Compounds containing Sulphur Chromophores. Part I. The Action of Bases on Heterocyclic Sulphide Quaternary Salts.*

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It is shown that quaternary salts of type XII (or XLI) on treatment with bases do not give the sulphides (XIII) required as examples of compounds containing chromophoric sulphur. The reactions lead to the elimination of the sulphur atom and the formation of amide type resonators (*e.g.*, XVI). In at least one case a complex disulphide (XXVI) is also formed in low yield. A mechanism of this reaction based on an intramolecular condensation with intermediate episulphide formation is proposed.

Schomaker and Pauling (*J. Amer. Chem. Soc.*, 1939, **61**, 1769) suggested that the low dipole moment of thiophen, compared with that of pyrrole or furan, is the result of contributions by resonance structures in which the sulphur atom expands its octet of electrons to a decet by utilizing its *d*-orbitals. Before their paper the concept of the expansion of the sulphur electron octet had been used to explain the activating influence of a sulphonyl group on an adjacent methylene-carbon atom (Ingold and Jessop, *J.*, 1930, 708; Shriner, Struck, and Jorison, *J. Amer. Chem. Soc.*, 1930, **52**, 2060; Kohler and Larsen, *ibid.*, 1936, **58**, 1448; Connor, Fleming, and Clayton, *ibid.*, p. 1386; Rothstein, *J.*, 1937, 309; 1953, 3991). Since then a number of workers have explained anomalous spectrographic characteristics of certain sulphur compounds on a similar basis (Rothstein, *J.*, 1940, 1550, 1553, 1558; Fehnel and Karmack, *J. Amer. Chem. Soc.*, 1949, **71**, 84, 231, 2889; 1950, **72**, 1292; Koch, *J.*, 1949, 387, 408, 2442; Szmant and Planisek, *J. Amer. Chem. Soc.*, 1950, **72**, 4042; Cilento, *ibid.*, 1953, **75**, 3748; Price and Morita, *ibid.*, p. 4747; see also Longuet-Higgins, *Trans. Faraday Soc.*, 1949, **45**, 173).

Szmant and McIntosh (*J. Amer. Chem. Soc.*, 1951, **73**, 4356) observed a bathochromic shift of 5 mμ on introducing a 4′-amino-group into *p*-nitrophenyl phenyl sulphide, to give (I*a*), and since no similar shift occurred in the diphenyl ether analogues they concluded that this was evidence of contribution by the extreme structure (I*b*). Mangini and Passerini (*J.*, 1952, 1168; see also Koch, *loc. cit.*, p. 387) pointed out, however, that since the benzene rings of (I) are not co-planar there is little likelihood of electronic interaction between them.

(I*a*)

Apart from the evidence of the above workers, there are also indications in the field of polymethin dyes that a sulphur (or selenium) atom may function as a resonance transmitter in much the same way as a vinylene (·CH:CH·) group. In the symmetrical cyanine series (II*a*) the absorption peaks of dyes from benzothiazole and benzoselenazole lie between these of the analogous dyes from benzoxazole and 2-quinoline. Since contributions to the hybrid by structures such as (II*b*) may be assumed to occur in the quinoline series but not in the benzoxazole dyes the intermediate positions of the peaks of the dyes from benzothiazole and benzoselenazole may indicate contributions by structures such as (II*b*).

Since they involve loss of aromaticity in one of the benzene rings contributions by (II*b*) would not be expected to be as large as those in the case of related thiazoles (III*b*; A = S). On such a basis we should expect that the bathochromic shift observed as we proceed from a symmetrical oxazole dye to the analogous thiazole dye would be greater

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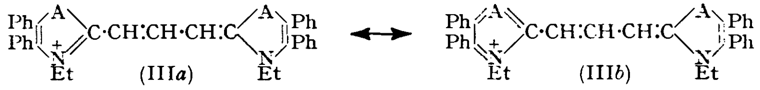
* The definitions of a chromophore and an auxochrome or antiauxochrome by Witt and by Dilthey and Witzinger have lead to a certain amount of confusion, as pointed out by Venkataraman ("The Chemistry of Synthetic Dyes," Vol. I, Academic Press Inc., New York, 1952). In this and subsequent papers a resonance system of a dye, or auxochromophoric system (Brooker), is defined as a chain of chromophoric atoms which allow the passage of π-electrons through their orbitals from a $-M$ atom of one auxochrome to a $+M$ atom of another auxochrome.

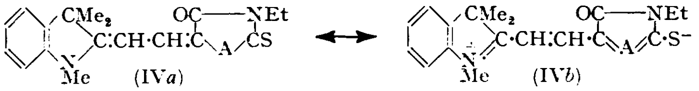
than that shown in the above series. This is found to be true: the shift on proceeding from (III*a*; A = O; Jeffreys, *J.*, 1952, 4823) ($\lambda_{max.}$ 504 mμ in MeOH) to (III*a*; A = S; Knott, *J.*, 1952, 4099) ($\lambda_{max.}$ 588 mμ) is 84 mμ whilst the related shift in (II; *n* = 1) is 72 mμ (Beilenson, Fisher, and Hamer, *Proc. Roy. Soc.*, 1937, *B*, **163**, 138), a difference corresponding to *ca.* 0·05 ev.


(II*a*) (II*b*)

Similarly *mero*cyanines derived from 3-ethyl-2-thio-oxazolid-4-one (IV; A = O) are always lighter in colour than the related dyes from 3-ethyl-2-thiothiazolid-4-one (IV; A = S) (see, *e.g.*, Brooker *et al.*, *J. Amer. Chem. Soc.*, 1951, **73**, 5332 and earlier papers; Jeffreys, *loc. cit.*). Brooker *et al.* (*loc. cit.*), have shown that the resonance responsible for


(III*a*) (III*b*)

the visible absorption of dyes (IV; A = O) is, energetically, less asymmetric than that for (IV; A = S), so that the deeper colour of the latter is certainly not attributable to an asymmetry effect. It is explicable, however, if such structures as (IV*b*; A = S) contribute to the hybrid since they represent an effective increase in the length of the conjugated path.


(IV*a*) (IV*b*)

A = O, $\lambda_{max.}$ = 474 mμ
A = S, $\lambda_{max.}$ = 500 mμ

Apart from the work mentioned above on the diphenyl sulphides little has been published on the synthesis of planar molecules in which a sulphur atom has been interposed in a conjugated system between an auxochrome (—*M* group) and an antiauxochrome (+*M* group) (cf. Cilento, *loc. cit.*; with Walter, *J. Amer. Chem. Soc.*, 1954, **76**, 4469). Whether the sulphur atom functions as an insulator or as a conductor in such molecules could be determined by a spectrographic comparison of the molecule with simpler molecules containing the essential structure of the two fragments on either side of the sulphur atom. It might also be possible to synthesize the related compounds in which the sulphur atom is replaced by an oxygen atom or a vinylene group, and in this way the electronic effects of those bridges could be directly compared.

