Compounds containing Sulphur Chromophores. Part III. Experiments on the Synthesis of Ionic Dyes.*

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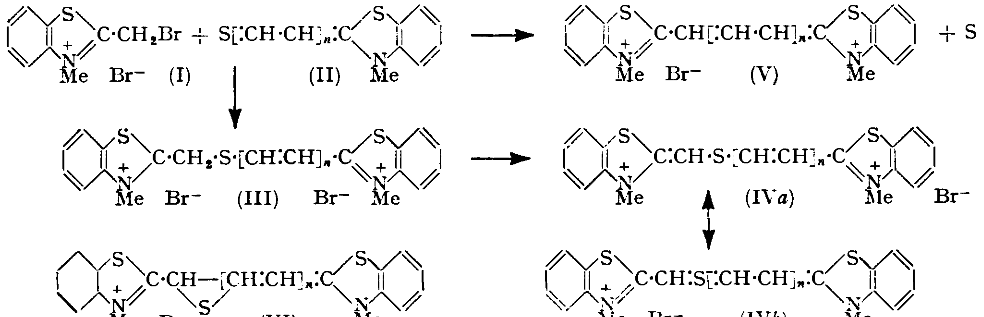
Reactions which were designed to give molecules related to cyanines and oxonols but carrying a sulphur atom in the conjugated chain between the end nuclei have led only to the parent cyanines and oxonols.

In Parts I and II * it has been shown that reactions which should lead to non-ionic compounds containing a sulphur atom in the conjugation path of a resonator usually give desulphurized products. The present paper is concerned with attempts to obtain cationic and anionic sulphides designed to show whether the sulphur atom is capable of functioning as a chromophore.

Cationic Dyes.—Synthesis of the sulphide (IV$a \longleftrightarrow b$; $n = 0$) was sought by quaternization of 3-methylbenzothiazolin-2-thione (II; $n = 0$) with 2-bromomethyl-3-methylbenzothiazolium bromide (I), followed by removal of hydrogen bromide from the bis-quaternary salt (III). Reaction in boiling methanol gave the yellow 3 : 3′-dimethylthiacyanine bromide (V; $n = 0$) (66·5% yield), the iodide from which was identical with a specimen obtained according to Mills's procedure (*J.*, 1922, 455), together with elementary sulphur and a small amount of blue dye which, however, was not (IV; $n = 0$). Similar attempts to obtain the dye (IV; $n = 1$) from the precursor (II; $n = 1$) gave only thiacarbocyanine (V; $n = 1$). The elimination of sulphur already encountered in Parts I and II is thus repeated, and it can be assumed once more that the episulphide (VI) is an intermediate.



As this direct method failed, two-stage syntheses by two routes were examined. Condensation of 2-bromomethylbenzothiazole with (II; $n = 0$) was intended to give the mono-quaternary salt (VII) and thence the dimethobromide (III; $n = 0$). However, it gave

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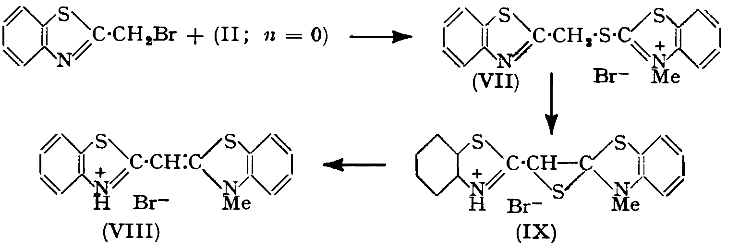
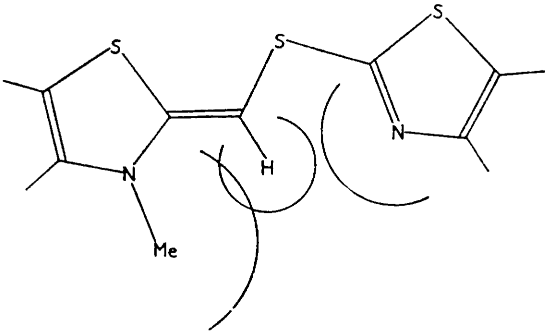
* Parts I and II, preceding papers.

