# 230. *Mercury Derivatives of Symmetrical Dichloroethylene.*

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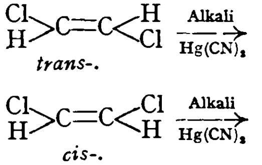
Optimum conditions are defined for the general reaction between unsaturated halogenated hydrocarbons having at least one remaining hydrogen atom and alkaline mercuric cyanide solution.

The reaction between *s*-dichloroethylene and mercuric cyanide has been reinvestigated, and it is shown that the two stereoisomeric forms of the chloro-hydrocarbon react differently under identical conditions, a phenomenon apparently not hitherto recorded.

A new compound, *mercury bisdichloroethylenide*, and derivatives have been prepared. Complex products accompany its formation.

The properties of mercury bischloroacetylide are found to differ from those recorded in the literature.

DURING a search for organo-mercury compounds suitable as fungicides for the treatment of seeds, it was decided to investigate the potentialities of halogen-substituted ethylene derivatives. The only compounds of the desired constitution recorded in the literature are the bistrihalogenoethylenides of mercury (Hofmann and Kirmreuther, *Ber.*, 1908, **41**, 314; 1909, **42**, 4234; Imperial Chemical Industries, B.P. 427,979). By suitable modification of reaction conditions, it was thought possible that a mercurated dichloroethylene might be obtained, instead of mercury chloroacetylide as reported by Hofmann and Kirmreuther. It was found that the envisaged compound could readily be prepared, but only from *trans*-dichloroethylene, the *cis*-isomer reacting with mercury in alkaline cyanide solution in a totally different manner, yielding only mercury bischloroacetylide. Hofmann and Kirmreuther do not mention this remarkable reaction of the *trans*-isomer, although they describe fully the preparation of the chloroacetylene derivative of mercury. This difference in the reaction of the two isomers of dichloroethylene furnishes a good example of *trans*-elimination (see Garner, *Chem. News*, 1919, **119**, 16). Michael (*J. pr. Chem.*, 1895, **52**, 307) observed that chlorofumaric acid loses hydrogen chloride some 50 times as rapidly as does the corresponding (*cis*) chloromaleic acid. In the example under consideration there is slight evidence of *cis*-elimination. The reactions may be expressed as follows:



$(CHCl{:}CCl)_2Hg$, together with more complex derivatives, *e.g.*, $(CHCl{:}CCl{\cdot}Hg{\cdot}CCl{:})_2$

*trans*-.

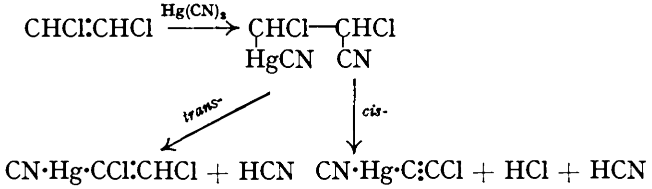
$(CCl{:}C)_2Hg$

*cis*-.

(*as*.-Dichloroethylene, $CCl_2{:}CH_2$, does not yield a mercury derivative.)

It is seen that the *cis*-isomer, with mercuric cyanide in alkaline solution, loses both chlorine and hydrogen, yielding a chloroacetylene compound, whereas the *trans*-form gives a C–Hg link by the loss of a hydrogen atom only. This behaviour, which is analogous to that shown by trichloroethylene under identical conditions, can extend to the removal of a further hydrogen atom, with the formation of a chain compound of the type $CHCl{:}CCl{\cdot}[Hg{\cdot}CCl{:}CCl]_n{\cdot}H$, the solubility in the usual organic solvents decreasing rapidly with increasing complexity. The ultimate product may be formed by ring closure, the terminal carbon atoms becoming attached to the same mercury atom.

The reaction in the case of *cis*-dichloroethylene is determined by the concentration of the alkali, which decreases owing to formation of sodium chloride, but with the *trans*-isomer it is independent of the alkali concentration above a certain minimum. In both cases the velocity of reaction is very slow in dilute solutions. It may be concluded, from the experimental data given herein, that in all mercurations involving the use of alkaline solutions of mercuric cyanide, the cyanogen radical functions catalytically, and a mere trace is sufficient to enable mercuration to proceed. The probable mode of interaction may be represented graphically thus:



Two molecules of each of these hypothetical intermediate products then react with elimination of mercuric cyanide, yielding respectively $(CHCl{:}CCl)_2Hg$ and $(CCl{:}C)_2Hg$.

