Compounds containing Sulphur Chromophores. Part IV. Derivatives of Heterocyclic Methylene Bases.*

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The synthesis of a series of substituted 2-methylene derivatives of 3-methylbenzothiazoline and of 1 : 2-dihydro-1-methylquinoline is described. Sulphur is readily removed from the 2-benzoylthiomethylene derivatives in alcoholic triethylamine, yielding the 2-phenacylidene analogues.

The stabilities of such sulphides in which a $+M$ and a $-M$ group are linked by a sulphur atom are compared with those of related compounds and are correlated with structures.

The absorption spectra of these compounds provide evidence that a sulphur atom may utilize its *d*-orbitals and function as a resonance transmitter, although it is not equivalent to a vinylene group. An oxygen atom may behave in the same way.

PRECEDING Parts * recorded unsuccessful attempts to synthesise compounds designed to show whether sulphur could function as a chromophoric atom, *i.e.*, a resonance transmitter. The present paper describes the synthesis of non-ionic sulphides (of type VI in Part I), derivatives of heterocylic methylene bases, and related compounds required for comparison of absorptions.

First, when it was believed that the sulphide (XV, of Part I) had been obtained it was of interest to prepare its isomer (III; X = S) in which the ·S·CH⁚ group was replaced by ⁚CH·S·. Condensation of 2-bromomethylbenzothiazole with potassium thiolbenzoate gave 2-benzoylthiomethylbenzothiazole (I; X = S). Removal of methyl hydrogen sulphate from the salt (II; X = S) at room temperature by triethylamine yielded the bright yellow 2-benzoylthiomethylene-3-methylbenzothiazoline, which, if the octet of the chain-sulphur atom expands, may be represented by the hybrid (III*a* $\longleftrightarrow$ *b*; X = S). The yellow colour of its solutions is discharged by mineralacid but not by acetic acid. This compound decomposes to a pale yellow tar with the evolution of hydrogen sulphide at

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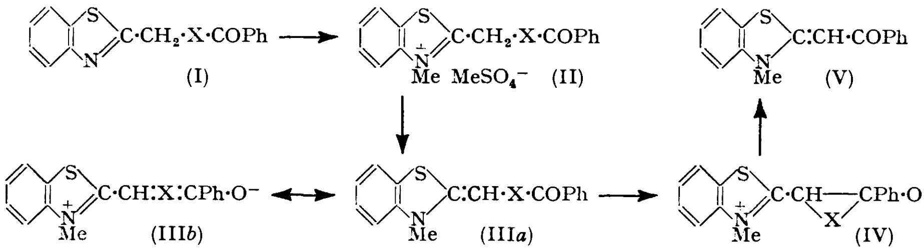
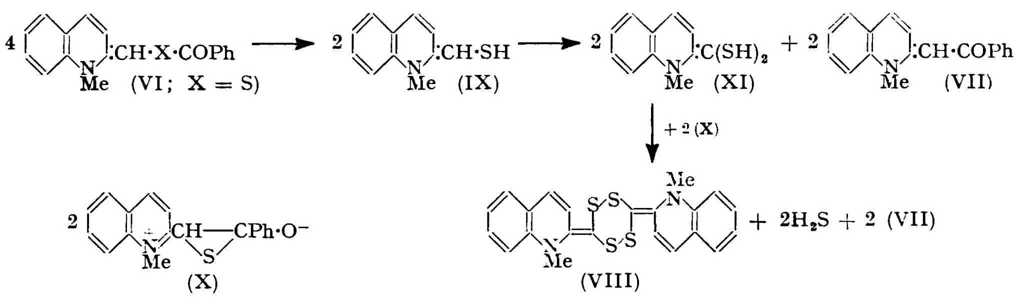
* Parts I—III, preceding papers.

20—25° during 7 days, and in boiling alcoholic triethylamine rapidly gives 3-methyl-2-phenacylidenebenzothiazoline (V), in 80% yield, and a bright orange solid of high sulphur content. As suggested in earlier parts, intermediate formation of the episulphide (IV; X = S) is a possible step in the decomposition.



Similar reactions gave the orange-coloured 2-benzoylthiomethylene-1 : 2-dihydro-1-methylquinoline (VI; X = S), which was also decomposed by alcoholic triethylamine to give 1 : 2-dihydro-1-methyl-2-phenacylidenequinoline (VII), in 53% yield, and a compound $(C_{11}H_9NS_2)_x$. The latter is very insoluble and its molecular weight has not been determined. It is insoluble in alkali and cannot, therefore, be the dithiol (XI). It is only the second compound (see Part I), isolated from such a desulphurization, which has been formed by the reaction of the starting material, or of a reaction product, with the sulphur liberated in the main reaction. This compound is probably (VIII), its stability ruling out a linear tetrasulphide structure. It may be formed by addition of sulphur to the hydrolysis product (IX) [from (VI; X = S)] by way of the episulphide (X) to give the dithiol (XI), followed by the oxidation of the last by more episulphide to give (VIII) and hydrogen sulphide. Such oxidation resulting in disulphide formation in the absence of atmospheric oxygen has been recorded in Parts I and II. Alternatively the thiol (IX) may have been oxidized to its disulphide before addition of sulphur occurred.



For comparison of absorptions the compounds related to (III; X = S) in which the chain-sulphur atom was replaced by an oxygen atom or a vinylene group were required. 2-Benzoyloxymethylbenzothiazole (Zubarowski, *J. Gen. Chem. U.S.S.R.*, 1951, **21**, 2055) gave the methyl sulphate (II; X = O), and thence an oil, presumably (III; X = O), on treatment with a base. The oil, which could not be distilled without decomposition, did not give the ketone (V) with boiling alcoholic triethylamine. This difference between the behaviour of (III; X = S) and (III; X = O) may indicate a greater resistance of the latter to formation of the epoxide (IV; X = O) or a higher stability of the hypothetical epoxide. Alternatively it may indicate that the expansion of the sulphur electron octet is instrumental in episulphide formation by a form of " short circuit " mechanism which may be depicted as (III*b*; X = S) ⟶ (IV; X = S).

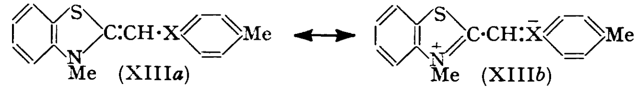
A very dilute alcoholic solution of 2-benzoyloxymethyl-1-methylquinolinium (methyl sulphate) (obtained from 2-bromomethylquinoline) with triethylamine gave a strong yellow colour believed to be due to the liberation of the base (VI; X = O). In more concentrated solution this initial colour faded rapidly as a pink solid was precipitated. The latter darkened in light and was converted into a purple dye on fusion or when heated with alcoholic triethylamine. It gave the correct analysis for (VI; X = O), but its high melting point, lack of colour, and low solubility in organic solvents are more consistent with its being the isomeric, mesoionic epoxide analogous to (X).

Condensation of 2 : 3-dimethylbenzothiazolium toluene-*p*-sulphonate with sodium hydroxymethyleneacetophenone gave 2-3′-benzoylallylidene-3-methylbenzothiazoline (III; X = ·CH:CH·), but the quinoline analogue could not be isolated in a pure form.

