Raney Nickel Reductions

Part III. Reduction of Anthraquinone and Its Derivatives

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It was reported earlier that the desulphurization of Cibanone Yellow R by treatment with Raney nickel gave a difficultly separable mixture of several substances, which apparently resulted from the reduction of 2-methylanthraquinone. It was necessary, therefore, to effect the desulphurization of the dye under conditions which would, if possible, leave the 2-methylanthraquinone residues in the dye unaffected after removal of sulphur and also to examine the products of the Raney nickel reduction of anthraquinone and some of its derivatives. With these objects in view the reduction of 2-methylanthraquinone, 2-mercaptopmethylanthraquinone (I), bis-2-anthraquinononylmethyl sulphide (II) and bis-2-anthraquinononylmethyl disulphide (III),

which may be intermediates in the formation of the dye, was studied. A comparative study of the reduction of anthraquinone was also carried out.

Anthraquinone and 2-methylanthraquinone have been converted to different hydro derivatives by the action of hydrogen in presence of metal catalysts, such as platinum in glacial acetic acid and nickel in alcohol under pressure. Raney nickel has been used in aqueous alkali, in dioxane,
and in alcohol at atmospheric pressure. Papa has effected desulphurizations in alkaline solutions by the addition of Raney alloy; under those conditions it was expected that Cibanone Yellow R, which is sparingly soluble in organic solvents, would vat and dissolve and then undergo desulphurization smoothly. The reduction of 2-methylanthraquinone was therefore studied particularly under these conditions.

Reduction of 2-methylanthraquinone with Raney alloy in aqueous alkali led to several derivatives of 2-methylanthraquinone. Using 2-methylanthraquinone (1 part) and Raney alloy (4 parts) for 10 hours, 5 crystalline products were obtained, which analysed for dihydro- (m.p. 126–7°), tetrahydro- (m.p. 170–1°), and octahydromethylanthraquinone (m.p. 136°, m.p. 146° and m.p. 163–4°). Raney alloy (2.5 parts) for 1 hour gave tetrahydro-2-methylanthraquinone (m.p. 170–1° identical with the tetrahydro derivative mentioned above). One part of Raney alloy for 1 hour gave some unreacted 2-methylanthraquinone (0.35 part), together with reduction products. Reduction of anthraquinone (1 part) with Raney alloy (2 parts) for 2 hours gave 1:2:3:4-tetrahydroanthraquinone.

The constitution of the reduction products was determined by oxidative degradation. 1:2:3:4-Tetrahydroanthraquinone on oxidation with potassium permanganate in acetone gave a mixture of phthalic and adipic acids, which were separated by taking advantage of the insolubility of the lead salt of phthalic acid in glacial acetic acid. Oxidation of tetrahydro-2-methylanthraquinone under similar conditions gave 4-methylphthalic acid and adipic acid, indicating that the tetrahydro derivative is 1:2:3:4-tetrahydro-6-methylanthraquinone. Reductive acetylation gave 9:10-diacetoxy-1:2:3:4-tetrahydro-6-methylanthracene.

Fusion of tetrahydroanthraquinone derivatives with caustic potash was not useful for determining their constitution, since tetrahydrobenzoic acids were not isolable. When tetrahydroanthraquinone was fused with caustic potash, anthraquinone was mainly formed, together with a small amount of benzoic acid. Dehydrogenation appeared to precede degradation.

In the course of their work on the constitution of vitamins K₂ and K₁, Fieser et al. synthesized several 2:3-dialkyl-1:4-naphthoquinones. They found a close correspondence between the spectra of the vitamins and the synthetic naphthoquinones, as well as their physiological and antihemorrhagic activity. Since 1:2:3:4-tetrahydroanthraquinone is structurally allied to 2:3-dialkyl-1:4-naphthoquinones and gives an absorption spectrum (Fig. 1) closely resembling the spectra of the naphthoquinones, it is likely to possess antihemorrhagic activity. The bathochromic shift
in the spectrum of 1:2:3:4-tetrahydromethylanthraquinone shows that
the methyl group is present in the unreduced benzene ring. The reduction
of the unsubstituted ring in 2-methylanthaquinone would appear to be in
agreement with the observation of Stork\(^{14}\) that "in a polycyclic aromatic
compound that ring will become reduced, the reduction of which will result
in the smallest loss of resonance energy by the system".

