Xanthones and Thioxanthones. Part V. The Preparation and Properties of 9-Thia-2-aza-anthrone and 9-Thia-4-aza-anthrone.*

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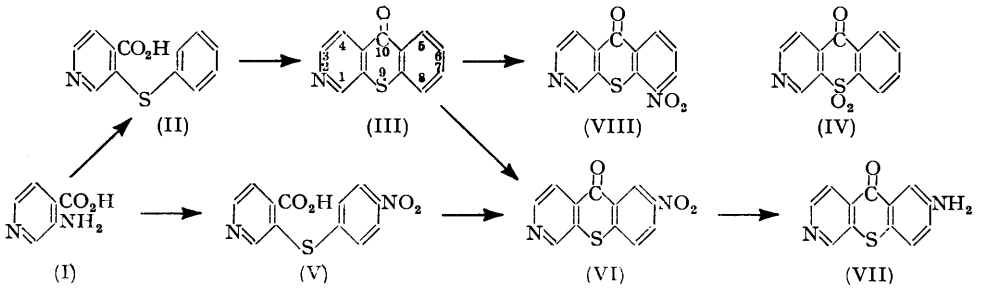
The synthesis of the two compounds named in the title and of various derivatives and kindred compounds is described. Certain of these compounds have been tested as possible schistosomicides but found to be ineffective.

IN Part IV,* Mann and Reid described the synthesis of 9-oxa- and 9-thia-1-aza-anthrone : these compounds and certain derivatives were prepared in order to investigate their possible value as schistosomicides.

We have now synthesised 9-thia-2-aza-anthrone (III) and 9-thia-4-aza-anthrone (XI) : our synthetic route in each case was unfortunately not applicable to the 9-oxa-analogues which still await preparation.

To prepare the 2-aza-anthrone (III), diazotised 3-amino*iso*nicotinic acid (I) was condensed with thiophenol in alkaline solution to form 4-carboxy-3-pyridyl phenyl sulphide (II). This was converted by thionyl chloride into the carbonyl chloride which when heated in nitrobenzene with aluminium chloride readily cyclised to give 9-thia-2-aza-anthrone (III). In this series, as in the 1-aza-series, the quaternary methochloride and the sulphone were chosen for therapeutic investigation. The anthrone (III) underwent ready quaternisation when heated with methyl toluene-*p*-sulphonate, and the product furnished in turn the methiodide and methochloride. Hydrogen peroxide in acetic acid oxidised (III) at 75—80° to the 9 : 9-dioxide (IV), the identification of which as the sulphoxide amine oxide, was confirmed by its infra-red spectrum



Diazotised 3-amino*iso*nicotinic acid (I) and *p*-nitrothiophenol in alkaline solution similarly formed the *p*-nitrophenyl sulphide (V), and thence, as before, pale yellow 6-nitro-9-thia-2-aza-anthrone (VI), which on reduction with tin (or stannous chloride) and hydrochloric acid gave the bright red crystalline 6-amino-derivative (VII).

The parent anthrone (III) when cautiously nitrated gave a product which was apparently a mixture of the 6- and the 8-nitro-derivative (VI and VIII), but these components could not be satisfactorily isolated by fractional crystallisation or sublimation. Reduction, followed by fractional sublimation, gave however the red 6-amino-derivative (VII), m. p. 227°, and a more volatile yellow crystalline product, m. p. 183°, which was presumably the 8-amino-derivative, although insufficient material precluded identification. The colour of the amine (VII) is discussed later.

In the 4-aza-series, 3-aminopicolinic acid (IX) was similarly converted into 2-carboxy-3-pyridyl phenyl sulphide (X), which, when treated as (II), furnished the 9-thia-4-aza-anthrone (XI). This compound was also converted into the methiodide, methochloride, and sulphone.