For comparison of the absorption of (III; X = S) with that of compounds containing the same fragments on either side of the chain-sulphur atom, phenacyl thiolbenzoate (XII)

Ph·CO·CH_2·S·CO·Ph

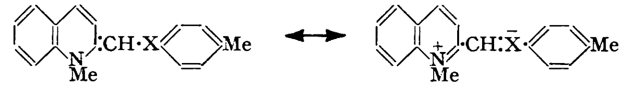
(XII)


(XIII*a*) (XIII*b*)

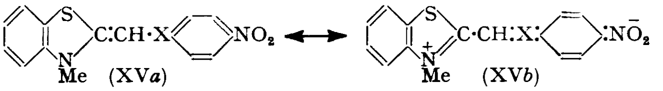
and 3-methyl-2-*p*-tolylthiomethylenebenzothiazoline (XIII*a*; X = S) were prepared. The latter was obtained by the condensation of 2-bromomethylbenzothiazole with *p*-thiocresol to give 2-*p*-tolylthiomethylbenzothiazole which was quaternized and then treated with triethylamine. For further spectrographic comparisons 3-methyl-2-*p*-tolyloxymethylenebenzothiazoline (XIII*a*; X = O) was obtained as a light-sensitive powder by reactions analogous to those employed for preparation of (XIII*a*; X = S).

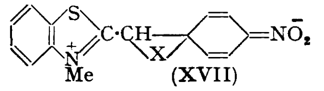
The 1 : 2-dihydroquinoline analogues (XIV*a*; X = S or O) were prepared similarly.

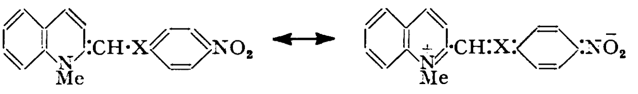
The second type of sulphide required is represented by 3-methyl-2-*p*-nitrophenylthiomethylenebenzothiazoline (XV*a*; X = S), the synthesis of its isomer (XLII of Part I) having proved unsuccessful. By a procedure analogous to that used for (XIII*a*) the required sulphide was obtained as stable, orange crystals.

(XIV*a*)

(XIV*b*)

The related 1 : 2-dihydro-1-methyl-2-*p*-nitrophenylthiomethylenequinoline (XVI*a*; X = S) was obtained similarly, as were also the analogous 2-*p*-nitrophenoxy-analogues (XV*a*, XVI*a*; X = O).


(XV*a*) (XV*b*)


(XVII)

(XVI*a*)

(XVI*b*)

There is considerable evidence (for references see Part I; also Koch and Moffitt, *Trans. Faraday Soc.*, 1951, **47**, 7; Bordwell and Cooper, *J. Amer. Chem. Soc.*, 1952, **74**, 1058) that a sulphone sulphur atom may expand its electron octet and function as a $+M$ rather than a $+I$ group. A variation of the present type of methylene base was therefore synthesized in order to substantiate this evidence. 2-Bromomethylquinoline and sodium toluene-*p*-sulphinate gave 2-*p*-tolylsulphonylmethylquinoline, which was treated with methyl sulphate. The resulting salt with triethylamine yielded the yellow 1 : 2-dihydro-1-methyl-2-*p*-tolylsulphonylmethylenequinoline (XIV; X = SO_2). The benzothiazoline analogue (XIII; X = SO_2) was obtained similarly. Both these compounds appear, from models, to be planar.

The Stabilities of the Above Sulphides and Those of Parts I, II, *and* III.—In most cases it has been shown that the instability of these sulphides is associated with the loss of the chain sulphur-atom and the formation of an unsaturated resonator. If episulphide formation is a necessary step in this decomposition, then the greater the energy difference between any sulphide and its episulphide the more stable will the sulphide be.

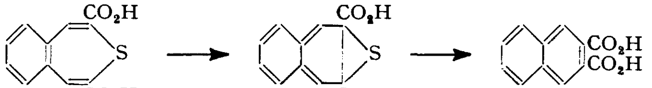
If the isomeric pairs (III; X = S) and (XV of Part I) are first considered, then the isomerization of the former to give the mesoionic (IV; X = S) requires the energy of charge separation. A similar change in (XV, Part I) to give (XXXI, Part I), however, involves charge neutralization to give a non-ionic molecule. The actual higher stability of (III ; X = S) over (XV of Part I) would therefore be expected.

Similarly, whereas the isomerization of (XV ; X = S) to (XVII ; X = S) requires the energy of charge separation and results in the loss of Kekulé resonance in the phenylene group the similar isomerization of its isomer (XLII, Part I) to (XLIV, Part I) results in a charge neutralization and a gain in Kekulé resonance. The stability of (XV ; X = S) and the instability of (XLII, Part I) is in agreement with this. It also explains why the higher stability of (XV ; X = S) exceeds that of (III ; X = S).

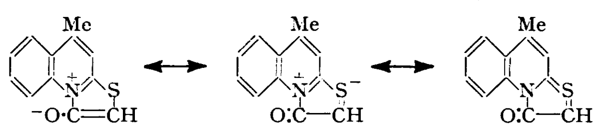
The inability to prepare (XV, Part II) compared with the ease of formation of (III ; X = S) is also explicable. It is known that the $+M$ effect of a 3-substituted rhodanine nucleus is greater than that of a benzoyl group, as is shown by the higher nucleophilic reactivity of the $C_{(5)}$-atom of a rhodanine compared with that of the methyl group of acetophenone. Consequently (XV, Part II) should isomerize more readily to (XVI, Part II) than will (III ; X = S) to (IV ; X = S).

The high stability of the base (X ; Part III) compared with (III ; X = S) may also be explained similarly on the basis of the greater $+M$ effect of the benzoyl group compared with that of the 2-benzothiazolyl group. The quaternization of (X, Part III) to give (IV, $n = 0$; Part III) reverses the above conditions since the $+M$ effect of the positively charged 3-alkylbenzothiazolium nucleus is here considerably greater than that of a benzoyl group. The formation of the episulphide (VI ; $n = 0$; Part III) is thus greatly facilitated and (IV ; $n = 0$; Part III) is too unstable to exist.

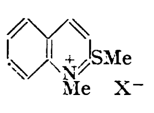
From the above it is clear that the stability of open-chain sulphides of the type in which one bond is attached to a $-M$ group and the other to a $+M$ group will decrease as the strength of the M effects of these groups increases. If the assumption is made that the sulphur atom can function as a resonance transmitter, then only compounds with an energetically highly asymmetric resonance system can be stable. When the sulphur atom is part of a cyclic system, and when the two atoms attached to the sulphur atom can no longer approach one another sufficiently closely for bond formation between them to occur, then a stable compound would be expected irrespective of the degree of energetic asymmetry of its resonance system. Scott (*J. Amer. Chem. Soc.*, **1953**, **75**, 6332) has, however, shown that 4 : 5-benzothiepin-2 : 7-dicarboxylic acid (XVIII), whilst stable in the solid state, readily decomposes in aqueous alcohol, or on fusion, to give naphthalene-2 : 3-dicarboxylic acid (XX) and sulphur (nacreous ?). He states that, from models, the 7-membered ring is not planar. This would facilitate the approach of the carbon atoms attached to the sulphur atom and the consequent decomposition, possibly through the episulphide (XIX).