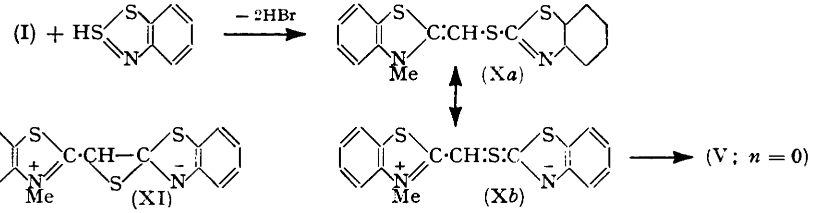
the hydrobromide (VIII) of the cyanine base (cf. Hamer, *J.*, 1940, 7991), probably by way of the episulphide (IX) similar to (VI).



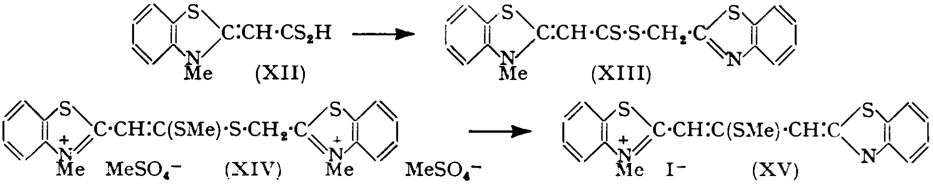
2-Bromomethyl-3-methylbenzothiazolium bromide (I) was made to react with 2-mercaptobenzothiazole in the presence of a base to give the required planar sulphide (X) (see Figure), analogous to a cyanine base and perhaps capable of the resonance (X*a* ⟷ *b*); its notable stability is discussed in Part IV (following paper) together with that of the



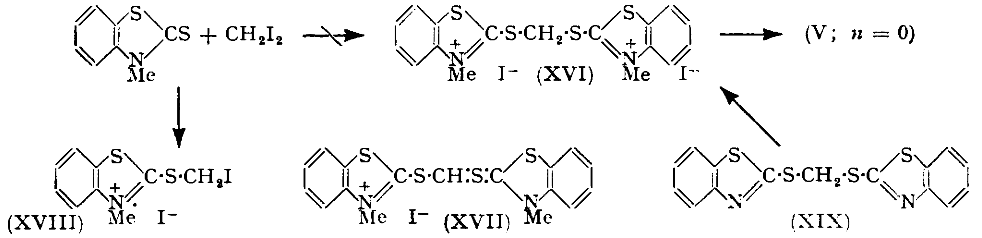
hypothetical episulphide (XI). Quaternization with methyl iodide or methyl sulphate again resulted in desulphurization and formation of the thiacyanine (V; $n = 0$).



Similarly, condensation of 2-dithiocarboxymethylene-3-methylbenzothiazoline (XII) (Kendall and Majer, B.P. 549,201) which with 2-bromomethylbenzothiazole gave the ester (XIII), with methyl sulphate gave a yellow tar, presumably the required diquaternary salt (XIV) since on its treatment with triethylamine the chain-substituted carbocyanine (XV) (cf. Fry, B.P. 678,626) was the only product isolated.

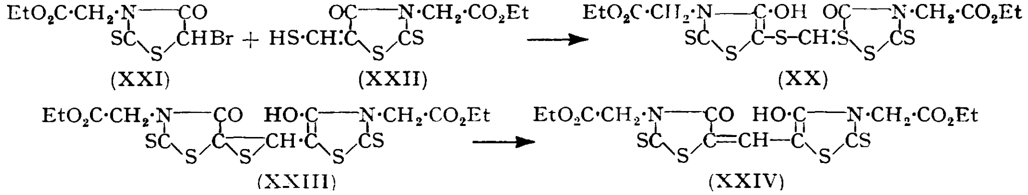


The introduction of two sulphur atoms into the chain of a polymethin dye could give a symmetrical molecule, and the synthesis of (XVII), which is planar, was attempted. The required intermediate was the diquaternary salt (XVI), from which it was hoped to remove hydrogen iodide to give (XVII). 3-Methylbenzothiazol-2-thione and methylene iodide at 95—100° gave only 2-iodomethylthio-3-methylbenzothiazolium iodide (XVIII) whilst at higher temperatures decomposition with evolution of methanedithiol (?) set in. 2-Mercaptobenzothiazole, however, gave the base (XIX) and thence a diquaternary compound (cf. XVI), isolated as the iodide or perchlorate. Treatment of the di-iodide (XVI) with a variety of bases failed, however, to give the compound (XVII) or indeed any significant colour change. Prolonged heating with alcoholic triethylamine gave traces of thiacyanine (V; $n = 0$) with slow evolution of hydrogen sulphide.