It is obvious from the experimental results that optimum conditions for the preparation of organo-mercury compounds by the alkaline mercuric cyanide reaction involve the employment of sodium ethoxide instead of aqueous solutions as stated in the literature. Finally, certain published results, *e.g.*, those of Hofmann and Kirmreuther on the m. p. and explosive properties of mercury bischloroacetylide, are not confirmed.

## EXPERIMENTAL.

*Comparison of the Reactions of* cis- *and* trans-*Dichloroethylenes under Identical Conditions with Alkaline Solutions of Mercuric Cyanide.*—The dichloroethylenes were the standard grades produced by Imperial Chemical Industries Ltd. Both samples were fractionally distilled and the fractions of b. p. 59° and 47·5° were collected and regarded as the pure *cis*- and *trans*-isomer respectively.

*Preparation of Mercury Bischloroacetylide and Bisdichloroethylenide.*—On account of the dangerously explosive nature of the former compound, it is advisable to carry out the preparation in aqueous solution; large-scale operations should not be attempted, since traces of impurities, probably alkali cyanide chiefly, may cause the dry substance to detonate violently (see below). The following experiment was conducted with aqueous solutions in order to follow visually the different behaviour of the two isomers; with sodium ethoxide in alcohol the turbidity of the mixture was such that no striking difference could be observed although the reaction was completed in a twentieth of the time.

Precipitated mercuric oxide (200 g.) was dissolved in an aqueous solution of sodium cyanide (100 g. in 250 ml. of water), 40 g. of sodium hydroxide in 100 ml. of water were added, and the whole was filtered through asbestos. The clear alkaline mercuric cyanide solution was diluted so as to contain 17·20% of mercury (by wt.). To 450 g. of this solution in each of two identical glass-stoppered bottles, were added 100 g. severally of *cis*- and *trans*-dichloroethylene. Continuous shaking was necessary to keep the mixtures emulsified. Within 30 mins., the *cis*-dichloroethylene commenced to show signs of reaction; the emulsion " broke " less readily and white glistening crystals formed at the interfaces; after 3 hours, a considerable quantity of crystals had formed, and in 24 hours there was a mass of crystals and unchanged dichloroethylene. The *trans*-isomer only began to show signs of reaction after 3 hours, and in 24 hours it had yielded a light grey, pasty mixture, rather flocculent and inclined to agglomerate upon shaking. After a further 24 hours' standing, the liquids were filtered and their mercury contents determined as 11·28 and 12·70% respectively. The residues, washed with water until free from alkali, and air-dried, weighed 43·7 and 51·0 g. respectively. The product from the *cis*-isomer formed white, shining plates of characteristic acetylene-like odour; and that from the *trans*-isomer was a light grey, rather pasty mass of pungent odour, very irritating when heated. The alkalinity in the former case had fallen from 11·20 to 8·60% (as NaOH), and in the latter to 11·0%.

Ether extraction (Soxhlet) afforded the undermentioned fractions:

| Isomer. | Wt. extracted, g. | (1) Very sol., g. | (2) Mod. sol., g. | (3) Insol., g. |
|---|---|---|---|---|
| *cis-* | 43·0 | nil | 42·8 | 0·2 |
| *trans-* | 51·0 | 11·2 | 12·2 | 24·7 |

The first product was homogeneous, and three samples taken at different periods during the extraction contained Hg, 63·03, 63·0, and 62·98%. The crude substance contained Hg, 63·60%. There is no doubt that this compound is mercury bischloroacetylide $(CCl\vdots C)_2Hg$, which was prepared in a similar manner by Hofmann and Kirmreuther. These workers, however, state that it melts at 185°, but explosion occurred well below that temperature, *i.e.*, at 174—175°, the substance being immersed in a bath pre-heated at 170°. Prolonged heating at 160° caused slow decomposition with formation of carbon. On one occasion the compound detonated so violently as to rock the m. p. apparatus and smash the thermometer bulb.

