View Article Online / Journal Homepage / Table of Contents for this issue

Published on 01 January 1955. Downloaded by Columbia University on 26/09/2014 18:03:25.

Compounds containing Sulphur Chromophores. Part II. Attempts to prepare Sulphide Analogues of* mero*Cyanines.*

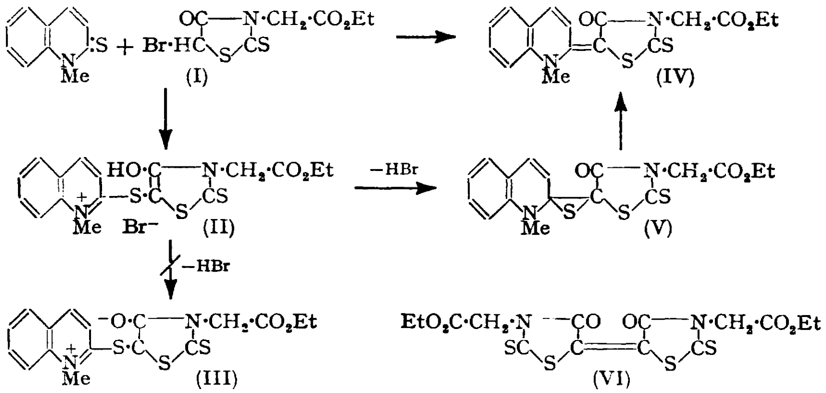
By E. B. Knott and R. A. Jeffreys

[Reprint Order No. 5457.]

Attempts to prepare sulphides (III, IX, and XV) analogous to *mero*cyanines but in which a sulphur atom is inserted in the bridge between the two end nuclei have given only the *mero*cyanines themselves. The elimination of the sulphur atom from the molecule is analogous to the reaction described in Part I.* In certain cases *mero*cyanine disulphides (XVIII) were isolated.

The preceding paper was concerned with experiments to obtain compounds containing chromophoric sulphur in which the $+M$ auxochrome was a nitro- or non-cyclic carbonyl group. Concurrent attempts were made to obtain related compounds, analogues of *mero*cyanines, in which the carbonyl auxochrome formed part of a heterocyclic ring.

In the first instance, compounds of type (VII) (Part I *) were sought. 3-Ethoxycarbonylmethylrhodanine was brominated to give the 5-bromo-derivative (I) which was used to quaternize 1 : 2-dihydro-1-methyl-2-thioquinoline. By analogy with similar reactions (*loc. cit.*) this should have yielded the quaternary salt (II), the removal of hydrogen bromide from which was expected to give the required non-planar sulphide (III). In fact, the salt obtained was not (II) but the hydrobromide of (IV) in which the sulphur had been eliminated. This phenomenon was analogous to those recorded in Part I, and the mechanism based on formation of an intermediate *spiro*episulphide (V) would apply equally.



Similar quaternization of other heterocyclic thiones with (I) proceeded much more slowly or not at all, the fused mixture on treatment with triethylamine giving only the thioindigoid dye (VI). The same dye was also obtained by treating (I) with alcoholic triethylamine. Synthesis of the planar higher vinylogue (IX; R = H) of (II) in the

---

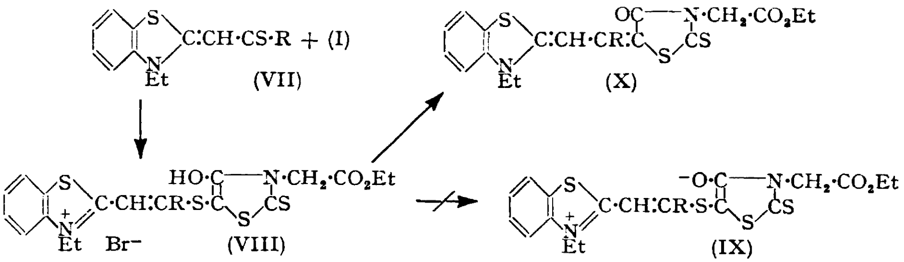
* Part I, preceding paper.