This unexpected stability of the salt (XVI) towards bases indicated the lack of acidity of the methylene group, the chain-sulphur atoms being unable to transmit the $+M$ effects of the quaternary nitrogen atoms sufficiently strongly to cause hyperconjugation of the methylene hydrogen atoms.

Anionic Dyes.—An attempt was next made to obtain the oxonol-type sulphide (XX). However, the 5-bromo-rhodanine (XXI) and the mercaptomethylene derivative (XXII) in the presence of triethylamine gave the triethylamine salt of di-(3-ethoxycarbonylmethyl 2-thio-5-thiazolid-4-one)methinoxonol (XXIV). The loss of sulphur from the presumed intermediate (XX) may also proceed through the intermediate episulphide (XXIII).



EXPERIMENTAL

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

Attempts to prepare the Sulphide (IV; $n = 0$).—(*a*) 2-Bromomethyl-3-methylbenzothiazolium bromide (1·6 g., 0·005 mole), 3-methylbenzothiazol-2-thione (0·9 g., 0·005 mole), and methanol (10 c.c.) were heated together for 2—3 min. on a steam-bath until a clear, deep yellow-green solution was obtained. The crystals (1·0 g.) which separated on chilling, together with a further crop (0·3 g.) obtained on concentration of the filtrate, formed canary-yellow needles (1·05 g., 53·5%), m. p. 292—293°, from methanol (Found: N, 7·1; Br, 19·9; S, 16·2. Calc. for $C_{17}H_{15}N_2BrS_2$: N, 7·35; Br, 20·45; S, 16·4%), identical with 3 : 3′-dimethylthiacyanine bromide obtained by Hamer's method (*J.*, 1930, 2522; m. p. 287°). The iodide formed yellow needles, m. p. 292°, from methanol (Found: I, 29·3; S, 14·8. Calc. for $C_{17}H_{15}N_2IS_2$: I, 29·0; S, 14·6%); Fisher and Hamer (*loc. cit.*) give m. p. 290—292°. The filtrate on concentration gave yellow crystals and a purple tar. A little cold ethanol was added to dissolve the tar and the crystals were collected. They formed flat needles (0·02 g.), m. p. 118°, from benzene–ethanol (Found: S, 99·7%). Addition of aqueous potassium iodide to the solution of the purple tar gave green crystals (0·05 g.) which after recrystallisation from methanol (blue solution) had m. p. 238° (Found: N, 6·0; I, 34·8; S, 13·0%).

(*b*) 2-Bromomethyl-3-methylbenzothiazolium bromide (3·25 g., 0·01 mole) in hot methanol (25 c.c.) was treated with a solution of 2-mercaptobenzothiazole (1·7 g., 0·01 mole) and potassium hydroxide (0·56 g., 0·01 mole) in methanol (15 c.c.). The mixture became cloudy, and addition of triethylamine (1·5 c.c., 0·01 mol.) after 1 min. caused separation of a granular precipitate, which was collected after 30 min. and washed with methanol, water, and methanol. 2-(*Benzothiazol-2-ylthiomethylene*)-3-*methylbenzothiazoline* (X) (2·4 g., 73%) was obtained as fawn leaflets, m. p. 197°, from pyridine–ethanol (Found : C, 58·4; H, 4·05; N, 8·6; S, 29·1. $C_{16}H_{12}N_2S_3$ requires C, 58·55; H, 3·65; N, 8·55; S, 29·3%).

(i) This product (X) (1·0 g.) and methyl iodide (10 c.c.) were refluxed for 2 hr., giving black flocks, forming rust-coloured needles from methanol in 8% yield (Found : S, 14·4), m. p. 292°, or 293° when mixed with the iodide of the dye (IV; $n = 0$).