Having arrived at a mild reduction procedure whereby at least a part
of the 2-methylanthaquinone was left unreduced, the desulphurization of
the simple sulphur-containing derivatives (I, II and III) of 2-methylantha-
quinone was next examined. The exocyclic sulphur in these compounds
was expected to poison part of the catalyst during reduction and thus prevent
the reduction of the 2-methylanthaquinone residue. 2-Mercaptomethylantha-
quinoine (I) gave a mixture of 2-methylanthaquinone, 2-hydroxy-
methylanthaquinone, anthraquinone-2-carboxylic acid, and \textit{bis}-2-anthra-
quinoynylnmethyl sulphide (II). \textit{Bis}-2-anthraquinonylnmethyl sulphide (II) gave
a-mixture of 2-methyloanthraquinone and traces of Anthraflavone. Bis-2-
anthraquinonylmethyl disulphide (III) gave a mixture of 2-methyloanthra-
quinone, 2-hydroxymethyloanthraquinone and anthraquinone-2-carboxylic acid. The preparation of compounds (I), (II) and (III), carried out by S. P. Chandavarkar will be reported separately. Desulphurization of benzyl mercaptan and di-p-tolyl sulphide under similar conditions has been studied by Papa, who obtained toluene as the only product.\(^8\) The behaviour of the anthraquinone derivatives is thus distinctive. The isolation of 2-hydroxy-
methyloanthraquinone and anthraquinone-2-carboxylic acid, in addition to 2-methyloanthraquinone, from the desulphurization products of (I) and (III) is of interest. In the desulphurization of (II), in addition to 2-methyloanthra-
quinone, Anthraflavone was isolated in small quantities. In the desulphuriza-
ton of (I), (II) was obtained as one of the products; the formation of a compound with lower sulphur content indicates the poisoning effect of the thiol group on the nickel catalyst.\(^15\)

The reduction of \(\alpha: \beta\)-bis-2-anthraquinonylethylene (Anthraflavone) with Raney alloy gave a mixture of products from which a compound analysing for decahydroanthraflavone and a small quantity of 1:2:3:4-tetrahydro-
6-methyloanthraquinone were isolated. Part of the Anthraflavone thus cleaved at the ethylene bridge during reduction. Fission of the carbon-
carbon linkage has been reported by Snyder and Cannon who obtained methane and ethane by the Raney nickel reduction of ethers of ethylenedi-
thiol.\(^16\) Earlier we have reported that reduction of thiouindigo with Raney alloy yields benzoic acid among other products.\(^17\) In view of the fact that the reduction of 2-methyloanthraquinone under mild conditions yields 1:2:3:4-tetrahydro-6-methyloanthraquinone, it is likely that the unsubstituted benzene rings and the ethylene link in Anthraflavone are reduced and that the decahydroanthraflavone mentioned earlier is constituted as \(\alpha: \beta-6: 6'-bis-(1:2:3:4\)-tetrahydroanthraquinonyl) ethane.

Another approach to the determination of the nature of the desulphuriza-
tion products obtained from Cibanone Yellow R would be to dehydrogenate the reduced anthraquinone derivatives to anthraquinone derivatives, which may be more amenable to separation. Dehydrogenation of 1:2:3:4-
tetrahydroanthraquinone and 1:2:3:4-tetrahydro-6-methyloanthraquinone was therefore studied. The conversion of anthrone to anthraquinone in 80-90% yield by passage of a benzene solution through an alumina-Celite column has been reported.\(^18\) We have now found that 1:2:3:4-tetra-
hydroanthraquinone and its 6-methyl derivative are converted to the cor-
responding anthraquinones in 95% yield, when a hexane solution is passed
through a column of alumina (Brockmann standard activity I). The tetrahydro derivatives were also dehydrogenated by shaking a hexane solution with excess of alumina. Alumina of lower activity was either ineffective or effected partial dehydrogenation. That light did not play a part in the dehydrogenation was shown by carrying out the reaction in the dark. Solvents more polar than hexane were unsuitable for the dehydrogenation, which also did not take place when other adsorbents such as Fuller’s earth and calcium sulphate were used.

