422. *The Structure and Properties of Certain Polycyclic Indolo- and Quinolino-derivatives. Part IV.* Derivatives of* 1-*Thiochroman*-4-*one and of* 2-*Thio*iso*chroman*-4-*one.*

By A. K. Kiang and Frederick G. Mann.

The phenylhydrazones of the above thiochromanones undergo normal indolisation, and the formation of ψ-indoles, which is a characteristic feature of several phenylhydrazones previously studied, does not occur. Both the above isomeric phenylhydrazones undergo ready oxidation to the corresponding sulphoxides in hot ethanolic solution, a property which is not shared by the parent thiochromanones or the indolo-derivatives.

The thiochromanones undergo the Pfitzinger reaction with isatin to give the quinolino-carboxylic acids, which can be decarboxylated to the corresponding quinolino-thiochromens. The latter compounds show one surprising difference, for the product from 1-thiochromanone when treated with cold permanganate is oxidised to the sulphone, whereas that from 2-thio*iso*chromanone is oxidised to the 1-keto-derivative, the sulphur being unattacked.

The cyclic keto-amines hitherto studied in this investigation have all contained essentially the 1 : 2 : 3 : 4-tetrahydro-4-ketoquinoline system (I), the nitrogen atom being either linked to an aryl group or forming part of another ring. Certain characteristics of this system have become apparent. (*a*) When the phenylhydrazone of the keto-amine is subjected to indolisation, a ψ-indole usually results. This is true for the phenylhydrazone of the parent tetrahydro-4-ketoquinoline (Clemo and Perkin, *J.* 1924, **125**, 1608), of the 1-phenyl derivative (Mann, *J.*, 1949, 2816) and of the 1-ketojulolidine (Mann and Smith, *J.*, 1951, 1898) but not of 1 : 2 : 2*a* : 3 : 4 : 5 : 8 : 9 : 10 : 10*a*-decahydro-5 : 8-diketo-2*a* : 10*a*-diazapyrene (Almond and Mann, *J.*, 1951, 1906). Salt formation by these ψ-indoles usually involves the acceptance of a positive charge by the 1-quinolino-nitrogen atom. (*b*) When the keto-amine is subjected to the Pfitzinger reaction with isatin, the resulting amino-acid is markedly different in colour from its salts; the decarboxylated amine, however, often resembles in colour the salts of the acid, whereas the salts of the amine resemble in colour the original amino-acid. These colour relations have been explained on the basis of the resonance of the amino-acid (which acts as a zwitterion)

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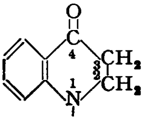
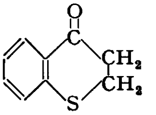
* Part III, preceding paper.

and of the ions produced by salt formation of the acid and the amine; this resonance also involves the possibility of the 1-nitrogen atom in the system (I) accepting a positive charge. (*c*) Finally, the decarboxylated amines undergo very ready oxidation, the 2-methylene group in (I) being converted into the CO group.



(I.)



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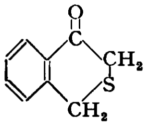
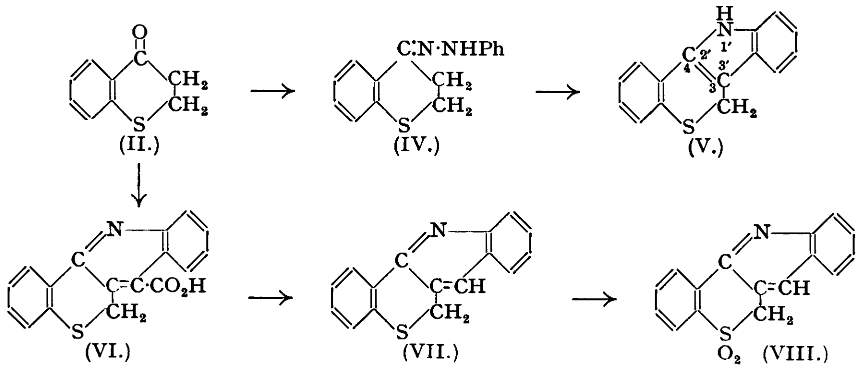


(III.)

