53. *The Constitution of the So-called Carbothialdines and the Preparation of some Homologous Compounds.*

By A. D. Ainley, W. H. Davies, H. Gudgeon, J. C. Harland, and W. A. Sexton.

Consideration of methods of formation lead to structure (VI; R = H, R′ = Me) for " carbothialdine " (or " thiuram carbomethyl ") and to (VI; R = Me, R′ = H) for the isomeric " dimethylformocarbothialdine " which is identical with " 2 : 4-dimethyl-2-methylenecarbothialdine." Absorption spectra are in accord with the proposed formulæ. The preparation of homologous compounds by interaction of formaldehyde with primary aliphatic amine salts of monoaryldithiocarbamic acids is described.

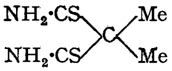
Although the reaction products of aldehydes with carbon disulphide and ammonia or primary amines have been known for nearly a century, none of the formulæ suggested for them is entirely satisfactory. The best known of the series, the reaction product of acetaldehyde, ammonia, and carbon disulphide, is " carbothialdine," which, despite its name, has not been shown to be related to the thialdines which are 1 : 3 : 5-dithiazines formed by the action of hydrogen sulphide on aldehyde-ammonias.

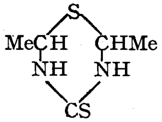
It appears to be generally agreed that the reaction of aldehydes ($R''\cdot CHO$) with carbon disulphide and primary amines or ammonia ($R'\cdot NH_2$) usually gives the same product as that obtained by reaction between the aldehyde and the dithiocarbamate $NHR'\cdot CS\cdot SH,NH_2R'$, and Levi (*Gazzetta*, 1931, **61**, 803) has shown that 2 mols. of aldehyde are involved in the reaction. He also showed (*ibid.*, 1930, **60**, 309) that potassium dithiocarbamates do not react with aldehydes.

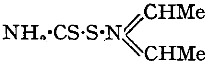
" Carbothialdine " ($C_5H_{10}N_2S_2$) has been prepared by the action of carbon disulphide on acetaldehyde-ammonia (Redtenbacher and Liebig, *Annalen*, 1848, **65**, 43) and by condensing acetaldehyde with ammonium dithiocarbamate or trithiocarbonate (Mulder, *Annalen*, 1873, **168**, 228). The product is thermally unstable, decomposing at 120° according to Cohn (*Pharm. Zentr.*, 1910, **51**, 149), though in the present work material with higher decomposition point has been obtained. " Carbothialdine " is very difficult to purify owing to its sensitivity even to solvents. It is reported to be soluble in dilute acids, though with decomposition (Mulder, *loc. cit.*). It is decomposed by water or alcohols, particularly when hot or in presence of acids; iodine, nitrous acid, or mercuric chloride causes a similar breakdown, ammonium thiocyanate being formed as well as the three main degradation products, acetaldehyde, ammonia, and carbon disulphide (Claus, *Ber.*, 1872, **5**, 362). Guareschi (*Gazzetta*, 1878, **8**, 246) reports that with ferric chloride, ferric thiocyanate is formed, but with ferric chloride in dilute acids or with chlorine water, the main product obtained is thiuram disulphide $(NH_2\cdot CS\cdot S-)_2$, thus suggesting that the dithiocarbamate structure is present in the molecule. Oxidation with permanganate, however, converted all the sulphur into sulphuric acid; this showed that the presence of the group $\cdot S\cdot CHR\cdot S\cdot$ was unlikely, as known products of this type, such as thialdine and trithioacetaldehyde, on similar treatment give good yields of ethane-αα-disulphonic acid.

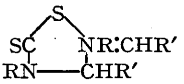
Mulder (*loc. cit.*) found that on treatment with certain heavy-metal salts, " carbothialdine " gave the corresponding metallic dithiocarbamate. Levi and Gimignani (*Gazzetta*, 1929, **59**, 757) showed that this reaction was more complex, and that unstable substituted dithiocarbamates containing aldehyde residues were also formed. These authors also studied alkylation of " carbothialdine " with methyl iodide and found the main product to be the hydriodide of dimethylthioformimine, $NH{:}C(SMe)_2$, a substance normally obtained by methylation of ammonium dithiocarbamate.

Four constitutional formulæ have been suggested for " carbothialdine." Hlasiwetz (*Ber.*, 1872, **5**, 803), without chemical evidence, put forward (I) by analogy with the thiuram sulphides, and suggested the name


(I.)