Dehydrogenation of 1:2:3:4-tetrahydroanthraquinone to anthraquinone by hot aniline and cyclohexylamine, by sulphuric acid, and by bromination of the hydrogenated nucleus and subsequent loss of hydrogen bromide have been reported. It has now been found that alkali fusion gave the dehydrogenated product together with a trace of benzoic acid. Tetrahydroanthraquinone was also dehydrogenated by boiling pyridine in good yield. Dehydrogenation by means of chloranil in boiling xylene was unsuccessful. Treatment of the reduced anthraquinones with sulphur at 200° gave the parent anthraquinones. Excellent yields of the anthraquinones were obtained when tetrahydroanthraquinone derivatives were treated with iodine and sodium acetate in boiling nitrobenzene. Iodine and sodium acetate in alcoholic solution has been used for dehydrogenation purposes. This method, however, failed with the reduced anthraquinones. Iodine has been used for aromatization at high temperatures, but the reaction was accompanied by partial dehydrogenation condensation. This is eliminated by the use of sodium acetate as acid-binding agent and nitrobenzene as solvent. Treatment of decahydroanthraflavone with iodine under these conditions gave α : β-bis-2-anthraquinonylethane (dihydroanthraflavone). The latter product was not further dehydrogenated by iodine in nitrobenzene, but treatment with excess of selenium dioxide in boiling nitrobenzene yielded Anthraflavone. The action of selenium dioxide on dibenzyl has been shown to result in benzene, benzaldehyde, stilbene and benzil, or a mixture of stilbene and benzil, depending on the conditions employed. In the case of Anthraflavone oxidation to the diketo derivative or fission of the carbon-carbon linkage does not occur in spite of the use of a large excess of selenium dioxide. When a mixture of 1 : 2 : 3 : 4-tetrahydroanthraquinone (1 mol.) and selenium dioxide (1·1 mol.) was heated at 170°, the major products were anthraquinone and α-hydroxyanthraquinone. With excess of selenium dioxide (4 mol.) tetrahydroanthraquinone gave quinizarin as one of the products. The action of selenium dioxide on reduced 2-methylanthaquinones is under investigation. By analogy with the formation of hydroxyanthraquinone derivatives, reduced 2-methylanthaquinone derivatives may lead
alcohol gave a 35% recovery of unchanged 2-methylantraquinone, m.p. 172°.

**Oxidation of 1:2:3:4-tetrahydroanthraquinone**

Tetrahydroanthraquinone (0·2 g.) was dissolved in acetone (25 c.c.) at 25° and powdered potassium permanganate was added slowly till a pink colour remained; the mixture was then refluxed, and since the pink colour was discharged more permanganate was added till a faint pink persisted. The total permanganate added was 0·7 g. The heating was continued for 2 hours. After distilling off acetone, the residue was extracted with hot water and the extract acidified with hydrochloric acid and evaporated to dryness. Ether extraction of the residue and evaporation of ether led to a sticky yellow substance (0·25 g.) which was dissolved in glacial acetic acid (15 c.c.) and warmed to 60°. A solution of lead acetate trihydrate (0·5 g.) in glacial acetic acid (2 c.c.) was added. The turbid solution was left overnight, and filtered from the precipitate (A). The filtrate was evaporated, acidified with dilute hydrochloric acid, evaporated to dryness, and the residue extracted with ether. The ether extract gave a yellow substance, which was triturated with chloroform and filtered. The residue crystallized from concentrated nitric acid in colourless prisms (0·07 g.), m.p. 151°, identified as adipic acid.