Since these reactions appeared to depend markedly on the position and properties of the 1-nitrogen atom, it was of interest to see if similar properties were shown by a heterocyclic system which would be closely similar to (I), except that the 1-nitrogen atom would be replaced by an element from a different Group, but which could nevertheless also accept a positive charge, so that the resonance possibilities would closely resemble those of the system already investigated.

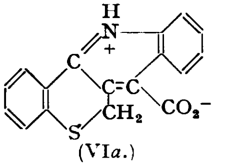
For this purpose, we have selected 1-thiochroman-4-one (II) which satisfies the above conditions, and also 2-thio*iso*chroman-4-one (III), in order to study the effect of the change in position of the hetero-atom. The derivatives of these ketones show many similarities but also some unexpected differences.

1-Thiochromanone (II) gives a pale yellow crystalline phenylhydrazone (IV) which when boiled with ethanolic hydrogen chloride undergoes indolisation to indolo(3′ : 2′-3 : 4)-thiochromen (V). No indication of the formation of a ψ-indole was detected. It is noteworthy, however, that whereas the chromanone (II) and its indolo-derivative (V) are apparently unaffected by air, either in the crystalline state or in hot organic solvents, the intermediate hydrazone (IV), when boiled in ethanolic, *n*-propanolic, or ethereal solution, undergoes ready atmospheric oxidation to the corresponding sulphoxide, the structure of which has been placed beyond reasonable doubt by an infra-red spectroscopic examination by Dr. N. Sheppard.

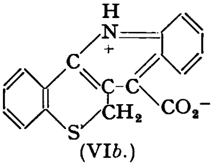


(II.) (IV.) (V.) (VI.) (VII.) (VIII.)

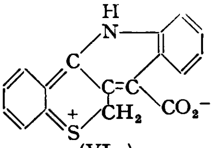
When 1-thiochromanone is boiled with isatin in alkaline solution, subsequent acidification ultimately gives quinolino(3′ : 2′-3 : 4)-1-thiochromen-4′-carboxylic acid (VI) as yellow crystals, m. p. 244—248° (decomp.), which however give a colourless potassium salt. The acid (VI) on decarboxylation gives quinolino(3′ : 2′-3 : 4)-1-thiochromen (VII) as almost colourless crystals, m. p. 101—102°, which however give an orange hydrochloride.



(VI*a*.)



(VI*b*.)



(VI*c*.)

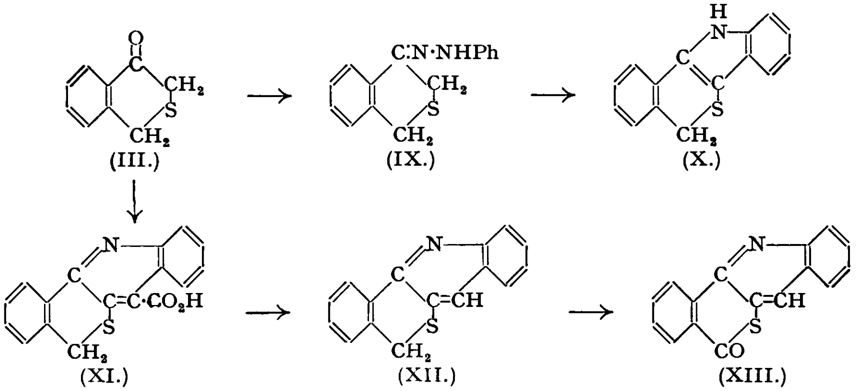
The interpretation of these colour relations must be closely similar to that already given (Mann, *loc. cit.*) for 1 : 2-dihydro-1-phenylquinolino(3′ : 2′-3 : 4)quinoline-4′-carboxylic acid and the corresponding decarboxylated amine. There is little doubt that the acid (VI) is a zwitterion, which will exist as a resonance hybrid to which the three canonical forms (VI*a*), (VI*b*), and (VI*c*) will contribute, and that it is this resonance, involving in particular the *o*-quinonoid structures, which is responsible for the yellow colour of the acid. When, however, this zwitterion structure is destroyed by the formation of a potassium salt, the resonance of the cation becomes much more limited and the salt is therefore colourless. The decarboxylated thio-amine (VII) will also show this very restricted resonance and is also colourless, but its hydrochloride will possess a cation which will have the three canonical forms precisely similar to (VI*a*—*c*), except that the CO_2^- group is replaced by an (uncharged) hydrogen atom, and hence this salt has the orange colour. The change from the highly polar structure of the zwitterion (VI) to the uncharged amine (VII) might also account for the considerable fall in melting point which accompanies this change.

