

766. *The Structure and Reactivity of Triazole Quaternary Salts.*

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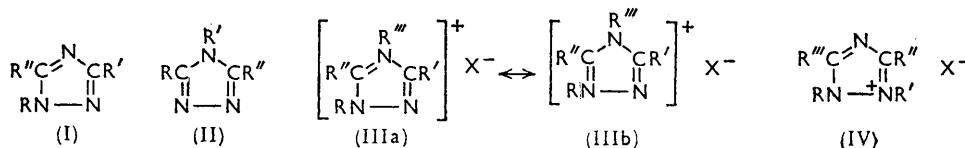
Quaternisation of some 1,3,5-trisubstituted and 1,3-disubstituted 1,2,4-triazoles is shown to take place at the N₍₄₎ atom to give salts of the general formula (III). Cyanine and merocyanine dyes are prepared from these salts, as well as from salts of various 3,4,5-trisubstituted 1,2,4-triazoles.

Some 1,2,4-triazolethiones (V, VI, and VII) have been prepared and their structures discussed.

Analysis of the absorption maxima of the dyes prepared indicates that the 1,2,4-triazole nucleus is strongly basic.

FEW triazole quaternary salts have been described; some do not have structures assigned to them,¹ and structures were proposed for others without supporting evidence.²

Atkinson and Polya³ claimed that alkaline degradation of the methiodide of 1,3,5-trimethyl-1,2,4-triazole (I; R = R' = R'' = Me) gave 1,2-dimethylhydrazine and con-



cluded that quaternization had taken place at the N₍₂₎ atom to give the salt (IV; R = R' = R'' = R''' = Me, X = I). The present authors reported⁴ that this degradation gave methylamine and methylhydrazine, and that the methiodides of 1,3,5- (I; R = R' = R'' = Me) and 3,4,5-trimethyl-1,2,4-triazole (II; R = R' = R'' = Me) were identical (m. p. and mixed m. p. and infrared absorption), thus proving that quaternisation had taken place at the N₍₄₎ atom to give the quaternary salt (III; R = R' = R'' = R''' = Me, X = I). In addition, a number of 1,2,4-triazoles have been studied and without exception quaternisation has been found to take place at the N₍₄₎ atom to give salts of the general structure (III).

Alkaline degradation of the methiodide of 3,5-dimethyl-1-phenyl-1,2,4-triazole (I; R = Ph, R' = R'' = Me) gave methylamine and phenylhydrazine,⁴ products which could be expected from the structure (III; R = Ph, R' = R'' = R''' = Me, X = I). It was also

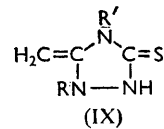
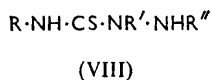
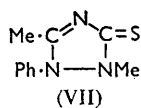
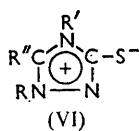
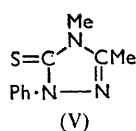
¹ Andreocci, *Atti R. Accad. Lincei*, 1890, **6**, II, 212; 1897, **6**, I, 294; Gabel and Schmidegg, *Monatsh.*, 1926, **47**, 748; Hernler, *ibid.*, 1927, **48**, 402.

² Engelhardt, *J. prakt. Chem.*, 1896, **54**, 153.

³ Atkinson and Polya, *Chem. and Ind.*, 1954, 462.

⁴ Duffin, Kendall, and Waddington, *ibid.*, 1954, 1458.

found that reaction ⁵ of the methotoluene-*p*-sulphonate of 3,5-dimethyl-1-phenyl-1,2,4-triazole (I; R = Ph, R' = R'' = Me) with 3-methyl-2-methylthiobenzothiazolium toluene-*p*-sulphonate gave the same cyanine dye (XI; D = residue of a benzothiazole nucleus, R = Ph, R' = R'' = R''' = Me, *m* = 0, X = I) as was formed in reaction between the methotoluene-*p*-sulphonate of 3-methyl-5-methylthio-1-phenyl-1,2,4-triazole (I; R = Ph, R' = Me, R'' = MeS) and 2,3-dimethylbenzothiazolium toluene-*p*-sulphonate. Since, as described below, 3-methyl-5-methylthio-1-phenyl-1,2,4-triazole (I; R = Ph, R' = Me, R'' = MeS) was shown to quaternise at the N₍₄₎ atom, with both methyl toluene-*p*-sulphonate and methyl iodide, it follows that 3,5-dimethyl-1-phenyl-1,2,4-triazole (I; R = Ph, R' = R'' = Me) quaternises at the N₍₄₎ atom. Quaternary salts of 3-methyl-1-phenyl-1,2,4-triazole (I; R = Ph, R' = Me, R'' = H) did not give rise to cyanine dyes and thus were assumed to have the structure (III; R = Ph, R' = R''' = Me, R'' = H). Neither the methiodide nor the methotoluene-*p*-sulphonate of 3-methyl-5-methylthio-1-phenyl-1,2,4-triazole (I; R = Ph, R' = Me, R'' = MeS) showed any sign of having a reactive methyl group. On the other hand, both quaternary salts gave the cyanine dye (XI; D = residue of a benzothiazole nucleus, R = Ph, R' = R'' = R''' = Me, *m* = 0, X = I), when treated with the corresponding quaternary salts of 2-methylbenzothiazole. Further, the methiodide and boiling pyridine gave a product C₁₀H₁₁N₃S which was shown to be 4,5-dihydro-3,4-dimethyl-1-phenyl-1,2,4-triazole-5-thione (V) since it was also obtained by acetylation of 4-methyl-2-phenylthiosemicarbazide (VIII; R = Me, R' = Ph, R'' = H) followed by ring closure with sodium ethoxide. The thione (V) rapidly reverted to the methiodide (III; R = Ph, R' = R''' = Me, R'' = MeS, X = I) when warmed with methyl iodide. Methylation of 3-mercapto-5-methyl-1-phenyl-1,2,4-triazole ⁶ (I; R = Ph, R' = SH, R'' = Me) gave 5-methyl-3-methylthio-1-phenyl-1,2,4-triazole (I; R = Ph, R' = MeS, R'' = Me) which was also prepared by condensing phenylhydrazine and methyl *N*-acetyldithiocarbamate. The identity of the two products was shown by conversion into identical cyanine dyes. Quaternisation of this base proceeded readily, and both the methiodide and methotoluene-*p*-sulphonate could be used to prepare the same cyanine dyes by reaction of the 5-methyl group, but no reactive methylthio-group was detectable; quaternisation at the N₍₄₎ atom therefore was indicated. Dequaternisation of this methiodide (III; R = Ph, R'' = R''' = Me, R' = MeS, X = I) with boiling pyridine gave a compound isomeric with with the thione (V) but with a much higher melting point. This new substance was identical (m. p. and mixed m. p. and ultraviolet absorption) with the product obtained by treating 4-methyl-1-phenylthiosemicarbazide (VIII; R = Me, R'' = Ph, R' = H) with boiling acetic anhydride and is therefore anhydro-3-mercapto-4,5-dimethyl-1-phenyl-1,2,4-triazolium hydroxide (VI; R = Ph, R' = R'' = Me). The compound (VI) reacted readily with methyl iodide to give the methiodide (III; R = Ph, R'' = R''' = Me, R' = MeS, X = I) again. 3-Ethylthio-5-methyl-1-phenyl-1,2,4-triazole (I; R = Ph, R' = EtS, R'' = Me), prepared from ethyl *N*-acetyldithiocarbamate and phenylhydrazine, also contained a reactive methyl group and formed cyanine dyes. It was of interest to prepare a member of the third type of thione, *e.g.*, (VII). 1-Methyl-2-phenylhydrazine was treated



