ANTHRAQUINONE AND ANTHRONE SERIES

Part VIII. 4-Halogenoalizarins and Their Derivatives

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HALOGENATION of α-hydroxyanthraquinone leads first to 4-halogeno- and then to 2:4-dihalogeno-1-hydroxyanthraquinones;[1] halogenation of β-hydroxyanthraquinone does not appear to have been studied. Direct chlorination or bromination of alizarin yields the 3-substituted halogeno derivatives, the directing group being the β-hydroxyl. When the β-hydroxyl group is methylated, the directing group is the α-hydroxyl and bromination gives 4-bromoalizarin-2-methyl ether.[2] Halogenated alizarins with the halogen atoms in the unsubstituted benzene ring of alizarin can be prepared synthetically by the condensation of halogenophthalic anhydrides with catechol.[3]

Chlorination of alizarin in aqueous suspension by sodium chlorate and hydrochloric acid,[4] or by passing chlorine through its solution in carbon disulphide in presence of iodine,[5] or by the action of iodine monochloride on alizarin[6] gives 3-chloroalizarin. When alizarin is heated with antimony pentachloride in a sealed tube at 100°, dichloro and tetrachloro derivatives of unknown constitution are obtained.[5] It has been stated that both 3-nitroalizarin and 4-nitroalizarin are "smoothly chlorinated" by sulphuryl chloride at 100°.[7] Chlorination of 3-methylalizarin with sulphuryl chloride in boiling nitrobenzene gives 4-chloro-3-methylalizarin.[8]

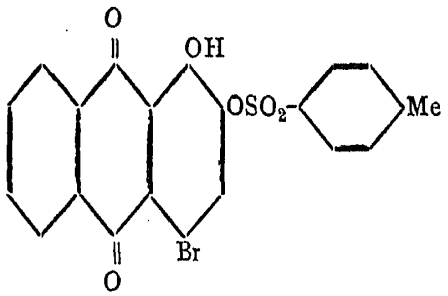
Bromination of hydroxyanthraquinones, such as alizarin, anthrapurpurin and flavopurpurin, is facilitated by reducing to the corresponding anthranol before treatment with bromine. Under these conditions bromine enters both the benzene rings and the *meso*carbon atoms; oxidation of the bromo derivative then gives a bromohydroxyanthraquinone.[9] Bromination of alizarin in carbon disulphide at 180°[10] or in boiling acetic acid in presence of sodium acetate,[11] leads to 3-bromoalizarin. Whereas bromination of alizarin with one mole of bromine in pyridine gives the 3-bromo derivative, two moles of bromine in the same solvent leads to 3-bromoalizarin pyridinium bromide.[12] Treatment of alizarin with excess of bromine and a little iodine in a sealed tube at 100° or 180° gives dibromo or tetrabromo

derivatives of unknown constitution,[5] while bromination in methanol at lower temperature yields 3:4-dibromoalizarin.[13]

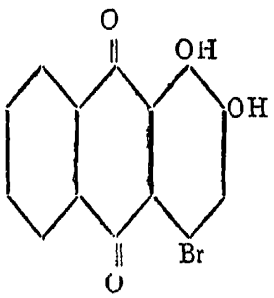
3-Iodoalizarin has been prepared by iodination of alizarin-1-methyl ether by means of iodine in warm pyridine and subsequent demethylation with hydrobromic acid in acetic acid.[14] It has also been synthesized from 3-nitroalizarin by methylation, reduction, replacement of the amino group by iodine, and final demethylation,[15] following the procedure employed earlier for the preparation of 4-iodoalizarin dimethyl ether.[16] This compound was prepared in the course of biological studies for which an alizarin derivative opaque to X-rays was required.[17]

4-Halogenoalizarins have not been reported so far, and their synthesis is now described. Although 4-bromoalizarin-2-methyl ether (IV) and 4-iodoalizarin dimethyl ether are known, their demethylation to 4-halogenoalizarins has not been reported.