The precipitate (A) was treated with dilute hydrochloric acid, evaporated to dryness and extracted with ether. The ether extract gave colourless needles (0·11 g.), m.p. 199–200° (dec.). On refluxing with acetyl chloride for 1 hour and evaporating, the residue crystallized from hexane in colourless needles, m.p. 131°, identified as phthalic anhydride.

**Oxidation of tetrahydromethylanthraquinone**

Oxidation of tetrahydromethylanthraquinone (0·2 g.) as above gave adipic acid (0·05 g.). A second acid was formed, which gave a lead salt insoluble in glacial acetic acid. After recovery from the lead salt and crystallization from benzene, the microcrystalline powder had m.p. 147° (Found: C, 60·5; H, 4·4. Calc. for C₉H₆O₄: C, 60·0; H, 4·4%). The acid appeared to be 4-methylphthalic acid, for which the m.p. quoted in the literature is 152°. This was confirmed by conversion into the anhydride, m.p. 92°.

**Reductive acetylation of tetrahydromethylanthraquinone**

Tetrahydromethylanthraquinone (0·4 g.), acetic anhydride (5 c.c.), zinc dust (0·8 g.) and pyridine (5 drops) were refluxed for 2 hours. On pouring
into ice and hydrochloric acid, the colourless precipitate (0.4 g.) was collected, washed, dried, dissolved in carbon tetrachloride and chromatographed on alumina. The colourless percolate gave a product which crystallized from alcohol in needles, m.p. 155° (Found: C, 72.6; H, 6.6. C₁₉H₂₉O₄ requires C, 73.1; H, 6.4%).

**Alkali fusion of tetrahydroanthraquinone**

Tetrahydroanthraquinone (0.5 g.) was slowly added to molten caustic potash (5.0 g.) under stirring at 200°, and the mixture was stirred for 3 hours at 210°. After cooling the melt was extracted with water and acidified with hydrochloric acid. The precipitate (0.47 g.) proved to be anthraquinone. Ether extraction of the filtrate gave a colourless product (0.02 g.), most of which was soluble in chloroform. The chloroform-insoluble residue gave the fluorescein test and was apparently phthalic acid. The chloroform-soluble portion crystallized from water in needles, m.p. 121°, undepressed when mixed with benzoic acid.

**Desulphurization of 2-mercaptomethylanthraquinone**

The thiol (5 g.) was heated with Raney alloy (5 g.) in 10% caustic soda solution (150 c.c.) on a water-bath for 1 hour. Filtration from nickel and aeration of the filtrate gave a reddish brown, sulphur-free precipitate (1.5 g.). The substance was extracted with alcohol (60 c.c.) and the insoluble residue (A) and the extract worked up separately. The latter was evaporated to dryness, and the residue was dissolved in acetone and chromatographed on alumina. The first percolate contained the major fraction (0.26 g.) which separated from alcohol as a yellow crystalline powder, m.p. 182° (Found: C, 75.2; H, 4.5. Calc. for C₁₅H₁₉O₅: C, 75.6; H, 4.2%). The m.p. and elementary analysis of the product are in agreement with those of 2-hydroxymethylanthraquinone, m.p. 183°.²⁴

The residue (A) crystallized from acetic acid in pale yellow needles (0.57 g.), m.p. 285-6°; undepressed when mixed with anthraquinone-2-carboxylic acid.

The nickel residue after treatment with hydrochloric acid was extracted with benzene in a Soxhlet for 3 days. The benzene extract gave a product (2.45 g.) containing sulphur. Extraction with alcohol (75 c.c.) effected a fractionation into an insoluble substance (B) and an alcoholic extract. The alcohol-soluble substance was dissolved in carbon tetrachloride and chromatographed on alumina, using chloroform as eluant. The first percolate gave a yellow compound (0.57 g.), which crystallized from alcohol in pale yellow needles, m.p. 172° undepressed when mixed with 2-methylantraquinone,
The alcohol-insoluble residue (B) crystallized from acetic acid in small needles (0.87 g.), m.p. 244\degree, and was identified as bis-2-anthraquinononylmethyl sulphide by a mixed m.p.