The thio-amine (VII) is in striking contrast to the corresponding diamines previously studied in that it does not undergo atmospheric oxidation, and in particular the 2-methylene group is quite stable. When the thio-amine is treated with potassium permanganate in acetone solution, however, oxidation occurs solely to the sulphone (VIII), the structure of which has been determined by both chemical and infra-red spectroscopic analysis.

It is noteworthy that the thio-amine (VII) is unaffected by boiling methyl iodide. This reluctance of the quinolino-nitrogen atom to undergo quaternisation has been shown by all similar compounds previously examined in this series. The thio-amine (VII) does, however, readily give a sulphilimine when boiled with an ethanolic solution of chloramine-T.

The corresponding reactions with 2-thio*iso*chroman-4-one (III) exhibit several points of considerable interest. This compound also gives a phenylhydrazone (IX) which in turn gives indolo(3′ : 2′-3 : 4)-2-thio*iso*chromen (X). Again, whereas the *iso*chromanone (III) and the indolo-derivative (X) are stable, the intermediate hydrazone (IX) when boiled in ethanolic solution undergoes ready oxidation to the sulphoxide. The reason for the high susceptibility to atmospheric oxidation shown by the isomeric hydrazones (IV) and (IX) is at present obscure.

The 2-thio*iso*chromanone (III) when subjected to the Pfitzinger reaction gave quinolino-(3′ : 2′-3 : 4)-2-thio*iso*chromen-4′-carboxylic acid (XI), m. p. 250—260° (decomp.), which also formed yellow crystals but gave an almost colourless potassium salt. Decarboxylation of the acid (XI) gave quinolino(3′ : 2′-3 : 4)-2-thio*iso*chromen (XII), m. p. 70°, which was almost colourless but gave a bright yellow hydrochloride. The acid (XI) also doubtlessly exists as a zwitterion, but differs from its isomer (VI) in that the resonance hybrid receives contributions only from the canonical forms corresponding to (VI*a*) and (VI*b*) : a form of type (VI*c*) having the *o*-quinonoid sulphonium group is not possible for the acid (XI). The same applies to the hydrochloride of the thio-amine (XII), in which the cation has forms corresponding only to (VI*a*) and (VI*b*), and it is probably this less complex resonance which causes this salt to be yellow whilst that of the isomer (VII) is orange.



The most remarkable property of the thio-amine (XII) is that, although it does not undergo atmospheric oxidation, it is readily oxidised by a cold acetone solution of potassium permanganate to 1-ketoquinolino(3′ : 2′-3 : 4)-2-thio*iso*chromen (XIII), the identity of which has again been established by chemical and infra-red spectroscopic analysis. This oxidation is of course parallel to that encountered in the diamines previously studied, except that in certain of the latter compounds it was necessarily the 2-methylene group of the pyridine ring which was oxidised. The striking factors are (*a*) that this oxidation should now occur only in the 2-thio*iso*chromen compound instead of the 1-thiochromen derivative, where the oxidation, had it occurred, would have affected the 2-methylene group and hence would have been precisely similar to previous examples, (*b*) that the sulphur atom in the 2-thio*iso*chromen compound (XII) should be so resistant to oxidation that it remains unaffected whilst the methylene group is oxidised to the keto-group, and (*c*) that the sulphur atom in (XII) readily reacts with chloramine-T to give a sulphilimine and hence in this reaction has normal reactivity.

Infra-red Absorption Spectra.—Dr. N. Sheppard reports : " *The oxidation product* (VIII). Barnard, Fabian, and Koch (*J.*, 1949, 2442) have shown that sulphone groups with normal aliphatic or aromatic substituents have strong absorption bands in the regions 1160—1120 and 1340—1295 cm.$^{-1}$, whereas sulphoxides have a single strong absorption in the region 1060—1030 cm.$^{-1}$. The infra-red spectrum of the product (VIII) as a powdered mull in Nujol has markedly strong absorption bands at 1158 and 1303 cm.$^{-1}$, which are consistent with the sulphone structure. No strong absorption band was found in the region characteristic of sulphoxides, or in the well-known infra-red spectral regions characteristic of OH or C:O groupings.