4-Bromoalizarin (III) has now been prepared by bromination of alizarin-2-*p*-toluenesulphonate to give (II), followed by hydrolysis of the latter compound by sulphuric acid. The orientation of the bromine atom in (III) was proved by methylation to the known 4-bromoalizarin-2-methyl ether (IV).[11] Treatment of alizarin with *p*-toluenesulphonyl chloride in chloroform and pyridine at 28–30° gave alizarin-2-*p*-toluenesulphonate (I), but with excess of *p*-toluenesulphonyl chloride in pyridine at 100°, alizarin-1:2-di-*p*-toluenesulphonate was obtained.



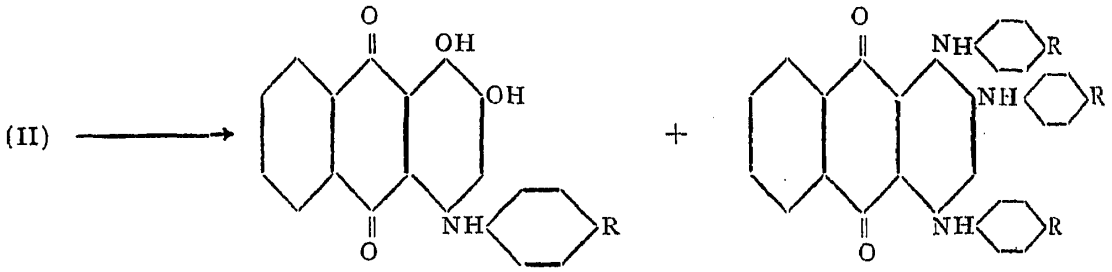
(II)



(III)

The bromine atom in (II) is reactive and by condensation with arylamines 4-arylaminoalizarins can be readily prepared. Thus, condensation of (II) with aniline in presence of anhydrous sodium acetate gave the alkali-soluble 4-anilinoalizarin (V; R= H), together with a deep blue-green alkali-insoluble product which has been shown to be 1:2:4-trianilinoanthraquinone (VI; R= H). When 4-halogeno- or 4-nitro-*o*-acylalizarins (see later) are condensed with arylamines and the products are treated with boiling hydrochloric acid to remove the excess of aniline, hydrolysis of the acyl groups takes place and 4-arylaminoalizarins are formed. 4-Anilino-

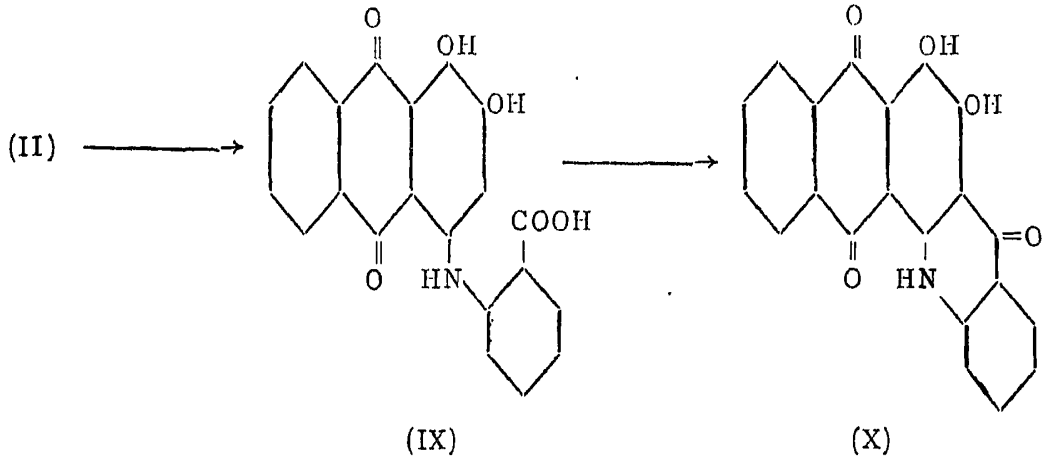
alizarin crystallized from hot toluene in shining violet plates, m.p. 263°, which were sparingly soluble in cold toluene. When the blue-green solution of the reaction product in toluene was chromatographed on alumina, a strongly adsorbed blue band and a green percolate were obtained. Removal of the solvent from the green percolate and crystallization from toluene and finally from acetic acid gave dark blue-green plates, m.p. 186°. The crystalline product was insoluble in hot aqueous sodium hydroxide and did not vat by the addition of sodium hydrosulphite. Elementary analysis and other properties indicated the constitution of the substance to be 1:2:4-trianilinoanthraquinone.[18] It has been noticed that 1:4-di-*p*-toluidinoanthraquinone is also non-vattable. Condensation of (II) with *p*-toluidine