in acid solution with potassium thiocyanate, to give 2-methyl-1-phenylthiosemicarbazide (VIII; R' = Me, R'' = Ph, R = H). This product could be 2-phenyl-1-methylthiosemicarbazide (VIII; R' = Ph, R'' = Me, R = H); but this appears unlikely because phenylhydrazine gives 1-phenylthiosemicarbazide ⁷ (VIII; R = R' = H and R'' = Ph) and

⁵ Kendall, B.P. 424,559/1933, 438,420/1934.

⁶ Wheeler and Beardsley, *Amer. Chem. J.*, 1902, **27**, 267.

⁷ Fischer and Besthorn, *Annalen*, 1882, **212**, 325.

methylhydrazine gives 2-methylthiosemicarbazide⁸ (VIII; $R = R'' = H$, $R' = Me$). Acetylation of 2-methyl-1-phenylthiosemicarbazide (VIII; $R' = Me$, $R'' = Ph$, $R = H$) and ring closure with sodium ethoxide gave 2,3-dihydro-2,5-dimethyl-1-phenyl-1,2,4-triazole-3-thione (VII) which reacted with methyl iodide to give 3-methylthio-2,5-dimethyl-1-phenyl-1,2,4-triazolium iodide (IV; $R' = R''' = Me$, $R'' = MeS$, $R = Ph$, $X = I$).

Whereas the thiones (V and VII) can be represented by a classical covalent structure, anhydro-3-mercapto-4,5-dimethyl-1-phenyl-1,2,4-triazolium hydroxide (VI; $R = Ph$, $R' = R'' = Me$) must be considered as a mesoionic compound.⁹ The difference between the three types of thione is illustrated by considering their absorption maxima. Whereas the mesoionic type (VI) absorbs with a maximum in the region of 2400–2500 Å, the other two (V and VII) do so in the region of 2900 Å.

The acylation and ring closure of substituted thiosemicarbazides (VIII; R' or $R'' = H$) could give rise to thiadiazole derivatives, a possibility considered by Pulvermacher,¹⁰ Freund,¹¹ and McKee.¹² However, the ease with which the thiones described in this paper are formed from, and converted into, triazole quaternary salts strongly indicates that they are in fact triazole derivatives. A second mesoionic thione, anhydro-3-mercapto-4-methyl-1-phenyl-1,2,4-triazolium hydroxide (VI; $R = Ph$, $R' = Me$, $R'' = H$) was formed by dequaternising 3-methylthio-1-phenyl-1,2,4-triazole methiodide (III; $R = Ph$, $R' = MeS$, $R'' = H$, $R''' = Me$, $X = I$) or by treating 4-methyl-1-phenylthiosemicarbazide (VIII; $R = Me$, $R'' = Ph$, $R' = H$) with formic acid, and readily reverted to the methiodide (III; $R = Ph$, $R' = MeS$, $R'' = H$, $R''' = Me$, $X = I$). The similarity between this thione and anhydro-3-mercapto-4,5-dimethyl-1-phenyl-1,2,4-triazolium hydroxide (VI; $R = Ph$, $R' = R'' = Me$) shows that the latter cannot possess the structure (IX; $R = Ph$, $R' = Me$) similar to that suggested by McKee¹² for the diphenyl analogue (IX; $R = R' = Ph$). It is clear that both thiones are best represented by the general formula (VI).

In analogy with the work of Freund,¹¹ 4-methyl-,¹⁰ 4-ethyl-,¹³ and 4-phenyl-thiosemicarbazides¹⁰ (VIII; $R' = R'' = H$, $R = Me$, Et , and Ph respectively) were acetylated and cyclised to give the corresponding triazoles (II; $R = SH$, $R'' = Me$, $R' = Me$, Et , or Ph). Alkylation of these triazoles gave the 4-alkyl(or -phenyl)-5-alkylthio-3-methyl-1,2,4-triazoles (II; $R = alkylthio$, $R'' = Me$, $R' = Me$, Et , or Ph) in good yield. All these bases were quaternised and converted into cyanine dyes by reaction of the 3-methyl group. Dequaternisation of the methiodide of 3,4-dimethyl-5-methylthio-1,2,4-triazole (II; $R' = R'' = Me$, $R = MeS$) gave rise to a third mesoionic thione (VI; $R = R' = R'' = Me$), the properties and absorption spectrum being very similar to those described earlier. These triazoles had quaternised, therefore, at the $N_{(2)}$ atom, *i.e.*, adjacent to the methyl group. This was to be expected by analogy with the quaternisation of certain pyridazine derivatives carried out by two of us.

Lastly, cyanine dyes were prepared from the methiodides of a number of 4-aryl-3,5-dimethyl-1,2,4-triazoles (II; $R = R'' = Me$, $R' = aryl$). These methiodides of course must all have the general structure (III; $R = R' = R'' = Me$, $R''' = aryl$, $X = I$).

Atkinson and Polya¹⁴ quote values (personal communication from Brown and Bassett) for the electron densities of the unsubstituted triazole molecule which give to the $N_{(4)}$ atom a higher value than to the other two N atoms. Therefore, quaternisation at the 4-position was understandable and, further, as a result of the experiments carried out, it is apparent that the $N_{(4)}$ atom retains the greater share of electron density irrespective of the influence of substituents present in the rest of the molecule. This is well illustrated by the fact that

⁸ Rodd, "Chemistry of Carbon Compounds," Elsevier, London, 1951, Vol. I, p. 929.

⁹ Baker and Ollis, *Quart. Rev.*, 1957, **11**, 15.