View Article Online

Published on 01 January 1955. Downloaded by Columbia University on 26/09/2014 18:03:25.

benzothiazole series was next attempted. 3-Ethyl-2-thioformylmethylenebenzothiazoline (VII; R = H) condensed with the ester (I) to give the red salt (VIII; R = H) smoothly at room temperature. Removal of hydrogen bromide from it gave either a tar or the dimethin*mero*cyanine (X; R = H) with the elimination of sulphur. Similar results were obtained when the starting point was the thioketone (VII; R = Me), the only product being the dye (X; R = Me).

The failure to isolate the salt (II), in view of the ease of formation of the analogous higher vinylogue (VIII), may be a consequence of the steric hindrance to coplanarity of the nuclei of the former salt.



After failure to obtain the required sulphide resonators of type (VII) (*loc. cit.*), attention was turned to the synthesis of their isomers, *i.e.*, of type (VI) (Part I). This required as intermediates a 2-bromomethylbenzothiazole quaternary salt and a 5-thioformylrhodanine. 2-Bromomethylbenzothiazole has been described by Zubarowski (*J. Gen. Chem., U.S.S.R.*, 1951, **21**, 2055), but its quaternary salts (XI) are best obtained by heating the quaternary salts of 2-hydroxymethylbenzothiazole (Anish, U.S.P. 2,508,324; Zubarowski, *loc. cit.*) with 70% aqueous hydrobromic acid. 3-Substituted-5-thioformylrhodanines (XIII; $R'' = H$) were readily obtained by treating 5-ethoxymethylene-rhodanines (XII; $R'' = H$) (Knott, *J.*, 1954, 1482) with sodium sulphide. The related thioketones (XIII; R'' = Me or Et) may be obtained similarly from (XII; R'' = Me or Et) (*idem, loc. cit.*). They are strongly acidic, forming yellow water-soluble salts, and thus may be formulated as 5-mercaptoalkylidenerhodanines.

Condensation of the salt (XI; R = Me) with the thioketone (XIII; $R' = C_3H_5$, $R'' = H$) in alcoholic triethylamine gave two dyes, one of which was the simple dimethin*mero*cyanine (XIV; R = Me, $R' = C_3H_5$, $R'' = H$), whilst the second dye (A) gave the correct analysis for the required sulphide (XV*a* $\longleftrightarrow$ *b*). In hot pyridine the condensation gave only the desulphurized dye (XIV), but alcoholic pyridine gave up to 16% of dye A, which separated during the reaction. This dye showed the same peak absorption (520 mμ) as the dimethin*mero*cyanine, but the absorption band was broader, giving the dye solutions a cherry-red colour instead of the purer magenta colour of the latter.

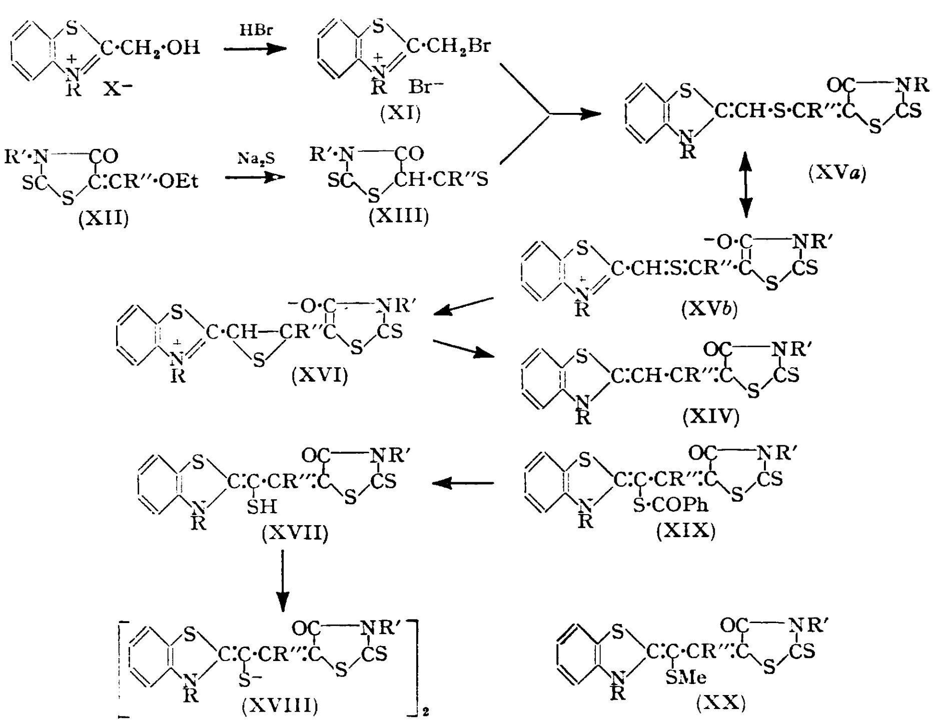
When dye A was dissolved in a solution of hydrobromic acid in acetic acid and the solution was added to alcoholic triethylamine, desulphurization occurred to give the *mero*cyanine (XIV). The red solution of the dye in pyridine–ethanol became an intense blue on addition of aqueous sodium hydroxide, the colour fading to yellow when the solution was heated. The blue solution remained clear on dilution with water, and red flocks were precipitated on acidification. This behaviour is similar to that of the chain hydroxy-dye analogous to the thiol (XVII) (Jeffreys, *J.*, 1954, 503), red solutions of which became blue with alkali or organic bases, the blue colour being attributable to the dye anion. Although its solution did not become blue with organic bases it seemed possible that dye A was the thiol (XVII), which is isomeric with (XV), or the disulphide (XVIII), analogous to the disulphide described in Part I. Such a disulphide would suffer disruption to the thiol anion with alkali hydroxide (cf. Schiller and Otto, *Ber.*, 1876, **9**, 1637; Fromm and Wittmann, *Ber.*, 1908, **41**, 2264). Syntheses of these substances were, therefore, undertaken.