*Desulphurization of bis-2-anthraquinonylmethyl sulphide*

The sulphide (5 g.) was treated with Raney alloy (5 g.) in 10% aqueous caustic soda solution (150 c.c.) as above for 1 hour. The reaction mixture was filtered and the red alkaline filtrate on passing air gave a yellow product (3.25 g.). Extraction with alcohol (225 c.c.) and concentration of the extract gave a product (2.5 g.), m.p. 171\degree; undepressed when mixed with 2-methylanthaquinone.

The alcohol-insoluble residue (0.22 g.) contained sulphur. On extraction with acetic acid a sulphur-free residue was obtained which crystallized from nitrobenzene in yellow needles, m.p. 434\degree, undepressed when mixed with Anthraflavone.

The nickel residue, after acidification, washing, drying and Soxhlet extraction with benzene, gave a product, which on chromatographic purification on alumina, led to 2-methylanthaquinone (0.75 g.).

*Desulphurization of bis-2-anthraquinononylmethyl disulphide*

The disulphide (5 g.) was treated with Raney alloy (5 g.) and 10% caustic soda solution (150 c.c.) on a water-bath for 1 hour. The greenish alkaline filtrate on aeration gave a brownish sulphur-free product (1.85 g.). On extraction with alcohol (50 c.c.) and chromatographic purification of the alcohol-soluble portion, 2-hydroxymethylanthaquinone (0.4 g.), m.p. 182\degree, was obtained. The alcohol-insoluble portion crystallized from acetic acid in needles (0.8 g.), m.p. 285–6\degree, undepressed when mixed with anthraquinone-2-carboxylic acid.

The nickel residue, after deactivation as usual and Soxhlet extraction with benzene, gave a sulphur-free sticky substance (1.55 g.). After chromatographing twice on alumina, using carbon tetrachloride as solvent and crystallizing from alcohol, 2-methylanthaquinone (0.87 g.) was obtained.

*Reduction of Anthraflavone*

Anthraflavone (5 g.) was dissolved in concentrated sulphuric acid and reprecipitated with water. The precipitate was filtered, washed free from acid, and the wet cake suspended in 10% caustic soda solution (150 c.c.). The mixture was treated with Raney alloy (15 g.) as above for 1 hour. The brownish red alkaline filtrate, on aeration, gave a yellow product (A) (2.65 g.). The alkaline solution after separation of (A) was poured into excess of
concentrated hydrochloric acid and the dark brown precipitate (B) was collected. Substance (A) was extracted with alcohol (100 c.c.) and product obtained from the alcoholic extraction was dissolved in carbon tetrachloride and chromatographed on alumina. The first fraction on concentration gave yellow needles, m.p. 170°, undepressed when mixed with 1:2:3:4-tetrahydro-6-methylanthaquinone. The major component was a brown uncry stallizable substance.

The alcohol-insoluble residue (1.6 g.) was dissolved in pyridine and chromatographed on alumina, using carbon tetrachloride as the eluant. The major fraction, which was eluted first, crystallized from acetic acid in yellow plates, m.p. 254° (Found: C, 79.3; H, 5.9. Decahydroanthra-
flavone, C_{30}H_{26}O_{4} requires C, 80.0; H, 5.8%). Substance (B) was extracted with aqueous sodium bicarbonate in which the major part went into solution. The extract on acidification gave a brown precipitate which could not be crystallized. Likewise, no crystalline material was recoverable from the nickel residue.

**Dehydrogenation of tetrahydroanthraquinone by activated alumina**

*Method 1.*—Tetrahydroanthraquinone (0.2 g.) was dissolved in hexane (50 c.c.) and passed through a column (25 cm. long and 1.5 cm. diameter) of alumina (35 g.; Grade I, Brockmann standard). Elution was effected with 2.5 l. of hexane. Removal of the solvent from the percolate and crystallization from acetic acid gave anthraquinone (0.16 g.), m.p. 286° and unconverted tetrahydroanthraquinone (0.03 g.), m.p. 157°.