" *The oxidation product* (XIII). The spectrum of this compound as a mull in Nujol showed no strong absorption bands in the regions characteristic of sulphone or sulphoxide groupings, nor could any OH absorption bands be detected. It did, however, have a strong absorption band near 1650 cm.$^{-1}$, which because of its intensity is probably caused by the presence of a C:O group. The frequency of this band is consistent with the structure (XIII). The conjugation of such a C:O group with the benzene ring would normally give rise to an absorption band between 1670 and 1690 cm.$^{-1}$ in purely hydrocarbon surroundings, and the neighbouring sulphur atom would probably cause a shift to lower frequencies to give the value found, near 1650 cm.$^{-1}$; cf. acetone (gas) 1724 cm.$^{-1}$, thioacetic acid (gas) 1696 cm.$^{-1}$ (Price, *J. Chem. Physics*, 1941, **9**, 725; Sheppard, *Trans. Faraday Soc.*, 1949, **45**, 693).

" *The oxidation products of the phenylhydrazones* (IV) *and* (IX). It was hoped to obtain infra-red spectroscopic evidence to show whether oxidation had resulted in the formation of an $N \rightarrow O$ or $S \rightarrow O$ (sulphoxide) grouping. As previous work on the infra-red spectrum of molecules containing $N \rightarrow O$ linkages seemed insufficient to give any reliable correlation rule for this grouping, reliance could be placed only on obtaining positive evidence for the $S \rightarrow O$ linkage which should give a strong absorption in the region 1060—1030 cm.$^{-1}$ when alkyl or aryl groups are joined to the sulphur atom (Barnard *et al.*, *loc. cit.*). The infra-red spectra of the oxidation products of (IV) and (IX) as Nujol mulls actually showed outstandingly strong absorption bands near 1020 and 1000 cm.$^{-1}$ respectively. Although these are somewhat outside the usual correlation region for $S \rightarrow O$ groupings, the fact that the sulphur atom is part of a ring might explain the slightly shifted frequencies, and hence it seemed possible that these absorption bands were those of the respective sulphoxides. In order to place the analysis on a firmer basis, the unoxidised phenylhydrazones (IV) and (IX) were also examined in the same spectral region. Their spectra had features in common with those of the oxidation products but lacked the outstandingly strong bands near 1020 and 1000 cm.$^{-1}$, thus providing confirmatory evidence for the assignment of the absorption in the latter cases to the presence of $S \rightarrow O$ linkages."

EXPERIMENTAL.

β-Phenylthiopropionic Acid.—This acid was prepared by the condensation of thiophenol and β-chloropropionic acid in alkaline solution (Arndt, *Ber.*, 1923, **56**, 1269).

1-*Thiochroman*-4-*one* (II).—This was most satisfactorily prepared by the following modification of Krollpfeiffer and Schultze's method (*Ber.*, 1923, **56**, 1819). The above acid (30 g.) was dissolved in concentrated sulphuric acid (200 c.c.) at 5°. The solution, which had become first orange and then dark red, was next removed from the cooling-bath and set aside overnight. It was then poured on ice, and the precipitated yellow oil was taken up in ether, washed with alkali and water, dried, and distilled. The thiochromanone was obtained as an oil, b. p. 113—114°/0·1 mm., which solidified and when recrystallised from light petroleum gave crystals, m. p. 29—30° (20 g., 74%).

Alternatively a solution of the acid (20 g.) in xylene (200 c.c.) was added to a mixture of phosphoric anhydride and " Hyflo Super Cel " (12 g.), and the whole then boiled under reflux for 2 hours with vigorous stirring. The xylene was filtered, the residue extracted with boiling xylene (100 c.c.), and the united xylene solutions were then distilled. The thiochromanone had b. p. 121—123°/0·2 mm. and when treated as above gave crystals, m. p. 29—30° (19 g., 50%).