(II.)


(III.)


(IV.)

" thiuram carbomethyl." Claus (*loc. cit.*) supported (II), originally proposed by Erlenmeyer, because he considered that the formation of thiocyanates in the decomposition reactions indicated that a thiourea group was present. This evidence is invalid, for it is known that aqueous ammonium dithiocarbamate, for example, readily gives ammonium thiocyanate on standing. Mulder (*loc. cit.*) proposed (III) to account for the ease with which metallic dithiocarbamates are formed on treating " carbothialdine " with heavy-metal salts. This formula was endorsed by Guareschi (*loc. cit.*) and has been accepted by Levi and Gimignani (*loc. cit.*) and by Powers (duPont, U.S.P., 1,732,532).

Delépine (*Bull. Soc. chim.*, 1897, **15**, 891) prepared an isomeric compound, " dimethylformocarbothialdine," m. p. 96°, by the action of carbon disulphide on trimethyltrimethylenetri-imine $(NMe{:}CH_2)_3$. As the Mulder type formula (III) could not be applicable to the new isomer, which from its formation must contain a methyl group attached to each nitrogen atom, Delépine suggested (IV; R = Me, R′ = H) for his new " dimethylformocarbothialdine," and (IV; R = H, R′ = Me) for " carbothialdine." He also showed that the new isomer on treatment with methyl iodide gave di(methylthio)-*N*-methylformimine (IX).

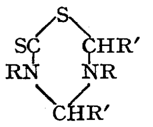
Bodendorf (*J. pr. Chem.*, 1930, **126**, 233) obtained from formaldehyde and methylammonium methyldithiocarbamate a compound, m. p. 106—107°, which he called " 2 : 4-dimethyl-2-methylenecarbothialdine " and to which he assigned the structure (IV; R = Me, R′ = H). Though no direct comparison appears to have been made, he assumed this to be the same as Delépine's " dimethylformocarbothialdine." We have now repeated both these preparations and find that the products are in fact identical.

The four formulæ proposed are, however, all unsatisfactory. Neither (I) nor (II) accords with the methods of formation and properties as outlined above; (III) has already been rejected for a sufficient reason by Delépine (*loc. cit.*), and moreover, this formula would demand salt-like properties which are not characteristic of the " carbothialdines " : (IV) also contains quinquevalent nitrogen and so is quite incorrectly described as a 1 : 2 : 4-thiodiazole (cf. Bodendorf, *loc. cit.*). If this type of structure is to be postulated, the modern implication is the unusual betaine-like immonium type $\overset{-}{S}\cdot CS\cdot NR\cdot CHR'\cdot\overset{+}{N}R{:}CHR'$ (V).

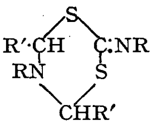
Alkyl-substituted immonium salts, $CR_2{:}\overset{+}{N}R_2\overset{-}{X}$ have been described by Stewart and Bradley (*J. Amer. Chem. Soc.*, 1932, **54**, 4172) and Reiber and Stewart (*ibid.*, 1940, **62**, 3026). The conditions for the formation of such salts and their general properties are such that (V) does not give a satisfactory picture of the properties of the " carbothialdines." Furthermore, it is very doubtful whether such a formula would accord with the ultraviolet absorption data given below.

More rational formulæ may be derived by considering the probable mechanism of formation of " carbothialdine " from dithiocarbamic acid, ammonia, and acetaldehyde. McLeod and Robinson (J., 1921, **119**, 1470) have shown that thiols, formaldehyde, and amines react to give $SR\cdot CH_2\cdot NR_2$, a reaction which may proceed *via* the methylol derivative of either the amine (Robinson and Robinson, J., 1923, **123**, 532) or the thiol (Levi, *Gazzetta*, 1932, **62**, 775) : in either case, the intermediate methylol compound loses water by condensation with the third reactant. If a similar mechanism is applied to the case in which the thiol compound is dithiocarbamic acid and the aldehyde Me·CHO, an intermediate di(hydroxyethyl) compound of the type $CHMe(OH)\cdot NH\cdot CS\cdot S\cdot CHMe\cdot OH$ or $NH{:}C(S\cdot CHMe\cdot OH)_2$ would be formed, which on condensation with ammonia would immediately cyclise to (VI or VII; R = H, R′ = Me) Either of these formulæ is in accord with the known properties of " carbothialdine," and corresponding isomeric structures (VI or VII; R = Me, R′ = H) would then be probable for Delépine's " dimethylformocarbothialdine." We hoped to distinguish between the two types of structure by converting the thionlactone sulphur postulated by (VI) into oxygen by means of mercuric oxide, but under the mildest conditions " dimethylformocarbothialdine " (a more stable compound than " carbothialdine " itself) was completely disrupted.