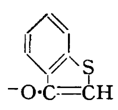
(XVIII) (XIX) (XX)



(XXI*a*) (XXI*b*) (XXI*c*)



(XXII)



(XXIII)

The Absorption Characteristics of Sulphides containing Conjugated M *Groups.*—(a) *Anhydro-(4-methyl-2-quinolylthio)acetic acid* (XXI) (Duffin and Kendall, *J.*, **1951**, **734** ; see also Part I). The broad absorption band in the blue region (Fig. 1) is somewhat sensitive to changes in solvent polarity (Table 1). This sensitivity is an indication that the resonance

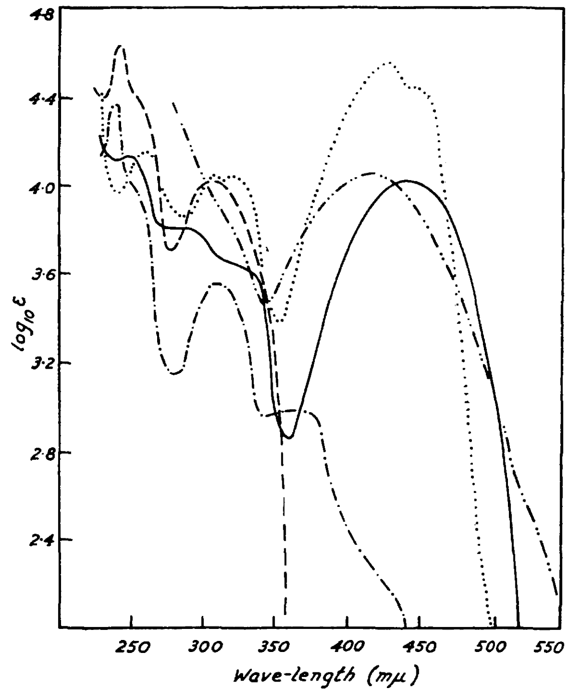
TABLE 1. *The absorption of the compound in various solvents.*

	C_6H_6	Pyridine	$CHCl_3$	$COMe_2$	MeOH	Aq. pyridine (1 : 1)
$\lambda_{max.}$ (mμ)	465	460	455	450	445	445
og ε	3·9	3·96	3·96	4·02	4·02	4·02

system responsible for the absorption in the long-wave-length band is of the charge-separation type represented by (XXI*a* ⟷ *c*) and not of the charge-transfer type (XXI*a* ⟷ *b*). The direction of the shift of $\lambda_{max.}$ indicates that the dipolar extreme structure (XXI*a*) is of lower energy than the non-polar structure (XXI*c*) (cf. Förster, *Z. Elektrochem.*, 1939, **45**, 572; Brooker, Keyes, Sprague, Van Dyke, Van Lare, Van Zandt, White, Crossman, and Dent, *J. Amer. Chem. Soc.*, 1951, **73**, 5332; Knott, *J.*, 1951, 3038) but the accompanying hyperchromic shift is the reverse of that expected.

The fragments of (XXI) on either side of the sulphur atom are contained in the 1-methyl-2-methylthioquinolinium salt (XXII) and in the anion (XXIII) of thioindoxyl.

FIG. 1. *Absorption in methanol of the compound* (XXI) *and related compounds.*



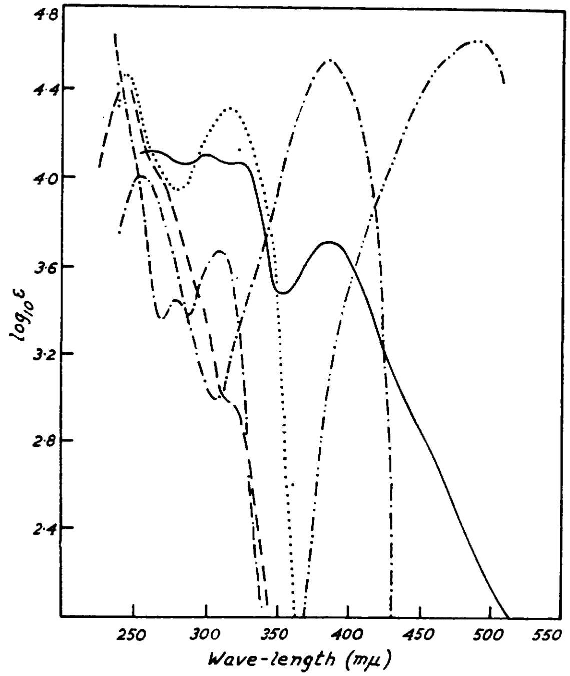
		$\lambda_{max.}$ (mμ), log ε (in parentheses), i = inflexion.
———	Anhydro-(4-methyl-2-quinolylthio)acetic acid (XXI)	250(4·14), 292(3·81), 325i(3·62), 445(4·02)
- - - - -	1-Methyl-2-methylthioquinolinium toluene-*p*-sulphonate (XXII)	243(4·64), 307(4·02)
. . . . .	1 : 2-Dihydro-1-methyl-2-phenacylidenequinoline (VII)	262(4·16), 311(4·04), 321(4·04), 414i(4·44), 430(4·56), 451(4·45)
— · —	Thioindoxyl anion (XXIII)	241(4·37), 310(3·55), 367(3·1)
— · · —	2-Benzoylthiomethylene-1 : 2-dihydro-1-methylquinoline (VI; X = S)	420(4·05)

Their absorption curves (Fig. 1) clearly show that neither fragment in itself is responsible for the long-wave-length band of (XIX) and confirm the occurrence of an interaction (XXI*a* ⟷ *c*) between the two fragments through the sulphur atom. Analogues of (XXI) in which the sulphur atom is replaced by an oxygen atom or vinylene group have not been synthesized but comparison with 1 : 2-dihydro-1-methyl-2-phenacylidenequinoline (VII) indicates that the sulphur atom is in no way equivalent to a vinylene group as a chromophore. The closest relative of (XXI) so far obtained is 2-benzoylthiomethylene-1 : 2-dihydro-1-methylquinoline (VI; X = S) and, as Fig. 1 shows, there is a certain resemblance between their curves. Since the structural relation between these two compounds becomes closer with greater tendency of the sulphur atoms to conjugate, the similarity of the curves may again be an indication of such conjugation.

(b) *2-Benzoylthiomethylene-3-methylbenzothiazoline* (III; X = S). The position of the long-wave-length band (Fig. 2) is practically insensitive to changes in solvent polarity. It is the same as for 3-methyl-2-phenacylidenebenzothiazoline (V; R = Me) which is also a decomposition product of (III; X = S). However, since this band of (III; X = S) fades it cannot be due to the presence of this stable decomposition product and must be considered to be a characteristic band of (III; X = S).

Because of the difficulty in purification, the absorption of 2-benzoyloxymethyl-3-methylbenzothiazoline (III; X = O) was measured on solutions obtained by treating the solution or suspension of its salt (II; X = O) with a base.* In methanol (Fig. 2) it showed the long-wave-length band at considerably shorter wave-length than that of the analogous band of (III; X = S). The curves for these compounds clearly show the bathochromic effect of proceeding from (III; X = O) to (III; X = S), an indication of conjugation through the sulphur atom in the latter compound.

FIG. 2. *Absorption in methanol of the sulphide* (III) *and related compounds.*



———	2-Benzoylthiomethylene-3-methylbenzothiazoline (III; X = S)	260(4·13), 295(4·13), 320(4·09), 385(3·72)
-----	Phenacyl thiolbenzoate (XII)	238(4·44), 263i(2·99)
.....	3-Methyl-2-*p*-tolylthiomethylenebenzothiazoline (XIII; X = S)	238(4·45), 314(4·32)
—•—	3-Methyl-2-phenacylidenebenzothiazoline (V)	250(4·01), 382(4·56)
—••—	2-3′-Benzoylallylidene-3-methylbenzothiazoline (III; X = ·CH:CH·)	481(4·66)
---•--	2-Benzoyloxymethylene-3-methylbenzothiazoline (III; X = O)	275(3·45), 307(3·67)

The replacement of the chain-sulphur atom of (III; X = S) by a vinylene group to give 2-3′-benzoylallylidene-3-methylbenzothiazoline (III; X = ·CH:CH·) results in very strong bathochromic and hyperchromic shifts (Fig. 2). This is striking evidence of the resistance offered by the sulphur atom to the passage of an electron through its *d*-orbitals.