Electrically Neutral Sulphides.—When a sulphur atom is interposed in the conjugated path of a resonance hybrid (V*a* ⟷ V*b*), where A is a —*M* atom or group and B a +*M* atom or group two types of compound may result. The first type is the sulphide (VI*a*) which may normally be represented by the hybrid (VI*a* ⟷ VI*b*). If the sulphur atom

$$\underset{(\mathrm{V}a)}{\mathrm{A{\cdot}CH{:}CH{\cdot}CH{:}B}} \longleftrightarrow \underset{(\mathrm{V}b)}{\mathrm{\overset{+}{A}{:}CH{\cdot}CH{:}CH{\cdot}\overset{-}{B}}} \qquad \underset{(\mathrm{VII}a)}{\mathrm{\overset{+}{A}{:}CH{\cdot}S{\cdot}CH{:}CH{\cdot}\overset{-}{B}}} \longleftrightarrow \underset{(\mathrm{VII}b)}{\mathrm{A{\cdot}CH{:}\overset{+}{S}{\cdot}CH{:}CH{\cdot}\overset{-}{B}}}$$

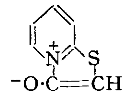
$$\underset{(\mathrm{VI}a)}{\mathrm{A{\cdot}CH{:}CH{\cdot}S{\cdot}CH{:}B}} \longleftrightarrow \underset{(\mathrm{VI}b)}{\mathrm{A{\cdot}CH{:}CH{\cdot}\overset{+}{S}{:}CH{\cdot}\overset{-}{B}}} \qquad \underset{(\mathrm{VII}c)}{\mathrm{\overset{+}{A}{:}CH{\cdot}\overset{-}{S}{:}CH{\cdot}CH{:}B}} \longleftrightarrow \underset{(\mathrm{VII}d)}{\mathrm{A{\cdot}CH{:}S{:}CH{\cdot}CH{:}B}}$$

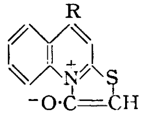
$$\underset{(\mathrm{VI}c)}{\mathrm{\overset{+}{A}{:}CH{\cdot}CH{:}\overset{-}{S}{\cdot}CH{:}B}} \longleftrightarrow \underset{(\mathrm{VI}d)}{\mathrm{\overset{+}{A}{:}CH{\cdot}CH{:}S{:}CH{\cdot}\overset{-}{B}}}$$

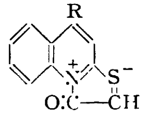
expands its octet then the hybrid may more truly be represented by (VI*a* ⟷ VI*b*), and (VI*c*) will be an important contributing structure. The second type results when the sulphur atom is interposed between carbon atoms adjacent to those divided by sulphur in (VI). This gives what would be called a mesoionic sulphide which is represented by (VII*a* ⟷ VII*b*) if the sulphur does not expand its octet. In such cases types (VI*a*) and (VII*a*) are distinct. If the *d*-orbitals are utilized then (VII*a*) is represented by (VII*a* ⟷ VII*d*) and the distinction between the hybrids (VI) and (VII) is reduced.

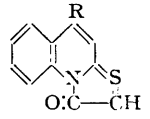
This present paper is concerned with the attempted synthesis of sulphides of type (VII).

Koenigs and Geisler Compounds.—Duffin and Kendall (*J.*, 1951, 734) showed conclusively that the product obtained by Koenigs and Geisler (*Ber.*, 1924, **57**, 2076) by heating (2-pyridylthio)acetic acid with acetic anhydride was the compound (VIII). They also made related compounds (IX) in the quinoline series and suggested that the intense, yellow colour of the solutions of these dyes was due to contributions by a number of resonance structures including (IX*b*) in which the sulphur *d*-orbitals are involved. If such an expansion of the sulphur octet does occur, then the resonance hybrid may more truly be represented by (IX*a* ⟷ IX*c*).


(VIII)

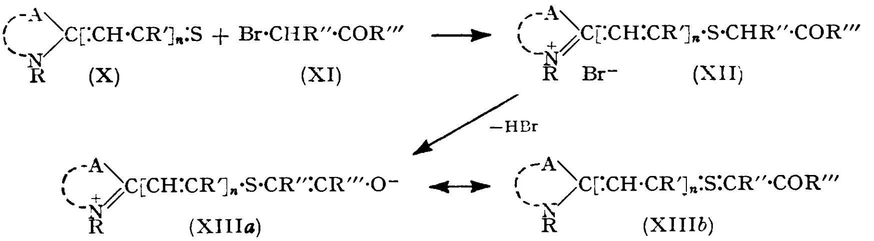

(IX*a*)


(IX*b*)


(IX*c*)

The compound (IX; R = Me), which Duffin and Kendall found to be the most stable of the series, has been examined spectrographically in a number of solvents. These results will be described in Part IV of this series.

Open-chain Analogues of the Compound (VIII).—The synthesis of open-chain benzothiazole analogues of (VIII) [*i.e.*, (XIII)] was then investigated. It is known (Fischer, *Ber.*, 1902, **35**, 3674; Rassow, Döhle, and Reim, *J. pr. Chem.*, 1916, **93**, 183; Hamer and Rathbone, *J.*, 1943, 243) that alkyl halides react with *N*-substituted cyclic thiones to form alkylthio-derivatives of cyclic quaternary ammonium salts. In the same way α-bromo-ketones (XI) condense with (X; $n = 0, 1$) to give the more complex substituted alkylthio- (XII; $n = 0$) or alkylthiovinyl (XII; $n = 1$) derivatives of quaternary bromides (cf. King, Ozog, and Moffat, *J. Amer. Chem. Soc.*, 1951, **73**, 300; Ozog, Comte, and King, *ibid.*, 1952, **74**, 6225). Similarly, unstable alkylseleno-derivatives were obtained from the related selenones. The removal of hydrogen bromide from the salt (XII) was expected to give the sulphide (XIII). Such compounds may be planar if A is a heteroatom (O, S, or Se) and R′, R″ are hydrogen atoms.

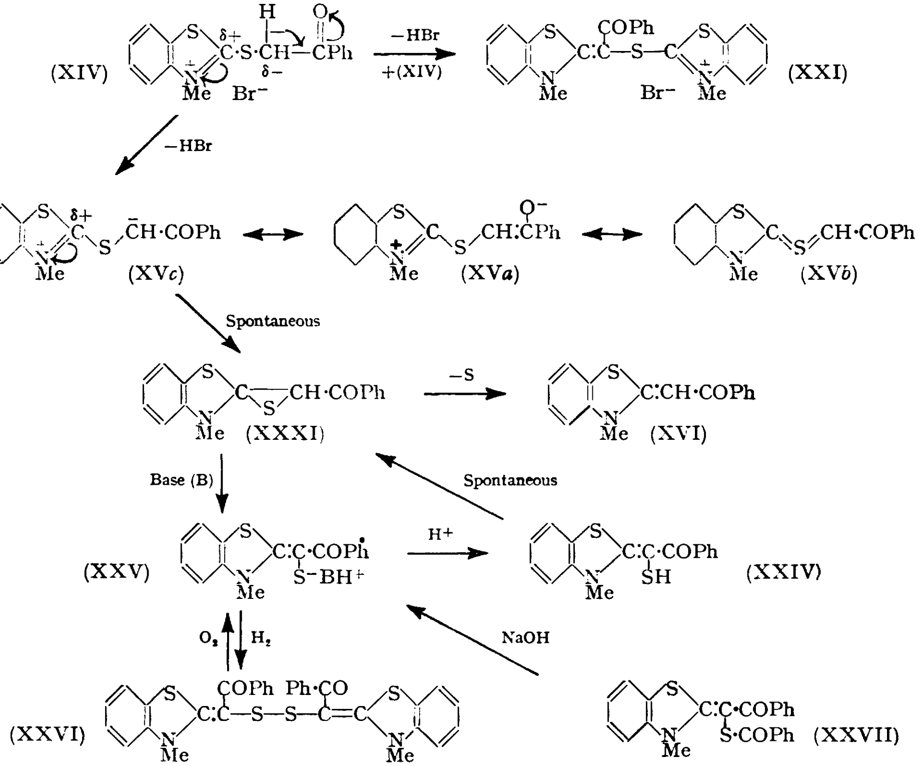


The treatment of 3-methyl-2-2′-phenacylthiovinylbenzothiazolium bromide (XII; $n = 1$; R′, R″ = H, R‴ = Ph) with a variety of bases gave no identifiable products. Similar treatment of the salt (XII; $n = 0$) gave crystalline products in all cases except where the heterocycle was a 1-alkylpyridinium nucleus.

