystals changed into a white powder whose composition corresponded to the mercuribromide (Found: N, 1·8; Br, 38·5; Hg, 48·6; C_2H_4, 3·4. $C_7H_9NBr_4Hg_2$ requires N, 1·7; Br, 38·6; Hg, 48·5; C_2H_4, 3·4%); m. p. in sealed tube 150—152° (slight decomp.; sintering from about 140°). When treated with ammonia solution, the *salt* (IV) partly dissolved; the solid left turned black with ammonium sulphide at once, and the filtrate gave with ammonium sulphide a whitish precipitate which blackened rapidly, but dissolved in excess and then was stable even on boiling. Analysis showed that only one mercury atom had remained in solution (Found: Hg, 24·1. $[C_7H_9NHg]HgBr_4$ requires Hg, 24·2%).

Mercuri-iodide (as IV). Cream-coloured needles were deposited from the filtrate from the sodium bromide precipitate after the addition of 50% acetic acid and potassium iodide solutions. When placed in a vacuum over concentrated sulphuric acid, they lost some volatile constituents without a visible change and attained constant weight only after more than a week (Found: N, 1·7; C_2H_4, 2·4. $C_7H_9NI_4Hg_2$ requires N, 1·4; C_2H_4, 2·8%); m. p. 105—109° (decomp.). The *substance* is soluble in methyl cyanide and insoluble in ammonium hydroxide.

Thiocyanate. Needles were precipitated by careful addition of potassium thiocyanate solution to the diluted filtrate from the chloride. They could be precipitated in the same way from a solution which was obtained by adding ethyl acetate after the absorption of ethylene and shaking with water. They lost constantly in weight and changed finally into a semi-liquid; that may account for the fact that the mercury content was always too high (Found: N, 10·0; S, 15·2; Hg, 48·3. $C_9H_9N_3S_2Hg$ requires N, 9·9; S, 15·1; Hg, 47·3%). The m. p. varied between 75° and 84°. Ammonium sulphide, added to the ammoniacal solution, gives a white precipitate in the first instance.

Determination of Ethylene.—The substance was decomposed by heating with a mixture of equal parts of concentrated hydrochloric acid and water, and the ethylene evolved was carried by a current of carbon dioxide through three absorption vessels filled with a 2N-solution of bromine in sodium bromide (10%) and subsequently through three absorption vessels filled with sodium bromide (10%). The amount of bromine consumed was iodometrically determined. A check on the compound $C_2H_4,Hg(OAc)_2$ gave C_2H_4, 8·5 (Calc.: 8·1%).

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