

**123.** *The Mercuration of some Simple Derivatives of  $\gamma$ -Pyrone.*

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The mercuration of  $\gamma$ -pyrone, dimethylpyrone and four hydroxy- $\gamma$ -pyrones, meconic acid, comenic acid, pyromeconic acid and kojic acid has been studied. The parent substance gives a dichloromercuri-derivative, and dimethylpyrone yields what is apparently a trichloromercuri-compound. The hydroxy- $\gamma$ -pyrones readily yield

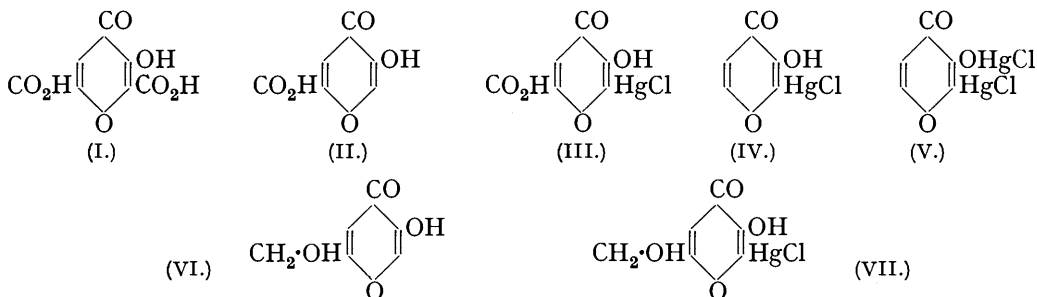
the anhydrides of mono-hydroxymercuri-derivatives, mercury entering the position ortho- to the hydroxyl group. These anhydrides are readily convertible into the corresponding chloromercuri-derivatives. Pyromeconic acid forms a dichloromercuri-derivative, which appears to contain an oxymercuri-group, together with a true mercurated (chloromercuri-) group. The behaviour of the hydroxy- $\gamma$ -pyrones on mercuration resembles that of the phenols, and treatment of the products with aqueous sodium iodide or sodium sulphide results in elimination of mercury. The mercuration of meconic acid is accompanied by decarboxylation, giving a derivative of comenic acid. The mercurated derivatives of comenic acid and pyromeconic acid are readily converted into known bromo-compounds. Iodopyromeconic acid is also obtained, thus establishing the position of the iodine atom. Almost all these mercurated products are amorphous, insoluble, infusible solids.

THE interaction of  $\gamma$ -pyrone and dimethylpyrone with mercuric chloride was investigated by Willstätter and Pummerer (*Ber.*, 1904, **37**, 3747) and by Gomberg and Cone (*Annalen*, 1910, **376**, 226) respectively. The resulting compounds were addition products. No other instances of the action of mercury salts on simple  $\gamma$ -pyrones are recorded. Information regarding the behaviour of  $\alpha$ -pyrones is also scanty. Sen and Chakravarti (*J. Indian Chem. Soc.*, 1929, **6**, 847) and Naik and Patel (*J.*, 1934, 1043) have, however, obtained mercurated derivatives from coumarin. This communication describes the mercuration of  $\gamma$ -pyrone and five simple derivatives in aqueous solution. In each case a carbon-mercury link is established. The products are invariably very sparingly soluble, decompose below their m. p.'s and are either compounds of the type RHgX or anhydrides. Mercurated derivatives of hydroxy- $\gamma$ -pyrones may be purified by solution in dilute alkali and re-precipitation with acids. They are therefore not mercuric chloride addition products, such compounds being decomposed by this treatment.

$\gamma$ -Pyrone with mercuric acetate gives a solid which with dilute hydrochloric acid yields a *dichloromercuri- $\gamma$ -pyrone*. Warm hydrochloric acid liberates mercuric chloride from this and similar compounds.

Dimethylpyrone with mercuric chloride and sodium acetate gives a *trichloromercuri-derivative*. This involves substitution in a methyl group. Such substitution by sodium was observed by Schorigin (*Ber.*, 1910, **43**, 1941) when diethylmercury and sodium (ethyl-sodium) were heated with *o*- or *p*-xylene, mesitylene or *p*-cymene.

Meconic acid (I) with mercuric chloride and sodium acetate, gives *hydroxymercuricomenic anhydride*, carbon dioxide and some calomel. The pure anhydride is obtained by the use of mercuric oxide at 100°. No mercuri-bis-comenic acid is produced, although mercury 2 : 4 : 6-trinitrobenzoate gives bis-2 : 4 : 6-trinitrophenylmercury on heating (Kharasch, *J. Amer. Chem. Soc.*, 1921, **43**, 2238).