In the first instance, 3-methyl-2-phenacylthiobenzothiazolium bromide (XIV) was treated with triethylamine in alcoholic solution to give bright yellow needles, the analysis of which indicated that the molecule contained one atom of sulphur less than that required for the sulphide (XV). It showed no depression in melting point with an authentic specimen of 3-methyl-2-phenacylidenebenzothiazoline (XVI) prepared by Brooker and White's procedure (U.S.P. 2,112,139) although its melting point (170—174°) was lower than that of (XVI) (176°) and it was bright yellow whilst (XVI) was cream-coloured. Careful extraction of the yellow needles with warm ethanol left undissolved a small amount of yellow grains which, after purification, formed glossy yellow flakes, m. p. 263° (Compound A), giving analytical figures agreeing well with those required for the sulphide (XV). The removal of compound A raised the m. p. of the main product to the correct value for the ketone (XVI). Further experiments on the removal of hydrogen bromide from (XIV) gave either only ketone (XVI) in yields of up to 50% or, when inorganic bases were used, in addition up to 12% of compound A and traces of a second yellow compound, m. p. 217°. Analysis of the compound, m. p. 217°, indicated that it might be the thione corresponding with (XV). The fate of the missing sulphur was partly accounted for by the isolation of nacreous (μ-)sulphur.

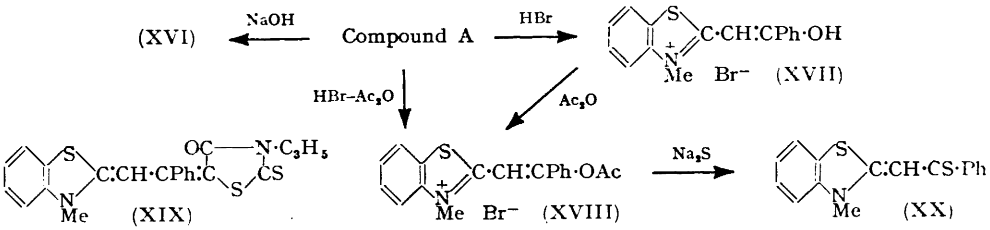
Heating a pyridine solution of compound A with aqueous sodium hydroxide caused the yellow colour to deepen to orange before fading, and a high yield of ketone (XVI) was obtained.

If compound A was the required sulphide (XV) it might be expected that the addition of hydrogen bromide to it would give the original quaternary bromide (XIV). The product obtained, however, was 2-α-hydroxystyryl-3-methylbenzothiazolium bromide (XVII), the same product being obtained by the addition of hydrogen bromide to the ketone (XVI). Its structure was proved by acetylation to give the 2-α-acetoxystyryl compound (XVIII), which with 3-allylrhodanine and with sodium sulphide yielded the dye (XIX) and thio-ketone (XX) respectively. Treatment of compound A with hydrogen bromide in acetic anhydride gave the acetate (XVIII) directly and elementary sulphur. Although the loss of sulphur from compound A in the above reactions seemed extraordinary it did indicate that a similar type of reaction could account for the high yields of ketone (XVI) in the primary reaction.



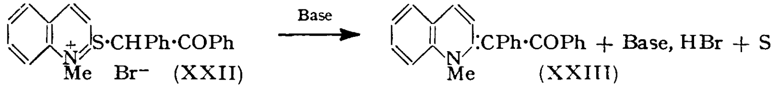
It is known (Kendall, B.P. 426,718) that 2-alkylthiobenzothiazolium salts and similar derivatives of other heterocycles contain an electrophilic $C_{(2)}$ atom which condenses with the nucleophilic methylene carbon atom of ketomethylene compounds under the influence of bases to yield *mero*cyanines, with the elimination of an alkanethiol. In the 3-alkyl-2-phenacylthiobenzothiazolium salt molecule (XIV) reactive centres of both types are present. The treatment of such molecules by bases may result, therefore, not only in simple elimination of hydrogen bromide, but also in either an intermolecular or an intramolecular condensation, on the assumption in the latter case that the reactive centres may approach each other sufficiently closely for bond formation between them to occur.

By analogy with *mero*cyanine formation the primary intermolecular reaction product would be (XXI) which might conceivably break down to give 3-methyl-2-phenacylidenebenzothiazoline (XVI) in a maximum yield of 50% based on starting material (XIV).



Although yields of (XVI) have never exceeded 50% the related 1-methyl-2-α-phenylphenacylthioquinolinium bromide (XXII) gave over 90% yields of the dihydroquinoline derivative (XXIII). If we assume that a similar mechanism accounts for both reactions, then such intermolecular condensations may be considered not to occur.

The primary reaction product to be expected from the intramolecular condensation of (XIV) is the thiol (XXIV). Such a compound would not be expected to lose its thiol sulphur atom to give (XVI). It should be very susceptible to oxidation, particularly in the form of its anion (XXV), to give the disulphide (XXVI) since it contains the strongly reducing fragment –NR·C:CH·SH similar to that of photographic developing agents. Since the thiol (XXIV) is isomeric with the sulphide (XV), and the disulphide (XXVI) would also give analytical figures similar to those of the sulphide (XV), the unambiguous syntheses of these two compounds was desirable.

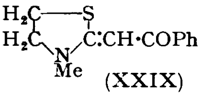


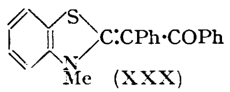
Condensation of 3-methyl-2-methylthiobenzothiazolium toluene-*p*-sulphonate with phenacyl thiolbenzoate gave the yellow dye (XXVII). Addition of aqueous sodium hydroxide to its alcoholic solution caused an intense red coloration, and warming caused yellow crystals to separate, the red colour gradually fading to yellow. The crystals had m. p. 263°, and were identical with compound A. The filtrate gave a 50% yield of 3-methyl-2-phenacylidenebenzothiazoline (XVI). Since the fading of the red solution occurred from the surface downwards it appeared that an oxidation was involved. Indeed hydrolysis under nitrogen gave a clear red solution which could be diluted with water without precipitation. The red colour is therefore ascribed to the thiol anion of (XXV) which forms an insoluble orange silver salt. Persulphate at once discharged the red colour and precipitated compound A in 80% yield. There is therefore no doubt that the latter is the disulphide (XXVI). It is readily reduced to the red thiol salt with sodium sulphide. Low molecular weights (Rast) found for the disulphide may be due to partial dissociation to the thiyl radicals (cf. Cutforth and Selwood, *J. Amer. Chem. Soc.*, 1948, **70**, 278), which may also account for the bright orange colour of the molten disulphide.

