15. *Chemical and Photochemical Degradation of Anthraquinone Mordant Dyes in Methanol. Part I.*

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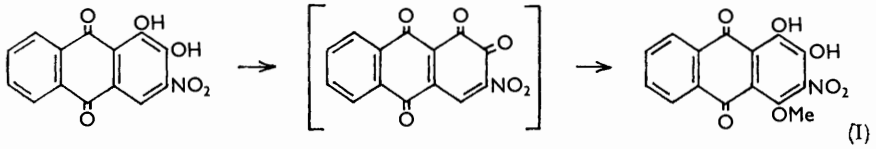
The chemical degradation of 3-nitro-alizarin and -purpurin in methanol by lead dioxide and potassium permanganate is elucidated. It involves cleavage of the substituted ring.

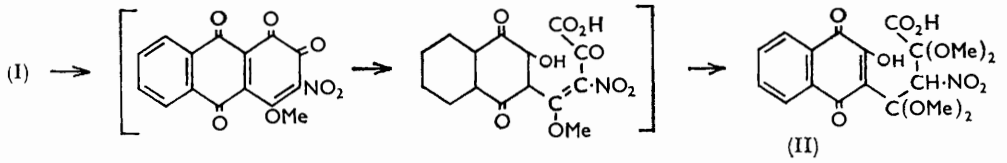
In studying the fading of 3-nitro-alizarin and -purpurin in methanol under irradiation by mercury-vapour lamps or by sunlight we noted that semiquinone radicals are known to be present in irradiated solutions of anthraquinone dyes in ethanol [1] and are produced also in the oxidation of hydroxyanthraquinones; [2] accordingly we assumed that the photochemical and the chemical oxidation of these dyes may, at least in part, follow the same course. This assumption has now been substantiated.[3] The present paper deals with the chemical oxidation of 3-nitro-alizarin and -purpurin by lead dioxide and potassium permanganate in methanol containing some acetic acid; in the following paper we compare the course of this oxidation with the photochemical degradation.

(a) 3-*Nitroalizarin*.—When 3-nitroalizarin was oxidised in methanol with lead dioxide the first relatively stable product was a methyl ether (I) of 3-nitropurpurin, which on hydrolysis with aqueous hydrobromic acid was converted into 3-nitropurpurin (I; OH in place of OMe), the methoxy-group being introduced, apparently, in the 4-position by participation of the solvent in the reaction. Analogous reactions have been described by Dimroth and Schultze,[4] and the structure is supported by the fact that the lake-forming properties are the same as those of 3-nitroalizarin, which indicates the presence of two adjacent hydroxyl groups. The intermediate 3-nitroanthra-1,2,9,10-diquinone could not be isolated, presumably because of its low stability in solution.



(I)

Further oxidation of 3-nitroalizarin or its 4-methoxy-derivative (I) cleaves the substituted ring with formation of a second, relatively stable, product (II). The reactions illustrated are presumed to occur. The structure of this product is based on its containing



(II)

four methoxyl groups and on its alkaline hydrolysis in good yield to 2-hydroxy 3-nitro-acetyl-1,4-naphthaquinone (III) and oxalic acid. On acid hydrolysis the acetal (II) is converted into 2-hydroxy-1,4-naphthaquinone and, in good yield, oxalic acid, along with carbon dioxide. The acetal (II) did not react with phenylhydrazine, the acetal groups

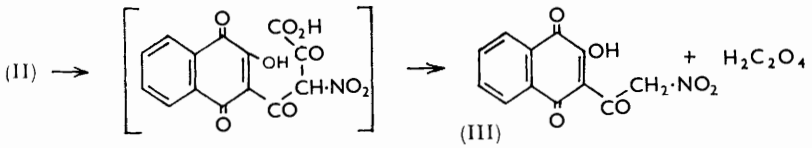
[1] Bolland and Cooper, *Proc. Roy. Soc.*, 1954, *A*, **225**, 405; Wells, *Nature*, 1956, **177**, 483; Bridge and Porter, *Proc. Roy. Soc.*, 1958, *A*, **244**, 259, 275; Bridge, *J. Soc. Dyers Colourists*, 1960, **76**, 484; Bridge and Maclean, *ibid.*, 1959, **75**, 147.

[2] James and Weisberger, *J. Amer. Chem. Soc.*, 1938, **60**, 98.