¹⁰ Pulvermacher, *Ber.*, 1894, **27**, 622.

¹¹ Freund, *Ber.*, 1896, **29**, 2483.

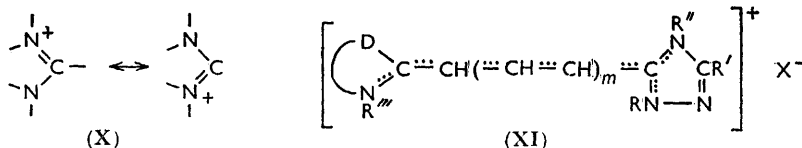
¹² McKee, *J.*, 1915, 1136.

¹³ Freund and Schwarz, *Ber.*, 1896, **29**, 2486.

¹⁴ Atkinson and Polya, *J.*, 1954, 3319.

3-methyl-5-methylthio- (I; R = Ph, R' = Me, R'' = MeS) and 3-methylthio-5-methyl-1-phenyl-1,2,4-triazole (I; R = Ph, R' = MeS, R'' = Me) both quaternise at the N₍₄₎ atom. Thus, while interchanging the 3- and the 5-substituent might alter the actual values of the electron densities, the relative values remain unaltered and the N₍₄₎ atom retains the greater share. On the other hand, the effect that the substituents had on the electron densities was illustrated when all attempts to quaternise 3,5-dimethylthio-1-phenyl-1,2,4-triazole (I; R = Ph, R' = R'' = MeS) met with failure owing to the reduction in basicity (*i.e.*, electron density) of the triazole nucleus by the two methylthio-groups.

All the triazole quaternary salts containing a 5-methyl substituent were used to prepare cyanine dyes by classical methods.¹⁵ It was not possible to classify the 1,2,4-triazole nucleus according to Brooker's table of deviations,¹⁶ since it proved impossible to prepare symmetrical cyanine dyes from 1,2,4-triazole quaternary salts. It was also necessary to use pyridine and triethylamine before the dyes could be formed, and this in itself indicated a general lack of reactivity of the quaternary salts which indicates, in Brooker's view,¹⁷ that the parent base is a strong one and, when incorporated in a cyanine dye containing a weakly basic nucleus at the opposite end of the methine chain, would give a large deviation.¹⁶



Cyanine dyes with a 1,2,4-triazole or a benzimidazole nucleus contain the grouping (X) and it might be expected that, since the benzimidazole nucleus acts as a strongly basic entity, the 1,2,4-triazole nucleus would behave similarly. For example, a trimethincyanine containing a 1,2,4-triazole nucleus and a weakly basic benzoxazole nucleus has three canonical forms. One form contains the positive charge on the benzoxazole nucleus and the other two contain the positive charge on the 1,2,4-triazole nucleus, the stronger basicity of the latter would result in electronic asymmetry of the dye. A measure of this asymmetry in a series of dyes of the general formula (XI; D = residue of a benzoxazole nucleus, R''' = Et) was obtained by applying Brooker's "sensitivity rule"¹⁸ when considering the absorption maxima of this series. Six dyes of this type were prepared (dyes nos. 1—6 in the experimental section) and their absorption maxima were measured. It was at once apparent that the absorption maxima were highly sensitive to changes in the nature and position of the substituents in the 1,2,4-triazole nucleus. The dyes thus had a high degree of electronic asymmetry. For example, replacement of a 4-methyl group by a 4-phenyl group, *i.e.*, conversion of dye (1) into (3) or of dye (2) into (5), results in a bathochromic shift of about 430 Å. This can be explained by assuming that the 1,2,4-triazole nucleus, being the more basic, retains the larger share of the positive charge in the cation but when phenyl replaces methyl this basicity is reduced and the dye becomes more degenerate, resulting in a bathochromic shift. The shift in going from dye (2) to (5) is slightly less than that in going from dye (1) to (3), presumably because the 3-methylthio-group present in dye (2) reduces the basicity of the triazole nucleus, making the dye rather more symmetrical than the dye (1). Consequently any change has slightly less effect on the absorption maximum than the corresponding change applied to dye (1). Similar chemical changes at the N₍₁₎ atom, *i.e.*, dye (1) to (4), or dye (2) to (6), result in somewhat larger bathochromic shifts. Once again, when a 3-methylthio-group is present the shift is smaller. If the degree of electronic asymmetry of dye (1) is assumed to be due more to

¹⁵ Hamer, *Quart. Rev.*, 1950, **4**, 327.

¹⁶ Brooker, Sklar, Cressman, Keyes, Smith, Sprague, Van Lare, Van Zandt, White, and Williams, *J. Amer. Chem. Soc.*, 1945, **67**, 1875.

¹⁷ Brooker, Dent, Heseltine, and Van Lare, *ibid.*, 1953, **75**, 4335.

¹⁸ Brooker and Sprague, *ibid.*, 1941, **63**, 3203.

the contribution of the structure containing a positively charged $N_{(1)}$ atom than it is to that containing a positively charged $N_{(4)}$ atom, then the overall larger bathochromic shifts due to changes at the $N_{(4)}$ atom are explained. Finally, the effect of replacing a 3-methyl substituent by a 3-methylthio-substituent is seen to vary somewhat, but in all cases, *i.e.*, conversion of dye (1) into (2), of dye (3) into (5), and of dye (4) into (6), the bathochromic shifts are much smaller than those encountered above. This is understandable since the 3-position of the 1,2,4-triazole nucleus is not part of the mesomeric chain of the dye.

EXPERIMENTAL

All products are colourless unless otherwise stated.

5-Methyl-3-methylthio-1-phenyl-1,2,4-triazole.—(a) Phenylhydrazine (11.6 g.), methyl *N*-acetyldithiocarbamate¹⁹ (16 g.), and benzene (100 c.c.) were refluxed for 2 hr. while the water formed was removed azeotropically. The benzene was evaporated and the residue dissolved in ether (200 c.c.). After being washed with 10% aqueous sodium hydroxide (3 × 50 c.c.), the ethereal solution was dried (K_2CO_3) and evaporated. Distillation of the residue gave the *triazole* as an orange liquid (10.5 g., 47.7%), b. p. 149–150°/2 mm. (Found: C, 58.2; H, 5.55; S, 15.2. $C_{10}H_{11}N_3S$ requires C, 58.5; H, 5.4; S, 15.6%).

(b) 3-Mercapto-5-methyl-1-phenyl-1,2,4-triazole⁶ (1.9 g.), *n*-sodium hydroxide (10 c.c.), and methyl iodide (0.62 c.c.) were placed in a stoppered vessel, shaken for 1 hr. Extraction with ether (3 × 20 c.c.), etc., as above, gave the pure triazole (1.5 g., 75%), b. p. 150°/2 mm. (Found: C, 58.3; H, 5.4; S, 15.5%).