gave the alkali-soluble 4-*p*-toluidinoalizarin (V; R= Me), violet plates, m.p. 228°, together with the alkali-insoluble 1:2:4-tri-*p*-toluidinoanthraquinone (VI; R= Me), shining dark blue plates, m.p. 220°.

Gonsalves, Kothare and Nadkarny have recently reported[19] the synthesis of 4-arylaminoalizarins by the interaction of arylamines with 4-nitroalizarin in presence of boric acid. They describe 4-anilinoalizarin as dark brown needles, m.p. 215°, and 4-*p*-toluidinoalizarin as brown needles, m.p. 204°. Since 4-anilino- and 4-*p*-toluidinoalizarins (V) prepared by us were different in melting point and other properties from the products described by Gonsalves, *et al.*, their reactions with 4-nitroalizarin were repeated. Pure 4-nitroalizarin (VIII), was prepared by nitration of alizarin dibenzoate to the 4-nitroderivative (VII), which was then hydrolysed with alkali. Condensation of (VII) or (VIII) with aniline, followed by treatment with boiling hydrochloric acid to remove the excess of aniline, gave the anilinoalizarin which was proved to be identical with 4-anilinoalizarin (V) prepared unambiguously from (II) as described earlier. Pure 3-nitroalizarin was also treated with aniline in presence of boric acid, but 3-anilinoalizarin was not formed, so that the "anilino-alizarin" of Gonsalves *et al.*, is not the 3-substituted derivative. Attempts to prepare 3-anilinoalizarin from 3-bromoalizarin likewise proved unsuccessful.

6:7-Dihydroxyanthraquinoneacridone (X), blue needles, m.p. 344-45°, was prepared by cyclization of 4-anilinoalizarin-2′-carboxylic acid (IX), prepared as usual from (II) and anthranilic acid. This acridone dyes cotton

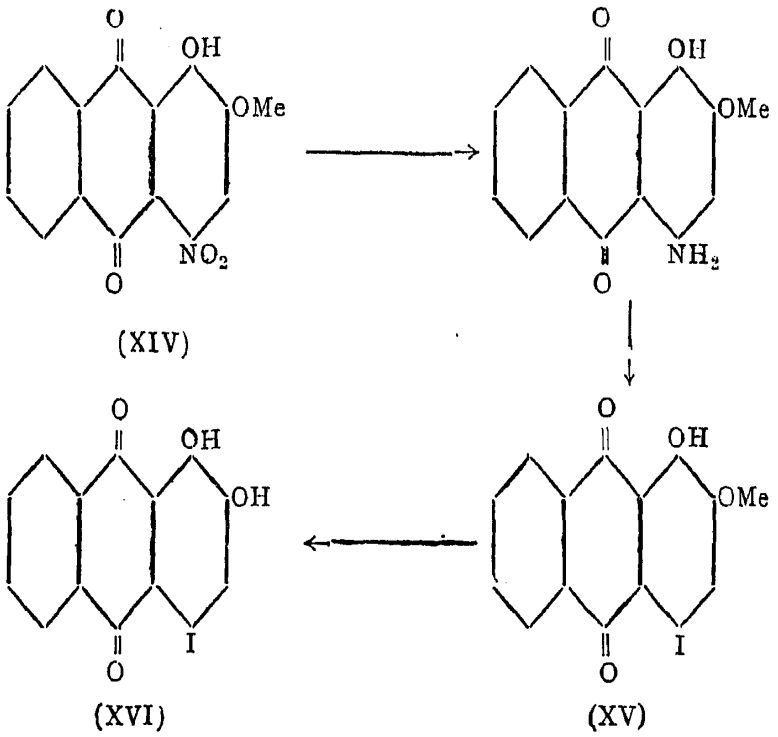


(IX) (X)

a blue-green shade which is not fast to soaping and changes to a blue-violet as a result of the presence of hydroxyl groups. In order to determine if the alkali sensitivity is primarily due to the β-hydroxyl group, the 2-methyl-ether (XI) of (IX) was prepared, but cyclization of (XI) with chlorosulphonic acid was accompanied by demethylation and the product was (X), instead of the expected 6-hydroxy-7-methoxyanthraquinoneacridone.