The fragments on either side of the chain-sulphur atom of (III; X = S) are contained in 3-methyl-2-*p*-tolylthiomethylenebenzothiazoline (XIII; X = S) and phenacyl thiolbenzoate (XII). A comparison of their absorption curves with that of (III; X = S) shows

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* The same procedure was adopted for absorption measurements on (VI, XIII*a*, XIV*a*, and XV*a* X = O).

that the long-wave-length band of the latter must be ascribed to the system (III*a* ⟷ *b*; X = S) in which the sulphur *d*-orbitals are utilized.

(c) 2-*Benzoylthiomethylene*-1 : 2-*dihydro*-1-*methylquinoline* (VI; X = S). The absorption curves in benzene, *cyclo*hexane (Table 2), acetone, or ethyl acetate are almost identical, but in methanol strong hypsochromic and hypochromic shifts result, probably because of some chemical interaction with the solvent. The analogue in which the sulphur atom has been replaced by a vinylene group could not be obtained pure. Comparison of the curve of (VI; X = S) with that of its sulphur-free analogue, 1 : 2-dihydro-1-methyl-2-phenacylidenequinoline (VIII), shows the non-equivalence of the sulphur atom and a vinylene group.

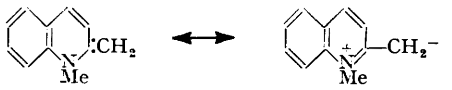
Comparison of the curve for (VI; X = S) with that for 1 : 2-dihydro-1-methyl-2-*p*-tolylthiomethylenequinoline (XIV*a*; X = S) indicates that conjugation through the sulphur atom of the former occurs. Here, but not in the benzothiazoline series, however, such conjugation is manifested by a broadening of the long-wave-length band accompanied by a hyperchromic shift and not by the appearance of a new band. This through-conjugation is also shown by bathochromic and hyperchromic shifts in the curves on proceeding from 2-benzoyloxymethylene-1 : 2-dihydro-1-methylquinoline (VI; X = O) to (VI; X = S).

TABLE 2. *Absorption in* cyclo*hexane of the compound* (VI) *and related compounds.*

2-Benzoylthiomethylene-1 : 2-dihydro-1-methylquinoline (VI; X = S)	273(4·5), 308i(3·88), 321i(3·76), 410(4·07)
1 : 2-Dihydro-1-methyl-2-*p*-tolylthiomethylenequinoline (XIV; X = S)	280(4·32), 305i(4·15), 405(3·97)
1 : 2-Dihydro-1-methyl-2-phenacylidenequinoline (VII)	330(4·1), 410(4·39), 429(4·42), 453i(4·15)
1 : 2-Dihydro-1-methyl-2-methylenequinoline (XXIV)	283i(3·89), 317(3·63), 330(3·56), 389(3·6)
2-Benzoylmethylene-1 : 2-dihydro-1-methylquinoline (VI; X = O)	345(3·77), 410(3·82)
1 : 2-Dihydro-1-methyl-2-*p*-tolyloxymethylenequinoline (XIV; X = O)	406(3·73)

Table 2 also shows the absorption curve of 1 : 2-dihydro-1-methyl-2-methylenequinoline, the long-wave-length band being ascribed to the resonance system (XXIV*a* ⟷ *b*). As in the benzothiazoline series (unpublished work) the replacement of the methylene group by a 2-*p*-tolylthiomethylene group (to give XIV; X = S) results in a strong hyperchromic shift. In this case, however, an appreciable bathochromic shift also occurs. This indicates that this band of (XIV; X = S) may be ascribed to the resonance system(XIV*a* ⟷ *b*; X = S) involving an expansion of the sulphur electron octet.

(XXIV*a*)



(XXIV*b*)

It is also noteworthy that similar, but smaller, bathochromic and hyperchromic shifts result on passing from (XXIV) to the *p*-tolyloxy-derivative (XIV; X = O). Such a shift was not observed in the benzothiazoline series. Whether this implies that the presence of the tolyloxy-group decreases the energetic asymmetry of the system (XXIV*a* ⟷ *b*) by virtue of its +*I* effect, or that the system (XIV*a* ⟷ *b*; X = O), involving the oxygen *d*-orbitals, is in operation, is not known. Since the +*I* effect of sulphur is weaker than that of oxygen the larger shift shown by the introduction of the *p*-tolylthio-group compared with that of the *p*-tolyloxy-group confirms the origin of the long-wave-length band of (XIV; X = S).

(d) 3-*Methyl*-2-p-*nitrophenylthiomethylenebenzothiazoline* (XV; X = S). It has not been found possible to synthesize the related compound in which the chain-sulphur atom is replaced by a vinylene group. The lower vinylogue of the latter, 3-methyl-2-*p*-nitrobenzylidenebenzothiazoline (Part I) already shows, however (Table 3), by its longer-wave-length band that the chain-sulphur atom of (XV; X = S) is not effectively conjugated.

The compounds used for comparison (see Table 3) are 3-methyl-2-*p*-tolylthiomethylenebenzothiazoline (XIII; X = S) and *p*-methylthionitrobenzene. The peaks of (XV; X = S) at 325 mμ and of (XIII; X = S) at 314 mμ are probably due to the resonance systems (XIII*a* ⟷ *b*). The long-wave-length band of *p*-methylthionitrobenzene does not appear in the spectrum of (XV; X = S) although it probably contributes to the band with the peak at 325 mμ. The inflexion at 415 mμ in the band of (XV; X = S) cannot be due to a simple displacement of the band of the the *p*-nitrophenylthio-group since it lies at a considerably lower intensity. The largest bathochromic displacement of the curve of the *p*-nitrophenylthio-group would be given by its anion which also has its $\lambda_{max.}$ at 415 mμ (Table 3) but at a considerably higher intensity than that of the inflexion of (XV; X = S).

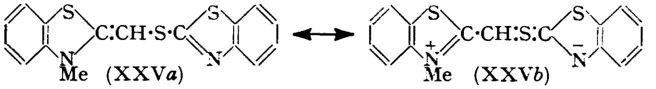
TABLE 3. *Absorption in methanol of the compound* (XV; X = S) *and related compounds.*

3-Methyl-2-*p*-nitrophenylthiomethylenebenzothiazoline (XV; X = S)	234(4·43), 325(4·42), 415(3·45)
3-Methyl-2-*p*-tolylthiomethylenebenzothiazoline (XIII; X = S)	238(4·45), 314(4·32)
3-Methyl-2-*p*-nitrobenzylidenebenzothiazoline	485(4·47)
p-Methylthionitrobenzene	341(4·1)
p-Nitrothiophenoxide ion	415(4·16)

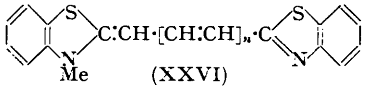
It is concluded, therefore, that this inflexion is, approximately, the peak of a new band arising from the system (XV*a* ⟷ *b*; X = S) in which the sulphur *d*-orbitals are engaged.

Brooker (Amer. Chem. Soc. Meeting, Autumn, 1937) prepared a dinitro-analogue of (XV; X = S) by the condensation of a 3-ethyl-2-methylbenzothiazolium salt with 2 : 4-dinitrobenzenesulphenyl chloride in pyridine and compared its absorption with that of the related compound in which the chain-sulphur atom was replaced by a vinylene group. The former has peaks at *ca.* 317 mμ (4·43) and *ca.* 472 (3·7) whilst the latter has a peak at *ca.* 583 mμ (4·2). From this Brooker concluded that this replacement substantially destroyed the main resonance system.