(ii) The intermediate (X) (1·0 g.) and methyl sulphate (0·3 c.c.) were heated together on a steam-bath for 15 min. The resulting black tar was dissolved in methanol (10 c.c.) and the solution was chilled overnight. The pale yellow crystals (0·2 g., 15%) were converted into the iodide and obtained as pale yellow needles, m. p. 292° (from methanol) alone or mixed with the preceding product (Found : S, 14·7%).

(*c*) 2-Bromomethylbenzothiazole (2·28 g., 0·01 mole), 3-methylbenzothiazol-2-thione (1·81 g., 0·01 mole), and benzene (10 c.c.) were refluxed together for 2 hr. Yellow needles (0·6 g.) which separated after 30 min. were collected after chilling and a further crop (total 1·5 g., 40%) was obtained from the filtrate. It was 2-*benzothiazol*-2′-*ylmethylene*-3-*methylbenzothiazolinium bromide* (VIII) and formed bright yellow needles, m. p. 256—257°, from ethanol (Found : N, 7·35; Br, 20·9; S, 17·1. $C_{16}H_{13}N_2BrS_2$ requires N, 7·45; Br, 21·2; S, 16·95%). The base formed orange-yellow needles, m. p. 172° (from ethanol) (Found : N, 9·45; S, 21·8. Calc. for $C_{16}H_{12}N_2S_2$: N, 9·45; S, 21·65%) alone or mixed with Dr. Hamer's specimen (*J.*, 1940, 799; m. p. 176°); Mills (*J.*, 1922, 455) reports m. p. 172°.

Attempt to prepare the Sulphide (IV; $n = 1$).—2-Bromomethyl-3-methylbenzothiazolium bromide (1·7 g.), 3-methyl-2-thioformylmethylenebenzothiazoline (1·1 g.), and methanol (10 c.c.) were heated together for 1 min. on a steam-bath, and then cooled to 20°. Triethylamine (0·8 c.c.) was added, and the solution was kept at 20° for 30 min. Hydrogen sulphide was evolved (smell; lead acetate wool). Addition of saturated aqueous potassium iodide (1 c.c.) resulted in the crystallization of 3 : 3′-dimethylthiacarbocyanine iodide corresponding to (V; $n = 0$). It (0·55 g., 22·4%) formed steel-blue needles, m. p. 264—265°, from methanol (Found : I, 25·7; S, 12·8. Calc. for $C_{21}H_{21}N_2IS_2$: I, 25·8; S, 13·0%); the mixed m. p. was 264—264° with an authentic specimen (Hamer, *J.*, 1927, 2796).

2-(*Benzothiazol*-2′-*ylmethyldithiocarbonylmethylene*)-3-*methylbenzothiazoline* (XIII).—2 : 3-Dimethylbenzothiazolium toluene-*p*-sulphonate (1·7 g., 0·005 mole) was dissolved in ethanol (15 c.c.), carbon disulphide (0·33 c.c., 0·0055 mole) and triethylamine (1·5 c.c., 0·1 mole) were added, and the deep orange solution was refluxed for 10 min. A solution of 2-bromomethylbenzothiazole (1·15 g., 0·005 mole) in ethanol (10 c.c.) was then added with vigorous shaking and the required *ester* separated at once as a thick, yellow meal. It was washed with ethanol and obtained as yellow threads (1·7 g., 87%), m. p. 239°, from pyridine–ethanol (Found : N, 7·1; S, 33·3. $C_{18}H_{14}N_2S_2$ requires N, 7·25; S, 33·2%).

Di-(3-*methyl*-2-*benzothiazole*)-β-*methylthiotrimethincyanine Iodide* (XV).—The ester (XIII) (1·25 g.) and methyl sulphate (2 c.c.) were fused together on a steam-bath for 30 min. The orange-red melt was dissolved in cold ethanol (20 c.c.), filtered from a small insoluble residue, and treated with triethylamine (2 c.c.). The dye (0·65 g., 42%) which crystallized was converted into the *iodide*, magenta threads, m. p. 252° (from methanol) alone or mixed with a specimen prepared by Fry's method (*loc. cit.*) (Found : N, 5·25; I, 25·1; S, 19·65. $C_{20}H_{19}N_2IS_3$ requires N, 5·5; S, 24·9; S, 18·85%).