[3] van Beek, Thesis, Delft, 1960.

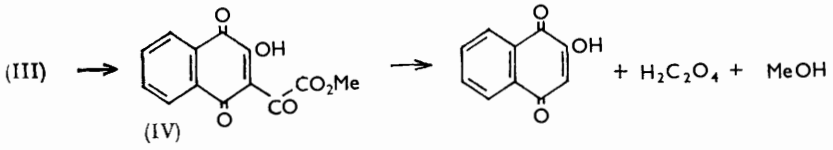
[4] Dimroth and Schultze, *Annalen*, 1916, **411**, 345.

being stable under these conditions. Except for the positions of the methoxy-groups the structure of the compound (II) follows from analyses and the above-mentioned reactions.



2-Hydroxy-3-nitroacetyl-1,4-naphthaquinone (III) can be obtained directly by oxidation of 3-nitropurpurin or, in higher yield, of 3-nitroanthra-1,4,9,10-diquinone. The latter compound was prepared in good yield by oxidation of 3-nitro-alizarin or -purpurin with nitric acid in acetic acid, this method being superior to the use of nitric acid alone described in the literature.[5] For the preparation of 2-hydroxy-3-nitroacetyl-1,4-naphthaquinone from the diquinone the following process was advantageous: The crude diquinone was dissolved in cold methanol. In a short time, without change in temperature, a yellow compound of the same composition but of unknown structure crystallised. This was filtered off and oxidised in sodium hydroxide solution with potassium permanganate. In this way higher yields of the quinone (III) were obtained than by oxidising the original diquinone directly. With phenylhydrazine hydrochloride in alcohol the quinone (III) gave a monophenylhydrazone, and with *o*-phenylenediamine in alcohol a phenazine derivative. The quinone (III) is hydrolysed by boiling dilute mineral acids to 2-hydroxy-1,4-naphthaquinone in good yield, together with carbon dioxide and nitromethane (identified by reaction with benzaldehyde in alkali to give β-nitrostyrene). These reactions establish the structure of the quinone (III).

The quinone (III) is oxidised by lead dioxide in boiling methanolic acetic acid to 2-hydroxy-3-methoxalyl-1,4-naphthaquinone, whose structure is established by the methoxyl content and by acid hydrolysis to 2-hydroxy-1,4-naphthaquinone and oxalic acid, formation of a phenylhydrazone, and conversion by *o*-phenylenediamine into methyl 5-hydroxybenzo[*a*]phenazin-6-ylglyoxylate.



(b) 3-*Nitropurpurin*.—When 3-nitropurin (I; OH in place of OMe) or 2-hydroxy-3-nitroanthra-1,4,9,10-diquinone is oxidised in methanol with lead dioxide or potassium permanganate 2-hydroxy-3-nitroacetyl-1,4-naphthaquinone (III) is formed directly; in this case the intermediate butyric acid derivatives are apparently not stabilised by reaction with methanol. Further oxidation with lead dioxide in methanolic acetic acid affords the methyl ester (IV).

Experimental

M. p.s are corrected.

2-*Hydroxy*-3-*nitroanthra*-1,4,9,10-*diquinone*.—Nitric acid (*d* 1·52; 400 ml.) was added to a stirred suspension of 3-nitroalizarin (60 g.) or alizarin (50 g.) in acetic acid (750 ml.) during 30 min. The temperature was kept between 20° and 25° (at higher temperatures the reaction products decompose exothermically; below 20° the reaction is very slow). The mixture was stirred for another 1½ hr. The *diquinone* was filtered off, washed with acetic acid, and dried *in vacuo* over potassium hydroxide (yield, 50 g., 80%) (Found: N, 4·7. $C_{14}H_5NO_7$ requires N, 4·7%).

[5] Schmidt, Stein, and Bamberger, *Ber.*, 1929, **62**, 1884; Brasch, *Ber.*, 1891, **24**, 1617.

3-*Nitropurpurin*.—2-Hydroxy-3-nitroanthra-1,4,9,10-diquinone (25 g.) was dissolved in methanol (300 ml.) at 10°. The resulting yellow solution was filtered rapidly, warmed to 25°, and kept at that temperature for 2 hr. The 3-nitropurpurin (16 g., 64%) formed was filtered off; it had m. p. 240—241° after crystallisation from methanol.