The thiol (XVII) was sought initially by condensation of the quaternary salt of 2-mercaptomethylbenzothiazole and a 5-ethoxymethylenerhodanine (XII; $R'' = H$).

View Article Online

Published on 01 January 1955. Downloaded by Columbia University on 26/09/2014 18:03:25.

2-Mercaptomethylbenzothiazole was obtained as an oil by alkaline hydrolysis of benzoylthiomethylbenzothiazole (Part IV, which follows) or by treatment of benzothiazol-2-ylmethylthiuronium bromide with sodium carbonate. It was soluble in alkali and oxidized slowly in air to the disulphide or more readily by persulphate. On gentle treatment of the thiol with methyl sulphate, hydrogen sulphide was evolved and the product, heated with a 5-ethoxymethylenerhodanine in alcoholic triethylamine, gave only the simple dimethin *mero*cyanine (XIV; R″ = H).



Condensation of 2-benzoylthiomethyl-3-methylbenzothiazolium (methyl sulphate) (Part IV, *loc. cit.*) with 3-allyl-5-ethoxymethylenerhodanine (Knott, *loc. cit.*) at room temperature gave the chain-substituted dimethin*mero*cyanine (XIX; R = Me, R′ = C_3H_5, R″ = H), which on hydrolysis with cold aqueous-alcoholic sodium hydroxide gave a deep blue solution completely miscible with water; acidification precipitated magenta flocks which, when fresh, redissolved readily in pyridine or alcoholic triethylamine to give a blue solution. The substance in solution must be the thiol (XVII; R = Me, R″ = H, R′ = C_3H_5) although it was not obtained pure. Recrystallization gave a product identical with dye A. That this was the disulphide (XVIII; R = Me, R″ = H, R′ = C_3H_5) was shown by oxidizing the blue solution of the thiol salt with persulphate. The blue colour was discharged immediately, and the red flocks proved to be identical with dye A obtained from (XI) and (XIII). The flocks were readily reduced to the thiol salt by sodium sulphide and less rapidly by hydrazine hydrate, the blue solution in the latter case soon fading. Methylation of the blue solution of the thiol salt readily gave the chain methylthio-substituted dye (XX).