The acid (IX) was also converted into 2-carboxy-3-pyridyl *p*-nitrophenyl sulphide (XII; R = NO_2), but attempts, under a wide variety of conditions, to cyclise this compound

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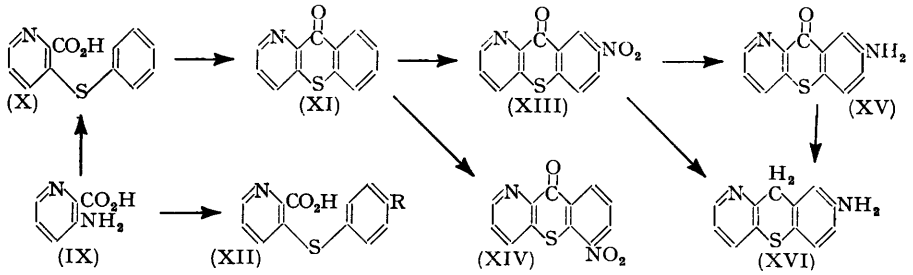
failed. This was unfortunate, because no mono-nitro-derivative of the anthrone (XI) of certain orientation was therefore available for reference purposes. Nitration of the anthrone (XI) gave two mononitro-derivatives: the one which formed considerably the major

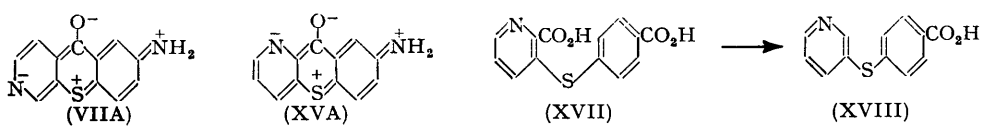


product separated as pale yellow crystals, m. p. 298°, and the other as bright yellow crystals, m. p. 249°. The former is almost certainly the 6-nitro-derivative (XIII) and the second is the 8-nitro-derivative (XIV), as nitration would occur more readily in the position *para* to the sulphur atom than in that *ortho* to this atom. This assumption (which for brevity of reference will be accepted) receives some confirmation from reduction of the former nitro-derivative to a scarlet amino-compound, presumably (XV)—in the 2-aza-series the derivative with the amino-group *para* to the sulphur has also this strikingly intense colour. The second nitro-compound (XIV) gave a brownish-yellow amino-compound, too small in quantity for further investigation.

It is suggested that the bright red colour of the 6-aminoanthrones (VII) and (XV) is due to charge separation, with the result that the resonance hybrids of these amines receive a considerable contribution from the forms (VIIA) and (XVA) respectively. This suggestion is supported by (*a*) the low solubility of these amines in organic solvents, and (*b*) the fact that the yellowish-brown ethanolic solution of (VII) immediately becomes very pale yellow on the addition of hydrochloric acid, when normal salt formation would suppress the charge separation shown in (VIIA).

The 6-nitro- and 6-amino-derivatives (XIII and XV) both showed an unexpected and very ready type of Clemmensen reduction with tin and hydrochloric acid, which converted them into the 6-amino-9 : 10-dihydro-9-thia-4-aza-anthracene (XVI).

The *p*-nitrophenyl sulphide (XII; R = NO_2) was also reduced to the amino-compound (XII; R = NH_2), which was both de-aminated to the sulphide (X) and converted into the urethane (XII; R = ·NH·CO_2Et). Although the yield of the sulphide (XII; R = NO_2) is markedly greater than that of the sulphide (X) from the acid (IX), this alternative route to (X) *via* the amine (XII; R = NH_2) offers no advantage.



The diazotised acid (IX) also underwent condensation with methyl *p*-mercaptobenzoate to give ultimately *p*-carboxyphenyl 2-carboxy-3-pyridyl sulphide (XVII), which, like (XII, R = NO_2), could not be cyclised to the corresponding thia-anthrone: it underwent ready monodecarboxylation however to *p*-carboxyphenyl-3-pyridyl sulphide (XVIII), the structure of which was proved by its non-identity with the isomeric acid (X).