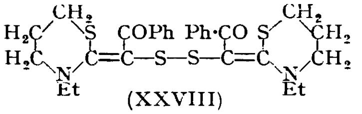
When the red solution obtained by hydrolysis of (XXVII) under nitrogen was neutralized with acetic acid, hydrogen sulphide was evolved and the precipitate contained the disulphide (XXVI) (8%) and 3-methyl-2-phenacylidenebenzothiazoline (XVI) (60%).

In one other case the treatment of a quaternary salt, 3-ethyl-4 : 5-dihydro-2-phenacylthio-1 : 3-thiazinium bromide, with triethylamine gave a product, which is probably the analogous disulphide (XXVIII). The red crystals obtained by treating 1-methyl-2-phenacylthioquinolinium bromide with triethylamine were not identified. The ketones (XXIX) and (XXX) were the sole products isolated from the treatment of the related quaternary salts (XII) with triethylamine.

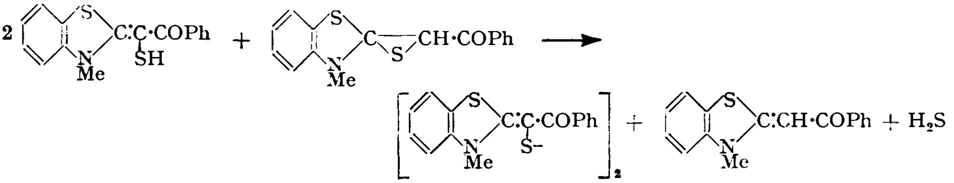
The seleno-analogue of (XXII) with triethylamine gave a small yield of the same dye (XXIII) as was obtained from (XII).


(XXIX)

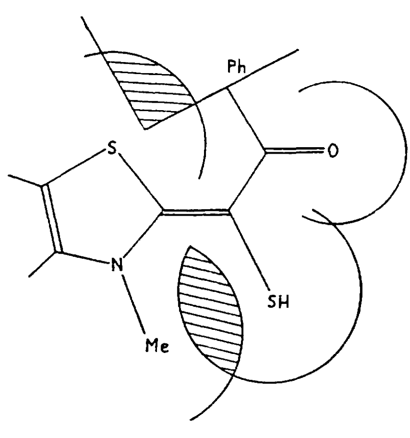

(XXX)


(XXVIII)

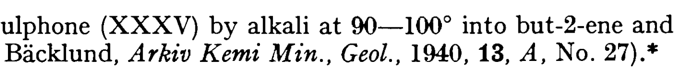
Possible Mechanisms of the Reactions.—The first step in the reaction of the quaternary cation (XIV) with a base is assumed to be the removal of a proton from the methylene-carbon atom. This would give (XV*c*) which is an excited structure of the sulphide resonance hybrid (XV*a* ⟷ XV*b*). If the angle of the chain sulphur bonds is 100° the distance between the negatively charged carbon atom and the electrophilic $C_{(2)}$-atom is *ca.* 2·75 Å but, because of the electrostatic attraction between these carbon atoms and the flexibility of the sulphur bonds, this distance may at times be considerably less. The formation of a bond by charge neutralization between these atoms to give the *spiro*-episulphide (XXXI) is thus feasible (see also Part IV).


(XXXII)

If the quaternary salt (XIV) is treated with aqueous sodium hydroxide the red thiol anion is formed (giving a 25% yield of disulphide on oxidation), a reaction which could indicate that the episulphide breaks down, at least in part, to the thiol anion. This breakdown is only slight with weaker bases such as triethylamine, as is indicated by the very low yield of disulphide obtained on treating the salt (XIV) with this base. In this case the splitting off of elementary sulphur, possibly by base catalysis, to give the ketone (XVI) occurs. The instability of the thiol (XXIV) itself is believed to be due to steric hindrance to coplanarity of the thiol-sulphur atom with the benzothiazoline nucleus (Figure). The evolution of hydrogen sulphide and the simultaneous formation of some disulphide on neutralization of the solution of the thiol anion seems to indicate a reductive process, possibly of the type giving rise to the compound (XXXII), above. In accordance, the vinylogue of (XXIV), namely (XXXIV), obtained by hydrolysis of the dye (XXXIII), does not suffer from steric hindrance to planarity and, in the absence of oxygen, is stable.



The hypothesis of the formation of episulphides is similar to that put forward by Bordwell and Cooper (*J. Amer. Chem. Soc.*, 1951, **73**, 5187) to explain the conversion


(XXXIII) (XXXIV)

of the bromo-sulphone (XXXV) by alkali at 90—100° into but-2-ene and sulphur dioxide (Ramberg and Bäcklund, *Arkiv Kemi Min., Geol.*, 1940, **13**, *A*, No. 27).* Loss of sulphur dioxide from such episulphones (XXXVI) has been reported by Staudinger and Pfenninger

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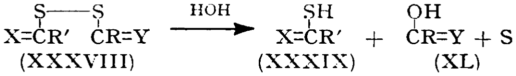
* Parham and Traynelis (*J. Amer. Chem. Soc.*, 1954, **76**, 4960) have shown that 2 : 5-diphenyl-1 : 4-dithiin is converted into 2 : 4-diphenylthiophen at 190° with the elimination of elementary sulphur and have postulated the intermediate formation of an episulphide.

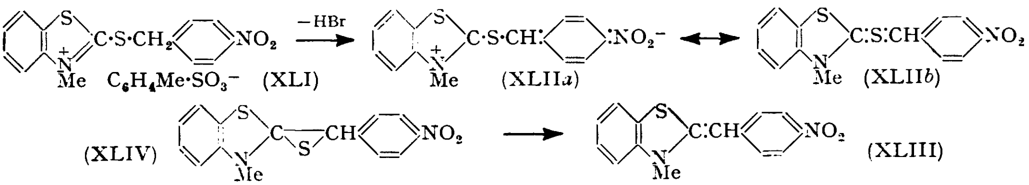
(*Ber.*, 1916, **49**, 1941). Loss of sulphur from the sulphide (XXXVII) on storage (Price and Kirk, *J. Amer. Chem. Soc.*, 1953, **75**, 2396) may also be related to the sulphur elimination described in the present paper and may not require the primary aerial oxidation to the sulphone suggested by these authors.