3-Ethylthio-5-methyl-1-phenyl-1,2,4-triazole was prepared by method (a) from phenylhydrazine (5.4 g.), ethyl *N*-acetyldithiocarbamate¹⁹ (8.15 g.), and benzene (50 c.c.) and distilled as an orange liquid (4 g., 36.5%), b. p. 157–159°/0.1 mm. (Found: S, 14.4; N, 19.0. $C_{11}H_{13}N_3S$ requires S, 14.6; N, 19.2%).

3-Methylthio-1-phenyl-1,2,4-triazole.—3-Mercapto-1-phenyl-1,2,4-triazole²⁰ (14.3 g.), *n*-sodium hydroxide (81 c.c.), and methyl iodide (5.1 c.c.) were shaken for 1 hr., then extracted with chloroform (3 × 50 c.c.). The chloroform solution was dried (K_2CO_3) and evaporated. Distillation of the residue gave the *triazole* (11.4 g., 74%), b. p. 194–196°/15 mm., needles, m. p. 43° (Found: S, 16.5. $C_9H_9N_3S$ requires S, 16.75%).

5-Methylthio-3-methyl-1-phenyl-1,2,4-triazole.—5-Hydroxy-3-methyl-1-phenyl-1,2,4-triazole²¹ (58 g.), phosphorus pentasulphide (74 g.), and toluene (500 c.c.) were refluxed for 3 hr. and filtered hot. On cooling, the filtrate deposited needles which recrystallised from benzene to give the *mercaptotriazole* (29 g., 45.3%) as needles, m. p. 182° (Found: S, 16.65. $C_9H_9N_3S$ requires S, 16.75%). The mercapto-compound (28 g.), *n*-sodium hydroxide (147 c.c.), and methyl iodide (9.2 c.c.) were shaken for 1 hr. and extracted with chloroform (3 × 100 c.c.). After drying (K_2CO_3), the chloroform was evaporated and the residue distilled to give the *methyl-triazole* (26 g., 86.5%), b. p. 125–127°/0.15 mm., needles, m. p. 34° (Found: S, 15.5. $C_{10}H_{11}N_3S$ requires S, 15.6%).

5-Mercapto-3,4-dimethyl-1,2,4-triazole.—Acetic anhydride (48 c.c.) was added to 4-methylthiosemicarbazide¹⁰ (50 g.), and the resulting hot solution was left for 1 hr. Dilution with water (60 c.c.) and cooling gave a solid which was recrystallised from water to give *acetyl-4-methylthiosemicarbazide* (50 g., 72%) as needles, m. p. 167° (decomp.) (Found: S, 21.7. $C_4H_9ON_3S$ requires S, 21.8%). The acetyl derivative (50 g.) was then added cautiously to a solution from sodium (9 g.) in ethanol (200 c.c.), and the mixture refluxed for 2 hr. After removal of the ethanol under reduced pressure, water (200 c.c.) was added and the solution filtered and acidified with concentrated hydrochloric acid (40 c.c.), to give a precipitate, which recrystallised from ethanol to give the pure *mercaptotriazole* (24 g., 55.8%) as needles, m. p. 210° (Found: S, 24.7. $C_4H_7N_3S$ requires S, 24.8%).

By similar methods, the following were obtained from the appropriate intermediates: *acetyl-4-ethylthiosemicarbazide* from ethanol as needles, m. p. 151° (45%) (Found: S, 20.1. $C_5H_{11}ON_3S$ requires S, 19.9%); *4-ethyl-3-methyl-5-mercapto-1,2,4-triazole* from ethanol as needles, m. p. 139° (65.7%) (Found: S, 22.6. $C_5H_9N_3S$ requires S, 22.4%); *acetyl-4-phenylthiosemicarbazide* which, being insoluble was crushed under ethanol to give needles, m. p. 170° (decomp.)

¹⁹ Delépine, *Bull. Soc. chim. France*, 1903, 29, 50.

²⁰ Pellizzari and Ferro, *Gazzetta*, 1898, 28, 552.

²¹ Andreocci, *ibid.*, 1889, 19, 448.

(74.5%) (Found: S, 16.25. $C_6H_{11}ON_3S$ requires S, 15.3%); 5-mercapto-3-methyl-4-phenyl-1,2,4-triazole as an amorphous solid, m. p. 220° (44.7%) (Found: S, 16.8. $C_6H_9N_3S$ requires S, 16.75%), by dissolving the crude triazole in dilute aqueous ammonia and precipitating it with concentrated hydrochloric acid.

3,4-Dimethyl-5-methylthio-1,2,4-triazole.—5-Mercapto-3,4-dimethyl-1,2,4-triazole (19.35 g.), N-sodium hydroxide (150 c.c.), and methyl iodide (9.36 c.c.), shaken for 1 hr. and then extracted with chloroform (3×100 c.c.), gave the methylated triazole (11.4 g., 53.2%), b. p. 200°/14 mm., hygroscopic plates, m. p. 55–57° (Found: S, 22.6; N, 28.65. $C_5H_9N_3S$ requires S, 22.4; N, 29.4%).

By use of the appropriate intermediate and alkyl iodide the following alkylated 1,2,4-triazoles were prepared similarly: 4-ethyl-3-methyl-5-methylthio, b. p. 186–188°/10 mm. (67%) (Found: S, 20.4; N, 26.4. $C_6H_{11}N_3S$ requires S, 20.4; N, 26.75%); 3-methyl-5-methylthio-4-phenyl, needles [from light petroleum (b. p. 100–120°)], m. p. 119° (70.7%) (Found: S, 15.4; N, 20.4. $C_{10}H_{11}N_3S$ requires S, 15.6; N, 20.5%); 5-ethylthio-3-methyl-4-phenyl, needles [from light petroleum (b. p. 100–120°)], m. p. 106° (76.3%) (Found: S, 14.3; N, 18.7. $C_{11}H_{13}N_3S$ requires S, 14.6; N, 19.2%).

5-Ethylthio-3,4-dimethyl-1,2,4-triazole.—5-Mercapto-3,4-dimethyl-1,2,4-triazole (13 g.), 20% aqueous sodium hydroxide (60 c.c.), and ethyl sulphate (16.25 c.c.) were stirred for 1 hr., then heated on a steam-bath for 30 min. after which the mixture was cooled and extracted with chloroform (3×100 c.c.). The chloroform solution was dried (Na_2SO_4) and evaporated, and the residue distilled to give the ethyltriazole (7.3 g., 46.5%), b. p. 206°/12 mm. (Found: S, 19.8; N, 26.3. $C_6H_{11}N_3S$ requires S, 20.4; N, 26.75%).

