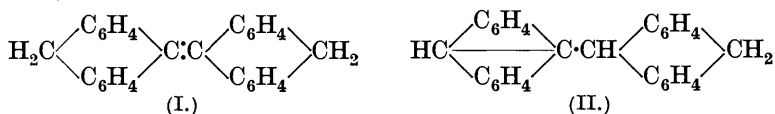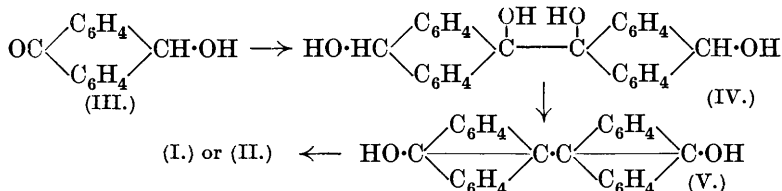# XXXV.—Reactions of the meso-Hydroxyanthrones.

By Marcus Aurelius Matthews.

THE reduction of 10-hydroxyanthrone * by zinc dust and glacial acetic acid leads to anthrone, probably through addition of hydrogen to the carbonyl group and subsequent loss of water across the ring (K. H. Meyer, *Annalen*, 1911, **379**, 37).

Anthrone itself on reduction with zinc and hydrochloric acid in glacial acetic acid undergoes the pinacol condensation (Barnett and Matthews, J., 1923, **123**, 380), and it has now been found that under similar conditions 10-hydroxyanthrone also undergoes the pinacol condensation, although the reduction goes further and leads to *dihydrodianthranyl*, which may be (I) or (II) or a tautomeric mixture of these. The powerful blue fluorescence renders (II) the more probable, but the existence of fluorescence cannot be taken as definite proof of the presence of a " bridge " (compare Padova, *Ann. Chim.*, 1910, **19**, 358, 435; Jüngermann, *Ber.*, 1905, **38**, 2868).

$$H_2C \Big\langle \genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4} \Big\rangle C\!:\!C \Big\langle \genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4} \Big\rangle CH_2 \qquad HC \Big\langle \genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4} \Big\rangle C\!\cdot\!CH \Big\langle \genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4} \Big\rangle CH_2$$

$$(I.) \qquad\qquad\qquad\qquad (II.)$$

The reduction of 10-hydroxyanthrone (III) to dihydrodianthranyl cannot take place through preliminary formation of anthrone, for, as already shown (Barnett and Matthews, *loc. cit.*), the reduction of this gives only dianthranyl and α-anthrapinacolin. Further, neither dianthranyl nor dianthranol is attacked under the experimental conditions employed, although dianthranol is reduced to dihydrodianthranyl by tin and hydrochloric acid. It therefore follows that in the reduction of 10-hydroxyanthrone with zinc and hydrochloric acid attack first takes place at the carbonyl group, involving the formation of a pinacol (IV), and that further reduction of the pinacol must be due to ready attack of the " nascent " dianthranol molecule (V) formed by loss of water across the rings.

$$OC \Big\langle \genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4} \Big\rangle CH\!\cdot\!OH \rightarrow HO\!\cdot\!HC \Big\langle \genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4} \Big\rangle \overset{OH}{\underset{}{C}}\!-\!\!-\!\!\overset{HO}{\underset{}{C}} \Big\langle \genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4} \Big\rangle CH\!\cdot\!OH$$

$$(III.) \qquad\qquad\qquad\qquad\qquad\qquad (IV.)$$

$$(I.)\ or\ (II.) \ \longleftarrow\ HO\!\cdot\!C \Big\langle \genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4} \Big\rangle C\!\cdot\!C \Big\langle \genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4} \Big\rangle C\!\cdot\!OH$$

$$(V.)$$

* All the anthrone formulæ given in this paper are numbered with the carbonyl group in position 9.