The formation of the disulphide (XVIII) from the precursors (XI) and (XIII) occurs rapidly even in the absence of oxygen and, since evolution of the hydrogen sulphide during the reaction was observed, it appears that the formation of the disulphide (XVIII) together with the dimethin*mero*cyanine (XIV) may be caused by the reductive desulphurization of the episulphide (XVI) by the thiol (XVII) (cf. disulphide formation in Part I):

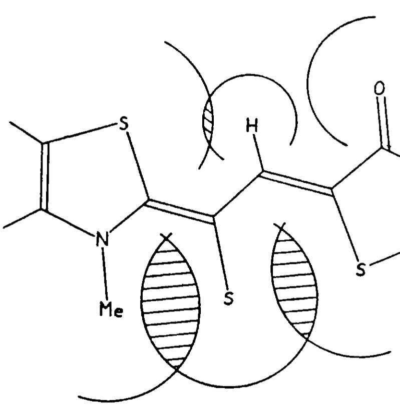
$$2(\text{XVII}) + (\text{XVI}) \longrightarrow (\text{XVIII}) + (\text{XIV}) + H_2S$$

View Article Online

Published on 01 January 1955. Downloaded by Columbia University on 26/09/2014 18:03:25.

Condensation of the bromide (XI) with the compound (XIII; R″ = Me) gave only one dye, the chain methyl-substituted dimethin*mero*cyanine (XIV; R″ = Me).

It is of interest that the free thiol (XVII) can be isolated, since the related 3-methyl-2-α-mercaptophenacylidenebenzothiazoline (Part I) decomposed immediately on neutralization of the solution of its sodium salt. Both of these compounds suffer from steric hindrance to planarity in that the thiol sulphur atom interferes with the 3-alkyl group (Figure). Episulphide formation would perhaps be a natural isomerization to relieve this strain; but it would destroy the main resonance systems, so it would be opposed by the resonance energy associated with this system. Such energy would be higher in the less asymmetric resonance of the thiol (XVII), since it is known that the $+M$ effect of a rhodanine nucleus is higher than that of a benzoyl group. This is shown by the higher nucleophilic reactivity of the $C_{(5)}$ atom of rhodanine compared with that of the methyl carbon atom of acetophenone.



The strong bathochromic shift from red ($\lambda_{max.}$ 510 mμ) to blue ($\lambda_{max.}$ 650 mμ), which accompanies the formation of the anion of (XVII) and is analogous to the colour shifts shown by the related chain hydroxy-dye, and of α-hydroxy-3 : 3′-dimethylthiacyanine salts (Jeffreys, *loc. cit.*), may be interpreted on the basis of the colour rule given in an earlier paper (*J.*, 1951, 1024).

EXPERIMENTAL

Microanalyses are partly by Mr. C. B. Dennis.

5-*Bromo*-3-*ethoxycarbonylmethyl*-2-*thiothiazolid*-4-*one* (I).—3-Ethoxycarbonylmethylrhodanine (21·9 g., 0·1 mole) was dissolved in chloroform (100 c.c.), and bromine (5·2 c.c., 0·1 mole) in chloroform (15 c.c.) was added in drops at 25°. Reaction was instantaneous; the solvent and hydrogen bromide were then removed in a stream of dry air. A thick pale yellow oil remained and was used for subsequent reactions. Addition of triethylamine to an alcoholic solution of the oil gave a quantative yield of *di*-(3-*ethoxycarbonylmethyl*-4-*oxo*-2-*thiothiazolid*-5-*ylidene*) (VI), brown needles, m. p. 178°, from benzene–ligroin (Found: C, 39·0; H, 3·3; N, 7·1; S, 29·7. $C_{14}H_{14}O_6N_2S_4$ requires C, 38·7; H, 3·2; N, 6·45; S, 29·5%). The same dye was obtained by fusion of equimolar amounts of the bromide (I) with 3-methylbenzothiazol-2-thione on the steam-bath for 1 hr., followed by treatment with alcoholic triethylamine.