3,4,5-Trimethyl-1,2,4-triazole.—As reported by us,⁴ preparation of this triazole by Meyer's method,²² gave a trihydrate. 2,5-Dimethyl-1,3,4-oxadiazole²³ (9.8 g.) and 10% w/v ethanolic methylamine (40 c.c.) at 100° (5 hr.) also the trihydrate (5.74 g., 35%), needles, m. p. 94° (Found: C, 36.15; H, 8.8; N, 25.15. Calc. for $C_5H_9N_3 \cdot 3H_2O$: C, 36.35; H, 9.1; N, 25.45%). Keeping this *in vacuo* over phosphoric oxide for about 14 hr. (loss, 32.7, 33.0. Calc. for $3H_2O$: 32.75%) gave the anhydrous triazole which crystallised from anhydrous benzene in plates, m. p. 178° (Found: N, 37.7. $C_5H_9N_3$ requires N, 37.85%). This readily reverted to the trihydrate in air or on crystallising from water. By the method used by Meyer²² for preparation of 3,5-dimethyl-4-phenyl-1,2,4-triazole were prepared: 4-p-methoxyphenyl-3,5-dimethyl-, needles [from benzene–light petroleum (b. p. 40–60°) (3 : 2)], m. p. 180° (45%) (Found: N, 20.6. $C_{11}H_{13}ON_3$ requires N, 20.7%), and 4-p-chlorophenyl-3,4-dimethyl-1,2,4-triazole, needles (from ethyl acetate), m. p. 236° (48%) (Found: Cl, 17.0. $C_{10}H_{10}N_3Cl$ requires Cl, 17.1%).

By refluxing a mixture of the appropriate triazole and methyl iodide (1 c.c. per g. of triazole; the reaction time is given in parentheses), adding anhydrous ether, filtering off the product, and recrystallising it, the following 1,2,4-triazole methiodides were prepared: 3,5-dimethyl-1-phenyl-³ (2 hr.), needles (from acetone), m. p. 167–168° (43%) (Found: I, 40.2. Calc. for $C_{11}H_{14}N_3I$: I, 40.3%); 3-methyl-1-phenyl-¹ (2 hr.), needles (from acetone), m. p. 183–185° (51%) (Found: I, 41.5. Calc. for $C_{10}H_{12}N_3I$: I, 42.2%); 5-methyl-3-methylthio-1-phenyl- (3 hr.), prisms (from acetone), m. p. 131° (55%) (Found: I, 36.0. $C_{11}H_{14}N_3SI$ requires I, 36.6%); 3-methylthio-1-phenyl- (20 hr.), needles (from ethanol), m. p. 186–188° (56.5%) (Found: I, 38.1. $C_{10}H_{12}N_3SI$ requires I, 38.1%); 3-methyl-5-methylthio-1-phenyl- (60 hr.), needles (from ethanol), m. p. 153° (51%) (Found: I, 36.5. $C_{11}H_{14}N_3SI$ requires I, 36.6%); 3,4-dimethyl-5-methylthio- (1 hr.), needles (from acetone), m. p. 164–166° (60%) (Found: I, 44.2. $C_6H_{12}N_3SI$ requires I, 44.6%); 3,5-dimethyl-4-phenyl- (1 hr.), needles [from acetone–ether (7 : 1)], m. p. 99–101° (67.5%) (Found: I, 39.7. $C_{11}H_{14}N_3I$ requires I, 40.3%); 4-p-methoxyphenyl-3,5-dimethyl (3 hr.), needles [from acetone–ether (17 : 1)], m. p. 174–176° (57%) (Found: I, 36.6. $C_{12}H_{16}ON_3I$ requires I, 36.8%); 4-p-chlorophenyl-3,5-dimethyl- (1 hr.), needles [from acetone–ether (2 : 1)], m. p. 206° (63%) (Found: I, 36.2. $C_{11}H_{13}N_3ClI$ requires I, 36.3%).

3,4,5-Trimethyl-1,2,4-triazole Methiodide.—3,4,5-Trimethyl-1,2,4-triazole (0.4 g.), methyl iodide (0.8 c.c.), and anhydrous benzene (10 c.c.) were refluxed for 4 hr., then cooled, and the resulting methiodide (0.5 g., 55%) was filtered off. This recrystallised from methanol–ether (1 : 2) as needles, m. p. and mixed m. p. with 1,3,5-trimethyl-1,2,4-triazole methiodide²⁴ 141° (Found: I, 50.7. Calc. for $C_6H_{12}N_3I$: I, 50.1%). The infrared absorptions of the two samples were identical.

²² Meyer, D.R.-P. 574,944/1933.

²³ Stolle, *Ber.*, 1899, **32**, 797.

²⁴ Atkinson and Polya, *J.*, 1954, 141.

Anhydro-3-mercapto-4,5-dimethyl-1-phenyl-1,2,4-triazolium Hydroxide.—(a) 5-Methyl-3-methylthio-1-phenyl-1,2,4-triazole methiodide (1.77 g.) and pyridine (10 c.c.) were refluxed for 1 hr. and poured into water (50 c.c.). After cooling, the resulting *thione* was filtered off and recrystallised from water to give needles (0.22 g., 21%), m. p. 292–294° (Found: C, 58.2; H, 5.6; S, 15.6. $C_{10}H_{11}N_3S$ requires C, 58.5; H, 5.4; S, 15.6%), λ_{max} (in ethanol) 2450 Å (ϵ 17,220).

(b) 4-Methyl-1-phenylthiosemicarbazide²⁵ (4 g.), acetic acid (5 c.c.), and acetic anhydride (5 c.c.) were refluxed for 30 min. On cooling, the pure *thione* (3.5 g., 74%) crystallised as needles, m. p. and mixed m. p. 292–294° (Found: C, 58.9; H, 5.6; S, 15.85%).

Anhydro-3-mercapto-4-methyl-1-phenyl-1,2,4-triazolium Hydroxide.—(a) 3-Methylthio-1-phenyl-1,2,4-triazole methiodide (2.2 g.) and pyridine (10 c.c.) as above gave the *thione* (0.35 g., 28%), needles (from ethanol), m. p. 267–268° (Found: S, 16.8. $C_9H_9N_3S$ requires S, 16.75%), λ_{max} (in ethanol): 2480 Å (ϵ 24,540).

