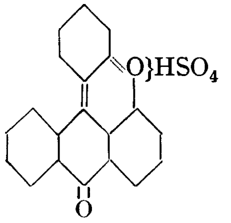
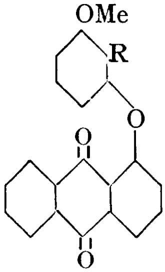
## **223.** *The Synthesis of Coeroxonones.*

By Frederick E. King.

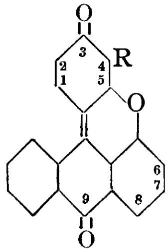
Decker (*Annalen*, 1906, **348**, 231) has shown that 1-phenoxyanthraquinone is converted by sulphuric acid into a dark red oxonium salt, coeroxonium sulphate (I), and several new aryl ethers of 1-hydroxy- and 1 : 5-dihydroxy-anthraquinone were synthesised (Decker and others, *ibid.*, p. 233; 1907, **356**, 317) with a view to their conversion into coeroxonium compounds. His experiments, however, do not appear to have included the preparation of anthraquinone ethers with methoxylated aryl substituents, and it will be seen that some of these, *e.g.*, resorcinol derivatives, possess still further synthetical possibilities. In the first place, the simple ethers such as (II) on ring-closure and demethylation should afford quinones of the type (III) which are related to the coeruleins, *e.g.*, coerulein A (IV) or (V), a class of dyes prepared from the phthaleins : on the other hand, the 1 : 5-resorcyl ethers can be regarded as the intermediates for an entirely new series of quinones having its prototype in (VI, R = H).



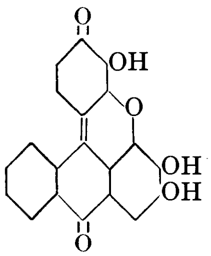
(I.)



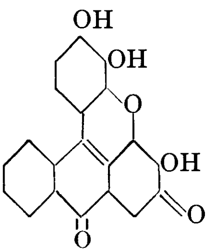
(II.)



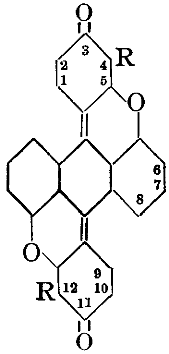
(III.)



(IV.)



(V.)



(VI.)

With these considerations in mind, *erythroxyanthraquinone 3'-methoxyphenyl ether* (II, R = H), obtained from 1-chloroanthraquinone and the sodium salt of resorcinol monomethyl ether, was submitted to the action of sulphuric acid under the conditions prescribed by Decker (*loc. cit.*). Instead of the water-soluble coeroxonium salt, the product was a dark red-brown precipitate of *coeroxonone*-3 : 9 (III, R = H) * which, however, had no dyeing properties. Similarly, 1 : 5-dichloroanthraquinone afforded *anthrarufin di-3'-methoxyphenyl ether*, and this was converted into the blue-black *coerdioxonone*-3 : 11 (VI, R = H), which is a strong vat dye.

The failure of (III, R = H) as a dye, despite its resemblance to the coeruleins, suggested that hydroxyl groups are the factor essential for dyeing properties. Accordingly, derivatives of pyrogallol were next investigated.

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* The nomenclature is Decker's and the figures refer to the position of the quinone oxygen atoms, but in preference to his scheme of numbering, which is based on the relationship of the coeroxonium compounds to 9-phenylanthracene, the system of Patterson (*J. Amer. Chem. Soc.*, 1925, **47**, 543) is employed.

The sodium salt of pyrogallol dimethyl ether and 1-chloroanthraquinone in a nitrogen atmosphere yielded *erythroxyanthraquinone* 2′ : 3′-*dimethoxyphenyl ether* (II, R = OMe), quantitatively transformed in one operation into 4-*hydroxycoeroxone*-3 : 9 (III, R = OH), a weak green dye characterised by an *acetyl* derivative. The related 4 : 12-*dihydroxycoerdioxonone*-3 : 11 (VI, R = OH), which was prepared from *anthrarufin bis*-2′ : 3′-*dimethoxyphenyl ether*, is a maroon dye resembling its analogue (VI, R = H).

It has been reported (D.R.-P. 294,447) that coerulein A and certain dimethylaminoquinones related thereto undergo condensation with aromatic bases, even at the ordinary temperature, and this property has been ascribed to the hydroxylated quinonoid ring which is present in these substances. The effect of aniline on the new compounds, (III, R = OH) and (VI, R = OH), was therefore investigated, but no reaction was observed; the quinone (III, R = OH) was dissolved by the boiling base but crystallised unchanged on cooling, while (VI, R = OH) was hardly soluble.