Under similar conditions, tetrahydromethylanthaquinone gave 2-methyl-
anthraquinone in 95% yield.

*Method 2.*—Tetrahydroanthraquinone (1 part) was dissolved in hexane and shaken with alumina (100 parts; Grade I, Brockmann standard) for 25 hours. Extraction of the alumina with alcohol gave anthraquinone. Tetrahydromethylanthaquione was similarly converted to 2-methylantha-
quinone.

These treatments were repeated with the exclusion of light, but the same results were obtained.

**Dehydrogenation of tetrahydroanthraquinone with pyridine**

Tetrahydroanthraquinone (0.05 g.) was refluxed with pyridine (5 c.c.) for 24 hours. The yellow solution slowly turned dark brown. On pouring into ice and hydrochloric acid, the precipitate (0.045 g.) had m.p. 279–80° and was identified as anthraquinone.
Tetrahydromethylandranthraquinone on similar treatment gave 2-methylanthraquinone.

Action of chloranil on tetrahydroanthraquinone

Tetrahydroanthraquinone (0·5 g.) and chloranil (1·25 g.) were added to sulphur-free xylene (40 c.c.) and refluxed for 20 hours. The mixture was then cooled, diluted with ether (40 c.c.) and filtered. The filtrate was extracted with 5% caustic soda solution (200 c.c.). The xylene layer was warmed to expel the ether and the xylene steam distilled. The residual solid crystallized from aqueous acetic acid in needles (0·35 g.), m.p. 158°, undepressed when mixed with tetrahydroanthraquinone.

Dehydrogenation of tetrahydroanthraquinone by sulphur

Tetrahydroanthraquinone (0·5 g.) was mixed with sulphur (0·22 g.) and heated at 200° for 3 hours. The mixture was then extracted with sodium sulphide solution to remove the excess of sulphur and then with acetic acid, some resinous material being left behind. The acetic acid extract gave a yellow substance (0·2 g.) on evaporation and it crystallized from alcohol in yellow needles, m.p. 278°, undepressed when mixed with anthraquinone.

Dehydrogenation of tetrahydromethylandranthraquinone by sulphur

Tetrahydromethylandranthraquinone (0·5 g.) was mixed with sulphur (0·42 g.) and heated at 200° for 5 hours when the evolution of hydrogen sulphide was nearly complete. The mixture was extracted with sodium sulphide solution to remove excess of sulphur and then with alcohol. The alcoholic solution on evaporation gave a yellow substance (0·22 g.), which was chromatographed on alumina using chloroform as solvent. 2-Methylanthraquinone (0·2 g.), m.p. 171–2°, was isolated as the main product.

Dehydrogenation of tetrahydroanthraquinone by iodine

Tetrahydroanthraquinone (0·5 g.), fused sodium acetate (2·0 g.) and iodine (1·5 g.) were refluxed with nitrobenzene (25 c.c.) for 6 hours. The solvent was steam distilled and the residue was treated with aqueous sodium thiosulphate solution to remove traces of unreacted iodine. On crystallization from alcohol, anthraquinone (0·4 g.) was obtained.

Dehydrogenation of tetrahydromethylandranthraquinone by iodine

Tetrahydromethylandranthraquinone (0·5 g.), fused sodium acetate (2·0 g.) and iodine (2·3 g.) were refluxed with nitrobenzene (25 c.c.) for 6 hours. On working up as described above, 2-methylandranthraquinone (0·35 g.) was obtained.
Dehydrogenation of decahydroanthraflavone by iodine

Decahydroanthraflavone (0·38 g.), sodium acetate (2 g.) and iodine (1·35 g.) were refluxed with nitrobenzene (20 c.c.) for 6 hours. Nitrobenzene was removed by steam distillation and the residue was crystallised from o-dichlorobenzene in needles (0·28 g.), m.p. 330°, undepressed when mixed with dihydroanthraflavone.