(b) 4-Methyl-1-phenylthiosemicarbazide (3 g.) and 98% w/w formic acid (10 c.c.) were refluxed for 24 hr. and poured into water (75 c.c.). Filtration and recrystallisation of the product from ethanol gave the *thione* (0.7 g., 41%) as needles, m. p. and mixed m. p. 267–268° (Found: S, 16.6%).

Anhydro-3-mercapto-1,4,5-trimethyl-1,2,4-triazolium Hydroxide.—3,4-Dimethyl-5-methylthio-1,2,4-triazole methiodide (1 g.) and pyridine (5 c.c.) was refluxed for 13 hr. and evaporated under reduced pressure. Recrystallisation of the residue from ethanol gave the *thione* (0.22 g., 44%) as needles, m. p. 257–259° (Found: S, 22.6. $C_5H_9N_3S$ requires S, 22.4%), λ_{max} (in ethanol) 2420 Å (ϵ 13,090).

4,5-Dihydro-3,4-dimethyl-1-phenyl-1,2,4-triazole-5-thione.—(a) 3-Methyl-5-methylthio-1-phenyl-1,2,4-triazole methiodide (4 g.) and pyridine (20 c.c.) were refluxed for 1 hr. and poured into water (50 c.c.). Filtration and recrystallisation from water gave the *thione* (0.85 g., 34%) as plates, m. p. 79–81° (Found: S, 15.7. $C_{10}H_{11}N_3S$ requires S, 15.6%), λ_{max} (in ethanol) 2870 Å (ϵ 10,250).

(b) 4-Methyl-2-phenylthiosemicarbazide²⁵ (8.2 g.) and glacial acetic acid (20.5 c.c.) were stirred at room temperature while acetic anhydride (5.1 c.c.) was added in one portion. After a further 30 minutes' stirring, the mixture was poured into water (100 c.c.), and the acetylated thiosemicarbazide was filtered off and recrystallised from ethyl acetate as needles (2.5 g., 25%), m. p. 166–168°. This compound (2.2 g.) was added to a solution from sodium (0.23 g.) in ethanol (20 c.c.), and the mixture refluxed for 2 hr. After cooling, the insoluble part was filtered off and recrystallised from water, to give the *thione* (1.5 g., 75%) as plates, m. p. and mixed m. p. 79–81° (Found: S, 15.8%).

2,3-Dihydro-2,5-dimethyl-1-phenyl-1,2,4-triazole-3-thione.—A solution of 1-methyl-2-phenylhydrazine (40 g.) in ethanol (40 c.c.) was treated cautiously with concentrated hydrochloric acid (33 c.c.) and then evaporated under reduced pressure. The residue was dried by azeotropic distillation with ethanol (2 × 50 c.c.), dissolved in ethanol (500 c.c.), and mixed with dried potassium thiocyanate (32 g.). After being refluxed for 15 hr., the mixture was filtered hot. The filtrate deposited 2-methyl-1-phenylthiosemicarbazide which recrystallised from alcohol as yellow needles (17.6 g., 30%), m. p. 200–202° (Found: C, 53.5; H, 6.1. $C_9H_{11}N_3S$ requires C, 53.0; H, 6.1%). The thiosemicarbazide (17.6 g.), acetic anhydride (9.5 c.c.), and acetic acid (40 c.c.) were refluxed for 1 hr., then poured into water to give the crude acetyl derivative (17.3 g., 80%) as buff needles, m. p. 184–188°. This was added to a solution from sodium (1.8 g.) in ethanol (100 c.c.), and the mixture refluxed for 15 hr. After cooling, the insoluble *thione* was filtered off and recrystallised from ethanol to give plates (10.8 g., 68%), m. p. 267–269° (Found: C, 58.6; H, 5.5; S, 15.6. $C_{10}H_{11}N_3S$ requires C, 58.5; H, 5.4; S, 15.6%), λ_{max} (in ethanol) 2910 Å (ϵ 12,812).

2,5-Dimethyl-3-methylthio-1-phenyl-1,2,4-triazole Methiodide.—2,3-Dihydro-2,5-dimethyl-1-phenyl-1,2,4-triazole-3-thione (1 g.) and methyl iodide (2 c.c.) were refluxed for 1 hr. and the crude *methiodide* was filtered off. Recrystallisation from acetone gave needles (1.1 g., 64%), m. p. 140–142° (Found: I, 36.2. $C_{11}H_{14}N_3SI$ requires I, 36.6%).

By similar methods, the following 1-phenyl-1,2,4-triazole *methiodides* were prepared from the corresponding thiones; they were identical (m. p. and mixed m. p.) with those prepared directly from the triazole bases: 5-methyl-3-methylthio-1-phenyl-, prisms (from acetone), m. p. 131° (79%) (Found: I, 36.6. $C_{11}H_{14}N_3SI$ requires I, 36.6%); 3-methylthio-, needles (from ethanol),

²⁵ Busch, Opfermann, and Walther, *Ber.*, 1904, **37**, 2332.

Trimethincyanines (XI; $m = 1$).