The mechanism of the decomposition of the disulphide (XXVI) by sodium hydroxide or hydrogen bromide is obscure. Fromm (*Annalen*, 1906, **348**, 144) collected evidence to show that disulphides (XXXVIII), in which the carbon atoms to which the disulphide group is bonded are unsaturated, are decomposed by alkali, or in some cases by water, to give sulphur and two fragments (XXXIX) and (XL). In the present case the thiol fragment would correspond to (XXIV), which has been shown to lose its sulphur atom to give the ketone (XVI).



$$\underset{\text{(XXXVIII)}}{\overset{\text{S——S}}{\text{X=CR}'\quad\text{CR=Y}}} \xrightarrow{\text{HOH}} \underset{\text{(XXXIX)}}{\overset{\text{SH}}{\text{X=CR}'}} + \underset{\text{(XL)}}{\overset{\text{OH}}{\text{CR=Y}}} + \text{S}$$

The Action of Bases on p-*Nitrobenzylthio-derivatives of Heterocyclic Quaternary Salts.*—After failure to obtain open-chain sulphides of type (VII) in which the group B contained a keto-group, attention was turned to related compounds in which group B contained a nitro-group. Condensation of *p*-nitrobenzyl chloride with 2-mercaptobenzothiazole gave 2-*p*-nitrobenzylthiobenzothiazole, which on quaternization gave the salt (XLI). Removal of toluenesulphonic acid from the latter by pyridine or aqueous-alcoholic triethylamine did not give the sulphide (XLII*a* ⟷ *b*). Two products were isolated, di-*p*-nitrobenzyl disulphide and 3-methyl-2-*p*-nitrobenzylidenebenzothiazoline (XLIII), the latter probably by way of the *spiro*episulphide (XLIV). The disulphide formation may be accounted for by aqueous hydrolysis of the quaternary salt, giving 3-methylbenzothiazol-2-one (not isolated) and *p*-nitrotoluene-ω-thiol the latter being oxidized aerially, or in the removal of sulphur from the episulphide. The product isolated from the pyridine treatment of (XLI) was again (XLIII).



EXPERIMENTAL

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

Heterocyclic Thiones (X; *n* = 0).—These were obtained (cf. Sexton, *J.*, 1939, 470) by treating the 2-alkylthio-derivative of the heterocyclic quaternary salt with aqueous sodium sulphide, best at room temperature. The related selenones were obtained similarly by using aqueous sodium selenide (cf. Michaelis and Holken, *Annalen*, 1904, **331**, 251).

1 : 2-*Dihydro*-1-*methyl*-2-*selenoquinoline*.—1-Methyl-2-methylthioquinolinium toluene-*p*-sulphonate (18·0 g.) was dissolved in water (50 c.c.) and added at 20° to a filtered solution of sodium selenide (12·5 g.) in water (50 c.c.). The thick precipitate was washed with water and obtained as orange-red needles, m. p. 115—116° (91%), from ethanol (Found : C, 54·15; H, 4·05; N, 6·1. $C_{10}H_9NSe$ requires C, 54·05; H, 4·05; N, 6·3%).

3-*Methyl*-2-*selenobenzothiazoline*, obtained similarly (87%), formed pale yellow flakes, m. p. 108—110°, from ethanol (Found : C, 42·35; H, 3·25; N, 6·2; S, 14·3. C_8H_7NSSe requires C, 42·15; H, 3·1; N, 6·15; S, 14·05%).

3-*Methyl*-2-*phenacylthiobenzothiazolium Bromide* (XIV).—3-Methyl-2-thiobenzothiazoline (1·8 g., 0·01 mole) and phenacyl bromide (2·0 g., 0·01 mole) were fused together for 10 min. on the steam-bath. The solid cake was dissolved in ethanol (10 c.c.), and dry ether was run in slowly to give 2·45 g. (64·5%) of the *thiazolium bromide.* This formed cream-coloured needles, m. p. 121°, from ethanol (Found: C, 50·4; H, 4·7; Br, 19·1; S, 15·25. $C_{16}H_{14}ONBrS_2,C_2H_5{\cdot}OH$ requires C, 50·7; H, 4·7; Br, 18·8; S, 15·05%).

1-*Methyl-2-phenacylthioquinolinium bromide,* obtained similarly (88%), formed similar needles, m. p. 179° (orange melt), from ethanol–ether (Found: Br, 19·15; S, 7·6. $C_{18}H_{16}ONBrS,C_2H_5{\cdot}OH$ requires Br, 19·05; S, 7·6%).

3-*Methyl-2-phenacylthiothiazolinium bromide* obtained by the above method (see also Batty and Weedon, *J.*, 1949, 786) from 3-methylthiazolidin-2-thione in 82% yield, formed white crystals, m. p. 117—120°, from ethanol (Found: Br, 23·8; S, 19·4. $C_{12}H_{14}ONBrS$ requires Br, 24·1; S, 19·3%).

3-*Ethyl*-4 : 5-*dihydro-2-phenacylthio*-1 : 3-*thiazinium bromide* was obtained from the related thione (Hamer and Rathbone, *loc. cit.*) as a tar which crystallised from ethanol (80% yield) and formed light brown needles, m. p. 135°, from ethanol–ether (Found: Br, 22·1; S, 17·75. $C_{14}H_{18}ONBrS_2$ requires Br, 22·25; S, 17·8%).

1-*Methyl-2-phenacylthiopyridinium bromide* formed yellow needles (93%), m. p. 180—181°, from ethanol (Found: Br, 24·55; S, 9·7. $C_{14}H_{14}ONBrS$ requires Br, 24·7; S, 9·9%).

1-*Methyl*-2-α-*phenylphenacylquinolinium Bromide* (XXII).—1-Methylquinoline-2-thione (1·75 g., 0·01 mole) and α-phenylphenacyl bromide (2·75 g., 0·01 mole) were dissolved separately in benzene (25 c.c.), and the solutions were mixed and heated for 15 min. on a steam-bath. The thick precipitate was washed with ether and obtained in 62% yield as a white crystalline powder, m. p. 175—177°, from ethanol–ether (Found: C, 62·1; H, 5·85; Br, 14·8; S, 6·1. $C_{24}H_{20}ONBrS,2C_2H_5{\cdot}OH$ requires C, 61·9; H, 5·9; Br, 14·75; S, 5·9%).

2-*Phenylcarbamylmethylthio*-1-*methylquinolinium bromide* (XII; $n = 0$, R = Me, R″ = H, R‴ = NHPh).—1-Methylquinoline-2-thione (3·5 g.) and ω-chloroacetanilide (3·4 g.) were fused together on the steam-bath for 5 min. The solid salt (5·3 g., 77%) formed yellow aggregates, m. p. 216° (red melt; effervesces), from methanol–ether (Found: C, 62·3; H, 5·05; N, 8·0; Cl, 9·95; S, 9·15. $C_{18}H_{17}ON_2ClS$ requires C, 62·75; H, 4·95; N, 8·15; Cl, 10·3; S, 9·3%).

3-*Ethyl-2-thioformylmethylenebenzothiazoline* (X; $n = 1$, R′ = H).—2-2′-Acetanilidovinyl-3-ethylbenzothiazolium iodide (45·0 g.) was suspended in acetone (100 c.c.), a solution of sodium sulphide nonahydrate (48·0 g.) in water (50 c.c.) added, and the whole shaken at 30°. The orange solution was filtered after 30 min. and diluted with water (500 c.c.). A red tar separated which gradually crystallised. From ethanol (400 c.c.) there was obtained a total of 18·2 g. (82·5%) of red crystals. This compound was dissolved in benzene, filtered, and reprecipitated by means of light petroleum (b. p. 60—80°). It was finally obtained as magenta needles, m. p. 87°, from ethanol (Found: S, 28·7. $C_{11}H_{11}NS_2$ requires S, 29·0%).

