CLXIII.—*Studies in the Anthracene Series. Part II.*

By EDWARD DE BARRY BARNETT and JAMES WILFRED COOK.

IN Part I of this series (T., 1921, **119**, 901) it was shown that when anthracene is treated with bromine in the presence of a large excess of pyridine it is converted almost quantitatively into a pyridinium salt. It seemed of interest to examine the application of this reaction to other compounds, and the present communication contains an account of the behaviour of some of the hydroxyanthraquinones when treated with bromine in the presence of a large excess of pyridine.

It has been found that under these conditions those hydroxyanthraquinones which do not contain two hydroxyl groups in the ortho- or para-position with reference to one another do not give pyridinium salts, but are merely brominated. Thus no pyridinium salt could be obtained from 1-hydroxyanthraquinone, 2-hydroxyanthraquinone, 1 : 3-dihydroxyanthraquinone (xanthopurpurin), or 1 : 5-dihydroxyanthraquinone (anthrarufin), all these compounds undergoing simple bromination. As a rule, the bromination takes place very smoothly and the brominated hydroxy-compound separates in the form of a pyridine additive compound, which, however, easily loses its pyridine when treated with dilute acids. These additive compounds are well-crystallised substances, and are probably salts of pyridine, for it is well known that hydroxyl groups, when attached to the anthraquinone ring system, are more acidic in nature than are hydroxyl groups in most phenols and, of course, the acidity would be increased by the entrance of halogen atoms. The formation of these additive compounds greatly facilitates the purification of the bromohydroxyanthraquinones, and this type of reaction is being studied in detail and will form the subject of a future communication. When a dihydroxyanthraquinone in which the two hydroxyl groups are present in the ortho- or para-position with reference to one another is treated with bromine in the presence of pyridine, a pyridinium salt is formed, and in this respect it resembles the dihydric phenols of the benzene series. Thus it has been shown (Ortoleva and di Stefano, *Gazzetta*, 1901, **31**, ii, 256; Ortoleva, *ibid.*, 1902, **32**, i, 447) that quaternary salts are formed when quinol and catechol are treated with halogens in pyridine solution, but that resorcinol gives no such compound. These salts are regarded by Ortoleva as additive compounds of the type

but these formulæ are almost certainly erroneous, and it will be shown in a future communication that the compounds are really hydroxyphenylpyridinium salts.

Now it has been shown (Lesser, *Ber.*, 1914, **47**, 2526; Dimroth and Schultze, *Annalen*, 1916, **411**, 345; Dimroth, Friedemann, and Kämmerer, *Ber.*, 1920, **53**, [B], 481; Dimroth and Hilcken, *ibid.*, 1921, **54**, [B], 3050) that both alizarin and quinizarin on oxidation give diquinones, and it seems certain that the formation of a pyridinium salt is preceded by the formation of the diquinone. The reaction is most simple in the case of quinizarin, as a dipyridinium salt (III) is produced, and the formation of this is easily explicable, since Dimroth, Schultze, and Heinze (*Ber.*, 1921, **54**, [B], 3035) have shown that quinizarinquinone adds on one molecule of bromine to form a dibromide (II). This must then unite with two molecules of pyridine and at the same time enolisation must take place :

The formation of the dipyridinium salt is interesting, as in most cases the action of pyridine on the halogen additive compounds of the aromatic series leads to pyridinium salt formation and simultaneous loss of halogen acid.

Quinizarin is not brominated by treatment with bromine in pyridine solution; if only 1 molecule of bromine is used, half the quinizarin can be recovered unchanged.

In the case of alizarin, the reactions which take place are rather more complicated. If only 1 molecule of bromine is used, scarcely any pyridinium salt is formed, almost the sole product being 3-bromoalizarin (IV). If 2 molecules of bromine are employed, or if 3-bromoalizarin is treated with 1 molecule of bromine under similar conditions, a bromoalizarinpyridinium bromide (VIII) is obtained. Assuming, as is probably the case, that 3-bromoalizarin is always formed as an intermediate compound, the formation of the bromoalizarinpyridinium bromide must be due to the oxidation of this to 3-bromoalizarinquinone (V), addition of bromine to form bromoalizarinquinone dibromide (VI); and then simultaneous pyridinium salt formation and loss of hydrogen bromide. This leaves a bromoalizarinquinonepyridinium bromide (VII), which is then reduced to bromoalizarinpyridinium bromide (VIII) by the hydrobromic acid produced by the oxidation of the bromoalizarin

and also simultaneously with the formation of the pyridinium salt :