10-Hydroxy-10-phenylanthrone differs from 10-hydroxyanthrone in giving on reduction a dianthranyl and not a dihydrodianthranyl derivative. Here the mechanism of the reaction probably consists in preliminary reduction to phenylanthrone, from which diphenyldianthranyl is very readily produced (Barnett and Cook, J., 1923, **123**, 2631).

The zinc–hydrochloric acid reduction of the two α-chloro-10-hydroxyanthrones gave compounds for which analytical figures corresponding to the α-chloroanthrones were obtained. The compounds were not the α-chloroanthrones, but each passed into the corresponding α-chloroanthrone on treatment with alcoholic sodium hydroxide. These compounds are at present under investigation and their structure will be discussed in a future communication.

Further information on the mechanism of reduction of a hydroxyanthrone was obtained by comparing the behaviour of 10-hydroxyanthrone itself towards acids and towards reducing agents with that of the two α-chloro-10-hydroxyanthrones :

With	10-Hydroxyanthrone gives	4-Chloro-10-hydroxyanthrone gives	1-Chloro-10-hydroxyanthrone gives
HBr	10-Bromoanthrone	4-Chloro-10-bromoanthrone	1-Chloro-10-bromoanthrone
HCl	10-Chloroanthrone	4 : 10-Dichloroanthrone	1-Chloroanthraquinone and 1-chloroanthrone
HI (1 or 2 mols.)	Anthraquinone and anthrone	1-Chloroanthraquinone and 4-chloroanthrone	4 : 4'-Dichloro-9 : 9'-dianthrone, 1-chloroanthrone, and a trace of 1-chloroanthraquinone
Sn and HCl	Anthrone and a small amount of dihydrodianthranyl	4-Chloroanthrone	4 : 4'-Dichloro-9 : 9'-dianthrone
H₂SO₄	Anthraquinone and anthrone	1-Chloroanthraquinone and 4-chloroanthrone	1-Chloroanthraquinone and 1-chloroanthrone
Al and H₂SO₄	Anthrone	4-Chloroanthrone	1-Chloroanthrone.

10-*Chloroanthrone* is an extremely stable substance and is readily prepared in good yield by the direct chlorination of anthrone, although Goldmann (*Ber.*, 1887, **20**, 2436; 1888, **21**, 1176) failed to obtain it by this method. It is best identified in the form of the *pyridinium* salt, $OH \cdot C \underset{C_6H_4}{\overset{C_6H_4}{<}} > C \cdot C_5H_5NCl$ (VI) or

$OC \underset{C_6H_4}{\overset{C_6H_4}{<}} > CH \cdot C_5H_5NCl$ (VII).
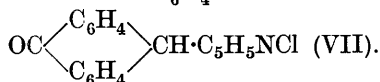
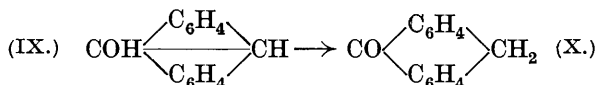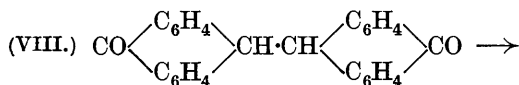The direct chlorination of 4-chloroanthrone gave 4 : 10-dichloro-

anthrone, whereas from 1-chloroanthrone the only product obtained was 4 : 4'-dichloro-9 : 9'-dianthrone, the 1 : 10-dichloroanthrone apparently being very unstable. It was not possible to prepare the last compound by the action of hydrogen chloride on the corresponding hydroxyanthrone, a disproportioning taking place with the production of the corresponding anthraquinone and anthrone. Other acids cause a disproportioning of the hydroxyanthrones, the mechanism of which has been discussed by Scholl (*Ber.*, 1923, **56**, 1065).

Hydroxyanthrone is readily converted into anthraquinol by boiling water in absence of air, this being the best method for preparing anthraquinol.