3-*Ethyl*-2 : 2′-*phenacylthiovinylbenzothiazolium Bromide* (XII; $n = 1$, R′ = R″ = H, R‴ = Ph).—3-Ethyl-2-thioformylmethylenebenzothiazoline (2·2 g.) was treated in benzene (20 c.c.) with phenacyl bromide (2·0 g.) in benzene (10 c.c.) at 20°. The precipitated tar crystallised and was collected, washed with water and ether, and dissolved in hot ethanol (20 c.c.). The required quaternary *salt* (3·2 g., 68·5%), which crystallised on chilling, formed pale yellow needles, m. p. 150—160° (softened and became orange at 94°), from ethanol (Found: Br, 17·6; S, 14·0. $C_{19}H_{18}ONBrS_2,C_2H_5{\cdot}OH$ requires Br, 17·4; S, 13·75%).

3-*Ethyl* 2-(2-α-*phenylphenacylthiovinyl*)*benzothiazolium Bromide* (XII; $n = 1$, R′ = H, R″ = R‴ = Ph).—3-Ethyl-2-thioformylmethylenebenzothiazoline (2·2 g.) and α-phenylphenacyl bromide (2·75 g.) were heated in benzene (10 c.c.) for 15 min. on a steam-bath. A tar separated and solidified during this time. Ether (30 c.c.) was added and the solid *bromide* was collected and washed with acetone. It (4·4 g., 89%) formed yellow crystals, m. p. 184° (effervesces and turns magenta) from ethanol (Found: Br, 15·95; S, 12·6. $C_{25}H_{22}ONBrS_2$ requires Br, 16·15; S, 12·9%).

Action of Bases on the Sulphide (XII; $n = 0$) *and its Analogues.*—(a) 3-*Methyl-2-phenacylthiobenzothiazolium bromide* (i) The quaternary salt (1·35 g.) was dissolved in pyridine (15 c.c.) by warming to 50°. The solution was allowed to cool and water (70 c.c.) was added. A yellow tar was precipitated which gradually set to a sticky solid. The aqueous layer which gave no sulphide reaction was decanted and the residual 3-methyl-2-phenacylidenebenzothiazoline (XVI) washed with cold ethanol. It (0·25 g., 29·5%) formed pale yellow flakes, m. p. 176°, from benzene (Found: C, 71·5; H, 4·8; N, 5·1; S, 12·1. Calc. for $C_{16}H_{13}ONS$: C, 71·8; H, 4·85; N, 5·25; S, 12·0%). Van Dormael and Ghys (*Bull. Soc. chim. belges*, 1950, **59**, 593) give m. p. 175—176°. A mixed m. p. with a sample obtained by Brooker and White's method (*loc. cit.*) was 176°.

(ii) The quaternary salt (4·25 g., 0·01 mole) was dissolved in ethanol (50 c.c.) and triethylamine (3 c.c.; 0·02 mol.) was added at 25°. After 2 min. water was run in until the solution was faintly turbid and the whole was chilled overnight. Crystals (1·8 g.) which separated formed bright yellow needles, m. p. 170—174°, from benzene–light petroleum (b. p. 60—80°) (Found: C, 71·1; H, 4·8; N, 5·1; S, 12·7%). Cautious extraction with warm ethanol left a little insoluble yellow residue. The ethanol on concentration gave 1·25 g. (47·0%) of the compound (XVI), m. p. 176°. The insoluble *di-[α-(3-methylbenzothiazolinylidene)phenacyl] disulphide* (XXVI) (0·06 g.) formed glossy, yellow flakes, m. p. 263°, from pyridine–ethanol (Found: C, 64·25; H, 4·2; N, 4·7; S, 21·75%; *M*, 274, 296. $C_{32}H_{24}O_2N_2S_4$ requires C, 64·45; H, 4·05; N, 4·7; S, 21·5%; *M*, 596). Its pyridine solution is instantly reduced to the orange-red sodium salt (XXV) with sodium sulphide.

(iii) The finely ground quaternary salt (20 g.) was stirred under benzene (250 c.c.). Sodium hydrogen carbonate (25 g.) and water (50 c.c.) were added and the whole was stirred rapidly at 25° for 1 hr. The yellow benzene layer then contained a pale yellow solid, and the original quaternary salt had disappeared. Nine such batches were united and the suspended solid (A) was collected. The benzene layer of the filtrate was dried and concentrated to 100 c.c. (B). The solid (A) was extracted with boiling ethanol (800 c.c.), leaving an insoluble yellow residue (C). The ethanol extract yielded the ketone (XVI) (23 g.) on concentration and a further 32 g. were obtained from the benzene solution (B) (total yield 44%). The yellow residue (C) was extracted with boiling benzene (4 l.) (D) to leave undissolved a bright yellow powder (0·45 g.), m. p. 215°. It formed bright yellow crystals, m. p. 217°, from pyridine–ethanol (Found: C, 61·55; H, 4·5; N, 4·6; S, 29·45. $C_{32}H_{24}N_2S_6$ requires C, 61·15; H, 3·8; N, 4·45; S, 30·6%). The compound may thus be the *disulphide* corresponding to (XXVI). Concentration of the benzene extract (D) yielded 11·2 g. (8%) of the disulphide (XXVI), m. p. 263°, after recrystallisation from pyridine–ethanol.

The benzene filtrates (B) were concentrated further, yielding nacreous sulphur (1·6 g.), m. p. 112°, and 3-methylbenzothiazolin-2-thione (6·5 g.), m. p. 87°.

(iv) Quaternary salt (2·15 g.), dissolved in ethanol (25 c.c.), was added at 25° to a solution of sodium (0·6 g.) in ethanol (25 c.c.). After 5 min. a slurry of potassium persulphate (2 g.) in water (20 c.c.) was added. The colour changed to light orange and yellow crystals separated. After chilling, the crystals were collected and washed with water and ethanol. The disulphide (XXVI) (0·65 g., 43·5%) formed glossy yellow flakes, m. p. 263°, from pyridine–ethanol, identical with the product obtained as under (iii).

(b) 1-*Methyl-2-phenacylthioquinolinium bromide*. The quaternary salt (3·75 g.) was dissolved in ethanol (20 c.c.) and cooled to 0°. Triethylamine (2·5 c.c.) was added and the temperature allowed to rise to 20°. The precipitated substance (2·6 g.) formed red crystals, m. p. 192°, from pyridine–ethanol (Found: C, 68·05; H, 4·55; N, 5·35; S, 17·25%). It was not identified.

(c) 3-*Methyl-2-phenacylthiothiazolinium bromide*. The quaternary salt (3·3 g.) was suspended in water (10 c.c.) and triethylamine (1·5 c.c.) was added. A thick yellow tar separated and became semi-solid. From ethanol (twice) there was obtained 0·3 g. (13·5%) of pale yellow needles, m. p. 125°, of 3-*methyl-2-phenacylidenethiazolidine* (XXIX) (Found: C, 65·0; H, 6·1; N, 6·4; S, 14·65. $C_{12}H_{13}ONS$ requires C, 65·75; H, 5·95; N, 6·4; S, 14·6%).