If alizarin is treated with 3 molecules of bromine in the presence of pyridine, or if bromoalizarin is treated with 2 molecules of bromine under similar conditions, the chief product is alizarindipyridinium dibromide (XIV). It will be observed that this compound contains the same number of bromine atoms as bromoalizarinpyridinium bromide, so that the extra molecule of bromine required for its formation does not appear in the final product. It was first thought that the conversion of the bromoalizarinquinonepyridinium bromide into bromoalizarinpyridinium bromide by the action of hydrobromic acid was a reversible reaction,

and that the function of the extra molecule of bromine was to force the equilibrium point towards the left in the above equation. If this were the case, the equilibrium should be forced towards the right by the presence of a large excess of hydrobromic acid, and consequently bromoalizarinpyridinium bromide should be obtained when alizarin is treated with three molecules of bromine in pyridine solution in the presence of a large excess of pyridine hydrobromide. This, however, is not the case, as the presence of a large excess of pyridine hydrobromide does not appear to affect the reaction appreciably. Now bromoalizarinpyridinium bromide is not converted into alizarindipyridinium dibromide by bromine in the presence of pyridine, the probable reason being that pyridine causes loss of hydrobromic acid and formation of a betaine* in which the

* Strictly speaking, a betaine is an internal salt formed by loss of water between a quaternary ammonium hydroxide group and a carboxyl group in another part of the same molecule (Meyer and Jacobson, "Lehrbuch der

two hydroxyl groups are no longer intact, so that oxidation to a quinonoid compound is not possible. The function of the extra molecule of bromine must therefore be to prevent the formation of the betaine. This it probably does by converting the bromoalizarinquinonepyridinium bromide into the perbromide (IX), the dipyridinium salt then being formed by oxidation (X), addition of bromine (XI), union with pyridine (XII), and subsequent loss of bromine (XIII) :

Alternatively, the conversion of the perbromide into the dipyridinium salt may be due to the alternate addition and loss of hydrogen bromide according to the scheme

as Ortoleva (*loc. cit.*) has shown that pyridinium salts are formed from benzoquinone by the action of the pyridine salts of the halogen

Organischen Chemie," 2nd ed., Vol. I, Part II (1913), p. 740; Beilstein, "Handbuch der Organischen Chemie," 4th ed., Vol. IV (1922), p. 333. In the compounds under consideration there is no carboxyl group present, salt-formation taking place with the phenolic hydroxyl group. Such compounds are conveniently named "phenobetaines" to distinguish them from the true "carbobetaines." In the same way the authors suggest the name "nitrolbetaine" for those betaines derived from the nitrolic acid formula for the nitrophenols.

acids, but the former scheme for the mechanism of the reaction seems the more probable.

In either case, the reduction of the alizarinquinonedipyridinium dibromide (XIII) to alizarindipyridinium dibromide must be effected at the expense of the hydrogen bromide produced partly during the earlier stages of the reaction and partly by the conversion of the dipyridinium dibromide into a phenobetaine.

It may be argued that the loss of bromine from the nucleus whereby XII is converted into XIII is improbable, but Dimroth, Schultze, and Heinze (*loc. cit.*) have shown that both bromoalizarinquinone dibromide and dibromoalizarinquinone dibromide lose bromine very easily and pass respectively into bromoalizarinquinone and dibromoalizarinquinone, the reaction being brought about by water at the ordinary temperature.

If 2:3-dihydroxyanthraquinone (hystazarin) is treated with bromine in pyridine solution, a dipyridinium dibromide (XVII) is formed, but it has not been found possible to isolate this in the pure state, as even when recrystallised from hydrobromic acid partial loss of hydrogen bromide takes place with the formation of a phenobetaine. Analysis both of the partly betainised substance and of the betaine itself shows, however, without any possibility of doubt, that two pyridinium groups have entered the molecule, so that it must be concluded that hystazarin is capable of oxidation to hystazarinquinone (XV), although the existence of this compound is not recorded in the literature. The formation of the dipyridinium salt must then take place by the addition of bromine to form a dibromide (XVI) and subsequent pyridinium salt-formation and enolisation :

The mechanism of the reaction is therefore similar to that involved in the formation of quinizarindipyridinium dibromide, but it will be observed that whereas quinizarinquinone dibromide is formed by the addition of bromine to one of the double bonds of the quinonoid ring, the corresponding hystazarin derivative is formed by the addition of bromine to the extreme ends of a conjugated system.