Dehydrogenation of dihydroanthraflavone by selenium dioxide

Dihydroanthraflavone (0·1 g.) and selenium dioxide (0·4 g.) were refluxed with nitrobenzene (10 c.c.) for 7 hours and filtered hot. The filtrate on cooling gave a substance, which crystallized from nitrobenzene in yellow needles (0·08 g.), m.p. 430–1°, identified as Anthraflavone by m.p. and mixed m.p. and the violet colouration with sulphuric acid.

Action of selenium dioxide on tetrahydroanthraquinone

Method 1.—Tetrahydroanthraquinone (0·5 g.; 1 mol) and selenium dioxide (1·05 g.; 4 mol.) were thoroughly mixed and heated in a test tube fitted with an air condenser. The mixture was slowly heated to 170° and maintained at this temperature for 2 hours. The reaction mixture was extracted repeatedly with alcohol. The alcoholic extract was taken down to dryness and extracted with 10% caustic soda solution. The minute amount of alkali-insoluble matter was not examined further. The violet alkaline extract on acidification gave a red solid which was sublimed at 200°/3 mm. The sublimate was dissolved in alcohol and the solution, on leaving in the refrigerator, slowly deposited a red crystalline product, m.p. 195–6°, undepressed when mixed with quinizarin. The mother liquor was evaporated and the residue was dissolved in acetone and chromatographed on heavy magnesium carbonate. An upper pink zone and a lower orange zone separated. The zones were cut out and treated with hydrochloric acid and ether. The ether extract from pink zone led to quinizarin, and orange band yielded α-hydroxyanthraquinone.

Method 2.—A mixture of tetrahydroanthraquinone (0·5 g.; 1 mol.) and selenium dioxide (0·29 g.; 1·1 mol.) was heated and worked up as above. The major product was insoluble in aqueous caustic soda; this was chromatographed on alumina using chloroform as solvent. A yellow percolate and an orange zone on the alumina were obtained. The percolate on evaporation gave anthraquinone. The strongly adsorbed substance was isolated by extraction of the alumina with alcohol containing a few drops of hydrochloric acid. The yellow solution gave yellow needles, which on recrystal-
lization from alcohol had m.p. 191°, undepressed when mixed with α-hydroxyanthraquinone.

**Summary**

Reduction of anthraquinone, 2-methylantraquinone, 2-mercaptopanthraquinone (I), bis-2-anthraquinononylmethyl sulphide (II) and bis-2-anthraquinononylmethyl disulphide (III) by Raney alloy in aqueous alkaline solution was studied. Anthraquinone gave 1:2:3:4-tetrahydroanthraquinone. When 2-methylantraquinone was reduced with varying amounts of Raney alloy, several hydro derivatives of 2-methylantraquinone were obtained. One was 1:2:3:4-tetrahydro-6-methylantraquinone, the constitution of which was proved by oxidation to adipic and 4-methylphthalic acids. Desulphurization of (I) gave 2-methylantraquinone, 2-hydroxymethylanthraquinone and anthraquinone-2-carboxylic acid; (II) gave 2-methylantraquinone and traces of Anthraflavone; and (III) gave 2-methylantraquinone, 2-hydroxymethylanthraquinone and anthraquinone-2-carboxylic acid. Anthraflavone gave decahydroanthraflavone as the major product and a small amount of 1:2:3:4-tetrahydro-6-methylantraquinone.

Dehydrogenation of tetrahydro- and tetrahydromethylantraquinones to the parent compounds was effected by several methods including treatment with iodine and sodium acetate in nitrobenzene and the action of activated alumina on a hexane solution. Treatment of tetrahydroanthraquinone with selenium dioxide at 170° gave a mixture of anthraquinone, α-hydroxyanthraquinone and quinizarin. Decahydroanthraflavone was dehydrogenated in two steps to Anthraflavone.

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**References**

2. Skita \( \rightarrow \) Ber., 1925, 58B, 2685.
4. Dufraisse and Houpillart \( \rightarrow \) Compt. rend., 1937, 205, 740.
5. U.S.P., 2,495,229.
11. Doisy' et al. Ibid., 1939, 61, 1295; 1612.
23. Niementowski Monatsh., 1891, 12, 625.