4-*Methoxy*-3-*nitroalizarin* (I).—(*a*) Lead dioxide (6·5 g.) was added in portions (0·5 g.) to a stirred suspension of 3-nitroalizarin (15 g.) in a boiling mixture of methanol (1 l.) and acetic acid (3 ml.) in 30 min. The mixture was refluxed for another 10 min. and then filtered. (During the reaction a rather large amount of 3-nitroalizarin was precipitated as lead salt or lead complex. This accounts for the low yield.) The filtrate was concentrated to 200 ml. and cooled, orange needles of 4-*methoxy*-3-*nitroalizarin* separating. When recrystallised from acetic acid, this (1·5 g., 9%) had m. p. 204—205° (Found: C, 57·8; H, 2·9; N, 4·4; OMe, 9·5. $C_{15}H_9NO_7$ requires C, 57·2; H, 2·9; N, 4·4; 1OMe, 9·8%).

(*b*) Potassium permanganate (10 g.) was added in portions (0·5 g.) during 60 min. to a stirred ice-cold suspension of 3-nitroalizarin (30 g.) in methanol (150 ml.) and acetic acid (150 ml.) in such a way that the temperature did not raise above 3°. (A yellow solution was obtained from which no 3-nitroalizarin or 4-methoxy-3-nitroalizarin could be isolated: 3-nitroanthra-1,2,9,10-diquinone is probably formed.) The mixture was stirred for another 4 hr. at 0°, then diluted with water, and filtered; the precipitate, crystallised from acetic acid (yield, 14·5 g., 44%), had m. p. 204—205°, not depressed upon admixture with the compound as obtained as under (*a*).

The compound was hydrolysed by boiling in 48% aqueous hydrobromic acid–acetic acid (1 : 1) to 3-nitropurpurin, m. p. and mixed m. p. 239—240° (from methanol).

γ-(3-*Hydroxynaphtha*-1,4-*quinon*-2-*yl*)-αα*γγ*-*tetramethoxy*-β-*nitrobutyric Acid* (II).—Lead dioxide (25 g.) was added in portions (1·5 g.) to a stirred boiling suspension of 4-methoxy-3-nitroalizarin (14 g.) in methanol (300 ml.) and acetic acid (25 ml.) during 85 min. The mixture was stirred and refluxed for another 30 min., then filtered and diluted with 4N-sulphuric acid (100 ml.) and water (500 ml.), lead sulphate being precipitated. The mixture was extracted several times with ether. The ether solutions were extracted with sodium acetate (10 g.) in water (1 l.). The latter solution was filtered, acidified with dilute hydrochloric acid, and again extracted with ether. The latter ether extracts were dried ($MgSO_4$), concentrated by distillation, and finally evaporated at room temperature. The residual pale yellow crystals (2·3 g.) contained mainly the acetal (II), together with a small amount of the quinone (III). The *compound* (II), crystallised once from methanol, had m. p. 95—97° (1·4 g., 7%), and after repeated crystallisation melted at 97—99° (Found: C, 50·7; H, 4·8; N, 3·3; OMe, 31·5. $C_{18}H_{19}NO_{11}$ requires C, 50·8; H, 4·5; N, 3·3; 4OMe, 29·2%).

The same compounds were obtained in smaller yield by oxidation of 3-nitroalizarin in methanol and acetic acid with lead dioxide.

The acetal (II) was heated in 2N-hydrochloric acid at 80° for 1 hr. Carbon dioxide was evolved. After cooling, brown crystals of 2-hydroxy-1,4-naphthaquinone separated: this crystallised from acetic acid and was identical with the quinone prepared as described by Fieser and Martin.[6] The filtrate was evaporated. The residue contained mainly oxalic acid, identified as the *S*-benzylisothiouronium salt, m. p. 203—204°.

Compound (II) (200 mg.) was heated with sodium acetate (1 g.) in 0·1N-sodium hydroxide (10 ml.) at 90° for ½ hr. On acidification, 2-hydroxy-3-nitroacetyl-1,4-naphthaquinone (III) (62%) separated. When crystallised from methanol this had m. p. 164—166° alone or with the substance described below. From the filtrate oxalic acid (56%) was isolated.

