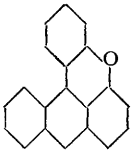
99. *Experiments in the Coeroxene and Coeramidine Series.*

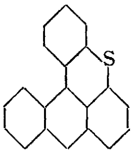
By A. H. Cook and W. Waddington.

A variety of 1-mono- and 1 : 5-bis-methoxyphenoxyanthraquinones were prepared, but although they were not converted into coeroxenones and coerodioxonones entirely satisfactorily, 1 : 4-bis-*m*-methoxyphenoxyanthraquinone was easily converted into a *cis*-coerodioxonone. On the other hand, the three 1-anisidinoanthraquinones and the three *s*-1 : 5-dianisidinoanthraquinones were cyclised and simultaneously demethylated to dihydroxycoerodiamidines; the acidity of the products may, it is suggested, be correlated with their bond structures.

The coeroxene, coerthiene, and coeramidine systems (I), (II), and (III) are the parents of a number of compounds of dye character, as are also coerodioxene, coerodithiene, and coerodiamidine (Houben, " Das Anthracen u. die Anthrachinone," 1929, 653, 790). Coeroxenone-9 * and coerodioxylium salts, (IV) and (V), are most readily obtained by cyclising 1-mono- or 1 : 5-di-aryloxyanthraquinones, *e.g.*, with 70% sulphuric acid (see, *e.g.*, Decker, *Annalen*, 1907, **356**, 319), and sulphur and nitrogen analogues have been similarly prepared (cf. D.R.-P. 126,444, which describes the cyclisation of 1-anilinoanthraquinones with a variety of acid reagents). Interest in this field is reviving. For instance, Scholl, Böttger, and Wanka (*Ber.*, 1934, **67**, 599) have prepared carboxylated compounds of this type. A series of patents describes the reduction of coeroxonols (B.P. 448,180; F.P. 794,596; D.R.-P. 639,168; U.S.PP. 2,176,421, 2,250,270), and the present work arose from the cyclisation of 1-*m*-methoxyphenoxy- and 1 : 5-bis-*m*-methoxyphenoxy-anthraquinones (King, J., 1934, 1064) by sulphuric acid. King showed that demethylation as well as cyclisation occurred and that compounds of the coeroxonone-3 : 9 (VI) or coerodioxonone-2 : 10 (VII*a*) type are formed. The work now reported indicates that demethylation is equally readily effected throughout the analogous coeramidone and coerodiamidine series. On repeat-



(I.)



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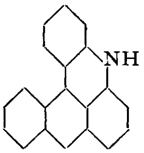

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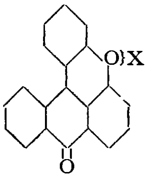

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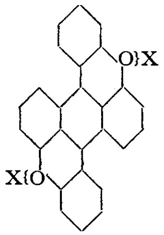

(V.)

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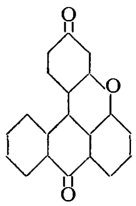
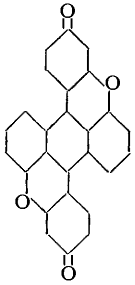
* The nomenclature and numbering are those adopted in " The Ring Index " (Patterson and Capell, 1940).

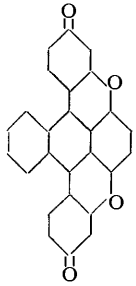
ing the preparation of coerodioxonone a satisfactory product of the expected composition could not be obtained; even by using sulphuric acid under milder conditions than those employed by King, the product always contained sulphur and, although there was no doubt of the structure suggested, it seemed certain that the product was to some extent sulphonated. Cyclisation by other methods, *e.g.*, by using zinc chloride, or zinc chloride and benzoyl chloride in nitrobenzene, led to dyes of the same character, though again they were analytically unsatisfactory and could not be obtained entirely free from chlorine. Attempts to prepare pure diacetyl and dimethyl derivatives were not successful. On the other hand, 1 : 4-*bis*-m-*methoxyphenoxyanthraquinone* was prepared without difficulty and cyclised in hot sulphuric acid. The sparingly soluble product did not contain methoxyl groups, gave intense magenta colorations in acetone, chloroform, or nitrobenzene, even in dilute solution, and gave a soluble vat. It is regarded as a cis-*coerodioxonone* (VII*b*).