(VI.)



(VII.)

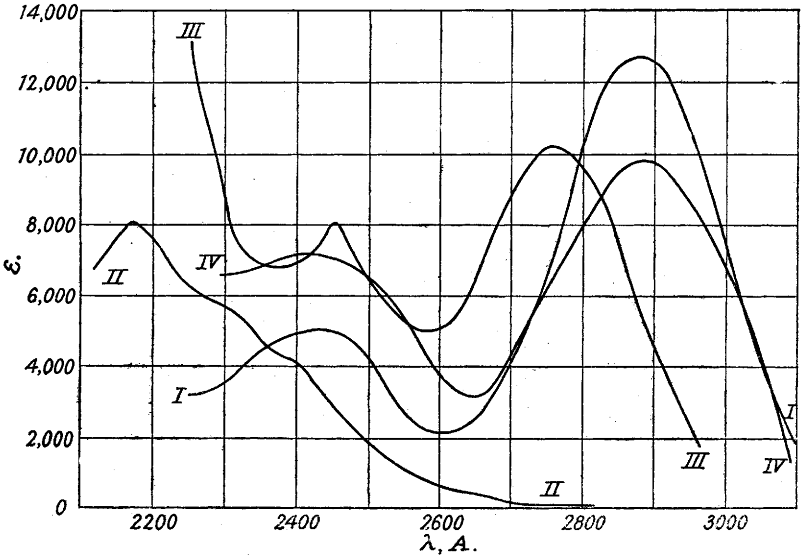


NMe$_2$·CS·SMe (VIII.)

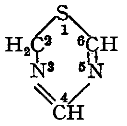
NMe:C(SMe)$_2$ (IX.)

The failure of chemical methods to decide the structure led us to examine the ultra-violet absorption spectra of the compounds. For this purpose " carbothialdine," " dimethylformocarbothialdine," methyl dimethyldithiocarbamate (VIII), analogous to (VI), and bismethylthio-*N*-methylformimine (IX), analogous to (VII), were examined. " Carbothialdine," " dimethylformocarbothialdine," and (VIII) gave similar types of curves with a marked peak between 2760 and 2890 A. and a subsidiary peak at about 2450 A.; (IX), on the other hand, gave only low general end absorption in this range (Fig. 1). It is concluded therefore that the available evidence supports the structure (VI; R = H, R′ = Me) for " carbothialdine " or " thiuram carbomethyl " and (VI; R = Me, R′ = H) for " dimethylformocarbothialdine " or " 2 : 4-dimethyl-2-methylenecarbothialdine." On account of the derivation from the unknown 1 : 3 : 5-thiadiazine (X), these compounds should be named 2-thio-4 : 6-dimethyltetrahydro-1 : 3 : 5-thiadiazine and 2-thio-3 : 5-dimethyltetrahydro-1 : 3 : 5-thiadiazine, respectively.

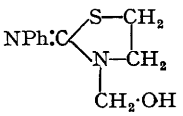
FIG. 1.



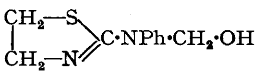
I. " Carbothialdine." II. NMe:C(SMe)$_2$. III. NMe$_2$·CS·SMe. IV. " Dimethylformocarbothialdine."



(X.)



(XI.)