$\overline{\text{C-D-N-R}}^{\text{***}}$	R	R'	R''	X	Yield (%)	Solvent	M. p.	Formula	Required (%)			Found (%)		
									C	H	Hal	C	H	Hal
A	Me	Me	Me	ClO ₄	20	MeOH ^a	240° (1)	C ₁₇ H ₂₁ O ₄ N ₄ Cl	—	—	8.95	—	—	8.9
A	Me	MeS	Me	I	20	H ₂ O ^a	214 (2)	C ₁₇ H ₂₁ O ₄ N ₄ SI	44.7	4.6	—	44.7	4.9	—
A	Me	Me	Ph	I	25	MeOH ^a	248–250 (3)	C ₂₂ H ₂₃ ON ₄ I [†]	54.3	4.7	26.1	54.3	5.1	25.9
A	Ph	Me	Me	I	20	EtOH ^a	236–237 (5)	2C ₂₂ H ₂₃ ON ₄ I [†] C ₂ H ₅ OH	54.2	5.1	24.95	53.7	4.8	24.7
A	Me	MeS	Ph	I	23	EtOH ^a	236–237 (5)	C ₂₂ H ₂₃ ON ₄ SI	51.0	4.4	24.5	50.9	4.7	23.8
A	Ph	MeS	Me	I	14	EtOH ^a	220–222 (6)	C ₂₂ H ₂₃ ON ₄ SI ₂ H ₂ O	—	—	23.7	—	—	23.8
B	Ph	Me	Me	I	36	MeOH ^b	247–248	2C ₂₂ H ₂₃ ON ₄ SI ₂ CH ₃ OH	52.1	4.8	24.5	52.2	4.7	24.8
B	Ph	MeS	Me	I	56	MeOH ^b	233–234	2C ₂₂ H ₂₃ ON ₄ SI ₂ CH ₃ OH	—	—	23.1	—	—	23.3
B	Ph	MeS	Me	I	36	MeOH ^b	233–234	2C ₂₂ H ₂₃ ON ₄ SI ₂ CH ₃ OH [†]	—	—	23.1	—	—	23.3
B	Ph	EtS	Me	I	32	EtOH ^b	223–224	2C ₂₂ H ₂₃ ON ₄ SI ₂ CH ₃ OH	—	—	22.8	—	—	22.7
B	Me	MeS	Et	ClO ₄	13	MeOH ^b	184–186	C ₁₈ H ₂₃ O ₄ N ₄ SI ₂ CH ₃ OH	—	—	6.8	—	—	6.85
B	Me	MeS	Ph	I	43	EtOH ^c	232–234	2C ₂₂ H ₂₃ ON ₄ SI ₂ CH ₃ OH	—	—	22.8	—	—	22.8
B	Me	EtS	Ph	I	24	MeOH ^c	225–227	C ₃₃ H ₃₅ N ₅ SI ₂ H ₂ O	—	—	22.4	—	—	22.35
B	Me	MeS	Me	ClO ₄	22	MeOH ^d	217–219	C ₃₃ H ₃₅ O ₄ N ₄ SI ₂ Cl	(S, 14.4)	—	—	(S, 14.3)	—	—
B	Me	Me	Ph	I	26	EtOH ^b	195	C ₃₂ H ₂₃ ON ₄ SI [†]	—	—	25.3	—	—	24.9
B	Me	Me	<i>p</i> -MeO·Ph	I	19	H ₂ O ^b	245	C ₃₃ H ₂₅ ON ₄ SI ₂ H ₂ O [†]	—	—	22.8	—	—	23.1
C	Ph	Me	Me	ClO ₄	11	EtOH ^b	212–213	C ₃₄ H ₂₇ O ₄ N ₄ Cl	—	—	7.5	—	—	7.4
C	Ph	MeS	Me	ClO ₄	20	MeOH ^e	220–221	C ₃₄ H ₂₇ O ₄ N ₄ SI	—	—	7.1	—	—	7.2
C	Ph	EtS	Me	ClO ₄	23	MeOH ^e	225	C ₃₅ H ₂₉ O ₄ N ₄ SI ₂ CH ₃ OH	—	—	6.1	—	—	5.9
A	Ph	EtS	Me	I	9	H ₂ O ^e	202–203	2C ₂₅ H ₂₉ O ₄ N ₄ SI ₂ H ₂ O	51.0	4.8	23.5	51.4	5.2	23.5
A	Me	EtS	Me	ClO ₄	12	EtOH ^a	191	C ₁₈ H ₂₃ O ₄ N ₄ SI	—	—	8.0	—	—	8.0
A	Me	MeS	Et	ClO ₄	14	MeOH ^a	197	C ₁₈ H ₂₃ O ₄ N ₄ SI ₂ CH ₃ OH	—	—	7.5	—	—	7.4
A	Me	Me	<i>p</i> -MeO·Ph	I	22	EtOH ^a	261	C ₃₃ H ₃₅ O ₄ N ₄ I [†]	—	—	24.6	—	—	24.5
E	Ph	Me	Me	I	25	EtOH ^c	231–232	C ₃₄ H ₃₅ N ₄ I [†]	—	—	25.6	—	—	25.1

* A = 3-Ethyl-2-benzoxazole; B = 3-ethyl-2-benzothiazole; C = 1,3,3-trimethyl-2-indoline; E = 1-ethyl-2-quinoline.

° Orange needles. ^b Purple needles. ^c Red needles. ^d Brown needles. ^e Yellow needles. λ_{max} (in ethanol): (1) 3940 Å; (2) 4080 Å; (3) 4370 Å; (4) 4430 Å; (5) 4500 Å; (6) 4530 Å.

† From the triazole methiodide.

m. p. 186—188° (87%) (Found: I, 38.2. $C_{10}H_{12}N_3SI$ requires I, 38.1%); 3-methyl-5-methylthio-, needles (from ethanol), m. p. 153° (98%) (Found: S, 9.4; I, 36.6. $C_{11}H_{14}N_3SI$ requires S, 9.2; I, 36.6%).

Degradation of 1,3,5-Trimethyl-1,2,4-triazole Methiodide.—The methiodide (5.9 g.) and 50% potassium hydroxide (40 c.c.) were refluxed for 2 hr. while the uncondensed vapours were passed through a tube of solid potassium hydroxide and thence into a solution of picric acid (5.4 g.) in anhydrous benzene (200 c.c.). The resulting methylamine picrate (1.7 g., 28%) was obtained as yellow needles, m. p. and mixed m. p. 208°. The residual alkaline solution was distilled and the distillate (15 c.c.) neutralised with 1.01N-sulphuric acid (25 c.c.). Addition of more 1.01N-sulphuric acid (25 c.c.) and evaporation of the solution under reduced pressure gave a crystalline residue which was dried by azeotropic distillation with ethanol (2 × 50 c.c.). Recrystallisation of the residue from methanol gave methylhydrazine sulphate (1.6 g., 54%) as needles, m. p. and mixed m. p. 144°.

Degradation of 3,5-Dimethyl-1-phenyl-1,2,4-triazole Methiodide.—The methylamine picrate (1.7 g., 33%) was recovered from the methiodide (6.3 g.) and 50% potassium hydroxide (20 c.c.) by the method used above. The residual alkaline mixture was diluted with water (30 c.c.) and distilled, and the distillate (30 c.c.) was treated with ethanol (5 c.c.), glacial acetic acid (2 c.c.), and benzaldehyde (2.1 c.c.) to give a crop of pale yellow needles. By repeating this process four times and recrystallising the assembled crops from ethanol, benzaldehyde phenylhydrazone (1.73 g., 45%) was obtained as pale yellow needles, m. p. and mixed m. p. 155—157°.

Conversion of 3,5-Dimethyl-1-phenyl- and 3-Methyl-5-methylthio-1-phenyl-1,2,4-triazole into the Same Cyanine Dye.—(a) 3,5-Dimethyl-1-phenyl-1,2,4-triazole (0.35 g.), methyl toluene-*p*-sulphonate (0.74 g.), and 2-methylthiobenzothiazole (0.36 g.) were fused for 1 hr. at 140°. Pyridine (5 c.c.) and triethylamine (2 c.c.) were added, the mixture was refluxed for 1 hr. and then poured into 4% aqueous sodium iodide (50 c.c.). The precipitate was filtered off, washed with ether, and recrystallised from ethanol, to give the dye (XI; D = the residue of a benzothiazole nucleus, R = Ph, R' = R'' = R''' = Me, *m* = 0, X = I) (0.23 g., 24%) as yellow leaflets, m. p. 207—209° (Found: I, 26.2. $C_{19}H_{19}N_4SI \cdot H_2O$ requires I, 26.5%).