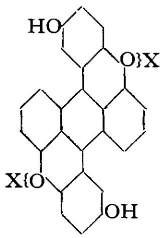
(VI.)



(VII*a*.)



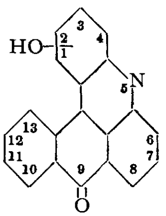
(VII*b*.)



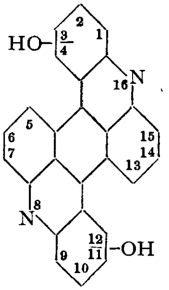
(VIII.)

A variety of 1-*mono-* and 1 : 5-*bis*-o- or -p-*methoxyphenoxyanthraquinones* were prepared, but although they were clearly cyclised by sulphuric acid, by boiling with acid chlorides, zinc chloride and nitrobenzene, or by fusion with sodium aluminium chloride, it was again impossible to obtain the products in satisfactory form. As the products would be formulated as complex pyrilium salts (VIII), this failure is not difficult to understand. Attention was then turned to the corresponding anisidino-anthraquinones. The three 1-*anisidinoanthraquinones* were obtained from the anisidines, 1-chloroanthraquinone, potassium acetate, and copper powder in boiling nitrobenzene. Heating 1 : 5-dichloroanthraquinone with 2 mols. of *m*- or *p*-anisidine under similar conditions gave only 1-*chloro*-5-m- or -p-*anisidinoanthraquinone.* 1 : 5-*Bis*-o-, -m-, and -p-*anisidinoanthraquinones* were obtained only with excess of anisidine. All these anisidinoanthraquinones underwent dehydration on heating with sulphuric acid, less satisfactorily with zinc chloride and an acid chloride in nitrobenzene, or with sodium aluminium chloride. Analytical data, the absence of methoxyl groups, and the preparation of representative acetyl and benzoyl derivatives indicated that again demethylation also had taken place to give *hydroxycoeramidones* (IX) or *dihydroxycoerodiamidines* (X).

(IX.)



(IX.)



(X.)

This reaction course was confirmed in that representative anisidinoanthraquinones were heated with zinc chloride in acetic acid (cf. D.R.-P. 126,444) to undergo cyclisation without demethylation; the resulting crude methoxycoeramidones afforded the corresponding hydroxy-compounds after hydrolysis with hydriodic acid or sodium hydroxide, though the reactions were less satisfactory than cyclisation with sulphuric acid.

All the hydroxy-coeramidones examined were remarkable in dissolving readily in dilute alkali carbonate or ammonia. It is suggested that an explanation of this rather unexpected acidity is to be found in a varying degree of unsaturation of the cyclic bonds due to mesomerism. Following a suggestion of Pauling ("The Nature of the Chemical Bond," 1940, 141) it can be shown that in (IX) the Δ^1-, Δ^3-, Δ^6- and Δ^8-linkages have three-fourths of the character of an ethylenic double bond, and that Δ^1- and Δ^3-linkages in (X) have nine-tenths of that character. Hydroxyl groups attached in these positions would then be comparable with those in acidic hydroxyquinones rather with those in phenols. The acidity of Bz.-hydroxybenzanthrones and the facile demethylation of 1-anisidino- and of 1 : 5-dianisidino-anthraquinones during cyclisation may be attributed to the same cause. It was shown that both coeramidone and coerodiamidone reacted with boiling aniline to give bases; the products were not well defined, possibly because they were mixtures, but there was no doubt that anilino-groupings had been introduced. The reactions of quinones, benzanthrone, and 1 : 2-benzophenazine with aniline are examples of similar reactivity in structures with partial or complete fixation of double bonds.

EXPERIMENTAL.

(Colours produced in concentrated sulphuric acid are noted in parentheses immediately after the name of the compound.)