(e) 2-*Benzothiazol*-2′-*ylthiomethylene*-3-*methylbenzothiazoline* (XXV). Table 4 describes the absorption curves of this planar compound (Part III) with those for the related compounds in which the sulphur atom has been replaced by a vinylene group, as in (XXVI; *n* = 1),



(XXV*a*) (XXV*b*)



(XXVI)

TABLE 4. *Absorption in methanol of compound* (XXV) *and related compounds.*

2-Benzothiazol-2′-ylthiomethylene-3-methylbenzothiazoline (XXV)	226(4·52), 236(4·54), 272(4·18), 318i(4·45), 326(4·49)
3-Methyl-2-*p*-tolylthiomethylenebenzothiazoline (XIII; X = S)	238(4·45), 314(4·32)
2-Benzothiazol-2′-ylmethylene-3-methylbenzothiazoline (XXVI; *n* = 0)	382(4·7), 395(4·7) *
2-3′-(Benzothiazol-2-yl)allylidene-3-methylbenzothiazoline (XXVI; *n* = 1)	451(4·73) †

Hamer (*J.*, 1940, 799) gives * 397(383i) mμ and † 455 mμ in methanol.

or eliminated, as in (XXVI; *n* = 0). This set again shows clearly how the chain-sulphur atom, by increasing the energetic asymmetry of the resonance system, causes hypsochromic and hypochromic shifts. A comparison of the absorption of (XXV) with that of 3-methyl-2-*p*-tolylthiomethylenebenzothiazoline (XIII; X = S) indicates a rather weak conjugation effect through the chain-sulphur atom. This is consistent with the weak +*M* effect of the benzothiazolyl group.

(f) 3-*Methyl*-2-p-*tolylsulphonylmethylenebenzothiazoline* (XIII; X = SO_2) *and* 1 : 2-*dihydro*-1-*methyl*-2-p-*tolylsulphonylmethylenequinoline* (XIV; X = SO_2). The absorptions of these sulphones in *cyclo*hexane are shown in Table 5 together with those of the related sulphides (XIII; X = S) and (XIV; X = S). In both cases the intensity of the long-wave-length band of the sulphone is higher than that of the related sulphide. In the

TABLE 5. *Absorption in* cyclo*hexane of the sulphone* (XVII) *and related compounds.*

3-Methyl-2-*p*-tolylsulphonylmethylenebenzothiazoline (XIII; X = SO_2)	329(4·53)
3-Methyl-2-*p*-tolylthiomethylenebenzothiazoline (XIII; X = S)	314(4·26)
1 : 2-Dihydro-1-methyl-2-*p*-tolylsulphonylmethylenequinoline (XIV; X = SO_2)	269(4·18), 293(4·82), 388(4·12)
1: 2-Dihydro-1-methyl-2-*p*-tolylthiomethylenequinoline (XIV; X = S)	280(4·32), 305i(4·15), 405(3·97)

benzothiazoline series there is also a slight increase in $\lambda_{max.}$ but a sharper falling-off on the long-wave-length side. In the dihydroquinoline pair, however, the long-wave-length band of the sulphone is displaced hypsochromically from that of the sulphide.

Although the greater intensity for both sulphones may indicate contributions by structures such as (XIV*b*; X = SO_2), involving the sulphur *d*-orbitals, the accompanying hypsochromic shifts are the reverse of what would be expected. It is possible that these anomalous shifts are the result of an increase in the energetic asymmetry of the molecules on proceeding from the sulphide to the sulphone. Although such a change invariably results in a hypochromic shift (cf. Brooker *et al.*, *J. Amer. Chem. Soc.*, 1951, **73**, 5332, 5350) when it is produced by a change in solvent polarity, in the present case an accompanying hyperchromic shift would be present as a result of the increase in the length of the conjugated path.

Such an increase in asymmetry could be brought about if the sulphone-oxygen atoms could not be freely accommodated without interference from the thiazole sulphur atom or the 3-hydrogen atom of the quinoline ring. There appears, however, from scale models, to be sufficient space available for the oxygen atoms on either side of these ring atoms.

The asymmetry would also be greater if the increase in the $+M$ effect of the anti-auxochrome on moving from –S– to $-SO_2-$ were sufficiently great to make the polar extreme structure (*b*) of lower energy than the non-polar extreme structure (*a*). This would be more likely to occur in (XIV; X = SO_2) than in (XIII; X = SO_2) because of the higher $-M$ effect of the dihydroquinoline nucleus. Then the absorption of the sulphones should shift hypsochromically with increasing solvent polarity. This has been found to be the case although the shifts of $\lambda_{max.}$ on changing from *cyclo*hexane to methanol as solvent are extremely small (5 mμ).

EXPERIMENTAL

2-3′-*Benzoylallylidene*-3-*methylbenzothiazoline* (III; X = ·CH:CH·).—2 : 3-Dimethylbenzothiazolium toluene-*p*-sulphonate (3·35 g., 0·01 mole), sodium hydroxymethyleneacetophenone (2·5 g., 0·015 mole), and methanol (20 c.c.) were refluxed together for 10 min. An orange colour developed immediately and a solid *product* separated (1·8 g., 61·5%), forming orange-yellow needles, m. p. 168°, from benzene–light petroleum (b. p. 60—80°) (Found: N, 4·5; S, 11·05. $C_{18}H_{15}ONS$ requires N, 4·3; S, 10·9%).

2-*Benzoylthiomethylbenzothiazole* (I; X = S).—2-Bromomethylbenzothiazole (Zubarowski, *J. Gen. Chem. U.S.S.R.*, 1951, **21**, 2055) (2·3 g., 0·01 mole), potassium thiolbenzoate (1·8 g., 0·01 mole), and ethanol (20 c.c.) were heated together on a steam-bath for 5 min. Water (75 c.c.) was slowly run in, precipitating the *ester* which was collected after chilling and washed with water (yield, 2·5 g., 86%) and formed colourless flakes, m. p. 76—77°, from ethanol (Found: N, 4·9; S, 22·6. $C_{15}H_{11}ONS_2$ requires N, 4·9; S, 22·45%).

2-*Benzoylthiomethyl*-3-*methylbenzothiazolium* (*methyl sulphate*) (II; X = S) was obtained in 86% yield by heating the ester (I; X = S) (1·4 g.) with methyl sulphate (0·5 c.c.) for 1—2 min on the steam-bath. The whole solidified when seeded, otherwise solidification was induced by the addition of a little hot acetone to the resultant tar. The salt formed pale yellow flakes, m. p. 164—166°, from ethanol–ether (Found: N, 3·6; S, 23·6. $C_{17}H_{17}O_5NS_3$ requires N, 3·4; S, 23·35%).

2-*Benzoylthiomethyl*-3-*ethylbenzothiazolium* (*ethyl sulphate*) was obtained in 50% yield by similar use of diethyl sulphate (0·65 c.c.) (2 hr.). The tar crystallised as cream-coloured flakes, m. p. 166°, from ethanol (Found: N, 3·25; S, 22·1. $C_{19}H_{21}O_5NS_3$ requires N, 3·2; S, 21·85%).