1-*Thiochroman*-4-*one phenylhydrazone* (IV). This was readily formed when a mixture of the chromanone (II) and phenylhydrazine (1·2 mols.) containing a small quantity of acetic acid was gently warmed. The *hydrazone* separated as a viscous liquid which solidified when stirred with light petroleum or methanol, and when recrystallised from the latter formed pale yellow needles, m. p. 77—80°, when rapidly heated (Found : C, 70·7; H, 5·6; N, 11·3. $C_{15}H_{14}N_2S$ requires C, 70·8; H, 5·55; N, 11·0%).

Indolo(3′ : 2′-3 : 4)-1-*thiochromen* (V).—A mixture of the hydrazone (IV) (5 g.) and saturated ethanolic hydrogen chloride (100 c.c.) was boiled under reflux for 30 minutes, cooled, filtered, and added with stirring to 10% aqueous sodium hydroxide (400 c.c.). The yellow rather sticky precipitate became powdery when set aside, and when collected, dried, and recrystallised from benzene gave the *indolo*-derivative (V) as very pale yellow crystals, m. p. 158—160° (Found : C, 76·0; H, 4·9; N, 5·8. $C_{15}H_{11}NS$ requires C, 75·9; H, 4·7; N, 5·9%).

Oxidation of the Phenylhydrazone (IV).—(*a*) A solution of the phenylhydrazone (1 g.) in ethanol (50 g.) was boiled under reflux for 6 hours and then concentrated to small bulk. The crude crystals, m. p. 165—180°, thus obtained were recrystallised repeatedly from ethanol to give pale yellow needless of 1-*thiochromanone phenylhydrazone* 1-*oxide*, m. p. 199—200° (Found : C, 67·0; H, 4·9; N, 10·6; S, 12·1. $C_{15}H_{14}ON_2S$ requires C, 66·6; H, 5·2; N, 10·4; S, 11·8%).

(*b*) Similar results were obtained on using solutions in *n*-propanol and in ether, but the phenylhydrazone was recovered almost unchanged when methanol was used.

(*c*) Sufficient acetone was added to a mixture of the phenylhydrazone (1 g.) and hydrogen peroxide (5 c.c.; " 100-vol.") to give a clear solution, which was then set aside. After 24 hours, a portion of the solution furnished a crude sample of the above sulphoxide, m. p. 190—194°; after 7 days another portion furnished a purer sample, m. p. 194—196°, undepressed on admixture with the pure material.

Quinolino(3′ : 2′-3 : 4)-1-*thiochromen*-4′-*carboxylic acid* (VI).—Potassium hydroxide (10·8 g.), isatin (9·6 g.), and the chromanone (II) (10·2 g.) were dissolved in this order in a mixture of ethanol (60 c.c.) and water (12 c.c.), which was then boiled under reflux for 1 hour, cooled, and poured with stirring into 5% aqueous acetic acid (300 c.c.). The yellow flocculent precipitate of the *acid* (VI) rapidly became crystalline when set aside, and was then collected, washed with ethanol and water, and dried : the yield was 15 g. (82%). A sample crystallised from acetic acid gave yellow crystals, m. p. 244—248° (decomp.) with softening at 223° (Found : C, 69·6; H, 4·0; N, 5·0. $C_{17}H_{11}O_2NS$ requires C, 69·6; H, 3·8; N, 4·8%).

To prepare the *potassium* salt, the acid (2 g.) was added to a boiling solution of potassium carbonate (0·75 g.) in water (50 c.c.) : after a short period of heating, the solution was filtered to remove a trace of a brownish-violet insoluble material, and was then evaporated until crystals appeared. After cooling, the pale yellow crystals were collected and recrystallised from water, furnishing the almost colourless dihydrated salt (Found : N, 3·75. $C_{17}H_{10}O_2NSK,2H_2O$ requires N, 3·8%). The crystals dissolved readily in cold water to give a solution having a slightly greenish fluorescence.

Quinolino(3′ : 2′-3 : 4)-1-*thiochromen* (VII).—The acid was decarboxylated by heating at 250°/0·2 mm. in a tube inclined slightly downward, so that the product condensed and flowed away from the heated end. The orange viscous liquid solidified when rubbed with ethanol, and when then recrystallised from this solvent gave colourless crystals of the *thiochromen* (VII), m. p. 101—102° (Found : C, 77·2; H, 4·5; N, 5·85. $C_{16}H_{11}NS$ requires C, 77·0; H, 4·45; N, 5·6%). This compound was recovered unchanged after prolonged boiling with methyl iodide.