3-*Ethoxycarbonylmethyl*-5-(1 : 2-*dihydro*-1-*methylquinolin*-2-*ylidene*)-2-*thiothiazolid*-4-*one* (IV).—1 : 2-Dihydro-1-methyl-2-thioquinoline (0·85 g., 0·005 mole) was dissolved in benzene (15 c.c.) and mixed at 25° with a solution of the bromide (I) (1·5 g., 0·005 mole) in benzene (15 c.c.), then heated at 70° for 10 min. to give a cream-coloured solid, m. p. *ca.* 168° (orange melt) with previous softening, after vacuum-drying (Found: C, 42·1; H, 4·05; N, 5·15; Br, 26·95; S, 11·0%). The ratio of N and S to Br indicates that it is a dihydrobromide of (IV), $C_{17}H_{14}O_3N_2S_2,2HBr$, containing some solvent. It was covered with ethanol and an excess of triethylamine was added to give a tar which soon crystallized and formed garnet flakes, m. p. 181°, from benzene–ethanol (Found: S, 18·05. $C_{17}H_{14}O_3N_2S_2$ requires S, 17·9%). It was identical with a specimen of the base (IV) obtained by the condensation of a 1-methyl-2-methylthioquinolinium salt with 3-ethoxycarbonylmethylrhodanine.

2-2′-(3-*Ethoxycarbonyl*-4-*oxo*-3-*thiothiazolidin*-5-*ylthio*)*vinyl*-3-*ethylbenzothiazolium Bromide* (VIII; R = H).—3-Ethyl-2-thioformylmethylenebenzothiazoline (1·1 g., 0·005 mole) in benzene (15 c.c.) was mixed at 23° with a solution of the bromide (I) (1·5 g., 0·005 mole) in benzene (10 c.c.). A red precipitate was formed at once. The mixture was left overnight, and the solid (2·4 g., 92·5%) was collected, washed with benzene, and vacuum-dried. It had m. p. 146°, with softening at 132° (Found: C, 41·9; H, 4·15; N, 5·45; Br, 15·25; S, 24·3. $C_{18}H_{19}O_3N_2BrS_4$ requires C, 41·6; H, 3·7; N, 5·4; Br, 15·4; S, 24·65%). This *salt* (5·2 g.) was covered with chloroform (100 c.c.) and shaken with water (100 c.c.) and sodium hydrogen carbonate (10 g.) for 5 min. The magenta chloroform layer was dried and concentrated to

View Article Online

Published on 01 January 1955. Downloaded by Columbia University on 26/09/2014 18:03:25.

5 c.c. Benzene (10 c.c.) was added and the flask was chilled. The purple flakes which separated (2·95 g.) formed magenta flakes, m. p. 189°, from benzene (Found: S, 23·85. $C_{18}H_{18}O_3N_2S_3$ requires S, 23·65%), identical with *3-ethoxycarbonylmethyl-5-(3-ethylbenzothiazolin-2-ylidene-ethylidene)-2-thiothiazolid-4-one* (X; R = H).

3-Ethoxycarbonylmethyl-5-[1-(3-ethylbenzothiazolin-2-ylidene)prop-2-ylidene]-2-thiothiazolid-4-one (X; R = Me).—The bromide (I) (3·0 g.) and 3-ethyl-2-thioacetylmethylenebenzothiazoline (VII; R = Me) (Brooker and Keyes, U.S.P. 2,369,647) (2·35 g.) in ethanol (15 c.c.) were heated on the steam-bath for 5 min. The *dye* which crystallized on chilling (1·3 g., 31%) formed magenta needles, m. p. 176°, from benzene (Found: S, 22·65. $C_{19}H_{20}O_3N_2S_3$ requires S, 22·85%). It was identical with a specimen prepared by the usual method.

Benzothiazol-2-ylmethylthiuronium Bromide.—2-Bromomethylbenzothiazole (10·2 g.) and thiourea (3·4 g.) were refluxed in ethanol (50 c.c.) for ½ hr. Cooling and filtration gave the *salt* (13·3 g.). It recrystallized from methanol–ether as colourless needles, m. p. 194° (Found: N, 13·8; Br, 26·2. $C_9H_{10}N_3BrS_2$ requires N, 13·8; Br, 26·3%).

2-Mercaptomethylbenzothiazole.—(*a*) Benzothiazol-2-ylmethylthiuronium bromide (9·1 g.) was dissolved in methanol and poured into an excess of 2N-sodium carbonate. The solution was made acid with acetic acid, and the thiol was extracted with ether and dried. On removal of the ether, an oil (4·5 g.) was obtained. It could not be distilled.