Nitration of dihydrodianthranyl leads to a *nitrodihydrodianthranyl*, a reaction which favours formula (II) without, however, excluding formula (I). The nitration is not preceded by oxidation as in the case of dihydroanthracene (Meisenheimer, *Annalen*, 1902, **323**, 205 ; 1904, **330**, 133), or of dichlorodihydrodianthranyl (Barnett and Matthews, J., 1923, **123**, 2549), the product isolated in the latter case being dichlorodinitrodianthranyl.

Dihydrodianthranyl reacts slowly with excess of bromine in carbon disulphide solution with the production of *dibromodihydro-dianthranyl*.

Dianthranol is converted by hydriodic acid in glacial acetic acid exclusively into anthrone and by tin and hydrochloric acid into a mixture of anthrone and dihydrodianthranyl. In these reactions it is improbable that anthrone is produced by the direct reduction of dianthranol and it seems almost certain that reduction is preceded by ketonisation to dianthrone, which is then reduced to anthrone. The suggestion was at first put forward (Barnett and Matthews, J., 1923, **123**, 380) that the reduction of dianthrone (VIII) to anthrone (X) was due to the instability of the dianthranyl ring system, reduction taking place at the bond joining the two *meso*-carbon atoms. Further work has rendered this view improbable, for if the single bond which joins the two anthracene ring systems in dianthrone shows this lack of stability, the corresponding double

(VIII.) $CO\big<{}^{C_6H_4}_{C_6H_4}\big>CH\cdot CH\big<{}^{C_6H_4}_{C_6H_4}\big>CO \longrightarrow$

(IX.) $COH\big<{}^{C_6H_4}_{C_6H_4}\big>CH \longrightarrow CO\big<{}^{C_6H_4}_{C_6H_4}\big>CH_2$ (X.)

bond in dianthraquinone should be even more susceptible to reduction. This, however, is not the case, dianthraquinone on reduction

giving dianthranol and not dianthrone. It therefore seems probable that hydrogen adds on to the carbonyl groups in dianthrone instead of to the single bond joining the two anthracene ring systems. In order to satisfy the requisite valencies, the " bridge " bond must be established with necessary rupture of the bond joining the two anthracene ring systems; the anthranol thus produced being at once ketonised to anthrone (X).

A similar explanation suffices to account for the reduction of 4 : 4'-dichloro-9 : 9'-dianthrone to the corresponding anthrone.

<center>EXPERIMENTAL.</center>

Dihydrodianthranyl (I or II).—To 20 g. of 10-hydroxyanthrone in 100 c.c. of boiling glacial acetic acid, 20 g. of zinc dust and 50 c.c. of concentrated hydrochloric acid were added simultaneously in small amounts. The addition of these two reagents must be simultaneous, since excess of hydrochloric acid causes decomposition of the hydroxyanthrone and excess of zinc dust brings about reduction to anthrone (Meyer, *loc. cit.*). After refluxing for 5 minutes the solid was separated from the hot solution. It crystallised from pyridine as an additive compound in greenish-yellow, flat needles, which lost pyridine on drying in the steam-oven for 3 days. The product (6 g.) became yellowish-grey and melted at 298—300° to a black liquid. In this state, it is pure enough for most purposes. For analysis it was recrystallised four times from benzene (Found : C, 94·5; H, 5·7. $C_{28}H_{20}$ requires C, 94·4; H, 5·6%).

Dihydrodianthranyl exhibits an intense violet-blue fluorescence in organic solvents. It is easily soluble in chloroform, but less so in carbon disulphide, pyridine, acetone, or ether.

Dibromodihydrodianthranyl.—Excess of bromine (1 c.c.) was added to a cold solution of dihydrodianthranyl in carbon disulphide. After 12 hours, most of the carbon disulphide was distilled off, ether added, and the resulting solid recrystallised twice from small quantities of pyridine and dried in the steam-oven (Found : C, 65·4; H, 3·6; Br, 31·1. $C_{28}H_{18}Br_2$ requires C, 65·4; H, 3·5; Br, 31·1%).