4-Chloro-2-*O*-*p*-toluenesulphonylalizarin (XII) was prepared by chlorination of (I) at 100° with sulphuryl chloride in nitrobenzene in presence of a little iodine. Hydrolysis of (XII) with sulphuric acid gave 4-chloroalizarin (XIII), orange plates, m.p. 239°. Reaction of (XII) with aniline gave 4-anilinoalizarin (V; R= H) and the alkali-insoluble blue-green 1:2:4-trianilinoanthraquinone (VI; R= H).

Iodination of (I) and alizarin di-*p*-toluenesulphonate by means of iodine monochloride in acetic acid and the iodination of alizarin-2-methyl ether and (I) by iodine in pyridine[14] were not feasible. Alizarin-2-methyl ether was nitrated to 4-nitroalizarin-2-methyl ether (XIV), m.p. 280°, the position of the nitro group being shown by the fact that demethylation with anhydrous aluminium chloride in nitrobenzene gave 4-nitroalizarin.[20] Condensation of (XIV) with aniline in presence of boric acid yielded 4-anilinoalizarin-2-methyl ether, obtained earlier from 4-bromoalizarin-2methyl-ether.[2] On reduction with yellow ammonium sulphide, (XIV) gave 4-aminoalizarin-2-methyl ether, from which by diazotization and treatment with aqueous potassium iodide 4-iodoalizarin-2-methyl ether (XV), crystallizing in red-orange needles, m.p. 235-37°, was prepared. Demethylation of (XV) by anhydrous aluminium chloride gave 4-iodoalizarin (XVI), m.p. 210°,



Experimental

4-*Bromo*-2-O-p-*toluenesulphonylalizarin* (*II*)

2-*O*-*p*-toluenesulphonylalizarin[21, 22] (4·0 g.), glacial acetic acid (80 c.c.), anhydrous sodium acetate (2·4 g.) and bromine (1·8 c.c.) were refluxed for one and a half hours and the solution filtered hot. Bright yellow needles (3·8 g.) separated on cooling, and the m.p. after crystallization from acetic acid was 180° (Found: Br, 16·8; S, 6·6. $C_{21}H_{13}BrO_6S$ requires Br, 16·9; S, 6·8%).

4-*Bromoalizarin* (*III*)

A solution of (II; 3·0 g.) in concentrated sulphuric acid (60 c.c.) was heated on a water-bath for one hour, and poured into ice-water. The orange precipitate (2·1 g.) obtained crystallized from acetic acid in bright orange plates, m.p. 230° (Found: C, 52·0; H, 2·3; Br, 24·8. $C_{14}H_7BrO_4$ requires C, 52·6; H, 2·2; Br, 25·0%). The substance gives violet solutions in aqueous sodium carbonate and sodium hydroxide, and a red solution in concentrated sulphuric acid.

4-*Bromoalizarin-2-methyl ether* (*IV*)

4-Bromoalizarin (90 mg.) was shaken with dimethyl sulphate (1 c.c.) in 10% sodium hydroxide (10 c.c.). The solution was kept alkaline by adding sodium hydroxide solution and warmed, when it turned yellow. It was cooled again and 10% caustic soda and dimethyl sulphate added. The process was repeated till the product gave a red precipitate in aqueous alkali,

The yellow solid which separated on acidification crystallized from acetic acid in lustrous orange needles, m.p. 236–37°; undepressed by adding the product of the bromination of alizarin-2-methyl ether.

4-Bromoalizarin (0·3 g.) and acetic anhydride (4 c.c.) were refluxed for 30 minutes and the mixture poured in ice-water. The *diacetate* (0·35 g.) crystallized from acetic acid in long lemon-yellow needles, m.p. 174–75° (Found: C, 54·1; H, 2·8; Br, 19·6. $C_{18}H_{11}BrO_6$ requires C, 53·6; H, 2·7; Br, 19·8%).