As already stated in the case of the alizarin derivatives, the quinonepyridinium salt is reduced to the hydroxy-compound by the hydrobromic acid formed during the reaction, alizarinquinone having great oxidising power. On the other hand, β -naphtha-

quinone is a much less powerful oxidising agent and is not reduced by hydrobromic acid, so that when treated with bromine in pyridine solution the quinonepyridinium salt is obtained. This and other similar reactions are at present being investigated and will be dealt with in a future communication.

As already stated, the pyridinium salts derived from the dihydroxy-anthraquinones form betaine-like compounds, and as in every case there are two hydroxyl groups present the question arises as to which of these is involved. Although it has not been found possible to obtain formal proof, the evidence points strongly to the fact that phenobetaine formation takes place most easily between a hydroxyl group in the β -position and a pyridinium group in the ortho-position to it, although a similar reaction between a pyridinium group and a hydroxyl group in other relative positions is not excluded. The evidence in support of the above contention may be summarised as follows :

(i) Quinizarindipyridinium dibromide does not form a phenobetaine easily and can be recrystallised from alcohol without loss of hydrogen bromide, although a monobetaine is formed when it is treated with a basic substance such as pyridine.

(ii) Alizarindipyridinium dibromide forms a monobetaine easily when recrystallised from a mixture of alcohol and ether. It is improbable that loss of hydrogen bromide takes place between the pyridinium group in position 3 and the hydroxyl group in position 1, as the relative positions of these groups are the same as in quinizarindipyridinium dibromide, and, as already stated, this compound does not readily form a betaine. If this is granted, there are still three possibilities, namely, betaine formation between (a) the pyridinium group in position 4 and the hydroxyl group in position 1, (b) the pyridinium group in position 4 and the hydroxyl group in position 3, and (c) the pyridinium group in position 3 and the hydroxyl group in position 2. Of these alternatives, the last-named is the most probable, as Ullmann and Ettisch (*Ber.*, 1921, 54, [B], 261) have shown that in the case of 2-hydroxy-1:4-naphthaquinone-3-pyridinium chloride betaine formation takes place with great ease, and in this case it must take place between a pyridinium group and a hydroxyl group in the ortho-position.*

The formation of a phenobetaine affords some evidence as to the position of the pyridinium group in bromoalizarinpyridinium bromide,

* In a future communication it will be shown that the pyridyl dichloro-hydroxybenzoquinone and the $\alpha\alpha'\beta\beta'$ -dipyridinobenzoquinone obtained by Imbert (*Compt. rend.*, 1901, 133, 162; *Bull. Soc. chim.*, 1898, [iii], 19, 1008) from tetrachlorobenzoquinone (chloroanil) and pyridine are really phenobetaines, and the same remark applies to the so-called pyridyldihydroxy-chlorobenzoquinone which Imbert (*Compt. rend.*, 1901, 133, 233) obtained by the action of alkali on the monochloro-compound.

as from the method of its formation this compound might have either of the structures

Of these, the first contains a pyridinium group in the ortho-position to a β -hydroxyl group and consequently a phenobetaine should be formed with great ease. In practice, however, loss of hydrogen bromide takes place only with difficulty unless a basic substance such as ammonia or pyridine is present, and for this reason the second formula is the more probable. If this is correct, and since a phenobetaine is formed under suitable conditions, the loss of hydrogen bromide must take place between the pyridinium group and a hydroxyl group either in the para- or in the meta-position to it. Salt formation between two groups in the meta-position to one another is unlikely and therefore it seems most probable that betaine formation has taken place with the *p*-hydroxyl group. There is still possible another structure (XVIII) in which one of the *meso*-carbon atoms is involved and this has much to recommend it on general grounds, although up to the present formal evidence on its behalf is lacking.

Zincke and Weisspfenning (*J. pr. Chem.*, 1910, [ii], **82**, 1) have found that 1 : 3-dichloro-4 : 6-dinitrobenzene gives a dipyridinium salt and that this on hydrolysis loses one of its pyridinium groups, the resulting dinitrophenolpyridinium chloride at once losing hydrogen chloride and passing into a betaine, the same betaine being obtained when 3-chloro-4 : 6-dinitrophenol is treated with pyridine. To this betaine Zincke and Weisspfenning ascribe the formula XIX, but this shows a meta-bridge, and the nitrolbetaine structure (XX) is more probable.