Dibromodihydrodianthranyl forms yellow crystals which do not melt at 320° and darken on exposure to light. Its solutions exhibit a blue fluorescence.

Nitrodihydrodianthranyl.—Excess of nitric acid (d 1·42; 2 c.c.) was added to 1·5 g. of finely powdered dihydrodianthranyl suspended in 50 c.c. of cold glacial acetic acid. After 12 hours, the solid was collected, washed with acetic acid, and dried in the steam-oven. The same compound was also obtained when the nitration was carried out at 80—100° and only one molecule of nitric acid

used. For analysis, it was recrystallised twice from glacial acetic acid, in which it was very sparingly soluble, separating in golden-yellow needles which melted and decomposed at 305° and darkened on exposure to light (Found : C, 83·6; H, 4·9. $C_{28}H_{19}O_2N$ requires C, 83·8; H, 4·7%).

Dichlorodinitrodianthranyl.—Dichlorodihydrodianthranyl * (Barnett and Matthews, J., 1923, **123**, 2549) in cold glacial acetic acid suspension was resistant to nitric acid, but oxidation and nitration took place when 3 g. of the finely powdered material were suspended in 30 c.c. of glacial acetic acid, 2 c.c. of nitric acid (d 1·42) added, and the whole slowly heated to the b. p. After cooling, the orange-red solid was collected, washed with acetic acid and ether, and recrystallised twice from small quantities of pyridine–alcohol. It then formed orange-red needles which became dark red on exposure to light and did not melt at 330° (Found : C, 65·5; H, 3·5; Cl, 13·8. $C_{28}H_{14}O_4N_2Cl_2$ requires C, 65·5; H, 2·7; Cl, 13·8%).

Reduction of 10-Hydroxy-10-phenylanthrone.—To 2·3 g. of hydroxy-phenylanthrone and 25 c.c. of boiling glacial acetic acid, 2 g. of zinc dust and 4 c.c. of concentrated hydrochloric acid were added simultaneously, and the whole was boiled under reflux for 5 minutes. After cooling, the solid was collected and the excess of zinc removed by digestion with dilute hydrochloric acid. The resulting diphenyl-dianthranyl (1·5 g.) was identified by analysis (C, 94·9; H, 5·2. Calc., C, 94·9; H, 5·1%) and by direct comparison with an authentic sample.

Reduction of Dianthranol.—(*a*) To 3 g. of dianthranol and 5 g. of zinc dust in 40 c.c. of boiling glacial acetic acid, 8 c.c. of concentrated hydrochloric acid were added during 2½ hours, and the boiling was continued for a further ½ hour. The yellow solid which separated from the filtered solution on cooling consisted mainly of unchanged dianthranol.

(*b*) Finely powdered dianthranol (3 g.) and zinc dust (12 g.) were heated on the water-bath with 50 c.c. of ammonia (d 0·880) and 50 c.c. of water for 3 days with occasional additions of more ammonia, sodium hydroxide, and zinc dust. The hot solution was filtered, the zinc dust extracted with dilute hydrochloric acid, and the residue recrystallised from pyridine; 0·6 g. of anthracene (m. p. 217°) was thus obtained.

(*c*) Dianthranol (1 g.) was boiled under reflux for 5 minutes with 20 c.c. of glacial acetic acid and 2 c.c. (2 mols.) of hydriodic acid (d 1·7), and the whole then diluted with hot water to incipient crystallisation. The dark crystals which separated on cooling were

* The m. p. of this compound, owing to a misprint, was given in the paper cited as 288° instead of 268°.

boiled with potassium iodide solution, and 0·9 g. of anthrone obtained. Dianthrone under similar conditions also gave anthrone.

(*d*) Dianthranol (5 g.), tin (8 g.), and glacial acetic acid (80 c.c.) were boiled under reflux and concentrated hydrochloric acid (15 c.c.) was added during 1 hour. After boiling for a further ½ hour, the hot solution was filtered. The dihydrodianthranyl which separated on cooling was recrystallised from benzene (yield 0·8 g.). The acetic liquors on dilution with water gave anthrone, which was recrystallised from glacial acetic acid and converted into anthranyl acetate.