(d) 3-*Ethyl*-4 : 5-*dihydro*-2-*phenacylthio*-1 : 3-*thiazinium bromide*. The quaternary salt (3·6 g.) was suspended in ethanol (20 c.c.), triethylamine (3 c.c.) was added, and the solid was dissolved with stirring. Triethylamine hydrobromide and a chrome-yellow solid slowly separated. The solids were collected after 2 days, and the triethylamine hydrobromide was washed out with ethanol and water. The yellow residual (?) *di-[α-(3-ethyltetrahydro-2-thiazinylidene)phenacyl] disulphide* (XXVIII) (0·8 g.) formed an orange-yellow crystalline powder, m. p. 188°, from pyridine–ether (Found: C, 60·3; H, 5·75; N, 4·9; S, 23·05. $C_{28}H_{32}O_2N_2S_4$ requires C, 60·4; H, 5·75; N, 5·05; S, 23·0%).

(e) 1-*Methyl*-2-α-*phenylphenacylquinolinium bromide* (XXII). (i) The quaternary salt (2·5 g.) was covered with ethanol (15 c.c.) and triethylamine (1 c.c.) added. The dye (1·55 g., 100%) which separated as the quaternary salt dissolved was obtained in 91% yield as orange plates, m. p. 218°, from benzene–light petroleum (b. p. 60—80°) (Found: C, 85·3; H, 5·5; N, 4·25. $C_{24}H_{19}ON$ requires C, 85·5; H, 5·65; N, 4·15%). It is 1 : 2-*dihydro*-1-*methyl*-2-α-*phenylphenacylquinoline* (XXIII). The m. p. showed no depression when the dye was mixed with a sample prepared by condensing 1-methyl-2-methylthioquinolinium toluene-*p*-sulphonate with deoxybenzoin in alcoholic triethylamine.

(ii) The quaternary salt (5·4 g.) was dissolved in pyridine (50 c.c.) at 55° in 5 min. After a further 5 min., water (20 c.c.) was slowly run in, the dye (XXIII) crystallising in 90%

yield. On concentration the filtrate yielded sulphur (0·06 g., 18·7%), and 1 : 2-dihydro-1-methyl-2-thioquinoline (0·36 g.). The same dye was obtained in 15% yield by treating 1-methyl-2-α-phenylphenacylselenoquinolinium bromide with alcoholic triethylamine. This quaternary salt which deposited selenium on attempted purification was formed in 82% yield as an orange powder by refluxing 1 : 2-dihydro-1-methyl-2-selenoquinoline (1·1 g.) and α-phenylphenacyl bromide (1·4 g.) in benzene (10 c.c.) for 5 min. on a steam-bath.

(f) 3-*Methyl*-2-α-*phenylphenacylbenzothiazolium bromide*. 3-Methylbenzothiazolin-2-thione (1·8 g.) and desyl bromide (2·75 g.) were fused together for 4 hr. on a steam-bath. The thick oil was dissolved in ethanol (10 c.c.), and triethylamine (1 c.c.) was added. Scratching caused solidification.

3-*Methyl*-2-α-*phenylphenacylbenzothiazoline* (XXX) (1·4 g., 41%) formed lemon-yellow needles, m. p. 203°, on recrystallisation from ethanol then from benzene–light petroleum (b. p. 60—80°) (Found: C, 76·8; H, 4·95; N, 4·3; S, 9·3. $C_{22}H_{17}ONS$ requires C, 77·0; H, 4·95; N, 4·1; S, 9·35%).

Alternative Synthesis of the Disulphide (XXVI).—*Phenacyl thiolbenzoate*. This compound has been obtained by Groth (*Arkiv Kemi, Min., Geol.*, 1924, **9**, 63) by the action of benzoyl chloride on acetophenone-ω-thiol. Preferably it is prepared as follows. Phenacyl bromide (10 g., 0·05 mole), potassium thiolbenzoate (8·9 g., 0·05 mole), and ethanol (20 c.c.) were warmed together for 2 min. on a steam-bath. Potassium bromide separated and was dissolved by the slow addition of water to the warm solution. The required ester commenced to crystallize and was fully precipitated by water (100 c.c.). It was obtained in 92% yield as cream-coloured flakes, m. p. 84—85°, from benzene–light petroleum (b. p. 60—80°) (Found: S, 12·55. Calc. for $C_{15}H_{12}O_2S$: S, 12·5%).

2-α-*Benzoylthiophenacylidene*-3-*methylbenzothiazoline* (XXVII). To 3-methyl-2-methylthiobenzothiazolium toluene-*p*-sulphonate (1·85 g.) and phenacyl thiolbenzoate (1·3 g.) in pyridine (10 c.c.) at 50° triethylamine (0·8 c.c.) was added and the whole was allowed to cool during 3 hr. Ethanol (50 c.c.) was run in slowly with scratching to give yellow crystals. The *product* (0·5 g., 25%) formed lemon-yellow needles in rosettes, m. p. 177°, from ethanol (Found: N, 3·65; S, 15·95. $C_{23}H_{17}O_2NS_2$ requires N, 3·45; S, 15·8%).

Hydrolysis of (XXVII). (*a*) The thiazoline (XXVII) (0·3 g.), ethanol (10 c.c.), and aqueous 4N-sodium hydroxide (0·5 c.c.) were heated for 2 min. on a steam-bath. A red solution resulted from which yellow crystals rapidly separated. The solution was chilled overnight, the red colour of the solution changing to yellow. The crystals, when washed with ethanol, gave the disulphide (XXVI) as yellow flakes, m. p. 262° (from pyridine–ethanol; 0·09 g., 40%) (Found: N, 4·55; S, 21·4), alone or mixed with compound obtained as under (a, ii). The reaction filtrate gave 0·1 g. (50%) of 3-methyl-2-phenacylidenebenzothiazoline (XVI), yellow flakes, m. p. 174—175°, from benzene–light petroleum (b. p. 60—80°).

(*b*) The thiazoline (XXVII) (0·5 g.) in ethanol (60 c.c.) was treated with aqueous 4N-sodium hydroxide (1 c.c.) under a stream of nitrogen. The solution was warmed at 40° for 2 min. and water (50 c.c.) was added. Addition of potassium persulphate (1 g.) in water (15 c.c.) discharged the orange-red colour and precipitated yellow flocks. These were washed with water and ethanol and gave 0·3 g. (80%) of yellow flakes, m. p. 263°, from pyridine–ethanol, identical with previous samples of the disulphide (XXVI).

(*c*) After reaction as described in (*b*) the alkaline solution of the thiol was neutralized with acetic acid, causing immediate discharge of the red colour, the formation of yellow flocks, and a strong odour of hydrogen sulphide (blackened lead acetate wool). The precipitate was washed with ethanol and extracted with boiling ethanol, leaving 0·03 g. (8%) of undissolved disulphide (XXVI), m. p. 262° (from pyridine–ethanol). The ethanol extract on concentration gave 0·2 g. (60%) of 3-methyl-2-phenacylidenebenzothiazoline (XVI), m. p. and mixed m. p. 176° (from ethanol).

The red alkaline solution of the thiol, on addition of ammonia and aqueous silver nitrate, gave an insoluble, orange silver salt.

Reactions of the Disulphide (XXVI).—(*a*) The disulphide (0·5 g.) was treated in pyridine (10 c.c.) with aqueous 2N-sodium hydroxide (10 c.c.) and heated on a steam-bath for 2 hr., the solution, initially orange, becoming almost colourless. Water (10 c.c.) was added, and the solution was concentrated until crystallization occurred. Water (100 c.c.) was added and the yellow flakes were collected. They were air-dried and dissolved in benzene (10 c.c.), and the solution was filtered, concentrated to 5 c.c., and treated with light petroleum (b. p. 60—80°) (25 c.c.). The pale yellow flakes (0·4 g., 90%), m. p. 175—176°, were identical with an authentic specimen of the thiazoline (XVI).