Exactly similar compounds are obtained from both 3-nitroalizarin and 4-nitroalizarin by the simultaneous action of bromine and pyridine, and in these cases the tendency to form the betaine is so great that the compounds separate from solution in hydrochloric or hydrobromic acid completely free from halogen. The boiling acid solutions, in which no doubt the compound is present as its chloride or bromide, are yellow, but on cooling become red and

the red, halogen-free betaine then crystallises out, the change in colour being particularly remarkable in the case of the 3-nitro-alizarin derivative. It is probable that the change in colour denotes change from the phenolic to the nitrolic form and that the halogen-free compounds have the structures

respectively.

It was thought desirable to ascertain if these compounds could be obtained indirectly from alizarin without the use of free bromine in the presence of pyridine, and in view of the fact that halogen atoms attached to the anthraquinone ring system are more reactive than when attached to other aromatic nuclei it seemed possible that the bromonitroalizarins would react directly with pyridine. Neither 3-bromo-4-nitroalizarin nor 4-bromo-3-nitroalizarin has been described in the literature, but there was every reason to believe that they would be easily obtained by nitrating 3-bromoalizarin and by brominating 3-nitroalizarin. Experiments were therefore undertaken on these lines, but the result was totally unexpected, as on nitrating 3-bromoalizarin the bromine atom was replaced by a nitro-group, whereas on brominating 3-nitroalizarin nitrogen dioxide was at once evolved and 3-bromoalizarin formed. These results are all the more surprising as Heller (*Ber.*, 1913, **46**, 2702) appears to have had no difficulty in nitrating 3-chloroalizarin, and in the patent literature (Brit. Pat. 120528) it has been claimed that both 3-nitroalizarin and 4-nitroalizarin are smoothly chlorinated by sulphuryl chloride at 100°. The reaction is being further investigated and will form the subject of a future communication.

EXPERIMENTAL.*

Action of Bromine and Pyridine.

On Quinizarin.—(a) A solution of 5 grams of quinizarin (purified by recrystallisation from xylene) in 50 c.c. of boiling pyridine was cooled

* All the pyridinium salts described in this communication appear to decompose, on heating, into some very stable substance, so that on analysis gas is evolved slowly for an hour or more after the whole tube has been heated to redness. For this reason, the values obtained for nitrogen are usually rather low. The high values found for hydrogen are due to bromine passing the silver spiral and being taken up by the sulphuric acid in the Travers tube used for absorbing the water. It has been proved that, provided the sulphuric acid is fairly fresh, no bromine passes into the potash bulb, so that the value found for carbon is not affected.

as rapidly as possible and the suspension thus obtained treated slowly with 2 c.c. of bromine (2 mols.), the whole being continually stirred and cooled. After keeping at the ordinary temperature for two hours, the precipitate was filtered, washed with pyridine and with ether, and recrystallised from boiling alcohol (Found : C = 51.6; H = 4.05; N = 4.96; Br = 28.6. $C_{24}H_{16}O_4N_2Br_2$ requires C = 51.8; H = 2.88; N = 5.04; Br = 28.8 per cent.).

Quinizarin-2 : 3-dipyridinium dibromide (III) forms a brown, crystalline powder which is rather sparingly soluble in alcohol, but very easily soluble in cold water. The aqueous solution is purple, but becomes pure blue on dilution. The compound melts and decomposes at 275–277°. It is moderately soluble in glacial acetic acid and crystallises from the boiling solution in minute, brown needles which melt and decompose at 285°. Their solution in water reacts acid towards litmus, and the crystals contain two molecules of acetic acid of crystallisation (Found : C = 49.8; H = 4.01; Br = 24.2. $C_{24}H_{16}O_4N_2Br_2 \cdot 2C_2H_4O_2$ requires C = 49.7; H = 3.55; Br = 23.7 per cent.).

The *monophenobetaine* was obtained by mixing a concentrated aqueous solution of the dibromide with its own volume of pyridine and heating the deep blue solution thus obtained under reflux on the water-bath for an hour. On diluting with a large volume of absolute alcohol and then cooling in ice, microscopic, deep blue needles separated. These were collected, washed with absolute alcohol, and dried in a vacuum desiccator (Found : Br = 16.3. $C_{24}H_{15}O_4N_2Br \cdot H_2O$ requires Br = 16.2 per cent.).

(b) Quinizarin (2.4 grams), suspended in 25 c.c. of pyridine, was treated with 0.5 c.c. of bromine (1 mol.). After keeping over-night, the whole was poured into a large volume of cold water and the precipitate collected and washed with boiling water. It weighed 1.3 grams, contained neither nitrogen nor bromine, and was identified as unchanged quinizarin by its general properties and by the method of mixed melting points.

On Alizarin and 3-Bromodalizarin.—The alizarin used in the following experiments was purified by recrystallisation from nitrobenzene, as it was found that unless this was done it was almost impossible to obtain products which were free from inorganic impurities.