Methoxyphenoxyanthraquinones.—A mixture of sodium *m*-methoxyphenoxide (7 g.) and 1-chloro-5-aminoanthraquinone (10 g.) was heated at 160—170° for 1 hour. The product was washed with water, recrystallised twice from acetic acid (charcoal) and finally from ethanol. 5-*Amino*-1-m-*methoxyphenoxyanthraquinone* (4·2 g.) formed small crimson prisms, m. p. 176—176·5° (Found : C, 73·1; H, 4·7. $C_{21}H_{15}O_4N$ requires C, 73·1; H, 4·4%).

1 : 5-Dichloroanthraquinone (2·8 g.), quinol monomethyl ether (7·5 g.), anhydrous potassium carbonate (3 g.), copper powder (0·1 g.), and nitrobenzene were refluxed for 1·5 hours. Aqueous sodium hydroxide was added, and solvent distilled in steam. The residual solid was crystallised from acetic acid (charcoal), giving 1 : 5-*bis*-p-*methoxyphenoxyanthraquinone* (magenta) (3 g.); it separated in orange plates, m. p. 226° (Found : C, 74·1; H, 4·7. $C_{28}H_{20}O_6$ requires C, 74·3; H, 4·5%). The following were prepared similarly. 1-p-*Methoxyphenoxyanthraquinone* (magenta) separated from acetic acid or ethanol in plates, m. p. 161·5° (Found : C, 76·6; H, 4·3. $C_{21}H_{14}O_4$ requires C, 76·4; H, 4·3%). 1-o-*Methoxyphenoxyanthraquinone* (purple-red) formed yellow prisms, m. p. 208°, from ethanol or acetic acid (Found : C, 76·3; H, 4·6%). 1 : 5-*Bis*-o-*methoxyphenoxyanthraquinone* (purple) was obtained by heating 1 : 5-dichloroanthraquinone (2·8 g.), guaiacol (27 g.), sodium carbonate (2·5 g.), and copper powder (0·1 g.) at 200° for 1 hour, diluting the product with ethanol and 10% sodium hydroxide solution, and crystallising the precipitate from acetic acid (yield, 2·9 g.); it formed yellow needles, m. p. 186° (Found : C, 74·4; H, 4·8. $C_{28}H_{20}O_6$ requires C, 74·3; H, 4·5%). 1 : 4-Dichloroanthraquinone (8 g.), *m*-methoxyphenol (7·5 g.), and sodium hydroxide (3 g.) in water (3 c.c.) were heated at 160—170° for 1 hour. After washing with hot water, residual 1 : 4-*bis*-m-*methoxyphenoxyanthraquinone* (intense magenta) was crystallised from acetic acid (charcoal) (yield, 9 g.); it formed golden-yellow needles, m. p. 149·5° (Found : C, 74·5; H, 4·7%).

1 : 4-Bis-*m*-methoxyphenoxyanthraquinone (4 g.) was heated with 75% sulphuric acid (80 g.) at 170° for 6 hours, the solution poured on ice (300 g.), and the dye filtered off and washed with aqueous potassium acetate. cis-*Coerodioxonone* (red-brown) (3·8 g.) was finally extracted with acetone (Soxhlet), and the extract allowed to crystallise; it formed very small needles, decomposing at 280—290°, and giving magenta solutions in chloroform, acetone, and nitrobenzene (Found : C, 80·3; H, 3·3. $C_{26}H_{12}O_4$ requires C, 80·4; H, 3·1%).

Anisidinoanthraquinones.—1-Chloroanthraquinone (2·4 g.), *o*-anisidine (25 c.c.), potassium acetate (1·5 g.), and copper powder (0·1 g.) were refluxed for 1 hour. The cold product was diluted with ethanol, acidified with 6N-hydrochloric acid, and the precipitate crystallised from acetone, forming red-brown plates, or from ethanol, forming red-purple prisms. 1-o-*Anisidinoanthraquinone* (olive-green) (yield, 2·5 g.) had m. p. 177° (Found : C, 76·6; H, 4·8. $C_{21}H_{15}O_3N$ requires C, 76·6; H, 4·6%). 1-m-*Anisidinoanthraquinone* (yellow) was prepared similarly, and purified by chromatography on alumina from benzene and elution with ethanol; it formed red-purple needles, m. p. 135—138°, from ethanol (Found : C, 76·5; H, 5·0%). 1-Chloroanthraquinone (9·2 g.), *p*-anisidine (5 g.), potassium carbonate (3 g.), nitrobenzene (50 c.c.), and copper powder (0·1 g.) were refluxed for 1 hour. The product was distilled in steam and the solid residue (11 g.) crystallised from benzene to give 1-p-*anisidinoanthraquinone* (green-yellow) in brown needles, m. p. 153—154° (Found : C, 76·6; H, 4·8%).