When the anhydride is treated with hydrochloric acid, *chloromercuricomenic acid* (III) is produced. Bromine converts this into 2-bromocomenic acid (How, *Annalen*, 1851, **80**, 85), which by the Fischer-Speier method gives ethyl 2-hydroxycomenate (see Reibstein, *J. pr. Chem.*, 1881, **24**, 286; Menzel, *ibid.*, 1882, **26**, 471).

Mercuration of comenic acid (II) is effected by mercuric acetate and by the chloride and sodium acetate, without evolution of carbon dioxide, giving hydroxymercuricomenic anhydride, which is thus obtained from both meconic and comenic acids. It is therefore

the carboxyl group in position 2 of meconic acid which is lost during mercuration. This is in agreement with the conversion of meconic into comenic acid on boiling with hydrochloric acid (Meyer, *Monatsh.*, 1905, **26**, 1328).

Loss of carbon dioxide during mercuration frequently occurs. Furan- $\alpha$ -carboxylic acid with hot aqueous mercuric chloride is decarboxylated to furan without mercuration, as is meconic to comenic acid (see p. 666), but with sodium acetate 2-chloromercurifuran is formed (Gilman and Wright, *J. Amer. Chem. Soc.*, 1933, **55**, 3303).

Benzoic and phthalic acids both give hydroxymercuribenzoic anhydride (Pesci, *Atti R. Accad. Lincei*, 1901, **10**, i, 362; Dimroth, *Ber.*, 1902, **35**, 2870). Whitmore and Culhane (*J. Amer. Chem. Soc.*, 1929, **51**, 602) proved that with nitrophthalic acid decarboxylation precedes mercuration. Salicylic acid also gives a mercurated anhydride (Dimroth, *loc. cit.*, p. 2872).

With pyromeconic acid mercuric acetate gives a product which appears to be the anhydride of hydroxymercuripyromeconic acid. This is probably also formed by the glycerol-bicarbonate-mercuric chloride reaction, the product of which gives monochloromercuripyromeconic acid (IV) with hydrochloric acid. Mercuric chloride and sodium acetate yield a product (V) having the composition of a dichloromercuripyromeconic acid. One of the chloromercuri-groups is removed by sodium hydroxide, or by dilute hydrochloric acid and is therefore probably linked through oxygen. The chlorine content of (V) excludes the possibility that it contains a co-ordinated molecule of mercuric chloride. Oxychloromercuri-derivatives were obtained by Neogi and Chatterji (*J. Indian Chem. Soc.*, 1928, **5**, 222) from catechol or quinol by the glycerol-bicarbonate method. Dimroth (*loc. cit.*, p. 2865), using other conditions, obtained C-Hg derivatives from resorcinol.

Replacement of the chloromercuri-group in (IV) by bromine yields 2-bromopyromeconic acid (Brown, *Annalen*, 1852, **84**, 41; Compagno, *Atti R. Accad. Lincei*, 1908, **17**, i, 73), thus establishing the position of the mercury atom. With iodine, the ?-iodopyromeconic acid first prepared by Brown (*Annalen*, 1854, **92**, 321) is obtained. The iodine must therefore be attached in the 2-position.

Kojic acid (VI) with mercuric chloride and sodium acetate or glycerol-bicarbonate gives hydroxymercurikojic anhydride. The position of the chloromercuri-group in the corresponding chloromercurikojic acid (VII) has not been determined, but analogy with pyromeconic acid suggests position 2. The molecular weights and therefore the structures of the mercuri-anhydrides derived from pyromeconic and kojic acids are unknown. The *o*-chloromercuri-derivatives of phenol and *p*-cresol, when dissolved in sodium hydroxide and treated with carbon dioxide, also yield anhydrides. *p*-Chloromercuriphenol behaves rather differently (Dimroth, *Ber.*, 1899, **32**, 764; 1902, **35**, 2858).

The mercuri-anhydrides described in this communication, like those of benzoic, phthalic and salicylic acids, are formed spontaneously without the use of alkali.

The action of sodium iodide on RHgCl may proceed according to three different equations: (1)  $\text{RHgCl} + \text{NaI} = \text{RHgI} + \text{NaCl}$ ; (2)  $2\text{RHgCl} + 4\text{NaI} = \text{R}_2\text{Hg} + \text{Na}_2\text{HgI}_4 + 2\text{NaCl}$ ; (3)  $\text{RHgCl} + 4\text{NaI} + \text{H}_2\text{O} = \text{RH} + \text{Na}_2\text{HgI}_4 + \text{NaCl} + \text{NaOH}$ . Reaction (3) is particularly associated with mercurated phenols, in which case Whitmore and Middleton (*J. Amer. Chem. Soc.*, 1921, **43**, 619) were able to titrate the sodium hydroxide (see also Naik and Patel, *loc. cit.*, p. 1046). The corresponding acetylated compounds did not react with sodium iodide (see Whitmore, "Organic Compounds of Mercury," Chemical Catalogue Company, 1921, p. 256).