(a) A suspension of alizarin (4.8 grams) in pyridine (50 c.c.) was prepared and treated with bromine (1 c.c.; 1 mol.) as described under (a) above, the whole being well stirred and cooled in cold water or a freezing mixture.* After keeping over-night at the

* In this and in other cases the product is apt to be very troublesome to filter if the reaction is carried out below 0°.

ordinary temperature, the whole was poured into water, the solution acidified with hydrochloric acid, and the precipitate collected and recrystallised from glacial acetic acid. It contained bromine, but no nitrogen, and was identified as 3-bromoalizarin by the method of mixed melting points. The yield was 5 grams.

(b) Alizarin (12 grams) was suspended in 100 c.c. of pyridine, and 5 c.c. of bromine were added drop by drop with stirring and cooling. After keeping at the ordinary temperature for five hours, the precipitate was collected, washed with pyridine and with ether, and extracted with boiling dilute hydrobromic acid to remove a small amount of alizarindipyridinium dibromide. The residue, recrystallised twice from about 2 litres of boiling, very dilute hydrobromic acid, formed glistening, pale brown needles and appeared to be unchanged after recrystallising three times from glacial acetic acid. It did not melt below 300° (Found: C = 45.0; H = 3.19; N = 2.68; Br = 31.5. $C_{19}H_{11}O_4NBr_2 \cdot 1\frac{1}{2}H_2O$ requires C = 45.2; H = 2.78; N = 2.78; Br = 31.7 per cent.).

The water of crystallisation is lost very slowly at 130° , but at the same time gradual darkening and decomposition take place.

Bromoalizarinpyridinium bromide (VIII) is almost insoluble in cold water and very sparingly soluble in boiling water or boiling alcohol, separating from the former in dark brown crystals, which become much paler when dried in a vacuum desiccator. It is only moderately soluble in boiling glacial acetic acid, and dissolves in dilute sodium hydroxide solution to form a deep purple solution, from which the original bromide is reprecipitated on acidifying with hydrobromic acid. Bromoalizarinpyridinium bromide is only partly converted into the betaine by boiling with alcohol, but the change is complete in the presence of a little ammonia or pyridine. This *phenobetaine* forms a deep purple, crystalline powder, which is insoluble in all the usual media, but dissolves in hot dilute acids owing to the formation of a salt, the sulphate, for example, separating in golden yellow plates when a hot solution in dilute sulphuric acid is cooled. For analysis, a sample of the betaine was thoroughly washed with alcohol and ether and dried in a vacuum desiccator (Found: Br = 19.9. $C_{19}H_{10}O_4NBr$ requires Br = 20.2 per cent.).

(c) 3-Bromoalizarin (6.4 grams) was treated with bromine (1 mol.) as described under (b). After keeping over-night, the precipitate was collected, washed with pyridine and ether, and recrystallised from a large volume of very dilute hydrobromic acid. The product appeared to be identical in every way with the bromoalizarinpyridinium bromide obtained from alizarin (Found: Br = 31.5 per cent.).

(d) Alizarinquinone dibromide was prepared by shaking com-

mercial alizarin paste, in which some potassium bromide had been dissolved, with a solution of bromine in aqueous potassium bromide. After two hours, the quinone dibromide was collected, washed with potassium bromide solution and with water, dried as far as possible by pressing on porous porcelain, and made into a thin cream with pyridine. Heat was evolved, and after standing for half an hour the solid was collected, washed with pyridine and with ether, and recrystallised from much dilute hydrobromic acid. It appeared to be identical in every way with the bromoalizarinpyridinium bromide described above (Found : Br = 31.9 per cent.).

(e) A suspension of bromoalizarinpyridinium bromide in pyridine was treated with bromine in the usual way. After keeping for some hours, the solid was collected and washed with pyridine and ether. It was almost insoluble in cold dilute hydrobromic acid and was identified by its general properties as being unchanged bromoalizarinpyridinium bromide. The same result was obtained when the experiment was carried out in the presence of a large excess of pyridine hydrobromide.

(f) Alizarin (4.8 grams) was treated with bromine (3 mols.) as described under (a). After keeping for four hours, the precipitate was collected and washed with pyridine and ether. The dark reddish-brown powder thus obtained was dissolved in 80 c.c. of hot dilute hydrobromic acid, the solution cooled and filtered to remove a small amount of bromoalizarinpyridinium bromide, and the alizarindipyridinium dibromide precipitated from the filtrate as its insoluble perbromide by the addition of bromine water. This was collected, washed with water, and dried in a vacuum desiccator over solid potassium hydroxide. When dry, it was reduced to the dibromide by boiling with acetone under reflux, and the dibromide collected and finally purified by recrystallisation from boiling hydrobromic acid (Found : Br = 28.5. $C_{24}H_{16}O_4N_2Br_2$ requires Br = 28.8 per cent.).