2-*Iodomethylthio*-3-*methylbenzothiazolium Iodide* (XVIII).—3-Methylbenzothiazol-2-thione (7·2 g., 0·04 mole) and methylene iodide (1·6 c.c., 0·02 mole) were fused together on a steam-bath for 5 hr. The crystalline cake was washed with warm ethanol to remove unchanged thione and the quaternary *salt* (78% yield) obtained as yellow needles, m. p. 190—193° (decomp.), from methanol (Found : I, 56·8; S, 14·6. $C_9H_9NI_2S_2$ requires I, 56·5; S, 14·25%).

Di(*benzothiazol*-2-*ylthio*)*methane* (XIX).—Potassium hydroxide (11·2 g., 0·2 mole) was dissolved in ethanol (200 c.c.), 2-mercaptobenzothiazole (36·7 g., 0·22 mole) and methylene iodide (8·1 c.c.; 0·1 mole) were added, and the whole was refluxed for 1 hr. Water (500 c.c.) was added to precipitate a yellow oil which crystallized rapidly. This *compound* (XIX) (30·8 g., 89%) formed pale yellow crystals, m. p. 75°, from benzene–light petroleum (b. p. 60—80°) (Found : N, 8·3; S, 37·3. $C_{15}H_{10}N_2S_4$ requires N, 8·1; S, 37·0%). The base (XIX) (1·75 g.) and methyl iodide (10 c.c.) were refluxed on a steam-bath for 48 hr. The precipitated *dimethiodide* was washed with acetone and obtained in 9·6% yield (0·3 g.) as buff needles, m. p. 153°

(effervescence), from methanol–ether (Found: N, 4·35; I, 39·95; S, 20·35. $C_{17}H_{16}O_2I_2S_4$ requires N, 4·45; I, 40·3; S, 20·3%). The *dimethoperchlorate* was obtained in 59% yield by fusing the base (1·75 g.) and methyl sulphate (1 c.c.) for 5 min. on a steam-bath, dissolving the melt in ethanol (20 c.c.), and adding saturated aqueous sodium perchlorate (0·5 c.c.). The resulting yellow tar was boiled with ethanol (20 c.c.) until it solidified and was then obtained as orange needles, m. p. 176—178°, from methanol (Found: N, 4·95; Cl, 12·15; S, 22·4. $C_{17}H_{16}O_8N_2Cl_2S_4$ requires N, 4·85; Cl, 12·35; S, 22·3%).

When the base (3·5 g.) and methyl sulphate (2 c.c.) were fused as above and the quaternary salt was refluxed in ethanol (10 c.c.) and triethylamine (1·5 c.c.) for 2 hr., hydrogen sulphide was evolved and addition of aqueous potassium iodide gave 0·05 g. of 3 : 3′-dimethylthiacyanine iodide (V; $n = 0$), m. p. and mixed m. p. 292° (from methanol) (Found: I, 28·7; S, 14·9%).

Attempt to obtain the Sulphide (XX).—5-Bromo-3-ethoxycarbonylmethylrhodanine (preceding paper) (1·5 g.) and 3-ethoxycarbonylmethyl-5-thioformylrhodanine (1·3 g.) were dissolved in ethanol (20 c.c.), then cooled to 20°, and triethylamine (1·5 c.c.) was added. Crystals of di-(3-ethoxycarbonylmethyl-4-oxo-2-thiothiazolid-4-ylidene) (VI of previous paper) separated rapidly. After chilling overnight the solution was filtered and the filtrate diluted with ether (100 c.c.). The precipitated tar gradually hardened. It was washed with ether, redissolved in ethanol (10 c.c.), and precipitated by slow addition of ether (50 c.c.). The green deliquescent crystals had no definite m. p. (Found: N, 8·05; S, 23·6. $C_{21}H_{31}O_6N_3S_4$ requires N, 7·9; S, 24·0%), $\lambda_{max.}$ 537 mμ (in methanolic triethylamine).

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