In Part IV it was noted that tests kindly undertaken by Mr. O. D. Standen at the Wellcome Laboratories of Tropical Medicine had shown that 9-thia-1-aza-anthrone and its sulphone had no significant effect on schistosomiasis infections. Subsequent tests by Mr. Standen have given the same result for the methochloride of this anthrone, for the acid (X), and also for the 2-aza- and 4-aza-anthrones (III and XI) and for their sulphones and methochlorides.

Experimental

4-Carboxy-3-pyridyl Phenyl Sulphide (II).—A solution of 3-amino*iso*nicotinic acid (I) (6·3 g.) (Gabriel and Colman, *Ber.*, 1902, **35**, 2832) in concentrated hydrochloric acid (10 c.c.) was stirred at 5° whilst a solution of sodium nitrite (3·6 g., 1·13 mols.) in water (25 c.c.) was added dropwise. Ten minutes after complete addition, urea was added to destroy excess of nitrous acid, and the solution was then added slowly with stirring to one of sodium hydroxide (10 g.) and thiophenol (5 c.c., 1 mol.) in water (50 c.c.) at 95°, heating being maintained until evolution of nitrogen ceased. The filtered chilled solution was then brought to pH 5 by the addition of acetic acid, whereupon the cream-coloured *sulphide* (II) was precipitated, m. p. 227° (decomp.) after crystallisation from acetic acid (yield, 4·7 g., 44%) (Found: C, 62·3; H, 3·9; N, 6·3. $C_{12}H_9O_2NS$ requires C, 62·3; H, 3·9; N, 6·1%).

9-Thia-2-aza-anthrone (III).—A mixture of the sulphide (II) (3 g.) and thionyl chloride (15 c.c.) was boiled under reflux for 1 hr., and the excess of chloride then removed in a vacuum. Nitrobenzene (30 c.c.) and aluminium chloride (8 g.) were added to the residue, and the mixture was then heated at 100° for 3 hr., poured on ice, and steam-distilled to remove the nitrobenzene. The hot solution was filtered, cooled, and strongly basified with sodium hydroxide. The precipitated solid was collected, washed, dried, and sublimed at 160—170°/0·2 mm., furnishing the *anthrone* (III) (2 g., 72%) as cream-coloured needles, m. p. 165° (Found: C, 67·6; H, 3·3; N, 6·6. $C_{12}H_7ONS$ requires C, 67·6; H, 3·3; N, 6·6%). It gives a reddish-yellow solution in concentrated sulphuric acid.

The anthrone (1·1 g.) and methyl toluene-*p*-sulphonate (22 g.) were heated at 165° for 4 hr., and when cold repeatedly extracted with ether; the oily residue, when dissolved in water and treated with concentrated aqueous sodium iodide, deposited the *methiodide*, orange needles, m. p. 250—251° (decomp.) after recrystallisation from water (Found: C, 43·8; H, 2·9; N, 3·8. $C_{13}H_{10}ONIS$ requires C, 43·9; H, 2·8; N, 3·9%). A suspension of an excess of freshly prepared silver chloride in a solution of the methiodide (1·5 g.) in methanol (100 c.c.) was boiled under reflux for 20 min. in the absence of light, then filtered, and the solvent was removed; the residue, recrystallised from methanol–ether, gave the yellow *methochloride monohydrate* (0·6 g.), m. p. 244° (decomp.) (Found: C, 55·7; H, 4·6; N, 5·0. $C_{13}H_{10}ONClS,H_2O$ requires C, 55·4; H, 4·6; N, 5·0%).

9-Thia-2-aza-anthrone 9 : 9-Dioxide (IV).—A solution of the anthrone (III) (0·9 g.) in acetic acid (90 c.c.) was kept at 75—80° whilst 30% hydrogen peroxide (6 c.c.) was added in three portions during 4 hr., the heating being then continued for 2 hr. more. On cooling, the *sulphone* (IV) (0·72 g., 69%) separated, and crystallised from ethanol as cream-coloured needles, melting indefinitely 230—250° (decomp.) (Found: C, 58·8; H, 2·7; N, 5·6. $C_{12}H_7O_3NS$ requires C, 58·8; H, 2·8; N, 5·7%). For infra-red data see below.