Alizarindipyridinium dibromide (XIV) forms a pale yellowish-brown powder which is easily soluble in water to form a red solution, the colour turning to deep purple on the addition of an alkali. The *mono-perbromide* is precipitated as a yellow powder when bromine water is added to an aqueous solution of the dibromide. It is insoluble or very sparingly soluble in the usual media and too unstable to be recrystallised. A sample was purified as far as possible by washing with alcohol and ether, and after drying over solid potassium hydroxide in a vacuum desiccator, a weighed sample was reduced by hydrazine hydrate and the total ionised bromine estimated (Found : Br = 45.8. $C_{24}H_{16}O_4N_2Br_4$ requires Br = 44.7 per cent.). If alizarindipyridinium dibromide is re-

crystallised from a mixture of alcohol and ether, deep blackish-red, hygroscopic needles are obtained which consist of the *monophenobetaine* (Found: C = 58.5; H = 3.52; Br = 16.1, 16.3. $C_{24}H_{15}O_4N_2Br \cdot H_2O$ requires C = 58.4; H = 3.45; Br = 16.2 per cent.). When heated, this betaine melts and decomposes at about 306°. When boiled for a short time with hydrobromic acid, it is converted back into the dibromide, which crystallises when the solution is cooled (Found: Br = 28.8 per cent.).

A *monoacetyl* derivative is obtained when the dibromide is recrystallised from boiling glacial acetic acid. It forms yellow needles which melt and decompose at about 308° (Found: C = 52.2; H = 3.33; N = 4.86; Br = 26.9, 27.1. $C_{26}H_{18}O_5N_2Br_2$ requires C = 52.2; H = 3.01; N = 4.68; Br = 26.8 per cent.). A small amount of the substance was warmed with a drop of amyl alcohol and a drop of concentrated sulphuric acid. On diluting the solution thus obtained, a strong odour of amyl acetate was detected. It has not been found possible to determine to which hydroxyl group the acetyl group is attached, but in view of the great ease with which the acetyl derivative is formed acetylation probably takes place with the same hydroxyl group as is involved in the formation of the betaine. The acetyl group is very easily removed by warming the compound on the water-bath with hydrobromic acid, and alizarindipyridinium dibromide crystallises when the solution is cooled. The acetyl group is also removed by heating at 100° with pyridine, the monophenobetaine mentioned above being obtained under these conditions.

(g) In order to ascertain whether the reduction of the alizarin-quinonedipyridinium dibromide (XIII) was brought about by the hydrogen bromide produced during the reaction or by the hydrobromic acid used during the purification of the crude substance, 4.8 grams of alizarin were treated as under (f). The crude product, which was very hygroscopic, was thoroughly washed with ether and then dried in a vacuum desiccator without further purification. It gave a strong odour of pyridine when treated with cold alkali and appeared to be a double salt consisting of 1 molecule of alizarindipyridinium dibromide with 1 molecule of pyridine hydrobromide (Found: Br = 35.4. $C_{29}H_{22}O_4N_2Br_3$ requires Br = 33.5 per cent.). It had no quinonoid properties and did not oxidise sulphurous acid.

(h) Alizarin was suspended in pyridine and treated with bromine (4 mols.) as described under (f). The product was worked up in the usual way and was found to consist of alizarindipyridinium dibromide.

(i) Alizarin, suspended in pyridine containing a large excess of pyridine hydrobromide, was treated with bromine (3 mols.) as

described under (f). The product was found to consist of alizarin-dipyridinium dibromide, the excess of hydrogen bromide appearing to have had no influence whatsoever on the reaction.

(j) 3-Bromoalizarin (6.4 grams) was suspended in 50 c.c. of pyridine and treated in the usual manner with 2 c.c. of bromine (2 mols.). After keeping for four hours, the product was worked up as described under (f) and was found to consist of alizarindipyridinium dibromide (Found : Br = 28.6 per cent.).