2-*Benzoylthiomethylene*-3-*methylbenzothiazoline* (III; X = S).—The salt (II; X = S) (2·05 g., 0·005 mole) in methanol (10 c.c.) was treated at 25° with triethylamine (0·8 c.c., 0·005 mole). An intense yellow colour developed, followed by immediate crystallization of the *compound* (1·25 g., 83%), which formed yellow flakes, m. p. 117° (orange melt), from ethanol or light petroleum (b. p. 60—80°) (Found: C, 64·4; H, 4·3; N, 4·65; S, 21·2. $C_{16}H_{13}ONS_2$ requires C, 64·2; H, 4·35; N, 4·7; S, 21·4%). When it (0·2 g.) was refluxed for 10 min. with ethanol (5 c.c.) and triethylamine (0·1 c.c.) a red, microcrystalline solid separated (Found: S, 55·6%). The filtered solution on chilling gave an 81% yield of 3-methyl-2-phenacylidenebenzothiazoline (V), m. p. and mixed m. p. 176° (Found: S, 12·1. Calc. for $C_{16}H_{13}ONS$: S, 12·0%).

2-Benzoylthiomethylene-3-ethylbenzothiazoline was obtained in 88% yield as yellow needles, m. p. 100—101°, from light petroleum (b. p. 60—80°) (Found: N, 4·45; S, 20·75. $C_{17}H_{15}ONS_2$ requires N, 4·45; S, 20·45%). It liquefied at 25° in 1 week with the evolution of hydrogen sulphide. It was stable at 0—5°.

2-Benzoyloxymethyl-3-methylbenzothiazolium (*Methyl Sulphate*) (II; X = O).—2-Benzoyloxymethylbenzothiazole (Zubarowski, *loc. cit.*) (2·2 g.) and methyl sulphate (1·0 c.c.), when heated together on a steam-bath for 2 mins., fused, then solidified. The *salt* (2·95 g., 75%) formed needles, m. p. 188°, from ethanol (Found: C, 51·4; H, 4·35; S, 16·3. $C_{17}H_{17}O_6NS_2$ requires C, 51·6; H, 4·3; S, 16·2%).

Its alcoholic solution on treatment with triethylamine gave an intense, blue colour. Addition of water then precipitated a pale yellow oil, presumably 2-benzoyloxymethylene-3-methylbenzothiazoline, which did not crystallize and decomposed on attempted distillation. Refluxing it with alcoholic triethylamine did not give a crystalline product.

2-Benzoylthiomethylquinoline.—2-Bromomethylquinoline (Brown, Hammick, and Thewlis, *J.*, 1951, 1145) (5·55 g.), potassium thiolbenzoate (4·5 g.), and ethanol (50 c.c.) were refluxed together on a steam-bath for 1 hr. The required *compound* was precipitated with water and recrystallized from a little ethanol. It (4·2 g., 75%) formed orange brown flakes, m. p. 76°, from light petroleum (b. p. 60—80°) (Found: N, 5·05; S, 11·65. $C_{17}H_{13}ONS$ requires N, 5·0; S, 11·5%).

2-Benzoylthiomethylene-1 : 2-dihydro-1-methylquinoline (VI; X = S).—2-Benzoylthiomethylquinoline (1·4 g.) and methyl sulphate (0·5 c.c.) were heated together on a steam-bath for 3 min. The resulting light brown tar of *2-benzoylthiomethyl-1-methylquinolinium* (*methyl sulphate*) was washed with ether and kept at 5° for several days to crystallize. It was washed with acetone-ether (2 : 1) and obtained in low yield as plates, m. p. 105°, from ethanol–ether (Found: N, 3·35; S, 16·0. $C_{19}H_{19}O_5NS_2$ requires N, 3·45; S, 15·8%).

The crude tar of quaternary salt was dissolved in ethanol (5 c.c.), and triethylamine (0·8 c.c.) was added at 20°. The solution became intensely yellow and solidified. The solid *dihydroquinoline* (0·8 g., 54·5%) was washed with a little ethanol and obtained as orange flakes, m. p. 102°, from light petroleum (b. p. 60—80°) (Found: N, 4·6; S, 10·95. $C_{18}H_{15}ONS$ requires N, 4·8; S, 10·9%). It darkened on exposure to light.

The base (2·2 g.) was refluxed in ethanol (50 c.c.) and triethylamine (1·5 c.c.) for 1 hr. Hydrogen sulphide was liberated and a crystalline precipitate formed which after chilling was washed with cold ethanol, the yellow filtrate and washings being united. The crystals (0·45 g.) formed brown needles, m. p. 239° (darkens at 227°), from pyridine–ethanol (Found: C, 60·25; H, 4·3; N, 6·45; S, 29·25. $C_{22}H_{18}N_2S_4$ requires C, 60·3; H, 4·1; N, 6·4; S, 29·2%). It is believed to be *3 : 6-di-(1 : 2-dihydro-1-methyl-2-quinolylidene)-1 : 2 : 4 : 5-tetrathia*cyclo*hexane* (VIII).

The yellow filtrates were diluted with water (200 c.c.) and chilled overnight. The crystalline precipitate (1·25 g.) was air-dried and obtained as orange needles (1·05 g., 53·5%), m. p. 112°, from light petroleum (b. p. 80—100°) (Found: C, 82·55; H, 5·55; N, 5·6. Calc. for $C_{18}H_{15}ON$: C, 82·75; H, 5·75; N, 5·35%). It is 1 : 2-dihydro-1-methyl-2-phenacylidenequinoline (VII) and gives no m. p. depression on admixture with a specimen prepared according to Vongerichten and Rotta's method (*Ber.*, 1911, **44**, 1419; they give m. p. 107—108°).

2-Benzoyloxymethylquinoline.—2-Bromomethylquinoline (13·8 g.), sodium benzoate (9 g.), ethanol (50 c.c.), and water (30 c.c.) were refluxed together on a steam-bath for 3 hr. Water (250 c.c.) was added, precipitating an oil which crystallized at 5° during 3 days. The sticky brown solid was washed with water by decantation and dissolved in hot light petroleum (b. p. 60—80°), and the solution was filtered and cooled to 25°, the solution being continuously freed from cloudiness by the addition of more petroleum. The *product* which separated during 24 hr. at room temperature was collected and the filtrate was concentrated. The cooling, clarification, and seeding were repeated. The total crop of yellowish needles, after four such concentrations, was 10·5 g., 61·0%. It formed needles, m. p. 50—51°, from petroleum (b. p. 60—80°) (Found: C, 77·4; H, 5·2; N, 5·2. $C_{17}H_{13}O_2N$ requires C, 77·5; H, 4·95; N, 5·3%).

2-Benzoyloxymethyl-1-methylquinolinium (*Methyl Sulphate*).—2-Benzoyloxymethylquinoline (1·35 g.) and methyl sulphate (0·5 c.c.) were fused together for 5 min. on a steam bath, the whole solidifying. The *salt* was dissolved in ethanol (20 c.c.), and ether (20 c.c.) was added to give crystals (1·45 g., 72·5%), which formed white needles, m. p. 147—148°, from ethanol (Found: N, 3·45; S, 8·05. $C_{19}H_{19}O_6NS$ requires N, 3·6; S, 8·2%). They were converted into a purple dye when refluxed in alcoholic triethylamine for 1 hr. The methyl sulphate (1·3 g.) was dissolved in methanol (50 c.c.), and triethylamine (0·5 c.c.) was added at 25°. An intense yellow colour developed which faded as a pink precipitate formed. The solid *substance* was collected after 5 min. and washed well with methanol and water. It (1·45 g.) darkened on exposure to light and had m. p. 155° (purple melt) (Found: C, 77·8; H, 5·7; N, 4·95. $C_{18}H_{15}O_2N$ requires C, 78·0; H, 5·4; N, 5·05%).