4-Carboxy-3-pyridyl p-Nitrophenyl Sulphide (V).—This *sulphide* was prepared in 93% yield precisely as (II) but with *p*-nitrothiophenol, and when recrystallised from acetic acid formed pale yellow needles, m. p. 279° (decomp.) (Found: C, 52·5; H, 3·2; N, 10·0. $C_{12}H_8O_4N_2S$ requires C, 52·2; H, 2·9; N, 10·1%).

6-Nitro-9-thia-2-aza-anthrone (VI).—This *compound* was prepared as (III), but with 6 hours' heating of the final mixture, and when sublimed at 200°/0·05 mm. furnished pale yellow needles, m. p. 290° (Found: C, 56·0; H, 2·45; N, 11·0. $C_{12}H_6O_3N_2S$ requires C, 55·8; H, 2·3; N, 10·8%).

6-Amino-9-thia-2-aza-anthrone (VII).—Stannous chloride (1 g.) was added to a suspension of the nitro-anthrone (VI) (50 mg.) in concentrated hydrochloric acid (5 c.c.), which was kept at 60° for 1 hr., and then cooled and made strongly alkaline with sodium hydroxide. When the precipitated material was heated at 205°/0·03 mm., the *amino*-compound (VII) (20 mg.) sublimed to form bright red crystals, m. p. 227° (Found: C, 63·3; H, 3·5; N, 12·1. $C_{12}H_8ON_2S$ requires C, 63·2; H, 3·5; N, 12·3%). The same compound was obtained when the stannous chloride was replaced by tin.

Nitration of the Anthrone (III).—Finely powdered potassium nitrate (75 mg.) was added to a stirred solution of the anthrone (100 mg.) in cold concentrated sulphuric acid (20 c.c.), the colour of the solution changing from reddish-yellow to pure yellow. The solution was poured on ice and made alkaline with ammonia. The yellow precipitate (100 mg.), when collected, washed with water, dried, and sublimed at 200—210°/0·2 mm., melted indefinitely between 230° and 280° and consisted of mixed mononitro-derivatives (Found: C, 55·9; H, 2·5; N, 10·7. $C_{12}H_6O_3N_2S$ requires C, 55·8; H, 2·3; N, 10·8%).

The mixed product was reduced as described for (VI), and the reduction product fractionally sublimed at 200°/0·03 mm. The less volatile amine formed bright red crystals, m. p. 227° alone or mixed with (VII) : the more volatile amine (probably the 8-amino-derivative) formed yellow crystals, m. p. 183°.

2-*Carboxy*-3-*pyridyl Phenyl Sulphide* (X).—This sulphide was prepared from the diazotised acid (IX) (6·3 g.) (Sucharda, *Ber.*, 1925, **58**, 1728) under the same conditions as were used for the preparation of (II) from the acid (I). The cautious addition of acetic acid to the final filtered solution to obtain pH 5 caused however a copious precipitate consisting apparently of a double sodium hydrogen salt, colourless plates (5·6 g.), m. p. 318° (decomp.), from ethanol (Found : C, 59·6; H, 3·4; N, 5·6. $C_{24}H_{17}O_4N_2S_2Na$ requires C, 59·5; H, 3·5; N, 5·8%). This recrystallised salt, when treated with glacial acetic acid, gave the pure cream-coloured *sulphide* (X), m. p. 162° (decomp.) (Found : C, 62·1; H, 4·2; N, 5·95. $C_{12}H_9O_2NS$ requires C, 62·3; H, 3·9; N, 6·05%). Alternatively, the sulphide was obtained by crystallisation of the crude sodium salt from acetic acid, a less soluble crop of diphenyl disulphide being rejected.

The sulphide, when heated above its m. p., underwent a ready decarboxylation to the liquid phenyl 3-pyridyl sulphide, which was volatile in steam and was characterised as its *picrate*, yellow leaflets, m. p. 126°, from water (Found : C, 49·7; H, 3·05; N, 13·6. $C_{11}H_9NS,C_6H_3O_7N_3$ requires C, 49·1; H, 2·9; N, 13·5%).