(*b*) To 2-benzoylthiomethylbenzothiazole (Part IV, *loc. cit.*) (5·7 g.), suspended in ethanol (20 c.c.), was added potassium hydroxide (2·5 g.) in water (5 c.c.), and the mixture was shaken for ½ hr., a clear solution being obtained. To this was added water (90 c.c.). The solution was extracted with ether to remove any ethyl benzoate, and acidified with hydrochloric acid. An oil separated, which was extracted with ether and dried (Na_2SO_4). The yield of crude product, on removal of the ether, was 4·6 g. When the oil was allowed to stand, it slowly precipitated crystals of the disulphide.

2-Mercaptomethylbenzothiazole (1·4 g.) and methyl sulphate (0·98 g.) were mixed at room temperature. During 1 hr. the temperature rose to 38° and hydrogen sulphide was evolved. The gum slowly solidified. To this quaternary salt were added 3-allyl-5-ethoxymethylenerhodanine (1·8 g.), triethylamine (1·1 c.c.), and ethanol (15 c.c.). The solution was heated for 10 min. on the steam-bath, chilled, and filtered. The dye (2·2 g.) recrystallized from pyridine–methanol as red needles, m. p. 243°, and was identical with 3-allyl-5-(3-methylbenzothiazolin-2-ylidene-ethylidene)-2-thiothiazolid-4-one (XIV; R = Me, R′ = C_3H_5).

Di(benzothiazol-2-ylmethyl) Disulphide.—A solution of 2-mercaptomethylbenzothiazole (2·8 g.) and sodium hydroxide solution (10%; 20 c.c.) in ethanol (20 c.c.) was shaken with potassium persulphate (5 g.) for ½ hr. Water (50 c.c.) was then added, and the precipitated *disulphide* was filtered off. It recrystallized from benzene–light petroleum as prisms (2·2 g.), m. p. 121° (Found: N, 7·7; S, 35·8. $C_{16}H_{12}N_2S_4$ requires N, 7·8; S, 35·6%).

2-Bromomethyl-3-methylbenzothiazolium Bromide (XI; R = Me).—2-Hydroxymethylbenzothiazole (Zubarowski, *loc. cit.*) (3·3 g.) and methyl toluene-*p*-sulphonate (3·8 g.) were fused together on a steam-bath until solid (15 min.). Aqueous hydrobromic acid (s.g. 1·7) (20 c.c.) was added and the whole heated on a steam-bath for 5 hr., and refluxed for 1 hr. on a gauze. The solvent was then removed under reduced pressure. Acetone (50 c.c.) was added and the crystalline *bromide* collected after chilling. It (5·0 g., 77·5%) formed colourless prisms, m. p. 198° (effervescence), from methanol (Found: Br, 49·1. $C_9H_9NBr_2S$ requires Br, 49·5%). With alcoholic triethylamine a purple colour developed.

2-Bromomethyl-3-ethylbenzothiazolium Bromide (XI; R = Et).—2-Hydroxymethylbenzothiazole (10 g.) and diethyl sulphate (8·0 c.c.) were heated together on a steam-bath for 1 hr. The thick reddish resin crystallized slowly. It was treated with hydrobromic acid (50 c.c.) by the method used for the 3-methyl homologue. The required *bromide* (5·8 g., 28·4%) formed fawn flakes, m. p. 190°, from ethanol (Found: Br, 47·3. $C_{10}H_{11}NBr_2S$ requires Br, 47·5%).

3-Allyl-2-thio-5-thioformylthiazolid-4-one (XIII; R′ = C_3H_5, R″ = H).—3-Allyl-5-ethoxymethylenerhodanine (2·3 g., 0·01 mole), ethanol (10 c.c.), and a solution of sodium sulphide nonahydrate (2·65 g., 0·011 mole) in water (5 c.c.) were shaken mechanically for 15—20 min., or until dissolution was complete. Water (100 c.c.) was added and the orange solution was filtered after 15 min. Addition of 2N-hydrochloric acid (20 c.c.) precipitated an orange oil which on chilling hardened to a friable resin. This *thiazolidone* (2·05 g., 94·5%) could not be crystallized. It was purified by dissolving it in benzene and precipitation with light petroleum (b. p. 60—80°). It was vacuum-dried for analysis (Found: C, 39·35; H, 3·5; N, 6·3; S, 43·6. C_7H_7ONS requires C, 38·75; H, 3·2; N, 6·45; S, 44·2%).