Excess of sodium iodide with hydroxymercuricomenic anhydride gives sodium comenate according to equation (3). Chloromercuricomenic acid and sodium iodide should therefore react thus:  $\text{C}_5\text{HO}_2(\text{OH})(\text{CO}_2\text{H})\cdot\text{HgCl} + 4\text{NaI} + \text{H}_2\text{O} = \text{C}_5\text{H}_2\text{O}_2(\text{OH})(\text{CO}_2\text{Na}) + \text{Na}_2\text{HgI}_4 + \text{NaCl} + \text{H}_2\text{O}$ . This was confirmed by titration of the acidic hydrogen atom (represented as being in the hydroxyl group) of the sodium comenate with sodium hydroxide (compare Verkade, *Rec. Trav. chim.*, 1924, **43**, 882).

According to equation (1) or (2) one molecule of chloromercuricomenic acid would give two equivalents of acid in the form of iodomercuricomenic acid or mercuri-bis-comenic acid. The reaction of chloromercuripyromeconic acid and chloromercurikojic acid with sodium iodide also follows equation (3), as shown by titration of the sodium hydroxide liberated.

Sodium sulphide can convert  $\text{RHgCl}$  into  $\text{R}_2\text{Hg}$ , thus: (4)  $2\text{RHgCl} + \text{Na}_2\text{S} \longrightarrow (\text{RHg})_2\text{S} \longrightarrow \text{R}_2\text{Hg} + \text{HgS}$ . The reaction (5)  $\text{RHgCl} + \text{Na}_2\text{S} + \text{H}_2\text{O} = \text{RH} + \text{HgS} + \text{NaCl} + \text{NaOH}$  may also occur (see Otto, *Annalen*, 1870, **154**, 191; Challenger and Miller, J., 1939, 1006). With sodium chloromercuricomenate (2 mols.) and sodium sulphide (1 mol.), mercuri-bis-comenic acid is not formed, although approximately half the mercury is eliminated. The reaction appears to be mainly: (5a)  $\text{C}_5\text{H}_2\text{O}_2(\text{ONa})(\text{CO}_2\text{Na})\cdot\text{HgCl} + \text{Na}_2\text{S} + \text{H}_2\text{O} = \text{C}_5\text{H}_2\text{O}_2(\text{ONa})(\text{CO}_2\text{Na}) + \text{NaCl} + \text{NaOH} + \text{HgS}$ . Unchanged sodium salt is detected as chloromercuricomenic acid on acidification.

With free chloromercuricomenic acid (2 mols.) and sodium sulphide (1 mol.), the equation (5b) is followed:  $2\text{C}_5\text{H}_2\text{O}_2(\text{OH})(\text{CO}_2\text{H})\cdot\text{HgCl} + \text{Na}_2\text{S} + \text{H}_2\text{O} = \text{C}_5\text{H}_2\text{O}_2(\text{OH})(\text{CO}_2\text{H})\cdot\text{HgOH}$  (probably as anhydride) +  $\text{C}_5\text{H}_2\text{O}_2(\text{OH})\cdot\text{CO}_2\text{H} + \text{HgS} + 2\text{NaCl}$ . This is shown by titration of the comenic acid and the chloride ion. With equimolecular proportions of the reactants all the mercury is eliminated (equation 5).

Chloromercurikojic acid (2 mols.) and sodium sulphide (1 mol.) give kojic acid and mercuric sulphide representing slightly under 50% of that required by (5); much mercurated kojic acid is recovered. With equimolecular proportions, equation (5) is closely obeyed.

#### EXPERIMENTAL.

(1)  *$\gamma$ -Pyrone*.—With mercuric chloride alone or in presence of sodium acetate or glycerol and sodium bicarbonate, only a trace of precipitate was formed at room temperature. On warming with mercuric chloride and sodium acetate, reaction was more rapid but the precipitate contained calomel. Mercuration was finally effected by warming  $\gamma$ -pyrone (1 g.) in water (50 c.c.) with mercuric acetate (3.2 g.) in dilute acetic acid (80 c.c.) for 4 hours at  $100^\circ$ . The resulting cream-coloured solid (A; 1.5 g.) was insoluble in organic solvents. Aqueous ammonia or sodium hydroxide had no action in the cold; boiling sodium hydroxide solution gave mercurous oxide, probably due to complete decomposition. Sodium sulphide formed mercuric sulphide. When triturated with dilute hydrochloric acid, (A) became white and more granular, giving a *dichloromercuri- $\gamma$ -pyrone* closely resembling the acetoxymercuri-compound (A) [Found: Hg, 70.0; Cl, 12.2. A second preparation gave Hg, 70.5; Cl, 12.2.  $\text{C}_5\text{H}_3\text{O}_2\text{ClHg}$  requires Hg, 60.6; Cl, 10.7.  $\text{C}_5\text{H}_2\text{O}_2(\text{ClHg})_2$  requires Hg, 70.6; Cl, 12.5%].