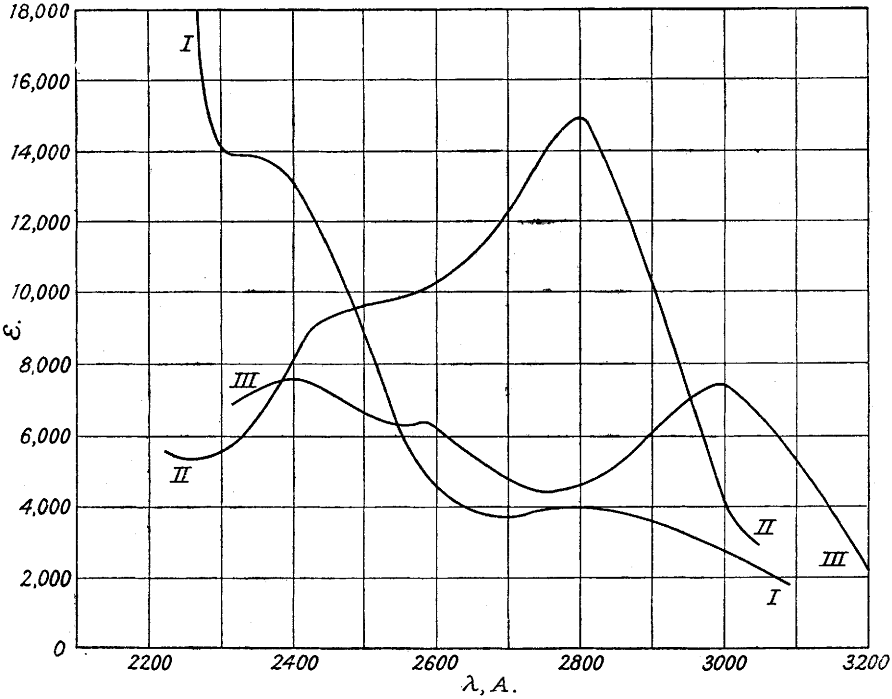
(XII.)

In the course of a study of the insecticidal and fungicidal properties of organic sulphur compounds (British Patent Specifications Nos. 554,729 and 555,795), we have prepared a series of 2-thio-3-aryl-5-alkyltetrahydro-1 : 3 : 5-thiadiazines. Methylammonium phenyldithiocarbamate (made by direct interaction of aniline, carbon disulphide, and aqueous methylamine) reacts rapidly with aqueous formaldehyde, precipitating *2-thio-3-phenyl-5-methyltetrahydro-1 : 3 : 5-thiadiazine* (type VI) in good yield. This is a crystalline compound, stable on storage in a dry state, very slowly decomposed by cold water and more rapidly by boiling water. Like the 3 : 5-dimethyl compound, it is completely decomposed under mild conditions by dilute acids or by mercuric oxide, and it is not possible to establish its structure by chemical degradation. Any doubt between the two possible formulæ of type (VI) and (VII) has been removed by a comparison of the ultra-violet spectrum of the compound with those of the " model " compounds, NPhMe·CS·SMe and NPh:C(SMe)$_2$.

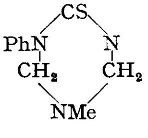
For the following comments on the results, we are indebted to Dr. R. A. Morton of Liverpool University. "The compound NMe:C(SMe)$_2$ (Fig. 1) has no powerful chromophore. The phenyl analogue NPh:C(SMe)$_2$ shows a spectrum (Fig. 2) probably due to the NPh: group, modified a little by the rest of the molecule, which however makes no direct contribution to the absorption. In NMe$_2$·CS·SMe (Fig. 1), it seems certain that ·CS·S· includes the absorbing unit, and in NPhMe·CS·SMe the contribution by NPh· is superimposed. Sufficient information is not available to assess the mutual effects of the NPh· and the ·CS·S· chromophore, but the additive nature of the curve is not to be doubted. In consequence, the two bands at *ca.* 2900 and 2430 A. in 2-thio-3-phenyl-5-methyltetrahydro-1 : 3 : 5-thiadiazine are consistent with the formula and name which have been assigned to the substance."

A number of homologous substances have been prepared (see Experimental), and their general properties have proved similar. For the preparation of the alkylammonium salt of the aryldithiocarbamic acid the procedure most generally adopted has been to prepare the barium salt first, and then bring about double decomposition with the alkylammonium sulphate. This ensured a satisfactory preparation, but the direct formation as described for methylammonium phenyldithiocarbamate was often very good.

FIG. 2.