The following were similarly prepared : 1-p-*Anisidino*-4-*benzamidoanthraquinone* (purple) (yield, 55%) separated from benzene, acetic acid, or acetone in small purple needles, m. p. 255—256° (Found : C, 74·9; H, 4·6. $C_{28}H_{20}O_4N_2$ requires C, 75·0; H, 4·5%). The m-*anisidino-isomer* (green) separated from benzene in purple needles, m. p. 202° (Found : C, 75·1; H, 4·8%).

1 : 5-Dichloroanthraquinone (2·8 g.), *p*-anisidine (2·5 g.), potassium acetate (1 g.), copper powder (0·1 g.), and anisole (25 c.c.) were refluxed for 1 hour and distilled in steam. Chromatography of the residue on alumina from benzene, elution with acetone, and crystallisation from acetic acid gave 5-*chloro*-1-p-*anisidinoanthraquinone* (2·5 g.) in purple, microcrystalline form, m. p. 157° (Found : Cl, 9·5. $C_{21}H_{14}O_3NCl$ requires Cl, 9·75%). A similar preparation using *o*-anisidine gave the 1-o-*anisidino*-analogue, which separated from acetone, ethanol, or acetic acid in red-purple plates, m. p. 164° (Found : C, 69·0; H, 3·8. $C_{21}H_{14}O_3NCl$ requires C, 69·3; H, 3·8%). 1 : 4-Dichloroanthraquinone (2·8 g.), *p*-anisidine (4·8 g.), potassium acetate (2·5 g.), and a little copper bronze were refluxed in nitrobenzene (20 c.c.) for 1 hour. On cooling, the crystalline product (1·5 g.) was recrystallised from acetic acid, and 1 : 4-*di*-p-*anisidinoanthraquinone* (blue, becoming intense blue-purple on warming and green on dilution) (Found : C, 74·7; H, 5·1. $C_{28}H_{22}O_4N_2$ requires C, 74·7; H, 4·9%) formed fine blue needles, m. p. 230°; a further quantity (1·5 g.) was obtained after distilling nitrobenzene in steam and crystallising the residue. The following were obtained similarly: 1 : 5-*Di*-o-*anisidinoanthraquinone* (green, becoming intense purple on warming) (total yield, 85%) separated from acetic acid or ethyl acetate in purple needles, m. p. 210° (Found : C, 74·4; H, 4·9. $C_{28}H_{22}O_4N_2$ requires C, 74·7; H, 4·9%). 1 : 5-*Di*-m-*anisidinoanthraquinone* (green $\rightarrow$ purple as above) (total yield, 60%), shining red-brown needles, m. p. 192°, from acetic acid (Found : C, 74·8; H, 4·6%). 1 : 5-*Di*-p-*anisidinoanthraquinone* (green) (total yield, 60%), brown needles, m. p. 243° from benzene (Found : C, 74·6; H, 5·3%).