Alizarin di-p-*toluenesulphonate*

Alizarin (0·9 g.), *p*-toluenesulphonyl chloride (3·1 g.) and dry pyridine (9 c.c.) were shaken at room temperature for 15 minutes when yellow flakes appeared. The mixture was heated on the water-bath for four hours and the solution kept overnight. The pale yellow product which separated was filtered, washed with methylated spirit (10 c.c.) and crystallized from acetic acid; the light yellow plates melted at 187–88° (Found: C, 61·0; H, 3·7; S, 11·9. $C_{28}H_{20}O_8S_2$ requires C, 61·3; H, 3·6; S, 11·7%). The substance is insoluble in boiling 10% sodium hydroxide solution; in concentrated sulphuric acid it gives a red-brown solution from which a yellow precipitate separates on dilution. Hydrolysis of the di-*p*-toluenesulphonate (0·27 g.) with sulphuric acid (2·7 c.c.) at 100° for 15 minutes gave alizarin (0·12 g.).

4-*Anilinoalizarin* (*V*; $R = H$)

Aniline (24 c.c.) and anhydrous sodium acetate (2·0 g.) were heated to 150°, then cooled to 130° and (II; 4·73 g.) was added and the mixture heated to 190° for four hours. The resulting blue mass was poured into dilute hydrochloric acid, boiled and the blue product collected (3·0 g.). It was treated with cold toluene (300 c.c.) and filtered. The violet toluene-insoluble residue (0·3 g.) was crystallized four times from hot toluene, when 4-anilinoalizarin was obtained as shining violet plates, m.p. 263° (Found: C, 72·8; H, 3·7; N, 4·1. $C_{20}H_{13}NO_4$ requires C, 72·4; H, 3·9; N, 4·2%). The substance forms a violet solution in aqueous sodium hydroxide; the violet solution in sulphuric acid changes to a red-violet on the addition of boric acid. 4-Anilinoalizarin dyes chromemordanted wool a dull violet shade.

The extract obtained by treatment of the reaction mixture with toluene in the cold was chromatographed on alumina. A blue band was found to be strongly adsorbed and a green percolate was collected. After removal of the solvent from the percolate, the residue was crystallized from toluene and finally from acetic acid when it was obtained as shining dark blue-green plates, m.p. 186° (Found: N, 8·6. $C_{32}H_{23}N_3O_2$ requires N, 8·7%). The

product is insoluble in boiling 10% sodium hydroxide and does not vat with alkaline sodium hydrosulphite solution. It dissolves in concentrated sulphuric acid giving a honey-yellow solution which gradually changes to an eosin-red solution. Elementary analysis and other properties suggest that the alkali-insoluble product is 1 : 2 : 4-trianilinoanthraquinone.

4-p-*Toluidinoalizarin* (*V*; *R* = *Me*)

A mixture of (II; 2·6 g.), *p*-toluidine (10 g.) and anhydrous sodium acetate (2 g.) was heated at 190° for two hours. The blue solution was poured into water and steam-distilled to remove the unreacted *p*-toluidine. The resinous blue product (2 g.) was treated with cold toluene (400 c.c.) and filtered. The residue (0·35 g.) after two crystallizations from boiling toluene gave 4-*p*-toluidinoalizarin as violet plates, m.p. 228° (Found: N, 4·1. $C_{21}H_{15}NO_4$ requires N, 4·1%).

The blue solution, obtained by extraction with cold toluene, was chromatographed on alumina. It gave two major fractions: (1) a blue-violet fraction which was strongly adsorbed and (2) a fraction which gave a greenish blue percolate. Concentration of the percolate and two crystallizations of the product from benzene gave dark blue plates with a metallic lustre, m.p. 220° (Found: C, 80·3; H, 5·5; N, 7·7. $C_{35}H_{29}N_3O_2$ requires C, 79·6; H, 5·9; N, 8·0%). The product is insoluble in boiling caustic soda solution and does not vat by addition of sodium hydrosulphite. Elementary analysis and its properties suggest that it is 1 : 2 : 4-tri-*p*-toluidinoanthraquinone.