3-Allyl-2-thio-5-thioacetylthiazolid-4-one (XIII; R′ = C_3H_5, R″ = Me).—This *compound*

View Article Online

Published on 01 January 1955. Downloaded by Columbia University on 26/09/2014 18:03:25.

was obtained similarly from 3-allyl-5-1′-ethoxyethylidenerhodanine (Knott, *loc. cit.*) (2·45 g.). The orange oil obtained on acidifying the reaction mixture crystallized rapidly. It (2·15 g., 93%) formed yellow needles, m. p. 58°, from *cyclo*hexane (Found: C, 42·4; H, 4·1; N, 6·0; S, 41·4. $C_8H_9ONS_3$ requires C, 41·9; H, 3·9; N, 6·05; S, 41·5%).

Di-[1-(3-*methylbenzothiazolin*-2-*ylidene*)-2-(3-*allyl*-4-*oxo*-2-*thiothiazolid*-5-*ylidene*)*ethyl*] *Disulphide* (XVIII; R = Me, R′ = C_3H_5, R″ = H).—(*a*) Solutions of 2-bromomethyl-3-methylbenzothiazolium bromide (3·23 g., 0·01 mole) in methanol (30 c.c.) and of 3-allyl-5-thioformylrhodanine (2·17 g., 0·01 mole) in methanol (20 c.c.) and triethylamine (3·0 c.c., 0·02 mole) were mixed at room temperature. A red tar which was formed immediately soon solidified. It was collected and washed with methanol and the filtrates were kept. From benzene (250 c.c.) followed by pyridine–ethanol the *disulphide* formed green flakes, m. p. 253°, in 10·4% yield (0·4 g.) (Found: C, 51·25; H, 3·55; N, 7·4; S, 33·85. $C_{32}H_{26}O_2N_4S_8$ requires C, 50·95; H, 3·45; N, 7·45; S, 34·0%), $\lambda_{max.}$ 520 mμ in pyridine. The original filtrate and the benzene filtrate on concentration yielded 0·4 g. (11·6%) of 3-*allyl*-5-(3-*methylbenzothiazolin*-2-*ylidene-ethylidene*)-2-*thiothiazolid*-4-*one* (XIV; R = Me, R′ = C_3H_5, R″ = H) as flat, dark red needles, m. p. 243°, from pyridine–ethanol (Found: S, 28·05. $C_{16}H_{14}ON_2S_3$ requires S, 27·75%). It was identical with a sample prepared by the conventional method.

(*b*) By heating the above quaternary salt and rhodanine (as in *a*) for 3 min. on a steam-bath in a mixture of pyridine (5 c.c.) and ethanol (25 c.c.) the dye, m. p. 253°, which crystallized during that time, was obtained in 16% yield.

(*c*) 2-Benzoylthiomethyl-3-methylbenzothiazolium (methyl sulphate) (Part IV) (4·1 g.), 3-allyl-5-ethoxymethylenerhodanine (2·3 g.), pyridine (25 c.c.), and triethylamine (1·5 c.c.) were dissolved with shaking and kept for 3 hr. at 25°. Ethanol (50 c.c.) was added and the solution was seeded. 3-*Allyl*-5-[2-*benzoylthio*-2-(3-*methylbenzothiazolin*-2-*ylidene*)*ethylidene*]-2-*thiothiazolid*-4-*one* (XIX; R = Me, R′ = C_3H_5, R″ = H) separated; after 3 hr. a further 150 c.c. of ethanol were added, and the solution was chilled overnight. The dye (2·3 g., 47·5%) formed red flakes with a gold reflex, m. p. 207°, from benzene (Found: N, 6·05; S, 26·95. $C_{23}H_{18}O_2N_2S_4$ requires N, 5·8; S, 26·55%).

It (0·5 g.) was dissolved in hot pyridine (10 c.c.), cooled to 30°, and mixed with sodium sulphide monohydrate (1·0 g.) or sodium hydroxide (0·5 g.) in water (2 c.c.) and ethanol (10 c.c.). Hydrolysis was instantaneous as indicated by the appearance of a brilliant blue colour. Water (40 c.c.) was added to give a clear blue solution.