(2) *Dimethylpyrone*.—When the addition product with mercuric chloride (Gomberg and Cone, *loc. cit.*) was heated alone, no mercuration occurred but dimethylpyrone sublimed. It was unchanged when 0.5 g. was heated with water (15 c.c.) at  $100^\circ$  for several days. On long heating of dimethylpyrone with aqueous mercuric chloride or acetate some calomel separated. No mercuration could be detected by the mercuric chloride-sodium bicarbonate-glycerol method.

When dimethylpyrone (1 g.), mercuric chloride (6.5 g.; 3 mols.), and sodium acetate (3.3 g.; 3 mols.) were dissolved in water (40 c.c.), the crystalline dimethylpyrone mercurichloride first separated, but dissolved on warming, being gradually replaced by a white solid. After 9 hours this was removed (2 g.). It was insoluble in organic solvents and in aqueous ammonia (no blackening). Sodium hydroxide gave yellow mercuric oxide after a few minutes in the cold, this behaviour strikingly differentiating the product from dimethylpyrone mercurichloride, which reacts immediately. The substance turned yellow at  $170^\circ$  and charred at about  $200^\circ$  without melting, but owing to its insolubility could not be purified [Found: Hg, 72.0, 72.2, 73.0, 73.4; Cl, 11.4, 11.2.  $\text{C}_7\text{H}_5\text{O}_2(\text{ClHg})_3$  requires Hg, 72.6; Cl, 12.8%.  $\text{C}_7\text{H}_5\text{O}_2(\text{ClHg})_2\cdot\text{HgCl}_2$  requires Hg, 69.6; Cl, 16.4%]. Most of these analyses were carried out with different preparations. 0.5 G. of this product was boiled with water (50 c.c.) for  $1\frac{1}{4}$  hours. The mercury content fell only from 72.2 to 71.4%. This experiment and the figures for Cl indicate the probable absence of addition products of mercuric chloride. Attempts to obtain a mono-mercurated compound by using equimolecular amounts of the three reagents gave the same product as before (Found: Hg, 72.8%). This was also obtained (0.25 g.) on warming dimethylpyrone mercurichloride (2 g.) with sodium acetate (0.7 g.; 1 mol.) in water (50 c.c.) for 12 hours (Found: Hg, 73.0%).

(3) *Meconic Acid*.—With mercuric chloride (2.7 g.) in water (250 c.c.), meconic acid (2.54 g.) gave only a trace of calomel after 2 days at room temperature. At  $100^\circ$  carbon dioxide was evolved and calomel deposited. After 6 hours this was separated. Evaporation of the filtrate and extraction of the residue with hot alcohol to remove mercuric chloride and meconic acid left a brown solid (1 g.), which was identified as comenic acid by conversion into the ethyl ester

(Reibstein, *loc. cit.*, p. 277), m. p. 127° and mixed m. p. 126·5° with ethyl comenate (m. p. 127°). Some carbon dioxide was evolved when the above quantities of meconic acid and water were heated alone for 6 hours.

Comenic acid would therefore appear not to be mercurated by aqueous mercuric chloride and this was confirmed in a separate experiment, only calomel being produced on heating.

*Mercuration of meconic acid.* Meconic acid (50 g.) in water (1000 c.c.) was warmed at 100°, mercuric chloride (108 g.) added, and the liquid filtered to remove any calomel. Sodium acetate (73 g.) in water (200 c.c.) was then added to the warm, well-stirred solution. Carbon dioxide was vigorously evolved and a cream-coloured precipitate (B) formed. After 4 hours' heating, by which time gas evolution had ceased, this was filtered off and washed with much hot water. Yield, 45 g. (Found: Hg, 50·5%). A further 10 g., obtained on adding more sodium acetate to the filtrate, was contaminated with a yellow basic product and was discarded. The main product was stirred with water (1000 c.c.) and dissolved by gradual addition of saturated aqueous sodium carbonate. About 2 g. of a black solid, presumably mercurous oxide, remained. The sodium salt of the mercurated product was sparingly soluble in excess of sodium carbonate, separating as a gelatinous solid on cooling. The warm solution was acidified with acetic acid, giving a gelatinous precipitate which, although difficult to manipulate, was well washed and dried (C). Bright sunlight caused some decomposition with formation of mercurous compounds. Chlorine was absent and therefore, presumably also from the original deposit (B). The solid (C) was shown to be a derivative of comenic acid by suspension (13·5 g.) in water (100 c.c.) and removal of mercury by hydrogen sulphide. Filtration and evaporation gave a residue (5·1 g.), which was converted into the ethyl ester as before, m. p. and mixed m. p. 127°.