I. NPh:C(SMe)$_2$. II. NMePh·CS·SMe. III.



Treatment of β-hydroxyethylammonium phenyldithiocarbamate with aqueous formaldehyde affords a mixture containing 75% of the expected *2-thio-3-phenyl-5-(β-hydroxyethyl)tetrahydro-1 : 3 : 5-thiadiazine* together with 25% of a substance believed to be a *hydroxymethyl* derivative of 2-anilino-4^2: 5-dihydrothiazole (XI or XII), since acid hydrolysis liberated formaldehyde and the (tautomeric) base. The latter was identified, together with its picrate, by mixed m. p. with authentic material. The available evidence is insufficient to adjudicate between formulæ (XI) and (XII). However, it is clear that formaldehyde plays an essential part in the cyclisation, since (i) in its absence, aqueous β-hydroxyethylammonium phenyldithiocarbamate remained substantially unchanged for several days at room temperature, and (ii) 2-anilinodihydrothiazole failed to react with formaldehyde at room temperature. It follows from (ii) that attachment of ·CH$_2$·OH to nitrogen precedes cyclisation.

Reaction of alcoholic *p*-anisidine, *p*-aminodimethylaniline, and *p*-aminodiethylaniline with carbon disulphide gave the aromatic base salts of the substituted phenyldithiocarbamic acids. Such salts are uncommon and are only known for a few of the stronger aromatic bases such as *p*-phenetidine (Hugershoff, *Ber.*, 1899, **32**, 2245). p-*Diethylaminophenylammonium* p-*diethylaminophenyldithiocarbamate* was indeed formed so readily that it seriously interfered with the formation of ammonium and sodium salts of the dithiocarbamic acid by reaction of ammonia and sodium carbonate respectively with carbon disulphide and the aromatic base. This is in accordance with the fact that diethylaniline is a much stronger base than dimethylaniline (Hall and Sprinkle, *J. Amer. Chem. Soc.*, 1932, **54**, 3469).

EXPERIMENTAL.

A. *Preparation of Compounds.*—2-*Thio*-4 : 6-*dimethyltetrahydro*-1 : 3 : 5-*thiadiazine* ("*Carbothialdine*") (VI; R = H, R′ = Me). This was obtained by the method of Redtenbacher and Liebig (*loc. cit.*), and purified after considerable difficulty by crystallisation first from methyl alcohol and finally from ethyl alcohol–ethyl acetate; m. p. 135° (decomp.) (Found: C, 37·4; H, 6·3; N, 16·8; S, 40·0. Calc. for $C_5H_{10}N_2S_2$: C, 37·0; H, 6·2; N, 17·5; S, 39·5%).

2-*Thio*-3 : 5-*dimethyltetrahydro*-1 : 3 : 5-*thiadiazine* ("*dimethylformocarbothialdine*") (VI; R = Me, R′ = H). Specimens of this substance were made (a) by Delépine's method (*loc. cit.*) from trimethyltrimethylenetri-imine and carbon disulphide and (b) by Bodendorf's method (*loc. cit.*) from methylammonium methyldithiocarbamate and formaldehyde. Both specimens had m. p. 106° (from benzene) and gave no depression on mixing. Delépine gives m. p. 96°, and Bodendorf 106—107°.

Methyl dimethyldithiocarbamate (VIII). A mixture of 25·3% aqueous dimethylamine (88 c.c.), 31% aqueous sodium hydroxide (48 c.c.), and water (50 c.c.) was treated with stirring with carbon disulphide (30·5 c.c.) at 25° for 1 hour. Methyl sulphate (47·3 c.c.) was then run in, the temperature being kept at 30—40°. After 1 hour's stirring the ester was extracted with ether, washed, dried (magnesium sulphate), and distilled, giving a yellowish solid (52 g.), b. p. 125—126°/17 mm. Recrystallisation from methyl alcohol and from light petroleum (b. p. 40—60°) gave white prisms, m. p. 45—46°.

Bismethylthio-N-*methylformimine* (IX). Methyl methyldithiocarbamate (30·3 g.; prepared from methylamine by the method used for the dimethyl derivative) in methyl alcohol (30 c.c.) was treated at 25—30° with methyl iodide (15·5 c.c.). After several hours' stirring, water was added to dissolve the precipitated hydriodide of the formimine. The solution was treated with charcoal, filtered, and made just alkaline to brilliant-yellow with sodium hydroxide. The yellow oil was extracted with ether and distilled, giving bismethylthio-*N*-methylformimine (26·2 g.), b. p. 188—192°.