The products in (*b*), (*c*), and (*d*) were each identified by comparison with an authentic specimen.

Reduction of Dianthraquinone.—Dianthraquinone (0·5 g.) and zinc dust (2 g.) were suspended in boiling glacial acetic acid (10 c.c.), and concentrated hydrochloric acid (3 c.c.) was added during 20 minutes. After filtration, dilute hydrochloric acid was added and the solid recrystallised from acetone. It was identified as dianthranol by its complete solubility in cold aqueous sodium hydroxide and by the preparation of dianthranyl diacetate.

1-*Chloro*-9-*anthranyl Acetate.*—A mixture of 5 g. of 1-chloro-9-anthrone, 30 c.c. of pyridine, and 7 c.c. of acetic anhydride was heated on the boiling water-bath for 15 minutes and then poured into boiling water. The solid after recrystallisation from alcohol formed long, yellow needles, m. p. 110—112° (yield 4·8 g.). Its alcoholic solutions exhibit a blue fluorescence (Found : Cl, 13·2. $C_{16}H_{11}O_2Cl$ requires Cl, 13·1%).

4-*Chloro*-9-*anthranyl Acetate.*—A similar mixture containing 4-chloro-9-anthrone * was heated for 10 minutes, the subsequent procedure being as above. The product formed almost colourless needles, m. p. 124—126° (yield 4·6 g.) (Found : Cl, 13·2%). Its solution in alcohol had a blue fluorescence.

1-*Chloro*-10-*bromoanthrone.*—Bromine (4 c.c.; 1 mol.) was added to 18 g. of finely powdered 1-chloroanthrone suspended in 50 c.c. of carbon disulphide. The solid (22·5 g.), after being washed with carbon disulphide and ether, was pure enough for most purposes, but for analysis a sample was recrystallised twice from chloroform, in which it was moderately soluble, separating in faintly yellow crystals, m. p. 165° (decomp.), which darkened on exposure to light (Found : Cl + Br, 37·75. $C_{14}H_8OClBr$ requires Cl + Br, 37·6%).

1-*Chloro*-10-*hydroxyanthrone.*—The above bromo-compound (22 g.) was boiled under reflux with 240 c.c. of acetone and 160 c.c. of water

* In preparing this compound by Barnett and Matthews's method (J., 1923, **123**, 2549) the reduction must not be too prolonged, since it has been found that 4-chloro-9-anthrone—unlike anthrone itself—slowly undergoes the pinacol condensation with tin and hydrochloric acid with the production of dichlorodihydrodianthranyl.

until an almost clear solution was obtained (about 5 minutes), the filtered solution was cooled in ice, and 160 c.c. of water were added slowly.* The resulting solid was recrystallised three times from benzene and then formed fine, white needles, m. p. 144—145°, which dissolved in boiling aqueous sodium hydroxide to form a deep red solution (Found : Cl, 14·6. $C_{14}H_9O_2Cl$ requires Cl, 14·5%).

4-*Chloro*-10-*hydroxyanthrone.*—4-Chloro-10-bromoanthrone (5 g.) was refluxed with 120 c.c. of acetone and 80 c.c. of water for 15 minutes, the filtered solution cooled in ice, and cautiously diluted with 100 c.c. of water. The yellow solid (2·5 g.) was washed with water, dried in a vacuum desiccator, and twice recrystallised from benzene; it then formed faintly yellow crystals, m. p. 144—145°. It is not altered in m. p. by mixing with 1-chloro-10-hydroxy-anthrone (Found : Cl, 14·5%).