2-p-*Tolylthiomethylbenzothiazole*.—2-Bromomethylbenzothiazole (4·6 g., 0·02 mole) was added to a solution of potassium hydroxide (1·12 g., 0·02 mole) and *p*-thiocresol (2·5 g., 0·02 mole) in ethanol (50 c.c.), at 40°. Potassium bromide separated and the reaction was completed by heating the mixture for 5 min. on a steam-bath. The required *sulphide* separated as a yellow oil on addition of water (250 c.c.). It solidified under ether (yield, 5·1 g., 94%) and formed flat, colourless needles, m. p. 62—64°, from light petroleum (b. p. 60—80°) (Found: N, 5·25; S, 23·8. $C_{15}H_{13}NS_2$ requires N, 5·15; S, 23·6%). The base (1·35 g.) and methyl sulphate (0·5 c.c.) on a steam-bath (1 min.) gave the *metho*(*methyl sulphate*) (0·95 g., 48%), white threads, m. p. 140—141°, from ethanol–ether (Found: N, 3·35; S, 23·95. $C_{17}H_{19}O_4NS_3$ requires N, 3·5; S, 24·2%).

3-*Methyl*-2-p-*tolylthiomethylenebenzothiazoline* (XIII; X = S).—The above metho(methyl sulphate) (1·0 g.) was treated in methanol (5 c.c.), cooled to 20°, with triethylamine (0·4 c.c.). The *base* separated immediately as a colourless cake (0·65 g., 91·5%) and formed colourless needles, m. p. 127°, from light petroleum (b. p. 60—80°) (Found: C, 67·3; H, 5·3; N, 4·95; S, 22·75. $C_{16}H_{15}NS_2$ requires C, 67·4; H, 5·25; N, 4·9; S, 22·5%).

2-p-*Nitrophenylthiomethylbenzothiazole*.—Sodium *p*-nitrophenyl sulphide (1·8 g.) was dissolved in hot ethanol (25 c.c.), the solution was cooled, and 2-bromomethylbenzothiazole (2·3 g.) was added. The orange colour was discharged rapidly and a crystalline precipitate formed. If the solution was heated a blue colour appeared. Water (25 c.c.) was added and the ochre *product* collected. It (2·65 g., 87·5%) formed orange flakes, m. p. 131°, from ethanol (Found: N, 9·1; S, 21·3. $C_{14}H_{10}O_2N_2S_2$ requires N, 9·25; S, 21·2%). The base (1·5 g.) and methyl sulphate (0·5 c.c.) in boiling benzene (5 c.c.) (30 min.) gave the *metho*(*methyl sulphate*) (1·6 g., 75%), white threads, m. p. 184° (decomp.), from ethanol (Found: N, 6·4; S, 22·4. $C_{16}H_{16}O_6N_2S_3$ requires N, 6·55; S, 22·4%).

3-*Methyl*-2-p-*nitrophenylthiomethylenebenzothiazoline* (XV; X = S).—The above metho-(methyl sulphate) (1·07 g.) was dissolved in hot methanol (25 c.c.) and the solution cooled to 25°. Triethylamine (0·4 c.c.) was added causing an immediate orange precipitate, the colour of which immediately changed to a deep violet. The *base* (0·7 g., 88·5%) formed violet needles, m. p. 170°, from benzene–ethanol (Found: C, 57·1; H, 3·85; N, 8·6; S, 20·1. $C_{15}H_{12}O_2N_2S_2$ requires C, 57·0; H, 3·8; N, 8·85; S, 20·3%). When triethylamine was added to a suspension of the quaternary salt in ethanol orange crystals were obtained. When the solution of the violet threads in benzene–ethanol was seeded with the orange crystals a mixture of orange flakes and violet threads resulted. When a benzene solution of the violet threads was diluted with light petroleum and seeded with the orange flakes the whole crystallized as orange flakes, m. p. 170° (Found: C, 57·2; H, 3·75; N, 9·1; S, 20·45%). The latter were readily converted into violet threads by recrystallization from ethanol or benzene–ethanol. A mixture of the two forms melted at 170°.

2-p-*Tolyloxymethylbenzothiazole*.—Potassium hydroxide (0·56 g.) was dissolved in ethanol (15 c.c.), and *p*-cresol (1·1 g.) was added followed by 2-bromomethylbenzothiazole (2·3 g.). The whole was refluxed for 15 min. and the required *compound* was precipitated by the addition of water. It (2·25 g., 88%) formed colourless needles, m. p. 114—115°, from light petroleum (b. p. 60—80°) (Found: N, 5·5; S, 12·75. $C_{15}H_{13}ONS$ requires N, 5·5; S, 12·55%). The *metho*(*methyl sulphate*) formed very pale yellow needles, m. p. 154° (red melt), from ethanol–ether (Found: N, 3·6; S, 17·05. $C_{17}H_{19}O_5NS_2$ requires N, 3·7; S, 16·8%). Its solution in ethanol developed a blue colour on addition of triethylamine. Water then precipitated a pale yellow oil, presumably of 3-methyl-2-*p*-tolyloxymethylenebenzothiazoline (XIII; X = O) which could not be distilled without decomposition.

2-p-*Nitrophenoxymethylbenzothiazole* was obtained in 66·5% yield by the method used for the preparation of the *p*-tolyloxy-analogue, with *p*-nitrophenol (1·4 g.) replacing *p*-cresol. The compound formed small, colourless needles, m. p. 192°, from benzene (Found: N, 9·9; S, 11·35. $C_{14}H_{10}O_3N_2S$ requires N, 9·8; S, 11·2%). 3-*Methyl*-2-p-*nitrophenoxymethylbenzothiazolium* (*methyl sulphate*) was obtained by fusing the base (1·4 g.) and dimethyl sulphate (1·0 c.c.) at 130° for 10 min. The resultant tar was refluxed with benzene (10 c.c.) for 30 min., to give yellow grains which were dissolved in methanol (20 c.c.). Ether was slowly added to the solution to give a meal of yellow crystals (1·8 g., 87·5%). They formed yellow needles (changing to buff on exposure to light), m. p. 198° (violet melt), from methanol–ether (Found: N, 6·6; S, 15·7. $C_{16}H_{16}O_7N_2S_2$ requires N, 6·8; S, 15·55%). Addition of triethylamine to its alcoholic solution gave violet crystals, m. p. 149°, of 3-*methyl*-2-p-*nitrophenoxymethylenebenzothiazoline* (XV*a*; X = O) which decomposed on attempted recrystallization from benzene (Found: C, 60·2; H, 4·4; N, 9·1; S, 10·8. $C_{15}H_{12}O_3N_2S$ requires C, 60·0; H, 4·0; N, 9·35; S, 10·65%).

1 : 2-*Dihydro*-1-*methyl*-2-p-*tolylthiomethylenequinoline* (XIV; X = S).—To a solution of potassium hydroxide (1·12 g.) and *p*-thiocresol (2·5 g.) in ethanol (20 c.c.) was added 2-bromomethylquinoline (4·4 g.), and the solution was gently warmed. An exothermic reaction set in and potassium bromide was precipitated. Water precipitated a brown oil which was dissolved in ether; the solution was dried and evaporated. The residual oil was extracted with hot light petroleum (b. p. 60—80), and the solvent distilled from the extracts. The residual oil was not purified.

It (5·6 g.) and methyl sulphate (2 c.c.) were heated together on a steam-bath for 2 min. or until quaternization set in, and the resulting tar was boiled with benzene (20 c.c.) to remove any unchanged material. The thick brown oil was dissolved in ethanol (20 c.c.), and triethylamine (4 c.c.) added at 25°. The orange solution was chilled overnight and the yellow crystals which had separated (0·8 g., 14·3%) were washed with ethanol. This *base* formed yellow needles, m. p. 88—89°, from methanol (Found: N, 4·85; S, 11·5. $C_{18}H_{17}NS$ requires N, 5·0; S, 11·45%).