9-*Thia*-4-*aza-anthrone* (XI).—This compound was prepared from the sulphide (X) (0·5 g.) as (III) was prepared from (II) : the final precipitate, when sublimed at 180—190°/0·07 mm., gave the cream-coloured *anthrone* (XI) (0·27 g., 59%), m. p. 224° (Found : C, 67·3; H, 3·3; N, 6·5. $C_{12}H_7ONS$ requires C, 67·6; H, 3·3; N, 6·6%). It gives a yellow solution in sulphuric acid.

On one occasion the anthrone (XI) was obtained by the action of phosphorus oxychloride on the sulphide (X) : the conditions require delicate adjustment, however, and the above method is preferable.

When cyclisation of (X) was attempted by treatment with sulphuric acid at 140—150° for 4 hr., only sulphonation occurred, with the formation of 2-*carboxy*-3-*pyridyl* p-*sulphophenyl sulphide*, pale yellow leaflets, m. p. 262° (decomp.), from water (Found : C, 45·8; H, 2·9; N, 4·5. $C_{12}H_9O_5NS_2$ requires C, 46·3; H, 2·9; N, 4·5%). (It is assumed that sulphonation has occurred in the *para*-position to the sulphur atom.)

The *methiodide* of the anthrone (XI), prepared as previously described, crystallised from hot water in orange rods and from cold water in yellow needles, both forms becoming scarlet on drying (Found : C, 43·7; H, 2·8; N, 3·75. $C_{13}H_{10}ONIS$ requires C, 43·9; H, 2·8; N, 3·9%); the methiodide decomposes at 181° with reversion to the anthrone (XI). The *methochloride*, prepared as before, and recrystallised from ethanol–ether, formed a sesquihydrate, yellow needles which readily decompose to the anthrone at *ca.* 150—160° (Found : C, 54·0; H, 4·5; N, 5·1. $C_{13}H_{10}ONClS,1{\cdot}5H_2O$ requires C, 53·7; H, 4·5; N, 4·8%). The readiness with which these two quaternary salts lose methyl halide when heated is noteworthy.

9-*Thia*-4-*aza-anthrone* 9 : 9-*Dioxide*.—This *sulphone*, prepared as was (IV), was obtained as colourless needles, m. p. 204°, from ethanol (Found : C, 58·8; H, 3·2; N, 6·0. $C_{12}H_7O_3NS$ requires C, 58·8; H, 2·85; N, 5·7%). For infra-red data, see below.

2-*Carboxy*-3-*pyridyl* p-*Nitrophenyl Sulphide* (XII; R = NO_2).—A solution of the diazotised acid (IX) (4·2 g.) was added rapidly to a boiling solution of *p*-nitrothiophenol (5·2 g., 1·1 mols.) in 5% aqueous sodium hydroxide (200 c.c.). When nitrogen evolution ceased, the solution was cooled, filtered, and acidified with hydrochloric acid. The precipitated *sulphide* (XII; R = NO_2) (7·0 g., 92%) gave yellow needles, m. p. 190° (decomp.), after recrystallisation from acetic acid and ethanol in turn (Found : C, 52·2; H, 3·1; N, 9·7. $C_{12}H_8O_4N_2S$ requires C, 52·2; H, 2·9; N, 10·1%). The sulphide, when heated above its m. p., smoothly formed p-*nitrophenyl* 3-*pyridyl sulphide*, pale yellow needles, m. p. 115°, from ethanol (Found : C, 56·8; H, 3·2; N, 12·0. $C_{11}H_8O_2N_2S$ requires C, 56·9; H, 3·4; N, 12·1%).