10-*Chloroanthrone.*—(*a*) Dry hydrogen chloride was passed for 10 minutes through a suspension of 5 g. of finely powdered 10-hydroxyanthrone in 40 c.c. of toluene, a yellow precipitate forming. After dilution with light petroleum, the solid was collected and recrystallised from benzene, from which it separated with benzene of crystallisation, which was lost on drying in the steam-oven (Found : Cl, 15·5. $C_{14}H_9OCl$ requires Cl, 15·5%).

10-*Chloroanthrone* forms colourless needles which melt and evolve gas at 225°. It is very much more stable than the corresponding bromo-compound and can be recrystallised from boiling xylene. It is stable towards boiling dilute solutions of alkali hydroxides, but dissolves in their alcoholic solution with a yellow colour. It is hydrolysed, but very much more slowly than 10-bromoanthrone, to 10-hydroxyanthrone by boiling with aqueous acetone.

(*b*) Finely powdered 10-hydroxyanthrone (1 g.) was boiled with 50 c.c. of concentrated hydrochloric acid for ½ hour. The product was recrystallised from xylene and identified by its conversion into anthronylpyridinium chloride (see below).

(*c*) Very finely powdered anthrone (40 g.) was added to 180 c.c. of a solution of chlorine in carbon tetrachloride (9·5% weight-volume). The reaction was extremely sluggish, but took place rapidly with evolution of heat on the addition of a trace of iodine, so that cooling with water became necessary. When it was complete (about 10 minutes) the whole was cooled in ice, and the solid, after being washed with carbon tetrachloride and ether, was dried in the steam-oven. The yield was 33 g. and the product pure enough for most purposes without further treatment. It was identified by its conversion into anthronylpyridinium chloride.

* In this and the succeeding preparation the addition of water must be made cautiously, otherwise the product separates as an oil.

10-*Hydroxyanthranyl*-9-*pyridinium Chloride* (VI) *or Anthronyl-pyridinium Chloride* (VII).—Chloroanthrone (2 g.) was heated with 15 c.c. of pyridine on the water-bath for 15 minutes, the crystals were washed with ether and then twice recrystallised from very dilute hydrochloric acid; orange-red needles, m. p. 204° (decomp.), were obtained (Found : Cl, 11·0. $C_{19}H_{14}ONCl,H_2O$ requires Cl, 10·9%).

This chloride is easily identified by its reactions, which are similar to those of the corresponding bromide (Barnett, Cook, and Grainger, J., 1922, **121**, 2059).

4 : 10-*Dichloroanthrone*.—(*a*) Dry hydrogen chloride was passed for 10 minutes through 3 g. of finely powdered 4-chloro-10-hydroxy-anthrone suspended in 20 c.c. of benzene; the solid slowly dissolved and crystals began to separate. After addition of light petroleum, these were collected and twice recrystallised from small quantities of chloroform and light petroleum, faintly yellow crystals being obtained, m. p. 127—128° (Found : Cl, 26·9. $C_{14}H_8OCl_2$ requires Cl, 27·0%).

1-Chloro-10-hydroxyanthrone, when treated with hydrogen chloride under identical conditions, gave a mixture of 1-chloro-anthraquinone and 1-chloro-9-anthrone.

(*b*) A solution of chlorine in carbon tetrachloride (10 c.c.; 9·5% weight-volume) was added to finely powdered 4-chloro-9-anthrone (3 g.) suspended in 10 c.c. of carbon tetrachloride. No reaction took place until a crystal of iodine was added; hydrogen chloride was then slowly evolved and the solid dissolved. After concentration to small bulk, light petroleum was added and the solid recrystallised from a small quantity of chloroform–light petroleum. It was identified as 4 : 10-dichloroanthrone by the method of mixed melting points.

1-Chloro-9-anthrone, when treated under identical conditions, gave 4 : 4'-dichloro-9 : 9'-dianthrone as the sole product.

Anthraquinol.—Finely powdered 10-hydroxyanthrone (3 g.) was boiled with 100 c.c. of air-free water in an atmosphere of carbon dioxide for 20 minutes. The precipitate was identified as anthra-quinol by its complete solubility in cold aqueous sodium hydroxide, by its facile oxidation to anthraquinone, and by the preparation of anthraquinyl diacetate. If the boiling with water is continued for a longer time, the product will be contaminated with some anthraquinone.