Ethyl meconate was found to melt at 157° (How, *Annalen*, 1852, **83**, 358, gives m. p. 158°) and at 117—119° in admixture with ethyl comenate.

The remainder of (B) was dried to constant weight at 115° without apparent decomposition (Found: Hg, 54·4, 54·5; Na, 1·1; CH<sub>3</sub>·CO·O, 2·8. C<sub>6</sub>H<sub>3</sub>O<sub>5</sub>·Hg·O·CO·CH<sub>3</sub> requires Hg, 48·1%. C<sub>6</sub>H<sub>3</sub>O<sub>5</sub>·Hg·OH requires Hg, 53·8%. C<sub>6</sub>H<sub>2</sub>O<sub>5</sub>Hg requires Hg, 56·5%).

These results suggest that (B) consists mainly of hydroxymercuricomenic acid, or its anhydride, together with a little of the acetoxymercuri-compound in the form of its sodium salt. Alternatively sodium acetate may be present. An attempt to convert it completely into acetoxymercuricomenic acid with glacial acetic acid failed, although the percentage of acetoxy rose (Found: Hg, 52·7; CH<sub>3</sub>·CO·O, 6·0%).

A product resembling (B) was obtained from meconic acid or its sodium salt and mercuric acetate (1 mol.). Carbon dioxide was evolved, especially on warming; the precipitate was dissolved in sodium carbonate to remove traces of mercurous salt and reprecipitated by acetic acid (Found: Hg, 54·7, 54·4, 55·0. C<sub>6</sub>H<sub>2</sub>O<sub>5</sub>Hg requires Hg, 56·5%). When sodium meconate and mercuric chloride were warmed in aqueous solution, the product contained no chlorine and appeared to be the hydroxymercuricomenic anhydride (B).

*Meconic Acid and Mercuric Oxide. Preparation of Hydroxymercuricomenic Anhydride free from Sodium Acetate.*—Mercuric chloride (2·7 g.) was converted into the oxide, which was washed six times by decantation and added to a warm solution of meconic acid (5 g.) in water (100 c.c.). Carbon dioxide was at once evolved, and the usual cream-coloured precipitate formed. Heating at 100° was continued till a test portion was soluble in sodium carbonate solution. Yield, 4 g. [Found: Hg, 57·0, 56·3. C<sub>6</sub>H<sub>2</sub>O<sub>5</sub>Hg requires Hg, 56·5. (C<sub>6</sub>H<sub>3</sub>O<sub>5</sub>)<sub>2</sub>Hg requires Hg, 39·3%]. Mercuri-bis-comenic acid is, therefore, not produced.

*Chloromercuricomenic Acid.*—The slightly impure anhydride (B) gave comenic acid with hot *n*-hydrochloric acid, but when 4 g. were added to 100 c.c. of *n*/5-acid (cooled in ice and well stirred), a white solid formed. This was separated, washed with water containing a few drops of dilute hydrochloric acid, and dried over potassium hydroxide (Found: Hg, 51·1, 51·1; Cl, 9·1. A second preparation gave Hg, 51·0; Cl, 8·8. C<sub>6</sub>H<sub>3</sub>O<sub>5</sub>ClHg requires Hg, 51·3; Cl, 9·1%).

*Chloromercuricomenic acid*, like other  $\beta$ -hydroxy- $\gamma$ -pyrones, turns red in presence of traces of iron. It is insoluble in water and most solvents, but slightly soluble in hot alcohol from which it separates in crystals. Some decomposition occurs, however, the solution becoming acid owing to anhydride formation.

*Chloromercuricomenic Acid and Bromine. Orientation of the HgCl Group.*—Chloromercuricomenic acid (1 g.) was finely powdered and suspended in water (15 c.c.), and bromine water added drop by drop until solution was almost complete, excess of bromine being avoided. The filtered solution deposited iridescent needles (0·4 g.), which after crystallisation once from

water and twice from alcohol decomposed at 189° without melting. An authentic specimen of 2-bromocomenic acid decomposed at 191°. 0.2 G. of the bromo-acid was esterified by the Fischer-Speier method. The product after crystallisation from alcohol and then from water was bromine-free and had m. p. 200—201° and mixed m. p. 202—203° with authentic ethyl 2-hydroxycomenate (m. p. 203°). It gave a fine blue colour with ferric chloride. Feist (*Ber.*, 1905, 38, 3572) and Tickle and Collie (*J.*, 1902, 81, 1006) showed that 2 : 3-dihydroxy- $\gamma$ -pyrones give a blue or violet colour with ferric chloride.

*Sodium Iodide and Hydroxymercuricomenic Anhydride.*—The anhydride on long boiling with sodium iodide in acetone or alcohol gave a yellow insoluble solid which was free from mercury and soluble in water. Acidification gave comenic acid, identified as before. Sodium comenate is yellow.