(b) By the same method, 3-methyl-5-methylthio-1-phenyl-1,2,4-triazole (0.62 g.), methyl toluene-*p*-sulphonate (1.12 g.), and 2-methylbenzothiazole (0.45 g.) gave the same dye (0.2 g., 14%), m. p. and mixed m. p. 207—209° (Found: I, 26.5%). The dye (0.1 g., 11%) was also obtained by refluxing a mixture of this methiodide (0.69 g.), 2,3-dimethylbenzothiazolium iodide (0.58 g.), pyridine (5 c.c.), and triethylamine (2 c.c.) for 1 hr., and then proceeding as above (Found: I, 26.4%).

4-[2-(3,4-Dimethyl-1-phenyl-1,2,4-triazolin-5-ylidene)ethylidene]-2-phenyl-5-oxazolone.—3,5-Dimethyl-1-phenyl-1,2,4-triazole (0.35 g.) and methyl toluene-*p*-sulphonate (0.37 g.) were fused for 1 hr. at 140°, then mixed with 4-ethoxymethylene-2-phenyl-5-oxazolone (0.43 g.), pyridine (5 c.c.), and triethylamine (2 c.c.). The mixture was refluxed for 1 hr. and poured into water (50 c.c.). The precipitate was filtered off and recrystallised from ethanol, to give the dye (0.24 g., 33%) as orange needles, m. p. 257—259° (Found: N, 15.3. $C_{21}H_{18}O_2N_4$ requires N, 15.6%).

By similar methods, the appropriate triazole and the oxazolone or 5-ethoxymethylene-3-ethyl-2-thiothiazolid-4-one gave 4-[2-(4-methyl-3-methylthio-1-phenyl-1,2,4-triazolin-5-ylidene)ethylidene]-2-phenyl-5-oxazolone, red needles (from ethanol), m. p. 241—242° (25%) (Found: N, 12.2. $2C_{21}H_{18}O_2N_4S \cdot 3C_2H_5 \cdot OH$ requires N, 12.2%), and 3-ethyl-5-[2-(3-ethylthio-1-methyl-4-phenyl-1,2,4-triazolin-5-ylidene)ethylidene]-2-thiothiazolid-4-one, red needles (from ethanol), m. p. 229° (40%) (Found: N, 13.3. $2C_{18}H_{20}ON_4S_3 \cdot C_2H_5 \cdot OH$ requires N, 13.2%).

The following merocyanines were made from the triazole methiodides: 3-ethyl-5-[2-(3,4-dimethyl-1-phenyl-1,2,4-triazolin-5-ylidene)ethylidene]-2-thiothiazolid-4-one, brown needles (from methanol), m. p. 231° (28%) (Found: S, 17.9. $C_{17}H_{18}ON_4S_2$ requires S, 17.9%); 3-ethyl-5-[2-(1,4-dimethyl-3-methylthio-1,2,4-triazolin-5-ylidene)ethylidene]-2-thiothiazolid-4-one, orange needles (from ethanol), m. p. 238° (30%) (Found: N, 16.1. $2C_{12}H_{16}ON_4S_3 \cdot C_2H_5 \cdot OH$ requires N, 15.95%); 3-ethyl-5-[2-(4-*p*-methoxyphenyl-1,3-dimethyl-1,2,4-triazolin-5-ylidene)ethylidene]-2-thiothiazolid-4-one, bronze plates (from ethanol), m. p. 229° (21%) (Found: N, 11.3. $C_{18}H_{20}O_2N_4S_2 \cdot 2C_2H_5 \cdot OH$ requires N, 11.7%); 5-[2-(4-*p*-chlorophenyl-1,3-dimethyl-1,2,4-triazolin-5-ylidene)ethylidene]-3-ethyl-2-thiothiazolid-4-one, red plates (from ethanol), m. p. 259—261° (35%) (Found: N, 13.9. $C_{17}H_{17}ON_4S_2Cl$ requires N, 14.3%).

5-Ethoxymethylene-3-ethyl-2-thiothiazolid-4-one was prepared as follows: 3-ethyl-2-thiothiazolid-4-one (32 g.), ethyl orthoformate (40 c.c.), and acetic anhydride (60 c.c.) were refluxed

for 18 hr. After cooling, the product was filtered off and recrystallised from ethanol forming yellow needles (22 g., 50%), m. p. 94° (Found: S, 29.5. $C_8H_{11}O_2NS_2$ requires S, 29.5%).

The following monomethincyanines (XI; $m = 0$) were prepared by a joint fusion process similar to that described earlier for the preparation of the dye (XI; D = residue of a benzothiazole nucleus, R = Ph, R' = R'' = R''' = Me, $m = 0$, X = I): (1,3,4-trimethyl-5-1,2,4-triazole)(3-methyl-2-benzothiazole)monomethincyanine perchlorate buff-coloured needles (from water), m. p. 235° (16%) (Found: Cl, 9.2. $C_{14}H_{17}O_4N_4S_2Cl$ requires Cl, 9.1%); (4-methyl-3-methylthio-1-phenyl-5-1,2,4-triazole)(3-methyl-2-benzothiazole)monomethincyanine iodide, buff-coloured needles (from ethanol), m. p. 132—134° (10%) (Found: I, 23.3. $C_{19}H_{19}N_4S_2I, C_2H_5, OH$ requires I, 23.5%); (1,4-dimethyl-2-methylthio-5-1,2,4-triazole)(3-methyl-2-benzothiazole)monomethincyanine perchlorate, yellow leaflets (from methanol), m. p. 236—237° (50%) (Found: S, 16.0. $C_{14}H_{17}O_4N_4S_2Cl$ requires S, 15.8%).

The trimethincyanines (XI; $m = 1$) contained in the Table were prepared by fusing the triazole and methyl toluene-*p*-sulphonate for 1 hr. at 140° and then refluxing the salt, the appropriate 2-2'-acetanilidovinyl heterocyclic quaternary salt, pyridine, and triethylamine for 1 hr. and pouring the whole into 4% aqueous sodium iodide or perchlorate. Numbers which have been given to the first six dyes correspond to those of the dyes discussed in the theoretical part.

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