2-*Thio*-3-*phenyl*-5-*methyltetrahydro*-1 : 3 : 5-*thiadiazine*. A stirred mixture of aniline (22·7 c.c.), carbon disulphide (15 c.c.), and water (100 c.c.) was treated during 20 minutes at room temperature with 10% aqueous methylamine solution (78 c.c.). After 2 hours' stirring, the solution was diluted to 2 l., filtered from a little insoluble material, and treated during 10 minutes, while stirred at 10°, with a solution of 37% formaldehyde (38 c.c.) in water (100 c.c.). After stirring for 1 hour, the precipitated solid was separated and dried (40 g.; 70%), and after crystallising from benzene had m. p. 148° (Found: C, 54·0; H, 5·5; N, 12·2; S, 28·6. $C_{10}H_{12}N_2S_2$ requires C, 53·6; H, 5·4; N, 12·5; S, 28·6%).

The same *compound* was prepared in somewhat better yield (80%) by interaction between equimolecular quantities of sodium carbonate, aniline, and carbon disulphide in water at 20—30° to yield sodium phenyldithiocarbamate solution, which, after addition of 2 mols. of formaldehyde in diluted solution and filtration from a slight sticky deposit, was treated at room temperature with 1 mol. of neutral aqueous methylammonium sulphate.

Substituted 2-*Thio*-3-*aryl*-5-*alkyltetrahydro*-1 : 3 : 5-*thiadiazines*.—The substances described below were obtained by one of two general methods. (1) The barium salt of the aryldithiocarbamic acid was precipitated by addition of barium chloride to a solution of the ammonium salt, and this was followed by double decomposition with the sulphate of the aliphatic amine. After separation of barium sulphate, formaldehyde was added, and the precipitated reaction product separated, dried, and crystallised from an appropriate solvent. (2) This was used in the case of the aminophenols. It is similar to method (1) except that the starting point was the sodium salt of the aryldithiocarbamic acid (instead of the ammonium salt), prepared from the sodium salt of the appropriate aminophenol.

2-*Thio*-3-α-*naphthyl*-5-*methyltetrahydro*-1 : 3 : 5-*thiadiazine* (Method 1), m. p. 159—160° (from benzene) (Found: C, 61·8; H, 5·0; N, 10·0; S, 23·0. $C_{14}H_{14}N_2S_2$ requires C, 61·3; H, 5·4; N, 10·2; S, 23·4%); 3-p-*chlorophenyl* analogue (Method 1), m. p. 139—140° (from dichloroethane) (Found: N, 10·5; Cl, 13·8. $C_{10}H_{11}N_2S_2Cl$ requires N, 10·8; Cl, 13·7%); 3-p-*anisyl* compound (Method 1), m. p. 160—161° (from dichloroethane) (Found: N, 11·1; S, 25·6. $C_{11}H_{14}ON_2S_2$ requires N, 11·0; S, 25·2%). An attempt to prepare the last substance by direct interaction of *p*-anisidine, methylamine, carbon disulphide, and formaldehyde failed owing to the formation of the *p*-anisidine salt of the aryldithiocarbamic acid.

2-*Thio*-3-(p-*hydroxyphenyl*)-5-*methyltetrahydro*-1 : 3 : 5-*thiadiazine* (Method 2), m. p. 163—164° (from ethyl alcohol) (Found: N, 11·5; S, 26·6. $C_{10}H_{12}ON_2S_2$ requires N, 11·7; S, 26·7%); 3-(3′-*chloro*-4′-*hydroxy*)-compound (Method 2), m. p. 146° (from alcohol or benzene–alcohol) (Found: N, 10·0; Cl, 12·5. $C_{10}H_{11}ON_2S_2Cl$ requires N, 10·2; Cl, 12·7%); 3-(p-*dimethylaminophenyl*) compound (Method 1), m. p. 168—169° (from acetone) (Found: N, 15·5; S, 24·4. $C_{12}H_{17}N_3S_2$ requires N, 15·7: S, 24·0%): addition of carbon disulphide (1·3 c.c.) to *p*-aminodimethylaniline (2·7 g.) in alcohol (10 c.c.) gave pale yellow crystals (m. p. 94—96°, decomp.) of the amine dithiocarbamate. Similarly, with *p*-aminodiethylaniline, p-*diethylaminophenylammonium* p-*diethylaminophenyldithiocarbamate* was obtained as yellow crystals, m. p. 97—99° (Found: N, 13·8. $C_{20}H_{32}N_4S_2$ requires N, 13·9%). This reaction interfered with the preparation of the thiadiazine by both methods (1) and (2).