*Sodium Iodide and Chloromercuricomenic Acid.*—The acid (0.3404 g.) was boiled with aqueous sodium iodide (1 g. in 50 c.c.) for 20 minutes. The clear solution was cooled and titrated with *N*/10-sodium hydroxide and phenolphthalein (Found : 8.6 c.c. corresponding to 0.98 equiv. of comenic acid). Verkade (*loc. cit.*) titrated comenic acid with sodium hydroxide and thymolphthalein, obtaining 78.4 for the equivalent. We used phenolphthalein, obtaining 78.8 and 78.7 (calc. for comenic acid, 78.0).

*Sodium Sulphide and Chloromercuricomenic Acid.*—A solution of the acid (2 mols.) in the calculated amount of *N*-sodium carbonate was filtered from traces of mercurous oxide, treated with freshly prepared and standardised aqueous 1% sodium sulphide (1 mol.), diluted to 100 c.c., and warmed. Mercuric sulphide was immediately precipitated and in 2 minutes the filtered solution was free from sulphide ions. The HgS represented 51% of the total mercury. Acidification of the filtrate with very dilute hydrochloric acid gave an almost white precipitate of chloromercuricomenic acid [Found : Hg, 50.8. Calc. for  $C_6H_3O_5ClHg$  : Hg, 51.3. Calc. for  $(C_6H_3O_5)_2Hg$  : Hg, 39.2%].

In similar experiments with sodium sulphide but omitting the sodium carbonate, the liberated comenic acid was titrated as before and the chloride ion also determined (Found : comenic acid, 0.97 mol.; Cl, corresponding to 98.4% of the 2 mols. of NaCl required by equation 5b, p. 666).

Equimolecular proportions of sodium sulphide and chloromercuricomenic acid being used, the total mercury was determined (Found : HgS, 103% of the theoretical). The high result is probably due to the presence of a trace of unattached chloromercuricomenic acid.

(4) *Mercuration of Comenic Acid.*—The acid, mercuric chloride, and sodium acetate were mixed in the molecular proportions of 1 : 1 : 2 and 1 : 4 : 8 (a) in the cold and (b) at 100°. A similar precipitate, having no m. p. (presumably hydroxymercuricomenic anhydride), was obtained in each case. No carbon dioxide was evolved.

Comenic acid (1.3 g.) in *N*-sodium hydroxide (8.5 c.c.) and water (10 c.c.) was added to mercuric acetate (2.6 g.) in 10% acetic acid (40 c.c.), and the mixture warmed. No carbon dioxide was evolved. The precipitate was dissolved in aqueous sodium carbonate and reprecipitated with acetic acid after filtration. The crude anhydride after repeated washing with dilute acetic acid still contained traces of sodium (Found : Hg, 54.9.  $C_6H_2O_5Hg$  requires Hg, 56.5%).

*Chloromercuricomenic Acid.*—Two separate preparations of the crude anhydride were converted into the chloride as before; both products were analysed (Found : Hg, 51.7, 51.8, 51.2; Cl, 8.7, 9.4. Calc. for  $C_6H_3O_5ClHg$  : Hg, 51.3; Cl, 9.1%).

(5) *Mercuration of Pyromeconic Acid.*—(1) *In presence of glycerol.* *Chloromercuripyromeconic acid.* Pyromeconic acid (5 g.; 1.2 mols.) and mercuric chloride (12 g.; 1 mol.) were dissolved in warm water (150 c.c.), and a saturated solution of sodium bicarbonate (4 g.; 1 mol.) and glycerol (8 c.c.) added. The resulting precipitate (probably the anhydride of hydroxymercuripyromeconic acid) was separated, and a further quantity obtained on addition of more bicarbonate. The whole was washed and stirred with cold *N*/2-hydrochloric acid. Yield, 10 g. The product was insoluble in water and organic solvents but soluble with difficulty in alcohol, from which white crystals were obtained. Prolonged contact with alcohol caused some loss of chlorine (compare chloromercuricomenic acid) (Found : Hg, 57.6, 57.7; Cl, 10.0. A second preparation gave Hg, 57.0; Cl, 10.1.  $C_6H_3O_5ClHg$  requires Hg, 57.8; Cl, 10.2%). Decomposition with hydrochloric acid or hydrogen sulphide gave pyromeconic acid (m. p. and mixed m. p.). Evaporation of aqueous solutions of this acid causes loss by volatilisation.