Addition of potassium persulphate (2·0 g.) in water (20 c.c.) resulted in discharge of the blue colour and precipitation of red flocks. They formed green flakes (0·355 g., 91%), m. p. 253°, from pyridine–ethanol, identical with the product (XVIII; R = Me, R′ = C_3H_5, R″ = H) obtained by the reactions (*a*) or (*b*). Oxidation with hypochlorite gave only a 20% yield of the same dye.

When the solution obtained by hydrolysis was acidified with acetic acid in an atmosphere of carbon dioxide it gave red flocks which were soluble in alcoholic triethylamine or in pyridine to give a deep blue solution. Recrystallization from pyridine–ethanol with access of air gave 0·385 g. (99%) of green flakes, m. p. 252°, identical with the disulphide obtained by the reaction (*a*), (*b*), or (*c*).

3-*Allyl*-5-[2-(3-*methylbenzothiazolin*-2-*ylidene*)-2-*methylthioethylidene*]-2-*thiothiazolid*-4-*one* (XX; R = Me, R′ = C_3H_5, R″ = H).—To the blue solution formed by the hydrolysis of (XIX; R = Me, R′ = C_3H_5, R″ = H), prepared as above, aqueous 2N-sodium hydroxide (10 c.c.) was added, and methyl sulphate (1 c.c.) was allowed to drip in at room temperature with shaking. The blue colour disappeared and red flakes of the *methyl sulphide* separated. They (0·45 g., 86·5%) formed flat magenta needles, m. p. 207°, from benzene–ethanol (Found: N, 7·35; S, 32·7. $C_{17}H_{16}ON_2S_4$ requires N, 7·45; S, 32·7%).

Di-[1-(3-*ethylbenzothiazolin*-2-*ylidene*)-2-(3-*allyl*-4-*oxo*-2-*thiothiazolid*-5-*ylidene*)*ethyl*] *Disulphide* (XVIII; R = Et, R′ = C_3H_5, R″ = H).—2-Bromomethyl-3-ethylbenzothiazolium bromide (3·4 g.) was dissolved in cold methanol (15 c.c.) and added to a solution of 3-allyl-5-thioformylrhodanine (2·2 g.) in methanol (10 c.c.) containing triethylamine (3 c.c.). A red tar was precipitated immediately. This *disulphide* (0·85 g.) recrystallized from benzene as green-red flakes (0·3 g., 7·65%), m. p. 241°, from pyridine–ethanol (Found: C, 52·15; H, 4·15; N, 6·9; S, 32·4. $C_{34}H_{30}O_2N_4S_8$ requires C, 52·15; H, 3·8; N, 7·15; S, 32·7%). The original filtrate and the benzene filtrate on concentration gave 0·65 g. (18·0%) of dark red needles, m. p. 225°, from pyridine–ethanol (Found: S, 26·9. $C_{17}H_{16}ON_2S_3$ requires S, 26·7%), identical with 3-*allyl*-5-(3-*ethylbenzothiazolin*-2-*ylidene-ethylidene*)-2-*thiothiazolid*-4-*one* (XIV; R = Et, R′ = C_3H_5, R″ = H) prepared by normal methods.

View Article Online

Published on 01 January 1955. Downloaded by Columbia University on 26/09/2014 18:03:25.

Action of Hydrogen Bromide on the Disulphide (XVIII; $R = Me$, $R' = C_3H_5$, $R'' = H$).—The disulphide (0·2 g.) was covered with benzene (20 c.c.), and a 40% solution of hydrogen bromide in acetic acid (5 c.c.) was stirred in until the dye had dissolved to a yellow solution. The benzene was decanted after 5 min. and the solution poured into a solution of triethylamine (10 c.c.) in ethanol (25 c.c.). Addition of water (50 c.c.) to the bright red solution precipitated a dye (0·12 g.) which, after recrystallization from benzene (twice) followed by pyridine–ethanol, formed flat red needles (0·06 g., 33%), m. p. 242°, identical with the *mero*cyanine (XIV; $R = Me$, $R' = C_3H_5$, $R'' = H$) (Found: N, 8·3; S, 27·8%).

RESEARCH LABORATORIES, KODAK LTD., WEALDSTONE,
HARROW, MIDDLESEX.

[*Received, June 11th*, 1954.]