O-*Dibenzoyl*-4-*nitroalizarin*[23] (*VII*)

Finely powdered *O*-dibenzoylalizarin[12] (3 g.) was slowly added under stirring to a mixture of 77% nitric acid (5·5 c.c.) and concentrated sulphuric acid (8 c.c.) keeping the temperature below 5°. A pasty mass was obtained after half an hour, and after two hours the pale orange solid was added to crushed ice. The precipitate (2·4 g.) was crystallized twice from glacial acetic acid and once from ethyl alcohol, when the nitro derivative was obtained as clusters of yellow needles.

4-*Nitroalizarin* (*VIII*)

Hydrolysis of (VII) with 10% sodium hydroxide in boiling water-bath gave 4-nitroalizarin as shining orange yellow needles, m.p. 289° (dec.) (Found: N, 5·3. Calc. for $C_{14}H_7NO_6$; N, 4·9%).

4-*Anilinoalizarin from* 4-*nitroalizarin*

Dibenzoyl-4-nitroalizarin (VII; 0·5 g.), boric acid (0·4 g.) and aniline (5 c.c.) were heated in an oil-bath at 120° for 9 hours. The mixture was

poured into dilute hydrochloric acid, boiled, and the dark precipitate (0·65 g.) dissolved in cold toluene (40 c.c.) and filtered. The violet residue (0·36 g.) was crystallized thrice from boiling toluene; the violet plates of 4-anilinoalizarin had m.p. 263°, undepressed when mixed with the anilinoalizarin obtained from (II). The properties of the products obtained by the two methods were also identical.

4-Nitroalizarin (VIII) on similar condensation with aniline also gave 4-anilinoalizarin, m.p. 263°.

4-Anilinoalizarin-2′-carboxylic acid (IX)

4-Bromo-2-O-p-toluenesulphonylalizarin (1·58 g.), anthranilic acid (1 g.) anhydrous sodium acetate (0·2 g.), potassium carbonate (0·5 g.), copper bronze (0·3 g.) and amyl alcohol (30 c.c.) were heated in an oil-bath at 150° for 20 hours. The reaction mixture was filtered, washed with methanol, and the residue (1·4 g.) was extracted with aqueous ammonia. The purple solution was acidified with hydrochloric acid and the product was purified by precipitation from 10% sodium carbonate solution. The blue-violet anthranilinoalizarin had m.p. 268° (Found: N, 3·7. $C_{21}H_{13}NO_6$ requires N, 3·7%).

6:7-Dihydroxyanthraquinoneacridone (X)

4-Anilinoalizarin-2′-carboxylic acid (0·2 g.) was dissolved in concentrated sulphuric acid (8 c.c.) and the violet solution heated on a water-bath for 30 minutes. On pouring into ice-water, the blue precipitate (0·18 g.) was collected. Two crystallizations from *o*-dichlorobenzene gave long blue violet needles, m. p. 344–45° (Found: N, 4·4. $C_{21}H_{11}NO_5$ requires N, 3·9%). The acridone dyes a blue-violet shade from an olive green vat. The shade is not fast to soaping and considerable bleeding takes place. The shade is sensitive to acid, the shade obtained after dyeing and oxidation changing to blue-violet on souring.

N-1′-(3′-Methoxy-4′-hydroxy)anthraquinonylanthranilic acid (XI)

4-Bromoalizarin-2-methyl ether (1·2 g.), anthranilic acid (1 g.) anhydrous potassium acetate (0·8 g.), copper bronze (20 mg.) and amyl alcohol (20 c.c.) were heated at 150° for 24 hours. The mixture was filtered hot, washed with alcohol and the residue boiled for 30 minutes with dilute hydrochloric acid. It was filtered and washed with 10% sodium carbonate solution (20 c.c.). The residue, after washing with water, crystallized from glacial acetic acid in violet needles, m.p. 319–20° (Found: N, 3·8. $C_{22}H_{15}NO_6$ requires N, 3·6%).