(2) *With mercuric acetate.* Pyromeconic acid (2 g.; 1 mol.) in water (70 c.c.) was heated at 100° with mercuric acetate (5 g.; 1 mol.) in 10% acetic acid (50 c.c.) until a test portion of the white gelatinous precipitate was found to be soluble in dilute sodium hydroxide solution

(25 mins.). Excess of the latter gave mercurous oxide owing to the instability of pyromeconic acid in presence of alkali. The precipitate, after being washed with very dilute acetic acid and with water, weighed 3.5 g. It was also soluble in acetic acid and in aqueous ammonia and sodium carbonate (Found: Hg, 63.0;  $\text{CH}_3\cdot\text{CO}\cdot\text{O}$ , 0.4. Monoacetoxy-derivative,  $\text{C}_7\text{H}_6\text{O}_5\text{Hg}$ , requires Hg, 54.1;  $\text{CH}_3\cdot\text{CO}\cdot\text{O}$  16.0%. Diacetoxy-derivative,  $\text{C}_9\text{H}_8\text{O}_7\text{Hg}_2$ , requires Hg, 63.7;  $\text{CH}_3\cdot\text{CO}\cdot\text{O}$ , 19.0. Hydroxymercuripyromeconic anhydride,  $\text{C}_5\text{H}_2\text{O}_3\text{Hg}$ , requires Hg, 64.6%). The product contained a trace of an acetoxy-derivative.

(3) *With mercuric chloride and sodium acetate.* *Oxymercurichlorochloromercuripyromeconic acid.* Pyromeconic acid (1 g.), mercuric chloride (3.5 g.), sodium acetate (7 g.), and water (100 c.c.) were warmed at 100°. The pale buff precipitate (3.2 g.) was separated after 1 hour. It was free from mercurous compounds (Found, for two different preparations: Hg, 68.6, 68.7, 68.6; Cl, 11.8, 11.4, 11.9.  $\text{C}_5\text{H}_2\text{O}_3\text{ClHg}$  requires Hg, 57.8; Cl, 10.2%.  $\text{C}_5\text{H}_2\text{O}_3\text{Cl}_2\text{Hg}_2$  requires Hg, 68.9; Cl, 12.2%). Cold dilute sodium hydroxide solution gave mercuric oxide; removal of this and careful acidification of the filtrate with dilute hydrochloric acid gave a white precipitate which, like monochloromercuripyromeconic acid, gave mercurous oxide on boiling with sodium hydroxide. The original product (Hg, 68.7%) was well washed with cold *N*-hydrochloric acid to remove the oxymercurichloro-group, and the residue dried (Hg, 58.4%). It was then soluble in alkali (no mercuric oxide was precipitated), but on boiling, mercurous oxide was formed. The washing with dilute acid was repeated, and the product dried over potassium hydroxide (Found: Hg, 58.0; Cl, 10.1.  $\text{C}_5\text{H}_2\text{O}_3\text{ClHg}$  requires Hg, 57.8; Cl, 10.2%).

*Bromine and Chloromercuripyromeconic Acid. Orientation of the HgCl Group.*—The mercury derivative was dissolved in ice-cold bromine water and kept below 0° for 5 days; needle-shaped crystals had then separated. These were recrystallised twice from alcohol and found to be free from mercury. They melted at 181°, alone and in admixture with 2-bromopyromeconic acid. Unless the reaction mixture was kept cold, mercurous salts separated and very little of this bromo-derivative was obtained.

*Iodine and 2-Chloromercuripyromeconic Acid. Orientation of the Iodine in Iodopyromeconic Acid.*—The mercury derivative (2 g.), suspended in alcohol (20 c.c.), was slowly treated with solid iodine until decolorisation ceased. The hot, filtered solution deposited crystals, which were separated from mercuric iodide by extraction with chloroform. Addition of light petroleum gave colourless crystals (0.95 g.), which decomposed at 110° without melting. Ferric chloride gave a purple colour. Iodopyromeconic acid decomposes at 108° (Brown, *loc. cit.*; Peratoner and Leonardi, *Gazzetta*, 1898, 28, ii, 297) (Found: I, 53.2, 53.4. Calc. for  $\text{C}_5\text{H}_3\text{O}_3\text{I}$ : I, 53.4%).

*Chloromercuripyromeconic Acid and Sodium Iodide.*—The mercury derivative (approx. 0.2 g.) was boiled with sodium iodide (0.5 g.) in water (100 c.c.) for 45 minutes. The solution was cooled and titrated with *N*/20-hydrochloric acid and methyl-orange (Found for NaOH per mol. of mercurated compound: 1.00, 0.99 equiv.). With thymol-blue the end-point was not so sharp as in the case of methyl-orange. Separate experiments showed that pyromeconic acid in *N*/10-solution is without effect on the titration of *N*/10-sodium hydroxide by *N*/20-hydrochloric acid and methyl-orange. The titration of *N*/10-sodium hydroxide by *N*/10-hydrochloric acid was also unaffected by a mixture of *N*/10-pyromeconic acid with *M*/5-sodium mercuric iodide and *M*/10-sodium iodide.