## EXPERIMENTAL.

*Erythroxyanthraquinone 3′-Methoxyphenyl Ether* (II, R = H).—Resorcinol monomethyl ether (Perkin, Rây, and Robinson, J., 1926, 945) and an equivalent of concentrated aqueous sodium hydroxide afforded the sodium salt (7 g.), which was thoroughly mixed with 1-chloroanthraquinone (10 g.) and heated in an oil-bath at 150—160°. The dark red viscid product, when washed with boiling water and twice crystallised from acetic acid (charcoal), gave a brown solid (9—10 g.), m. p. 127—130°, and by further crystallisation from benzene, the pure *erythroxyanthraquinone* 3′-*methoxyphenyl ether* was obtained as golden-yellow rectangular leaflets, m. p. 130—131° (Found : C, 76·1; H, 4·5. $C_{21}H_{14}O_4$ requires C, 76·4; H, 4·2%). The compound has the anticipated high solubility in non-hydroxylic solvents except ether and ligroin; it is only moderately soluble in alcohols. It dissolves readily in cold concentrated sulphuric acid, and the solution is dark red.

*Coeroxonone*-3 : 9 (III, R = H).—Erythroxyanthraquinone 3′-methoxyphenyl ether (3·5 g.) and sulphuric acid (70 g. of 75%) were heated under reflux in an oil-bath at 180°, in the first experiment, for 12 hours. A red-black precipitate, m. p. *ca.* 300°, was obtained by the addition of ice and water (200 g.), and was purified by extraction in a Soxhlet apparatus with chloroform, followed by two crystallisations from large volumes of xylene. *Coeroxonone*-3 : 9 forms dark maroon needles with metallic lustre, m. p. (capillary) 310° following slight decomposition below this temperature (Found : C, 80·2; H, 3·1. $C_{20}H_{10}O_3$ requires C, 80·5; H, 3·3%). The quinone is very slightly dissolved by high-boiling solvents, acetic acid, and chloroform to deep red solutions, and is otherwise insoluble. With alkaline hydrosulphite a scarlet vat is formed, but it has no dyeing power.

*Anthrarufin Di-3′-methoxyphenyl Ether.*—A mixture of the sodium salt of resorcinol monomethyl ether (12 g.) and 1 : 5-dichloroanthraquinone (8 g.) was heated for an hour at 160°. After washing with hot water, the black tarry product was boiled with acetic acid (*ca.* 40 c.c.) (charcoal) and filtered. The brown solid separating from the filtrate was recrystallised from acetic acid, but the material retained some dichloroanthraquinone until purified through ethyl acetate. Pure *anthrarufin di*-3′-*methoxyphenyl ether* crystallises in golden-brown pointed tablets, m. p. 177—178° (Found : C, 74·3; H, 4·6. $C_{28}H_{20}O_6$ requires C, 74·3; H, 4·4%). The double ether resembles the monoresorcyl compound in its ready solubility. The sulphuric acid solution is an intense purple-red.

*Coerdioxonone*-3 : 11 (VI, R = H).—Addition of ice (50 g.) to the dark purple-red solution obtained by heating the anthrarufin ether (1·9 g.) with sulphuric acid (40 g. of 75%) at 180° for 6 hours, gave a blue-black precipitate (1·8 g.). By extraction in a Soxhlet apparatus the *coerdioxonone* was obtained as a dark green microcrystalline powder, which formed intense magenta-coloured solutions with nitrobenzene, acetic acid and chloroform, although only very sparingly soluble. On account of its insolubility in organic media, the quinone was purified through its solution in hot sulphuric acid (75%), which was filtered (sintered glass filter) and diluted with water. The precipitate, after being washed with hot water and alcohol, contained sulphuric acid, which was largely removed by warm potassium acetate (Found : C, 63·6; H, 3·1; S, 6·6. $C_{26}H_{12}O_4,H_2SO_4$ requires C, 64·2; H, 2·9; S, 6·6%. Found for a specimen after potassium acetate treatment : C, 77·4; H, 3·4. $C_{26}H_{12}O_4$ requires C, 80·4; H, 3·1%).