When a solution of the base in hot saturated ethanolic hydrogen chloride was cooled, orange crystals of the *hydrochloride* separated, and when recrystallised from this solvent gave the hemihydrate as yellow needles, m. p. 192—194° (Found : C, 65·3; H, 5·1; N, 5·0. $C_{16}H_{11}NS,HCl,\frac{1}{2}H_2O$ requires C, 65·2; H, 4·5; N, 4·8%).

When ethanolic solutions of equal quantities of the base and hydrated chloramine-T were mixed and warmed, a pale yellow crystalline precipitate rapidly formed. This, when collected, washed with water, and recrystallised from ethanol, gave colourless crystals of *quinolino*(3′ : 2′-3 : 4)-1-*thiochromen toluene*-p-*sulphonylimine*, m. p. 182—183° (Found : C, 65·5; H, 4·7; N, 6·9. $C_{23}H_{18}O_2N_2S_2$ requires C, 66·0; H, 4·3; N, 6·7%).

Oxidation of the Base (VII).—(*a*) Air was drawn for 4 hours at 85—90° over the finely powdered base, which was subsequently recovered unchanged.

(*b*) A cold solution of the base (0·5 g.) in acetone (150 c.c.) was shaken mechanically whilst potassium permanganate was added in small quantities. Oxidation occurred slowly and was complete after *ca.* 48 hours. The filtered solution was then allowed to evaporate. The residue was washed with water and extracted with boiling ethanol, which on cooling deposited crystals which when further recrystallised from acetone furnished *quinolino*(3′ : 2′-3 : 4)-1-*thiochromen* 1 : 1-*dioxide* (VIII) as very pale yellow crystals, m. p. 202—204° (Found : C, 68·4; H, 3·75; N, 4·8. $C_{16}H_{11}O_2NS$ requires C, 68·3; H, 3·9; N, 5·0%).

Benzylthiolacetic Acid.—Toluene-ω-thiol (10 g.) was added to a solution of chloroacetic acid (9 g.) in 4N-sodium carbonate (24 c.c.), to which 4N-sodium hydroxide (24 c.c.) was then slowly added with vigorous shaking and cooling. The mixture was then heated on a water-bath for 1 hour, cooled, filtered, and acidified. The precipitated oily acid (yield, almost theoretical) crystallised when vigorously stirred with light petroleum. Recrystallisation from light petroleum gave colourless crystals, m. p. 62—63° (cf. Gabriel, *Ber.*, 1879, **12**, 1641; Lesser and Mehrländer, *Ber.*, 1923, **56**, 1642).

2-*Thio*iso*chroman*-4-*one* (III).—A thin paste of phosphoric anhydride (30 g.), " Hyflo Super Cel " (15 g.), and dry benzene (100 c.c.) was slowly added to a vigorously stirred solution of the above dry acid (20 g.) in benzene (75 c.c.), which was then heated on a boiling water-bath for 3·5 hours. The benzene solution was filtered, the residue extracted with boiling benzene (75 c.c.), and the solvent removed by distillation from the united extracts, which were then basified with sodium hydroxide solution and distilled in steam. The 2-thio*iso*chromanone separated as an oil which subsequently crystallised, and a further quantity was obtained by ether-extraction of the distillate; the total yield was 6·5 g. (37%). After recrystallisation from light petroleum, the 2-thio*iso*chroman-4-one was obtained as colourless leaflets, m. p. 59—60°. It was unaffected by prolonged boiling with methyl iodide. Lesser and Mehrländer (*loc. cit.*) and Braun and Weissbach (*Ber.*, 1929, **62**, 2419) prepared this compound by cyclisation of the intermediate acid chloride.

2-*Thio*iso*chromanone phenylhydrazone* (IX). This *compound* was prepared as was the isomer (IV) and after recrystallisation from methanol was obtained as pale yellow needles, m. p. 114—116° (Found: C, 71·0; H, 5·4; N, 11·0. $C_{15}H_{14}N_2S$ requires C, 70·8; H, 5·55; N, 11·0%).