2-*Thio*-3-*phenyl*-5-(β-*diethylaminoethyl*)*tetrahydro*-1 : 3 : 5-*thiadiazine* (Method 1), m. p. 103—104° (from benzene–light petroleum) (Found: C, 58·8; H, 7·6; N, 13·6. $C_{15}H_{23}N_3S_2$ requires C, 58·5; H, 7·5; N, 13·6%). The 5-(β-*hydroxyethyl*) analogue of this was obtained by Method 1 in a yield of 13 g. after recrystallisation from acetone (300 c.c.); m. p. 136° (not raised further by another crystallisation) (Found: N, 11·1; S, 25·3. $C_{11}H_{14}ON_2S_2$ requires N, 11·0; S, 25·2%); the crude product weighed 30 g.

Hydroxymethyl derivative of 2-*anilino*-4 : 5-*dihydrothiazole*. The mother-liquors from the above acetone crystallisation were concentrated, giving three successive crops of crystals, which were combined and recrystallised to constant m. p. from ethyl acetate; yield 6·0 g., m. p. 165° (Found: C, 57·2; H, 5·7; N, 13·5; S, 15·6. $C_{10}H_{12}ON_2S$ requires C, 57·6; H, 5·8; N, 13·6; S, 15·4%). On boiling with dilute sulphuric acid, the *compound* evolved formaldehyde, and when the cooled liquid was made alkaline, anilinodihydrothiazole was precipitated, m. p. (from benzene) 160—161°; picrate, m. p. 201—205° (from alcohol). Neither the base nor its picrate gave m. p. depressions when mixed with authentic samples. The base was prepared by the action of concentrated hydrochloric acid on *N*-phenyl-*N′*-β-hydroxyethylthiourea (cf. Dains *et al.*, *J. Amer. Chem. Soc.*, 1925, **47**, 1981) and had m. p. 160°, picrate m. p. 201—203° (Menne, *Ber.*, 1900, **33**, 657, gives 159—160° and 198—202°, respectively). 2-Anilinodihydrothiazole failed to react with formaldehyde when heated for 20 hours at 70—80° in aqueous-alcoholic solution. β-Hydroxyethylammonium phenyldithiocarbamate very slowly deposited thiocarbanilide, but otherwise remained unchanged in aqueous solution during 3 days at room temperature.

B. *Absorption Spectra* (with F. R. Cropper).—The compounds were dissolved in cold *cyclo*hexane (with the exception of "carbothialdine" which, being very sparingly soluble in *cyclo*hexane, was examined in ethyl alcohol) in concentrations from 0·45 mg. to 10·4 mg. per 50 ml., in 1 mm., 5 mm., and 2 cm. cells. The solvents had been purified by standard methods (*cyclo*hexane, extracted with oleum, washed, dried and distilled; ethyl alcohol, distilled from solid potassium hydroxide and silver nitrate).

The absorption-spectra determinations were carried out on a Hilger E498 Medium Quartz Spectrograph, with a " Spekker " photometer. The results are summarised in the following table, and plotted in Figs. 1 and 2.

Substance.	$\lambda_{\text{max.}}$, A.	$\varepsilon_{\text{max.}}$	$\lambda_{\text{min.}}$, A.	$\varepsilon_{\text{min.}}$
" Carbothialdine "	2880	12,800	2620	2100
	2430	5,000	—	—
" Dimethylformocarbothialdine "	2890	9,900	2640	3100
	2420	7,150	—	—
Methyl dimethyldithiocarbamate	2760	10,100	2600	4950
	2460	8,000	2370	6750
Bismethylthio-*N*-methylformimine	2170	*ca.* 8,000	—	—
2-Thio-3-phenyl-5-methyltetrahydro-1 : 3 : 5-thiadiazine	2990	7,500	—	—
	2580	6,400	2760	4400
	2410	7,600	2560	6150
Methyl phenylmethyldithiocarbamate	2800	15,000	2260	*ca.* 5300
	2400—2650 *	10,000	—	—
Bismethylthio-*N*-phenylformimine	280	4,100	2690	3700
	2330—2370 *	*ca.* 14,100	—	—

* Inflexion.

The last three compounds in the table were examined in alcohol as well as in *cyclo*hexane, and no significant differences were observed.

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