6:7-*Dihydroxyanthraquinoneacridone* (*X*)

(*a*) The above acid (XI; 0·2 g.) was finely powdered and added to sulphuric acid (5 c.c.), and the violet solution heated on a water-bath for 30 minutes. Part of the product was sulphonated under these conditions and dissolved in water; the water-insoluble portion was the uncyclized acid.

(*b*) The acid (XI; 0·5 g.) was dissolved in chlorosulphonic acid (5 c.c.). After leaving for two days in a stoppered bottle, the resulting green solution was poured into crushed ice and the product collected (0·42 g.). It crystallized from *o*-dichlorobenzene in long blue-violet needles, m.p. 344–45°, undepressed when mixed with the 6:7-dihydroxyanthraquinoneacridone described above.

4-*Chloro*-2-O-p-*toluenesulphonylalizarin* (*XII*)

2-*O*-*p*-toluenesulphonylalizarin (5 g.), nitrobenzene (10 c.c.), sulphuryl chloride (5 c.c.) and a trace of iodine were heated on a water-bath for two hours. Nitrobenzene was removed by steam distillation, and the residue (5·9 g.) after two crystallizations from glacial acetic acid was obtained as yellow needles, m.p. 167° (Found: C, 58·4; H, 3·4; Cl, 8·2; S, 7·5. $C_{21}H_{13}ClO_6S$ requires C, 58·9; H, 3·0; Cl, 8·3; S, 7·5%).

4-Chloro-2-*O*-*p*-toluenesulphonylalizarin (XII; 1 g.) was condensed with aniline (5 c.c.), as in the case of (II) in presence of fused sodium acetate. The reaction mixture was treated with hydrochloric acid and dissolved in cold toluene. Two crystallizations of the residue from toluene gave blue-violet plates, m.p. 263°. The mixed m.p. of this product with 4-anilinoalizarin was undepressed. The toluene-soluble portion after chromatographic separation gave 1:2:4-trianilinoanthraquinone, m.p. 186° (Found: C, 79·1; H, 4·8; N, 8·6. $C_{32}H_{23}N_3O_2$ requires C, 79·8; H, 4·8; N, 8·7%).

4-*Chloroalizarin* (*XIII*)

The toluenesulphonyl derivative (XII; 1·5 g.) was heated on water-bath with concentrated sulphuric acid (30 c.c.) for one hour and the solution poured into ice. The product (1 g.) crystallized from acetic acid (60 c.c.) in orange plates, m.p. 239° (Found: C, 60·8; H, 3·0; Cl, 12·7. $C_{14}H_7ClO_4$ requires C, 61·2; H, 2·6; Cl, 12·7%).

4-Chloroalizarin (0·2 g.), acetic anhydride (2·5 c.c.) and anhydrous sodium acetate (0·1 g.) were refluxed for one hour and the yellow solution poured into crushed ice. The yellow *diacetate* crystallized from acetic acid in bright yellow plates, m.p. 168° (Found: C, 59·9; H, 2·9; Cl, 9·7. $C_{18}H_{11}ClO_6$ requires C, 60·3; H, 3·1; Cl, 9·9%).

4-*Nitroalizarin-2-methyl ether* (*XIV*)

Alizarin-2-methyl ether (1·0 g) was added to concentrated nitric acid (10 c.c.) at 28–30°. A red-brown solution was obtained from which yellow plates separated. It was poured into ice-water, and the yellow residue collected and crystallized twice from acetic acid. The shining yellow plates melted at 280° (Found: N, 4·7. $C_{15}H_9NO_6$ requires N, 4·7%).

4-*Nitroalizarin*

4-Nitroalizarin-2-methyl ether (0·5 g.) was dissolved in nitrobenzene (9 c.c.) at 150° and anhydrous aluminium chloride (0·7 g.) was added, when the yellow-orange solution changed to a purple red. After 30 minutes, it was poured into dilute hydrochloric acid, steam distilled, and the solid crystallized twice from acetic acid, when orange-yellow needles, m.p. 289° (dec.), were obtained. Mixed with 4-nitroalizarin (VIII), the melting point was not depressed.