It was also shown that phenolphthalein cannot be used in the titration of *N*/10-pyromeconic acid by *N*/10-sodium hydroxide, a pink colour being given with 0.6 equivalent.

(6) *Kojic Acid.* Mercuric chloride (3 g.; 1 mol.) in water (150 c.c.) with kojic acid (3 g.; 2 mols.) showed no apparent reaction. Addition of sodium acetate (3 g.; 2 mols.) in water (20 c.c.) gave a pale yellow, crystalline precipitate (P). This was separated, washed, and found to give mercuric oxide with sodium hydroxide. After this was removed, the filtrate gave a white precipitate with hydrochloric acid. This was soluble in sodium hydroxide without separation of mercuric oxide and was therefore a true mercurated compound. Analysis of two separate preparations of (P) indicated mixtures of variable composition free from acetate. They probably contained the mercury salt of kojic acid together with some mercurated compound, possibly hydroxymercurikojic anhydride.

*Hydroxymercurikojic Anhydride.*—The remainder of (P) was dissolved in boiling water (200 c.c.); a pale yellow, gelatinous precipitate (Q) quickly formed. This was insoluble in water and organic solvents, but dissolved in aqueous sodium carbonate or ammonia when warm and also in cold sodium hydroxide solution, being precipitated on acidification. Q was free from chlorine. Analysis indicated *hydroxymercurikojic anhydride* (Found for two separate preparations: Hg, 58.7, 58.8.  $\text{C}_6\text{H}_4\text{O}_4\text{Hg}$  requires Hg, 58.9%).

*Chloromercurikojic Acid.*—A product identical with or similar to (Q) was obtained by the

interaction of kojic acid (5 g.) in hot water (300 c.c.) with mercuric chloride (10 g.) in water (150 c.c.), glycerol (2—3 c.c.), and sodium bicarbonate (3 g.). Yield, 8 g. This contained no chlorine, but with water and a few c.c. of dilute hydrochloric acid it gave a white solid, shown to be *chloromercurikojic acid*. This was insoluble in organic solvents but dissolved in aqueous sodium hydroxide or ammonia. It decomposed at 185—190° without melting (Found for two separate preparations : Hg, 53·8, 53·3; Cl, 9·5, 9·6.  $C_6H_5O_4ClHg$  requires Hg, 53·2; Cl, 9·5%).

*Chloromercurikojic Acid and Sodium Iodide*.—The reaction was carried out as described for chloromercuripyromeconic acid (Found, for NaOH per mol. of mercurated compound : 1·01, 1·01 equiv.). It was shown that the titration of *N*/10-sodium hydroxide by approximately *N*/10-hydrochloric acid and methyl-orange was unaffected by kojic acid or by a mixture of this substance with sodium mercuric iodide in the amounts present in these experiments. The behaviour of kojic acid when titrated with *N*/10-sodium hydroxide and phenolphthalein is similar to that of pyromeconic acid.

*Chloromercurikojic Acid and Sodium Sulphide*.—(a) *With equimolecular proportions according to equation (5)*. Chloromercurikojic acid (0·5246 g.) and sodium sulphide (0·33 g.) in water (100 c.c.) were boiled for 15 minutes. Sulphide ions were absent from the filtered solution. The mercuric sulphide was washed with sodium carbonate to remove traces of mercurated compound. The filtrate was titrated with *N*/10-sodium hydroxide (Found : HgS, 97% of the theoretical; NaOH, 0·96 equiv.).

(b) *With 0·5 mol. of sodium sulphide*. Chloromercurikojic acid (0·94 g.) in water (150 c.c.) was boiled with 1% sodium sulphide solution (9·75 c.c.) for 2 minutes. Sulphide ions were then absent. Kojic acid was determined in the filtrate as the copper salt by Barham's method (*Ind. Eng. Chem. Anal.*, 1939, 11, 31). The mercury sulphide was washed with sodium carbonate as before, much mercurated kojic acid being removed (Found : kojic acid, 48%; HgS, 49% of that corresponding to the chloromercurikojic acid taken).

*Chelidonic Acid*.—Attempts to mercurate chelidonic acid ( $\gamma$ -pyrone-2 : 6-dicarboxylic acid) by (1) the acetate or (2) the chloride and sodium acetate method failed. Carbon dioxide was not evolved and the products appeared to be mainly impure mercuric salts of chelidonic acid. By method (2) some calomel was also formed. No mercuration was observed on heating the product from (1) up to 260°. At no stage was a test portion soluble in or stable to aqueous sodium hydroxide or carbonate. There appears to be no record of the direct formation of any substitution products from this acid. Chloro- and bromo-derivatives of the ester were, however, obtained from ethyl acetonedioxalate by Feist and Baum (*Ber.*, 1905, 38, 3574; 1906, 39, 3662, *et seq.*).

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