(*b*) The disulphide (XXVI) (0·5 g.) was suspended in benzene (20 c.c.) and a 50% solution of hydrogen bromide in acetic acid (0·5 c.c.) was added, with shaking until the solid had dissolved. The benzene was decanted and acetone (2 c.c.) was added. The yellow crystals (0·55 g., 95%) formed yellow needles, m. p. 203—204°, from ethanol–ether (Found : Br, 22·7; S, 9·05. $C_{16}H_{14}ONBrS$ requires Br, 23·0; S, 9·2%). They are *2-α-hydroxystyryl-3-methylbenzothiazolium bromide* (XVII), identical with a specimen obtained by passing hydrogen bromide into a benzene solution of the ketone (XVI).

(*c*) The disulphide (XXVI) (2·0 g.) was suspended in acetic anhydride (100 c.c.) and saturated with hydrogen bromide. The temperature rose from 22° to 29° and a mass of crystals separated (2·35 g.). From acetic anhydride saturated with hydrogen bromide, then from acetic anhydride, they formed pale yellow needles, m. p. 140° (red) (Found: C, 55·7; H, 4·3; Br, 20·5; S, 7·9. $C_{18}H_{16}O_2NBrS$ requires C, 55·45; H, 4·1; Br, 20·5; S, 8·2%), of *2-α-acetoxystyryl-3-methylbenzothiazolium bromide* (XVIII), identical with specimens obtained by dissolving the enol (XVII) (1 g.) in boiling acetic anhydride (10 c.c.) and chilling it immediately.

The acetic anhydride filtrates were evaporated to dryness to yield 0·095 g. (44·5%) of sulphur (flakes, m. p. 118°, from benzene) and 0·22 g. (12·3%) of ketone (XVI).

The structure of the acetate (XVIII) was determined as follows : (i) The acetate (1·95 g.), 3-allylrhodanine (0·9 g.), ethanol (10 c.c.), and triethylamine (0·8 c.c.) were refluxed for 2 min. The crystals (0·9 g., 42·5%) of *3-allyl-5-[2-(3-methylbenzothiazolin-2-ylidene)-2-phenylethylidene]-2-thiothiazolid-4-one* (XIX) formed green-gold flakes, m. p. 233°, from benzene–ethanol (Found : C, 62·6; H, 4·6; S, 22·9. $C_{22}H_{18}ON_2S_3$ requires C, 62·5; H, 4·25; S, 22·75%). (ii) To the acetate (1·3 g.) suspended in ethanol (20 c.c.) sodium sulphide nonahydrate (1·0 g.) in water (5 c.c.) was added and the whole was heated for 2 min. on the steam-bath. The flocculent red precipitate of 3-methyl-2-thiophenacylidenebenzothiazoline (XX), collected after chilling, formed scarlet needles, m. p. 175° (0·6 g., 63·5%) from benzene–light petroleum (b. p. 60—80°) (Found : S, 22·9. Calc. for $C_{16}H_{13}NS_2$: S, 22·6%). de Smet and Mees (G.P. 740,773) give m. p. 176°.

2-(3-Benzoyl-3-benzoylthioallylidene)-3-ethylbenzothiazoline (XXXIII).—2-2′-Acetanilidovinyl-3-ethylbenzothiazolium iodide (2·25 g.), phenacyl thiolbenzoate (1·3 g.), ethanol (10 c.c.), and triethylamine (0·8 c.c.) were refluxed together on a steam-bath for 10 min. The *dye* separated when the solution was chilled. It (1·25 g., 58%) formed garnet tablets, m. p. 172—173°, from benzene (Found : N, 3·2; S, 14·65. $C_{26}H_{21}O_2NS$ requires N, 3·15; S, 14·45%). Hydrolysis with sodium hydroxide gives an orange, water-soluble product forming an insoluble silver salt. Acidification of the solution of the sodium salt under nitrogen gave orange-red grains which could not be crystallized but readily redissolved in alkali.

*2-*p*-Nitrobenzylthiobenzothiazole.*—To potassium hydroxide (5·6 g., 0·1 mole) in ethanol (250 c.c.) 2-mercaptobenzothiazole (16·7 g., 0·1 mole) and *p*-nitrobenzyl chloride (17·15 g., 0·1 mole) were added. The mixture was warmed gently to start the reaction and was then left for 1 hr. and chilled. The solids were filtered off and washed well with ethanol and water. The *sulphide* (28·1 g., 97·5%) formed pale yellow flakes, m. p. 95°, from ethanol (Found : N, 8·9; S, 21·1. $C_{14}H_{10}O_2N_2S_2$ requires N, 9·25; S, 21·2%). It yielded *3-methyl-2-*p*-nitrobenzylthiobenzothiazolium toluene-*p*-sulphonate* (XLI) on fusion for 12 hr. on a steam-bath with 1 mol. of methyl toluene-*p*-sulphonate. This (92% yield) formed white crystals, m. p. 209—211° (red melt), decomposing on attempted recrystallization (Found : S, 19·4. $C_{22}H_{20}O_5N_2S_3$ requires S, 19·7%). It (3·9 g.), water (20 c.c.), and triethylamine (1·0 c.c.) were ground together in a boiling-tube and warmed gently until the quaternary salt was converted into a soft black solid. The water was decanted and the residue washed with ethanol. From ethanol containing a little triethylamine the first crop (1·5 g., 66%) formed purple-bronze or red flakes, m. p. 224° after a further recrystallization from benzene–light petroleum (b. p. 80—100°) (Found : C, 63·15; H, 4·3; N, 10·1; S, 11·35. $C_{15}H_{12}O_2N_2S$ requires C, 63·4; H, 4·3; N, 9·85; S, 11·25%). It is *3-methyl-2-*p*-nitrobenzylidenebenzothiazoline* (XLIII). The second crop (0·3 g., 22·4%) formed pink needles, m. p. 125° [from benzene–light petroleum (b. p. 60—80°)] (Found : C, 50·3; H, 3·8; N, 7·95; S, 18·95. Calc. for $C_{14}H_{12}O_4N_2S_2$: C, 50·0; H, 3·6; N, 8·35; S, 19·05%), of di-(*p*-nitrobenzyl) disulphide, identical with an authentic specimen (Price and Twiss, *J.*, 1908, 1401).

*2-*p*-Nitrobenzylthioquinoline.*—This was obtained in 86·5% yield from equimolar quantities of 2-mercaptoquinoline, *p*-nitrobenzyl chloride, and alcoholic potassium hydroxide, as colourless needles, m. p. 87° (from ethanol) (Found : C, 64·7; H, 4·2; N, 9·35; S, 10·95. $C_{16}H_{12}O_2N_2S$ requires C, 64·8; H, 4·05; N, 9·45; S, 10·8%). Its *methotoluene-*p*-sulphonate*, obtained in 52% yield on a steam-bath (6 hr.), formed flat, buff needles, m. p. 177°, from ethanol–ether

(Found: S, 13·35. $C_{24}H_{22}O_5N_2S_2$ requires S, 13·2%). Its ethanolic solution gave a purple precipitate with triethylamine which resinified on attempted purification.

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