Coeramidones.—The monoanisidinoanthraquinone (2 g.) in 75% sulphuric acid (40 g.) was heated at 160° for 3 hours. The intensely coloured solution was poured on ice, and the crude product purified by solution in dilute aqueous ammonia and precipitation with acid. 4-*Hydroxycoeramidone*-9 (from 1-*o*-anisidinoanthraquinone) crystallised from aqueous pyridine and was finally sublimed in a high vacuum at 270°, forming brown needles, m. p. 290° after sintering at 280° (Found : C, 81·1; H, 3·9. $C_{20}H_{11}O_2N$ requires C, 80·8; H, 3·7%); it gave blue solutions in alkali which became red on reduction with hyposulphite (dithionite). 1(or 3)-*Hydroxycoeramidone*-9 (from 1-*m*-anisidinoanthraquinone) separated from aqueous pyridine as a brown powder, m. p. 310° (decomp.) (Found : C, 80·8; H, 3·8%); it gave green-brown solutions in alkali becoming crimson with hyposulphite. 2-*Hydroxycoeramidone*-9 (from 1-*p*-anisidinoanthraquinone) formed a purple powder sintering at 290—295° and sparingly soluble in the common solvents (Found : C, 80·8; H, 3·9%); the same compound was obtained by fusing the anisidino-compound (1 g.) with sodium aluminium chloride (10 g.) at 160° for 15 mins. and extracting inorganic salt with hot N-hydrochloric acid; the colour in alkali was blue changing to crimson with hyposulphite or zinc dust. 1-*m*- and -*p*-Anisidino-4-benzamidoanthraquinone were partly debenzoylated during cyclisation with sulphuric acid and quantities of benzoic acid were collected in the condensate. 1 (or 3)-*Hydroxy*-8-*benzamidocoeramidone*-9 (red purple) formed a brown solid subliming in a high vacuum, m. p. >350°, sparingly soluble in organic solvents but dissolving in alkali to a red solution (Found : C, 77·8; H, 3·7. $C_{27}H_{16}O_3N_2$ requires C, 77·8; H, 3·9%). 2-*Hydroxy*-8-*benzamidocoeramidone*-9, sublimed in a high vacuum, had m. p. 313—315°, and gave similar colours (Found : C, 77·7; H, 4·2%). 10-*Chloro*-2-*hydroxycoeramidone*-9 (green) (Found : C, 72·7; H, 3·3; Cl, 10·8. $C_{20}H_{10}O_2NCl$ requires C, 72·4; H, 3·0; Cl, 10·7%) had m. p. > 360°; it was blue in alkali, becoming red-purple on reduction with sodium hyposulphite or zinc dust. The dye (1 g.) was boiled with acetic anhydride (10 c.c.) and acetic acid (1 c.c.) for 2 hours. The product was precipitated with water, and repeatedly dissolved in boiling chloroform and reprecipitated with light petroleum, and then had m. p. $> 360°$; it gave brown-red solutions in organic solvents, was insoluble in cold alkali, and appeared to be a *monoacetyl* derivative (Found : C, 70·7; H, 3·4. $C_{22}H_{12}O_3NCl$ requires C, 70·7; H, 3·2%). Similarly, treatment with benzoyl chloride in alkaline solution appeared to give a *monobenzoyl* derivative which, after repeated solution in chloroform and precipitation with light petroleum, formed an amorphous powder, m. p. 212—215° (Found : C, 74·4; H, 3·7. $C_{27}H_{14}O_3NCl$ requires C, 74·1; H, 3·2%).

Coerodiamidines.—Cyclisation of dianisidinoanthraquinones was carried out in sulphuric acid, and the products purified as with the preceding coeramidones. 1 : 9-*Dihydroxycoerodiamidine* (purple) formed a purple black solid, m. p. $>360°$ from aqueous pyridine; it was blue in alkali, giving a crimson vat (Found : C, 80·9; H, 4·1. $C_{26}H_{14}O_2N_2$ requires C, 80·8; H, 3·7%); light absorption (pyridine) : max. at 5990, 5550 A., I $>$ II. 2 : 10(or 4 : 12)-*Dihydroxycoerodiamidine* (purple), after repeated precipitation from ammoniacal solution by acetic acid, formed a purple-black powder, m. p. $>360°$ (Found : C, 80·8; H, 3·9%); it was brown-green in alkali and gave a crimson vat solution; light absorption (pyridine), max. at 5860, 5410 A., I $>$ II. 3 : 11-*Dihydroxycoerodiamidine* (red-purple) formed a purple-black powder, m. p. $>360°$, from aqueous pyridine (Found : C, 80·7; H, 3·7%); it was blue in alkali, and gave a red vat solution; light absorption (pyridine), max. at 6540, 6000 A., I $>$ II.

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