4-*Aminoalizarin-2-methyl ether*

4-Nitroalizarin-2-methyl ether (1 g.) was refluxed with yellow ammonium sulphide (40 c.c.) for one hour, when a red-brown precipitate was obtained. It was collected, washed with hot water, dried (0·8 g.) and crystallized from aqueous pyridine. The dark red needles did not melt below 400° (Found: N, 5·0. $C_{15}H_{11}NO_4$ requires N, 5·2%). With concentrated sulphuric acid a yellow-red solution with an orange fluorescence is obtained; on addition of boric acid it changes to a bluish red solution with a strong yellow fluorescence.

4-*Iodoalizarin-2-methyl ether* (*XV*)

4-Aminoalizarin-2-methyl ether (0·5 g.) was dissolved in boiling acetic acid (15 c.c.) and hydrochloric acid (8 c.c.) added. On cooling, brown yellow needles of the hydrochloride separated. After addition of sodium nitrite solution (0·25 g. in 5 c.c. water) at 0°, and keeping for about 30 minutes the clear solution was poured into 10% aqueous potassium iodide (50 c.c.) and heated on water-bath for one hour. The brown precipitate was collected, washed and dried (0·62 g.). It crystallized from acetic acid in red-orange needles, m.p. 236–37° (Found: C, 47·6; H, 2·4; I, 33·1. $C_{15}H_9IO_4$ requires C, 47·4; H, 2·4; I, 33·4%).

4-*Iodoalizarin* (*XVI*)

The 2-methyl ether (XV; 0·1 g.) was dissolved in nitrobenzene (3 c.c.) at 120° and anhydrous aluminium chloride (0·1 g.) added. The brown

solution changed to violet. After 45 minutes, the solution was poured in dilute hydrochloric acid, steam-distilled to remove the nitrobenzene, and the dark-red residue (0·095 g.) collected. It crystallized from acetic acid in red-orange needles, m.p. 210° (Found: C, 46·0; H, 1·8; I, 34·4. $C_{14}H_7IO_4$ requires C, 45·9; H, 1·9; I, 34·7%). It dissolves in aqueous sodium carbonate and caustic soda giving violet solutions.

4-Anilinoalizarin-2-methyl ether

4-Nitroalizarin-2-methyl ether (XIV; 0·3 g.), boric acid (0·3 g.) and aniline (3 c.c.) were heated in a oil-bath at 120° for 8 hours. The solution was poured into hydrochloric acid, and the violet residue dissolved in cold benzene (100 c.c.) and filtered. The residue crystallized from hexane in violet plates, m.p. 198° (Found: N, 4·2. $C_{21}H_{15}NO_4$ requires N, 4·1%). The blue-violet solution in concentrated sulphuric acid changes to a fuchsine red on the addition of boric acid.

Summary

The synthesis of 4-chloro-, bromo- and iodo- alizarins is described. Bromination of 2-*O*-*p*-toluene sulphonylalizarin (I) in glacial acetic acid gave a monobromo derivative (II), which on hydrolysis yielded a new bromoalizarin (III). Methylation of (III) gave the known 4-bromoalizarin-2-methyl ether, showing that (III) is 4-bromoalizarin. Chlorination of (I) with sulphuryl chloride in nitrobenzene gave 4-chloro-2-*O*-*p*-toluenesulphonylalizarin (XII), which on hydrolysis yielded 4-chloroalizarin. Condensation of (II) and (XII) with aniline and *p*-toluidine led to 4-anilino- and 4-*p*-toluidinoalizarins. In addition to the 4-arylaminoalizarins, 1:2:4-trianilino and 1:2:4-tri-*p*-toluidinoanthraquinones were isolated by chromatography. Condensation of 4-nitroalizarin with aniline in presence of boric acid gave 4-anilinoalizarin, which was different from the product described by Gonsalves, *et al.*, as 4-anilinoalizarin. 6:7-Dihydroxyanthraquinoneacridone was prepared from (II) in the usual manner and examined as a vat dye. 4-Iodoalizarin-2-methyl ether (XV) was prepared from alizarin-2-methyl ether by nitration, reduction, and replacement of the amino group by iodine *via* the diazonium salt. Demethylation of (XV) with aluminium chloride gave 4-iodoalizarin.

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