2-*Hydroxy*-3-*nitroacetyl*-1,4-*naphthaquinone* (III).—Crude 2-hydroxy-3-nitroanthra-1,4,9,10-diquinone (50 g.) was dissolved in methanol at 0°. The solution was filtered rapidly and stirred for ½ hr. at 0—3°. The yellow precipitate (40 g.) was filtered off, washed with cold methanol, and dried in a vacuum (KOH). The dry compound is stable for 1—2 weeks. This substance (10 g.) was stirred in 0·2N-potassium hydroxide (500 ml.) and potassium permanganate (2·8 g.) in water (50 ml.) was added rapidly at 20—25°. The whole was stirred for ½ hr. and then filtered. On acidification 2-*hydroxy*-3-*nitroacetyl*-1,4-*naphthaquinone* (III) (3·9 g., 41%) separated and after crystallisation from methanol containing some acetic acid had m. p. 164—166° (Found: C, 55·6; H, 2·8; N, 5·4. $C_{12}H_7O_6N$ requires C, 55·2; H, 2·7; N, 5·4%). The sample analysed was crystallised from benzene because adhering methanol was difficult to remove. During the acidification (above) hydrogen cyanide was evolved.

[6] Fieser and Martin, *Org. Synth.*, Coll. Vol. III, 1955, 465, 633.

This quinone was also obtained by oxidation of 3-nitropurpurin or 3-nitroalizarin with lead dioxide in methanol or with potassium permanganate in alkali. It was heated in suspension in dilute hydrochloric acid until about 40% of the liquid had distilled into a vessel containing benzaldehyde and potassium hydroxide solution. Acidification of the distillate afforded β-nitrostyrene. 2-Hydroxy-1,4-naphthaquinone separated in good yield from the residue in the distillation flask.

The *phenylhydrazone* was prepared by heating compound (III) with phenylhydrazine hydrochloride in methanol and had m. p. 215—220° (decomp.) when crystallised from acetic acid (Found: C, 61·6; H, 3·6; N, 12·0. $C_{18}H_{13}N_3O_5$ requires C, 61·5; H, 3·7; N, 12·0%).

To the quinone (III) (1 g.) in boiling methanol (100 ml.) and acetic acid (2 ml.), *o*-phenylenediamine (0·8 g.) in methanol (10 ml.) was added. The yellow precipitate of *5-hydroxy-6-nitroacetylbenzo*[a]*phenazine* was filtered off and extracted several times with hot methanol. It decomposed above 240° (Found: C, 65·3; H, 3·5; N, 12·7. $C_{18}H_{11}N_3O_4$ requires C, 64·9; H, 3·3; N, 12·6%).

2-Hydroxy-3-methoxalyl-1,4-naphthaquinone (IV).—To a boiling suspension of the quinone (III) (0·7 g.) in methanol (7 ml.) and acetic acid (7 ml.) lead dioxide (7·5 g.) was added in portions (0·5 g.) during 15 min. The mixture was boiled for 10 min. After removal of the excess of lead dioxide the solution was diluted with an equal volume of water. The precipitate of the lead salt was filtered off, washed with methanol–water (1 : 1), and shaken with 4N-sulphuric acid (30 ml.) and ether (50 ml.). The ether layer was separated, dried ($MgSO_4$), and evaporated at 0—5° under slightly reduced pressure. The yellow *ester* (IV) separated, was filtered off, washed with ether, and dried. The compound (IV) is very unstable, so that it could not be recrystallised. It had m. p. 135—137° (Found: C, 60·0; H, 3·1. $C_{13}H_8O_6$ requires C, 60·0; H, 3·1%).

The orange *phenylhydrazone*, prepared as above and recrystallised from methanol, had m. p. 177—178° (decomp.) (Found: C, 65·2; H, 4·1; N, 8·3; OCH_3, 8·6. $C_{19}H_{14}N_2O_5$ requires C, 65·1; H, 4·0; N, 8·0; 1OMe, 8·8%).

Equimolar amounts of the ester (IV) and *o*-phenylenediamine in methanol were refluxed for 3 min. Orange crystals of *methyl 5-hydroxybenzo*[a]*phenazin-6-ylglyoxylate* separated. They were filtered off, washed several times with hot methanol, and dried, (m. p. 204—210°). The compound is insoluble in the normal organic solvents (Found: N, 8·6. $C_{19}H_{12}N_2O_4$ requires N, 8·4%).

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