2-p-*Nitrophenylthiomethylquinoline*.—2-Bromomethylquinoline (3·8 g.) was added to a solution of sodium *p*-nitrothiophenol (3·0 g.) in ethanol (50 c.c.). The deep orange colour was discharged and a thick meal of crystals separated. The whole was refluxed for 15 min., then chilled, and crystalline *sulphide* was collected. It (4·05 g., 80%) formed buff needles, m. p. 118°, from ethanol (Found: N, 9·2; S, 10·65. $C_{16}H_{12}O_2N_2S$ requires N, 9·45; S, 10·8%). 1-*Methyl*-2-p-*nitrophenylthiomethylquinoline* (*methyl sulphate*), obtained in 40% yield (steam-bath; 5 min.), formed buff needles, m. p. 191°, from methanol–ether (Found: N, 6·45; S, 15·2. $C_{18}H_{18}O_6N_2S_2$ requires N, 6·65; S, 15·15%).

1 : 2-*Dihydro*-1-*methyl*-2-p-*nitrophenylthiomethylenequinoline* (XVI; X = S) was obtained by adding triethylamine (0·3 c.c.) to a solution of the above quaternary salt (0·75 g.) in methanol (10 c.c.). The deep orange precipitate solidified rapidly. It (0·475 g., 86·5%) formed orange flakes, m. p. 149°, from benzene–light petroleum (b. p. 60—80°) (Found: N, 8·9; S, 10·3. $C_{17}H_{14}O_2N_2S$ requires N, 9·05; S, 10·3%).

2-p-*Nitrophenoxymethylquinoline*, obtained in 73% yield by the method used for the benzothiazole analogue, formed white needles, m. p. 141—142°, from ethanol (Found: N, 9·8. $C_{16}H_{12}O_3N_2$ requires N, 10·0%). 1-*Methyl*-2-p-*nitrophenoxymethylquinolinium* (*methyl sulphate*), obtained in 76% yield, formed white needles, m. p. 192°, from methanol–ether (Found: N, 6·8; S, 8·05. $C_{18}H_{18}O_7N_2S$ requires N, 6·9; S, 7·9%). A dilute solution of this salt in ethanol developed an immediate orange colour with triethylamine. In more concentrated solutions the orange colour appeared momentarily on addition of triethylamine and was followed by the separation of a pink, light-sensitive solid. This was washed with methanol and water and dried in vacuum. 1 : 2-*Dihydro*-1-*methyl*-2-p-*nitrophenoxymethylenequinoline* (XVI*a*; X = O) formed a yellow powder, m. p. 136° (purple melt), darkening at 120° (Found: C, 69·0; H, 5·1; N, 9·1. $C_{17}H_{14}O_3N_2$ requires C, 69·3; H, 4·75; N, 9·5%).

2-p-*Tolyloxymethylquinoline* was obtained, as was the benzothiazole analogue, in 93% yield, as buff flakes, m. p. 94°, from ethanol (Found: N, 5·65. $C_{17}H_{15}ON$ requires N, 5·65%). 1-*Methyl*-2-p-*tolyloxymethylquinolinium* (*methyl sulphate*) (77% yield) formed white needles, m. p. 150—151°, from ethanol–ether (Found: N, 3·65; S, 8·55. $C_{19}H_{21}O_5NS$ requires N, 3·75; S, 8·55%). On its treatment in dilute alcohol with triethylamine a yellow colour developed; in more concentrated solution a light-sensitive solid, m. p. 108—112°, separated which decomposed on attempted recrystallization, namely, 1 : 2-*dihydro*-1-*methyl*-2-p-*tolyloxymethylenequinoline* (XIV*a*; X = O) (Found: C, 81·8; H, 6·45; N, 5·05. $C_{18}H_{17}ON$ requires C, 82·2; H, 6·45; N, 5·3%).

2-p-*Tolylsulphonylmethylbenzothiazole*.—2-Bromomethylbenzothiazole (4·6 g.), sodium toluene-*p*-sulphinate dihydrate (4·3 g.), and ethanol (25 c.c.) were refluxed for 15 min. The *sulphone* separated rapidly during this time. The solution was chilled and the crystals (4·15 g., 68·5%) were washed with water and ethanol. From ethanol they formed flat, colourless needles, m. p. 171—172° (Found: N, 4·76; S, 21·2. $C_{15}H_{13}O_2NS_2$ requires N, 4·65; S, 21·1%). The base (1·5 g.) and methyl sulphate (1·0 c.c.) in 10 min. on a steam-bath yielded 2·05 g. (95·5%) of 3-*methyl*-2-p-*tolylsulphonylmethylbenzothiazolium* (*methyl sulphate*), white flakes (from ethanol–ether), m. p. 189—191° (Found: N, 3·25; S, 22·4. $C_{17}H_{19}O_6NS_3$ requires N, 3·25; S, 22·4%).

3-*Methyl*-2-p-*tolylsulphonylmethylenebenzothiazoline* (XIII; X = SO_2).—The above quaternary salt (1·05 g.) was dissolved in methanol (10 c.c.), and triethylamine (0·4 c.c.) was added at

20°. The methylene *base* separated rapidly, was washed with ethanol, recrystallized from the same solvent, and obtained in 90% yield (0·7 g.) as white needles, m. p. 171° (Found : N, 4·4; S, 20·3. $C_{16}H_{15}O_2NS_2$ requires N, 4·4; S, 20·2%).

2-p-*Tolylsulphonylmethylquinoline*.—2-Bromomethylquinoline (1·1 g.), sodium toluene-*p*-sulphinate dihydrate (1·1 g.) and ethanol (10 c.c.) were refluxed together for 1 hr. Water (20 c.c.) was added and the buff needles (1·27 g., 85·5%) which separated were recrystallized from benzene–light petroleum (b. p. 60—80°). The *sulphone* formed almost colourless needles, m. p. 150—152° (Found : N, 4·7; S, 10·95. $C_{17}H_{17}O_2NS$ requires N, 4·7; S, 10·8%).

The base (1·5 g.) and methyl sulphate (1·0 c.c., 100% excess) were fused together on a steam-bath for 15 min. The solid, 1-*methyl*-2-p-*tolylsulphonylmethylquinolinium* (*methyl sulphate*) (1·9 g., 90%) recrystallized from ethanol–ether as white needles, m. p. 195° (softened at 185°) (Found : N, 3·5; S, 15·2. $C_{19}H_{21}O_6NS_2$ requires N, 3·3; S, 15·15%).

1 : 2-*Dihydro*-1-*methyl*-2-p-*tolylsulphonylmethylenequinoline* (XIV; $X = SO_2$).—The above quaternary salt (1·0 g.) was dissolved in methanol (5 c.c.), and triethylamine (0·4 c.c.) was added at 20°. The granular yellow precipitate (0·6 g., 82%) which separated rapidly was recrystallized, first from ethanol, then from benzene–light petroleum (b. p. 60—80°), and obtained as yellow grains, m. p. 159° (Found : N, 4·4; S, 10·25. $C_{18}H_{17}O_2NS$ requires N, 4·5; S, 10·3%).

Ultra-violet and visible absorption curves were determined in a Hilger Uvispek Spectrophotometer. The author thanks Mr. R. A. Jeffreys and Mrs. M. E. Weston for the preparation of certain intermediates, Mr. C. B. Dennis for analyses, and Mr. R. Searle for absorption measurements.

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