On Hystazarin.—A solution of hystazarin* (2.4 grams) in 24 c.c. of boiling pyridine was cooled as rapidly as possible and then 1 c.c. of bromine (2 mols.) added drop by drop with stirring and cooling. After keeping over-night, the precipitate was collected, washed with pyridine and ether, and recrystallised from boiling hydrobromic acid (about 15 per cent.). The product (XVII) thus obtained consisted of large, brown crystals, but analysis showed that partial conversion into a phenobetaine had taken place (Found : C = 53.7; N = 4.89; Br = 26.0. $C_{24}H_{16}O_4N_2Br_2$ requires C = 51.8; N = 5.04; Br = 28.8 per cent.). Owing to the small amount of material available, it was not possible to attempt to obtain the dibromide in the pure state by recrystallising from more concentrated hydrobromic acid. The crude substance was very easily soluble in water to give a brown solution, which became blue on dilution, the same colour being produced by the addition of an alkali. When boiled with alcohol, it was converted into a deep purple powder, which analysis showed to consist of the *monophenobetaine* (Found : N = 5.55; Br = 17.1. $C_{24}H_{15}O_4N_2Br$ requires N = 5.89; Br = 16.8 per cent.).

On Nitroalizarin.—(a) 3-Nitroalizarin was prepared by treating alizarin, suspended in glacial acetic acid, with nitric acid, and was purified through its pyridine additive compound (Möhlau and Bucherer, "Farbenchemischespraktikum," 1908, p. 211), this method being found to give excellent results. The pure substance (5.6 grams) was suspended in 75 c.c. of pyridine and treated with 2 c.c. of bromine (2 mols.) under the usual conditions. After keeping for three hours, the precipitate was collected, washed with pyridine and ether, and recrystallised from aqueous hydrobromic acid. After drying in a vacuum desiccator over solid potassium hydroxide, it was found to be completely free from bromine (Found : C = 57.8; H = 4.14; N = 6.75. $C_{19}H_{10}O_6N_2 \cdot 2H_2O$ requires C = 57.3; H = 3.52; N = 7.03 per cent.).

Alizarin-4-pyridinium-3-nitrolbetaine (XXI) forms deep red needles which do not melt. It is almost insoluble in water, but

* The sample of hystazarin used was generously presented to the authors by the Farbenfabriken vorm. Friedr. Bayer & Co., Leverkusen.

dissolves in boiling dilute hydrochloric and hydrobromic acids to form yellow solutions. On cooling, the colour of these solutions changes to red and the betaine then crystallises free from halogen. It is sparingly soluble in boiling pyridine and can be recrystallised from its solution in this solvent.

If in the above experiment only 1 gram-molecule of bromine is employed, approximately half the nitroalizarin can be recovered unchanged from the reaction product.

(b) 4-Nitroalizarin was prepared by nitrating dibenzoylalizarin* (D.R.-P. 66811), and this method was found to give satisfactory results. The pure product (2.8 grams), suspended in 35 c.c. of pyridine, was treated in the usual manner with 1 c.c. of bromine (2 mols.). After keeping over-night, the precipitate was collected, washed with pyridine and ether, and recrystallised from 500 c.c. of hydrobromic acid (about 12 per cent.). The resulting red needles contained a small amount of bromine, but lost this completely when boiled with water (Found: C = 60.3; H = 3.75; N = 7.1. $C_{19}H_{10}O_6N_2 \cdot H_2O$ requires C = 60.0; H = 3.16; N = 7.4 per cent.).

Alizarin-3-pyridinium-4-nitrobetaine (XXII) forms a red, crystalline powder, which is almost insoluble in water, but dissolves in boiling dilute acids to form a yellow solution, from which red crystals separate on cooling. When heated, it decomposes without melting.

On Purpurin and Anthragallol.—Attempts were made to obtain pyridinium salts from purpurin (1 : 2 : 4-trihydroxyanthraquinone) and anthragallol (1 : 2 : 3-trihydroxyanthraquinone) by the methods already described. In the case of purpurin a product was formed which contained nitrogen and bromine, but owing to its insolubility it was found impossible to obtain it in the pure state. The crude product seemed to be contaminated with a large amount of bromo-purpurin. Similar results were obtained in the case of anthragallol, but in this case the amount of nitrogenous matter formed was very small.