Mercury bischloroacetylide is moderately soluble in hot ether but only sparingly so in cold. It is soluble to various extents in all the usual organic solvents. Concentrated hydrochloric acid rapidly decomposes it with liberation of spontaneously inflammable chloroacetylene. If a small quantity of fairly concentrated hydrochloric acid is added to some of the mercurial in a tall beaker, and the mixture gently warmed, a crackling sound is audible, accompanied sometimes by small flashes of light, and ozone is evolved. From the very rapid oxidation of lead sulphide papers it would appear that considerable quantities of ozone are formed by the slow oxidation of chloroacetylene—a phenomenon not previously recorded. The formation of traces of a highly unstable ozonide might account for the dangerously explosive nature of the crude, unextracted compound : about 30 g. of the crude crystals in a small bottle were left untouched upon a shelf, the back of which consisted of a $\frac{5}{8}''$ wooden partition, and about 60 hours later a violent explosion occurred; the partition immediately behind the bottle was shattered, and the shelf itself, a 5″ × 4″ beam, was indented to a depth of $\frac{1}{4}''$ with the imprint of the bottom of the bottle. Jars and tins, some weighing over 1 lb., which were within 3 feet of the spot were scattered.

The pure substance appears to be stable : 1 g. in a glass-wool-plugged test-tube shows no alteration after 6 months' standing. Kept under alcohol, mercury bischloroacetylide undergoes slow decomposition, which becomes more rapid after several weeks' standing and is complete at the end of 3 months. This reaction has not been further studied, but chloroacetic acid appears to be one of the products, and is present chiefly as the ethyl ester. The mercury is present both in the inorganic state and as an insoluble organo-compound, possibly a mercurated acetic acid.

*Identification of the reaction products of* trans-*dichloroethylene.* The ether extraction results showed that at least three different compounds had been produced. The oily, not readily crystallisable derivative was purified by steam-distillation, followed by crystallisation from alcohol. The residue from steam-distillation contained a small quantity of coloured non-volatile matter, which was rejected; the purified derivative, which had solidified in the condenser, was removed on gentle heating.

*Mercury bisdichloroethylenide* formed rhombohedra, m. p. 50·3° [Found : C, 12·3;* H, 0·7;* Cl, 35·9;* Hg, 51·2. $(C_2HCl_2)_2Hg$ requires C, 12·2; H, 0·5; Cl, 36·2; Hg, 51·1%]. It was very soluble in chloroform, ether, and acetone, insoluble in water. Boiling concentrated hydrochloric acid decomposed it, yielding mercuric chloride and dichloroethylene, and hot aqueous sodium sulphide similarly gave mercuric sulphide. The above composition was confirmed by treating the compound with excess of iodine in hot chloroform and titrating the excess with thiosulphate : 1 mol. required 504, 506 g. of iodine [Calc. for $Hg(C_2HCl_2)_2 + 2I_2 = HgI_2 + C_2Cl_2I_2 + 2HCl$ : 508 g.].

Mercury bisdichloroethylenide was heated with mercuric chloride in alcoholic solution, and the mixture steam-distilled, yielding white crystals of *chloromercury dichloroethylenide* (Found : C, 7·5;* H, 0·4;* Cl, 31·8;* Hg, 60·75. $C_2HCl_3Hg$ requires C, 7·2; H, 0·3; Cl, 32·1; Hg, 60·4%). Recrystallisation from perchloroethylene, in which it was sparingly soluble in the cold, afforded long, silky, white fibrous needles, m. p. 80·6°, slightly soluble in water, readily so in alcohol. Dilute mineral acids were without action upon the compound, but hot concentrated hydrochloric acid effected quantitative decomposition into dichloroethylene and mercuric chloride. Solutions of strong bases converted it into an insoluble white amorphous substance. Hot aqueous sodium sulphide quantitatively decomposed the crystals into mercuric sulphide and dichloroethylene.

The preparation of this derivative is analogous to that of hydrocarbon mercury halides from mercury dihydrocarbons and mercuric halides, whence it is reasonable to conclude that it is dichloroethylene mercury chloride, and this was confirmed by its reaction with iodine : 1 g.-mol. required 250, 256 g. (Calc. : 254 g.).

The iodide, $CHCl{:}CCl{\cdot}HgI$, was obtained as white micro-crystalline plates, m. p. 115°

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* Microanalyses by Dr. G. Weiler, Oxford.

(decomp. 125°), by addition of potassium iodide to an aqueous solution of the chloride, but it could not be recrystallised owing to its decomposition into iodine and mercuric iodide.