Nitration of the Anthrone (XI).—This anthrone (400 mg.) was nitrated as was (III), with potassium nitrate (240 mg.), the complete mixture being kept at 30—35° for 15 min.; the initial deep yellow colour faded almost completely, and a green fluorescence developed. The final yellow precipitate (420 mg.) was collected, washed, dried, and extracted repeatedly with boiling ethanol. The insoluble residue (353 mg.), after sublimation at 200°/0·03 mm. and recrystallisation from acetic acid, gave 6-*nitro*-9-*thia*-4-*aza-anthrone* (XIII), pale yellow leaflets m. p. 298° (Found : C, 55·9; H, 2·4; N, 10·8. $C_{12}H_6O_3N_2S$ requires C, 55·8; H, 2·3; N, 10·8%).

The ethanolic extracts on evaporation gave a residue (63 mg.) which, recrystallised from

ethanol, furnished the bright yellow 8-*nitro*-derivative (XIV), m. p. 249° (Found : C, 56·1; H 2·6; N, 10·7. $C_{12}H_6O_3N_2S$ requires C, 55·8; H, 2·3; N, 10·8%).

Reduction of 6-*Nitro*-9-*thia*-4-*aza*-*anthrone* (XIII).—(*a*) Stannous chloride (1 g.) in concentrated hydrochloric acid (15 c.c.) was added to the anthrone (XIII) (0·3 g.) in acetic acid (20 c.c.). The mixture was then kept at 50—60° for 1 hr., then made strongly alkaline with aqueous sodium hydroxide, and the reddish-brown precipitate (0·13 g.) collected, washed, and dried. Sublimation at 220°/0·03 mm. slowly gave the 6-*amino*-derivative (XV) as a scarlet microcrystalline powder, m. p. 246°; alternatively, recrystallisation from acetic acid gave brownish-red rhombs, also m. p. 246° (Found : C, 63·4; H, 3·3; N, 12·0. $C_{12}H_8ON_2S$ requires C, 63·2; H, 3·5; N, 12·3%).

(*b*) Granulated tin (270 mg.) and concentrated hydrochloric acid (*ca.* 0·1 c.c.) were added in turn to a suspension of the anthrone (150 mg.) in 70% acetic acid (10 c.c.) which was then kept at 90° for 1 hr.; a clear pale yellow solution remained. This was worked up as in (*a*). Sublimation at 175—180°/0·03 mm. readily gave 6-*amino*-9 : 10-*dihydro*-9-*thia*-4-*aza*-*anthracene* (XVI) (50 mg., crude), m. p. 159·5—160° (Found : C, 67·3; H, 4·9; N, 13·1. $C_{12}H_{10}N_2S$ requires C, 67·3; H, 4·7; N, 13·1%). A very small residue of the amino-anthrone (XV) remained unsublimed.

The 6-amino-anthrone (XV) when similarly treated also yielded (XVI), m. p. and mixed m. p. 159—160°.

Reduction of 2-*Carboxy*-3-*pyridyl* p-*Nitrophenyl Sulphide* (XII; R = NO_2).—Concentrated hydrochloric acid was added dropwise to the sulphide (2 g.) and granulated tin (2 g.) in ethanol (20 c.c.), which was kept at 40—50° until all the tin had dissolved. The solution was concentrated in a vacuum, mixed with water, filtered, and saturated with hydrogen sulphide; precipitated sulphides were collected, and the filtrate was acidified with hydrochloric acid, evaporated to small volume, and whilst hot diluted with acetone until a turbidity became just apparent. The solution on cooling deposited the p-*aminophenyl* 2-*carboxy*-3-*pyridyl sulphide hydrochloride* (XII; R = NH_2,HCl), pale cream-coloured needles, m. p. 195° (decomp.) after crystallisation from ethanol–ether (Found : C, 50·7; H, 4·2; N, 9·6. $C_{12}H_{10}O_2N_2S$,HCl requires C, 50·9; H, 3·9; N, 9·9%).

This amino-compound underwent ready deamination under conditions analogous to those employed by Brewster and Page (*J. Amer. Chem. Soc.*, 1939, **61**, 2418). A solution of the hydrochloride (500 mg.) was diazotised, added to hypophosphorous acid (10 c.c.), and set aside overnight at 1—2°. On adjustment of the pH to 4, the pale yellow sulphide (X) (220 mg.) was precipitated; after recrystallisation from aqueous ethanol, it had m. p. 162° (decomp.), alone and mixed with the former sample.