On 2-Hydroxyanthraquinone and Xanthopurpurin.—(a) 2-Hydroxyanthraquinone (4.5 grams) was suspended in 50 c.c. of pyridine

* The preparation of dibenzoylalizarin by heating alizarin with benzoyl chloride is mentioned by Schützenberger ("Die Farbstoffe," 1870, Vol. II, p. 114), who purified his product by recrystallisation from alcohol. The best results are obtained if alizarin is heated under reflux with 3.5 parts of benzoyl chloride for one and a half hours on the oil-bath at 200°. The crude product is sufficiently pure for nitration, after washing with light petroleum and hot alcohol. If a purer product is desired, it can be obtained by recrystallisation from methyl ethyl ketone, from which solvent it separates as yellow needles. A sample purified in this way melted at 187° and the melting point did not change after three further recrystallisations. Schützenberger gives an analysis of the compound, but does not mention the melting point.

and treated in the usual manner with 3 c.c. of bromine (3 mols.). After keeping over-night, the red, crystalline precipitate was collected, and washed with a little pyridine and then with ether. It consisted of a pyridine additive compound and was decomposed by boiling, dilute hydrochloric acid, the resulting yellow precipitate, recrystallised from xylene, being identified as 1:3-dibromo-2-hydroxyanthraquinone, m. p. 214—215° (Found: Br = 41·8 per cent.). The yield was 6·85 grams, equivalent to 90 per cent. of the theoretical. The same compound has previously been described by Baeyer (*Annalen*, 1880, **202**, 136), who obtained it by heating tetrabromophenolphthalein with concentrated sulphuric acid at 150° for eight hours. He gives the melting point as 207—208°.

(b) Xanthopurpurin was prepared by reducing purpurin with sodium hyposulphite in cold ammoniacal solution (D.R.-P. 212697). The reaction was found to take place very smoothly and to yield a product which was easily purified. The pure product (2·4 grams), suspended in 25 c.c. of pyridine, was treated in the usual manner with 1·5 c.c. of bromine (3 mols.). After keeping over-night, the whole was poured into water and boiled with excess of dilute hydrochloric acid. The yellow precipitate of dibromoxanthopurpurin thus obtained was collected, washed, and recrystallised from tetrachloroethane. It melted at 225—226°. The same compound has previously been prepared by Plath (*Ber.*, 1876, **9**, 1205) by brominating xanthopurpurin, and by Heller (*ibid.*, 1895, **28**, 315) by loss of water from 3:5-dibromo-2:4-dihydroxybenzophenone-2'-carboxylic acid. They give the melting point as 227—230°.

Attempt to Prepare Bromonitroalizarin.

(a) Ten grams of 3-bromoalizarin were suspended in 80 c.c. of glacial acetic acid, and 4 c.c. of nitric acid (*d* 1·42) added. After keeping over-night at the ordinary temperature, the whole was warmed at 40—45° for thirty minutes, cooled, and filtered. The filtrate was found to contain free bromine. The precipitate was washed and then purified by recrystallisation first from glacial acetic acid and then from methyl ethyl ketone. It contained nitrogen, but no bromine, and was identified as 3-nitroalizarin by the method of mixed melting points and by conversion into the pyridiniumnitrolbetaine.

(b) 3-Nitroalizarin (2·8 grams) was suspended in 100 c.c. of glacial acetic acid, and 0·6 c.c. of bromine added. The whole was warmed, evolution of nitrogen dioxide commencing at about 50°. On gently boiling under reflux, the nitroalizarin slowly dissolved and at the end of two hours the clear solution was cooled and the crystalline

precipitate collected and recrystallised from glacial acetic acid. The product contained no nitrogen and was identified as 3-bromoalizarin by the method of mixed melting points.

Summary.

The behaviour of certain hydroxyanthraquinones when treated with bromine and pyridine has been examined and it has been found that :

(i) Monohydroxyanthraquinones and dihydroxyanthraquinones in which there are not two hydroxyl groups present in the ortho- or para-position with reference to one another are brominated.

(ii) Alizarin under suitable conditions gives 3-bromoalizarin.

(iii) Alizarin, 3-bromoalizarin, 3-nitroalizarin, 4-nitroalizarin, quinizarin, and hystazarin all give pyridinium salts.

(iv) These pyridinium salts all pass into betaines with varying ease.

It has also been found that 3-bromoalizarin on nitration gives 3-nitroalizarin and that this is reconverted into 3-bromoalizarin when treated with bromine.

In conclusion, the authors desire to express their thanks to British Dyestuffs Corporation, Ltd., for the supply of anthraquinone derivatives, to the South Metropolitan Gas Co., Ltd., for the supply of pyridine, and to the Research Fund Committee of the Chemical Society for a grant which has partly defrayed the expenses of this research.

DEPARTMENT OF ORGANIC CHEMISTRY,

SIR JOHN CASS TECHNICAL INSTITUTE,

JEWRY ST., ALDGATE, LONDON, E.C.3.

[Received, May 18th, 1922.]