Indolo(3′ : 2′-3 : 4)-2-*thio*iso*chromen* (X).—A saturated ethanolic solution of hydrogen chloride (5 c.c.) was added to a solution of the phenylhydrazone (IX) (2·5 g.) in ethanol (50 c.c.). After 15 minutes, the solution was poured into an excess of dilute aqueous sodium hydroxide, and the precipitated yellow powder was collected and recrystallised first from benzene and then repeatedly from aqueous ethanol. The *indolo*-derivative (X) was obtained as very pale yellow leaflets, m. p. 140—142° (Found: C, 76·15; H, 4·6; N, 5·9. $C_{15}H_{11}NS$ requires C, 75·9; H, 4·7; N, 5·9%).

Oxidation of the Phenylhydrazone (IX).—This was performed by boiling an ethanolic solution of the hydrazone as described for the isomer (IV). The crystals which were obtained on concentration were thrice recrystallised from ethanol and furnished 2-*thio*iso*chromanone phenylhydrazone* 2-*oxide* as pale yellow needles, m. p. 225—226° (decomp.) (Found: C, 66·8; H, 5·4; N, 10·4; S, 12·2. $C_{15}H_{14}ON_2S$ requires C, 66·6; H, 5·2; N, 10·4; S, 11·8%). Similar results were obtained in *n*-propanol and in ethereal solution, but no oxidation was detected in boiling methanolic solution.

Quinolino(3′ : 2′-3 : 4)-2-*thio*iso*chromen*-4′-*carboxylic Acid* (XI).—This was prepared as was the isomer (XI) but the heating was continued for 5 hours. The average yield of crude acid was 74%. Recrystallisation from methanol gave yellow crystals, m. p. 255—260° (decomp.) with darkening at 230° (Found: C, 69·6; H, 4·0. Calc. for $C_{17}H_{11}O_2NS$: C, 69·6; H, 3·8%). Braun and Weissbach (*loc. cit.*) give m. p. 255—260° with darkening at 220°.

The *potassium* salt, prepared as before, formed needles of the monohydrate readily soluble in water (Found: C, 58·9; H, 3·5; N, 4·3; K, 11·35. $C_{17}H_{10}O_2NSK,H_2O$ requires C, 58·4; H, 3·5; N, 4·0; K, 11·2%).

Quinolino(3′ : 2′-3 : 4)-2-*thio*iso*chromen* (XII).—The above acid is not decarboxylated as readily as its isomer (VI). An intimate mixture of equal parts of the acid (XI) and soda-lime was therefore heated at 250—280°/0·1 mm. in a small retort, a viscous greenish distillate being obtained. A solution of the latter in hot methanol deposited pale green crystals, which when recrystallised from methanol (charcoal) gave the *thio-amine* (XII) as colourless crystals, m. p. 69—70° (Found: C, 76·8; H, 4·2; N, 5·6. $C_{16}H_{11}NS$ requires C, 77·0; H, 4·45; N, 5·6%).

The *hydrochloride*, prepared and purified as its isomer, was obtained as yellow crystals, m. p. 195—196° (decomp.) (Found: C, 66·1; H, 4·3; N. 4·7. $C_{16}H_{11}NS,HCl,0{\cdot}25H_2O$ requires C, 66·2; H, 4·3; N, 4·8%).

Treatment of the thio-amine with chloramine-T gave colourless crystals of *quinolino*(3′ : 2′-3 : 4)-2-*thio*iso*chromen toluene*-p-*sulphonylimine*, m. p. 199—200° (decomp.) after crystallisation from ethanol (Found: C, 66·4; H, 4·35; N, 6·95. $C_{23}H_{18}O_2N_2S_2$ requires C, 66·0; H, 4·3; N, 6·7%).

Oxidation of the Amine (XII).—The amine was recovered unchanged after it had been heated in a stream of air at 75—80° for 6 hours. When, however, the base in cold acetone was oxidised with permanganate as with the isomer (VII), the residue after washing with water and recrystallisation from acetone furnished pale lemon-yellow needles of *quinolino*(3′ : 2′-3 : 4)-2-*thio*iso*chromen*-1-*one* (XIII), m. p. 185—187° (Found: C, 72·9; H, 3·4; N, 5·3. $C_{16}H_9ONS$ requires C, 73·0; H, 3·4; N, 5·3%).

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