*Erythroxyanthraquinone 2′ : 3′-Dimethoxyphenyl Ether* (II, R = OMe).—Pyrogallol dimethyl ether (Baker and Smith, J., 1931, 2544 )(7·5 g.) and 1-chloroanthraquinone (10 g.) were mixed to a paste with a solution of sodium (1 g.) in alcohol (25 c.c.) and heated in an oil-bath. The alcohol was removed in a slow current of nitrogen, and after 30 minutes at 150—160°, the dark brown melt was cooled, powdered, and washed with hot water. Once crystallised from acetic acid, the product (11 g.) had m. p. 161—163°; it was obtained in yellow elongated tablets, m. p. 165°, from ethyl acetate (Found : C, 73·5; H, 4·5. $C_{22}H_{16}O_5$ requires C, 73·5; H, 4·4%). *Erythroxyanthraquinone* 2' : 3'-*dimethoxyphenyl ether* is readily soluble in benzene and toluene, and dissolves in most other organic solvents except light petroleum. It forms with cold sulphuric acid a red-brown solution.

4-*Hydroxycoeroxonone*-3 : 9 (III, R = OH).—The solution obtained by heating the foregoing erythroxyanthraquinone dimethoxyphenyl ether (3 g.) and sulphuric acid (50 c.c. of 80%) under reflux in an oil-bath at 180—190° for 6 hours, when poured into water, gave a green-black solid (2·8 g.). This was crystallised from xylene, and the pure *hydroxycoeroxonone* formed dark blue, long, rectangular plates with metallic lustre, of high but indefinite m. p. (Found : C, 76·4; H, 3·5; OMe, nil. $C_{20}H_{10}O_4$ requires C, 76·4; H, 3·2; OMe, 0·0%). High-boiling solvents dissolve the quinone to blue or blue-green solutions. It is insoluble in aqueous sodium hydroxide, but dissolves easily in warm hydrosulphite solution, the crimson vat dyeing cotton and silk a pale green colour. The compound was dissolved in boiling aniline, forming a deep blue solution; the solid which separated on cooling was the unchanged quinone. Acetic anhydride (10 c.c.) was boiled with the quinone (1 g.) for several minutes until the solution was dark red. The solid which separated on cooling was removed and crystallised from acetic acid, whereby the *acetyl* derivative was obtained as maroon-coloured short needles, m. p. 235—240° (decomp.) (Found : C, 74·0; H, 3·8. $C_{22}H_{12}O_5$ requires C, 74·2; H, 3·4%).

*Anthrarufin Bis*-2' : 3'-*dimethoxyphenyl Ether*.—A well-mixed paste of 1 : 5-dichloroanthraquinone (6 g.) and pyrogallol dimethyl ether (8·5 g.) with a solution of sodium (1·2 g.) in alcohol (25 c.c.), in a nitrogen atmosphere, was heated in an oil-bath. After evaporation of the alcohol, the bath temperature was increased to 160—170° for 40 minutes. The powdered product, when washed with hot water, dried, and crystallised from ethyl acetate and from toluene, gave an orange-yellow solid (5—6 g.), m. p. 177—180°. Several recrystallisations from either solvent afforded the pure *anthrarufin ether* in orange-yellow hexagonal plates, m. p. 183°, which slowly acquired a red-brown tint (Found : C, 70·1; H, 4·9. $C_{30}H_{24}O_8$ requires C, 70·3; H, 4·7%). Benzene and chloroform readily dissolve the substance, which is soluble in most solvents except petroleum. The sulphuric acid solution is purple-red.

4 : 12-*Dihydroxycoerdioxonone*-3 : 11 (VI, R = OH).—The foregoing anthrarufin ether (3·9 g.) and sulphuric acid (75 c.c. of 80%), heated under reflux at 180—190° for 6 hours, gave by addition of water, an almost black powder, practically insoluble in organic solvents. It was purified by precipitation with water from a filtered solution (sintered glass filter) in sulphuric acid (75%), and washing with water and alcohol. As with its analogue (VI, R = H), the purified *quinone* contained sulphuric acid (Found : C, 66·9, 66·5; H, 3·2, 3·0; S, 3·0. $C_{26}H_{12}O_6,\frac{1}{2}H_2SO_4$ requires C, 66·5; H, 2·8; S, 3·4%). The crimson solution in alkaline hydrosulphite dyes cotton and silk a maroon colour.

From a boiling acetic anhydride solution of the quinone, a small amount of maroon-coloured microcrystalline powder was obtained which, on account of its limited solubility, could not be purified. It dissolved in concentrated sulphuric acid to an olive-green solution, changing in 2—3 minutes to the intense purple-red characteristic of the free hydroxycoerdioxonone.

The quinone is only very sparingly soluble in boiling aniline, forming a dark red solution with a green fluorescence.

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