The action of acids and reducing agents on 10-hydroxyanthrone and on the two α-chlorohydroxyanthrones, the results of which are given in the theoretical part of this paper, were carried out as follows :

Hydrobromic acid. The conditions were similar to those already described in the case of hydrochloric acid.

Hydriodic acid. The hydroxyanthrone (1 g.) was dissolved in boiling glacial acetic acid (10 c.c.), 1 or 2 mols. of hydriodic acid (*d* 1·7) were added, the whole was boiled for 1 minute in an atmosphere of carbon dioxide, and the solution then diluted with water.

Tin and hydrochloric acid. The hydroxyanthrone (1 g.), glacial acetic acid (10 c.c.), and tin (2 g.) were boiled under reflux, and concentrated hydrochloric acid (2 c.c.) was added during 5 minutes. The dianthrone or dihydrodianthranyl was filtered from the boiling solution. The filtrate on cooling deposited the anthrone.

Sulphuric acid. The hydroxyanthrone was dissolved in a small quantity of concentrated sulphuric acid in an atmosphere of carbon dioxide, kept in the cold for 15 minutes, and the product precipitated by pouring into ice-water.

Aluminium and sulphuric acid. The hydroxyanthrone (1 g.) was dissolved in concentrated sulphuric acid (11 c.c.), and aluminium powder (0·25 g.) added with cooling. A series of colour changes took place, the end of the reaction being determined by frothing and by the changing of the dark colour of the solution to light yellow or green (about $\frac{3}{4}$ hour). The product was precipitated by pouring into ice-water and purified by recrystallisation.

The identification of the compounds formed in the above reactions was effected usually by means of direct comparison with authentic samples. 1-Chloro- and 4-chloro-9-anthrone were differentiated by the preparation of the respective anthranyl acetates. When an anthrone occurred together with an anthraquinone, separation was not practicable by means of fractional crystallisation. The anthraquinone was detected by the anthraquinol test. The anthrone was detected by dissolving some of the mixture in boiling alcoholic sodium hydroxide and adding a drop of chloroform : if anthrone is present, a green colour is produced (compare Padova, *Compt. rend.*, 1909, **148**, 290); if 1-chloro-9-anthrone is present, a green colour will also develop; but if 4-chloro-9-anthrone is present, a dirty brown colour appears, thus affording a means of differentiating between 1- and 4-chloroanthrones. The most effective way of identifying 4 : 4'-dichloro-9 : 9'-dianthrone was by reducing 0·5 g. with tin (1 g.) in boiling glacial acetic acid (40 c.c.) and adding concentrated hydrochloric acid (3 c.c.) until all the solid matter had gone into solution (1½ hours). After filtration from the undissolved tin, water was added to incipient crystallisation, and the 1-chloro-9-anthrone thus obtained identified by direct comparison with an authentic sample.

Summary.

1. The reduction of 10-hydroxyanthrone and 10-hydroxy-10-phenylanthrone has been studied. Both compounds undergo the pinacol condensation with the production of dihydrodianthranyl and diphenyldianthranyl respectively.

2. The reduction of dianthranol under various conditions has been found to give anthracene, anthrone, and dihydrodianthranyl.

3. The mechanism of the reduction of a dianthrone to an anthrone has been discussed.

4. 10-Chloroanthrone, a substance of remarkable stability, has been prepared by the action of hydrochloric acid on 10-hydroxyanthrone and of chlorine on anthrone.

5. The action of acids and reducing agents on hydroxyanthrone and 1- and 4-chloro-10-hydroxy-9-anthrones has been examined. With some acids a disproportioning to the corresponding anthraquinone and anthrone takes place; reduction usually leads to the corresponding anthrone.

6. Hydroxyanthrone is easily enolised to anthraquinol by boiling water.