Examination of the less soluble ether extraction fraction (2) and the insoluble residue (p. 1219) indicated that a close relationship existed between all three obviously different substances. Fraction (2) did not melt even at 185°, although it became pasty and discoloured, and the insoluble residue blackened at 192° but did not melt. Both compounds burned slowly with a pale green flame or glow, emitting clouds of irritating fume and mercury vapour. Both substances were heated in an inert atmosphere to about 200°, and the resulting blackened masses steam-distilled; a mixture of mercury bisdichloroethylenide and dichloroethylenemercuric chloride was obtained in each case, the better yield being from fraction (2), and the residues consisted of carbon, unchanged compound, and some inorganic mercury.

These complex mercurials could not be thoroughly examined, but consideration of their reactions with sodium sulphide and the fact that mercury bisdichloroethylenide in the presence of alkali and mercuric cyanide yielded identical products, suggest that they are formed by lengthening of the chain by loss of one of the terminal hydrogen atoms and formation of an additional C–Hg linkage. The residue after 4 days' ether extraction yielded very little mercury bisdichloroethylenide after heating and subsequent steam-distillation. Upon analysis, fraction (2) contained Hg, 59·2% ($C_6H_2Cl_6Hg_2$ requires Hg, 58·2%), and the residue Hg, 63·0% ($C_8H_2Cl_8Hg_3$ requires Hg, 61·2%). An attempt to determine the percentage of dichloroethylene liberated upon heating the compounds with sodium sulphide was carried out in a Tate and Warren moisture-determination apparatus, the volume of liberated dichloroethylene being read off directly in the collecting tube. The simpler compound gave $C_2H_2Cl_2$, 38·1 (Calc.: 42·3%), and the more complex gave $C_2H_2Cl_2$, 34·9 (Calc.: 39·4%). It is obvious that with increasing chain length the percentage of mercury will show only a relatively small increase, and the quantity of mercury bisdichloroethylenide obtained after pyrolysis and steam-distillation will very rapidly fall until only traces are detectable. The completely ether-insoluble portion of the residue yielded chiefly carbon and inorganic mercury and mercuric chloride when heated.

The best yields of the compounds described are obtained as follows:

10 G. of sodium are dissolved in 250 ml. of 95% alcohol (distilled methylated spirit) with suitable cooling, and the solution is added with shaking to 50 g. of yellow mercuric oxide and 2 g. of mercuric cyanide in a flask; then 75 g. of *trans*-dichloroethylene are added and the mixture is heated in a bath at 40° under a reflux condenser. The yellow mass becomes almost white at the end of 1 hour, and the reaction is complete after a further ½ hour's warming. The mixture is poured on a Buchner filter, and the residue washed with warm alcohol until the filtrate runs almost free from alkali. The yield of dry polymercurated dichloroethylenes is about 58 g. The filtrate, after addition of sufficient hydrochloric acid to neutralise the alkali and removal of the sodium chloride precipitated, is steam-distilled, and as soon as the greater part of the alcohol has been removed, mercury bisdichloroethylenide collects in the condenser. The white solid can readily be removed by allowing the water in the condenser to warm to about 50°. The yield of crude product should be 16 g., and a further 2—3 g. may be recovered from the alcoholic first runnings after dilution with water and steam-distillation. The crude dichloroethylenide is best purified by recrystallisation from absolute alcohol, separating in excellent crystals, m. p. 50·3° (sharp).

*Preparation of Dichloroethylenemercury Chloride.*—4 G. of the bisdichloroethylenide are heated in alcohol with 3 g. of mercuric chloride for 10 minutes at 70°, and the solution steam-distilled. The white solid which collects in the condenser is removed by allowing the water to become warm. The crude product is dissolved in 20 ml. of perchloroethylene at 90°, and on cooling, the complex chloride crystallises in long, fibrous needles, m. p. 85·6°; yield *ca.* 4 g. From the steam-distillation condensate, the corresponding iodide may be obtained by addition of a solution of potassium iodide. The white precipitate is filtered off, washed with cold water, and dried in a desiccator.

*Preparation of Mercury Bistrichloroethylenide* (cf. B.P. 427,979).—10 G. of sodium are dissolved in 200 ml. of alcohol in a long-necked flask, 50 g. of yellow mercuric oxide added, followed by 2 g. of potassium cyanide dissolved in 2 ml. of warm water. The flask is then immersed in water at 40°, and 50 g. of trichloroethylene added with agitation. The temperature must be kept below 60° in order to avoid formation of monochloroacetylene and its mercury derivative. Reaction is complete in about an hour, and the crude trichloroethylenide is separated by addition of water and filtration; it may be crystallised from alcohol, m. p. 141° (yield 83 g., over 90% calculated upon trichloroethylene).

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