A solution of the above hydrochloride (140 mg.), diethylaniline (0·2 c.c.), and ethyl chloroformate (0·1 c.c.) in ethanol (50 c.c.) was boiled under reflux for 15 min., concentrated, and diluted with water. The p-*ethoxycarbonylaminophenyl* 2-*carboxy*-3-*pyridyl sulphide* (XII; R = ·NH·CO_2Et) which separated crystallised from aqueous ethanol as cream-coloured crystals, m. p. 179—180° (decomp.) (Found : C, 56·8; H, 4·6; N, 9·0. $C_{15}H_{14}O_4N_2S$ requires C, 56·6; H, 4·4; N, 8·8%). Attempts to cyclise this compound failed, although the comparable cyclisation of other urethanes has been recorded (cf. Walls, *J.*, 1947, 67).

p-*Carboxyphenyl* 2-*Carboxy*-3-*pyridyl Sulphide* (XVII).—A solution of the diazotised acid (IX) (1·05 g.) was added to boiling 20% aqueous sodium hydroxide (15 c.c.) to which methyl *p*-mercaptobenzoate (1·3 g.) had been added immediately before. The cooled solution was acidified to pH 3 with hydrochloric acid, and the precipitated *sulphide* (XVII) (1·4 g., 67%), after recrystallisation from dioxan, gave colourless crystals, m. p. 215° (decomp.) (Found : C, 57·1; H, 3·3; N, 5·3. $C_{13}H_9O_4NS$ requires C, 56·8; H, 3·3; N, 5·1%). The use of *p*-mercaptobenzoic acid on one occasion gave (XVII) in low yield, but on all others gave an unidentified solid of high m. p.

The sulphide, when heated above its m. p., underwent smooth decarboxylation to p-*carboxyphenyl* 3-*pyridyl sulphide* (XVIII), crystals, m. p. 173·5—174·5° from aqueous ethanol (Found : C, 62·4; H, 3·9; N, 5·9. $C_{12}H_9O_2NS$ requires C, 62·3; H, 3·9; N, 6·05%).

9-*Thia*-1-*aza*-*anthrone Methochloride*.—This salt, which has not previously been described, was prepared from the corresponding methiodide (Mann and Reid, *loc. cit.*) precisely as the above 2-aza- and 4-aza-analogues, and obtained as buff-coloured hygroscopic needles, m. p. 226° (decomp.), of the *hemihydrate* from methanol–ether (Found : C, 57·4; H, 4·2. $C_{13}H_{10}ONClS$,0·5H_2O requires C, 57·3; H, 4·1%).

Infra-red Investigation of 9-*Thia*-2-*aza*-*anthrone* 9 : 9-*Dioxide* (IV) *and its* 4-*Aza*-*isomeride*.—These compounds were identified as sulphones by the method already described (Mann and

Reid, *loc. cit.*), based on the fact that sulphones normally have strong absorption bands in the regions of 1340—1295 and 1160—1120 cm.$^{-1}$, whereas sulphoxides show a single strong absorption band at 1060—1030 cm.$^{-1}$. The compound (IV) had two strong bands at 1299 and 1160 cm.$^{-1}$, and the 4-aza-compound similarly at 1295 and 1164 cm.$^{-1}$ (cf. the 1-aza-isomer, which showed bands at 1315 and 1165 cm.$^{-1}$). This provides very strong evidence that the two compounds were sulphones and not pyridine oxide sulphoxides. The compound (IV) and the 4-aza-isomer also showed a considerably weaker band at 1157 cm.$^{-1}$, which does not however indicate a sulphoxide group.

We are greatly indebted to Dr. Joan A. Reid for a preliminary investigation of the synthesis of compounds (II) and (III), to Mr. O. D. Standen for the therapeutic tests, and to the Medical Research Council for a grant (S. K.).

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