230. 2-*Mercaptoglyoxalines. Part X.* The Acylation of 2-Mercaptoglyoxalines.*

By Alexander Lawson and H. V. Morley.

2-Mercaptoglyoxalines, which show an absorption maximum in the 2600 Å region due mainly to contributions from the thione form, are acylated in basic media at a nitrogen atom, probably as a result of rearrangement of the *S*-acyl isomer first formed. In the case of acyl derivatives such as 1-ethoxycarbonyl-2-mercapto-4- or -5-methylglyoxaline (III), possible reasons for the bathochromic shift in the absorption maximum from the 2600 to the 3050 Å region are advanced.

Interest in the acylation of 2-mercaptoglyoxalines arose owing to the necessity of protecting the sulphur and the nitrogen atom of 2-mercaptohistidine during the methylation which led to the synthesis of ergothioneine by Heath, Lawson, and Rimington.[1] The product obtained by the action of ethyl chloroformate on 2-mercaptohistidine was designated as 2-ethoxycarbonylthiohistidine since methylation affected only the side-chain amino-group and the ultraviolet absorption failed to show a maximum at *ca.* 2600 Å (in ethanol) believed to be characteristic of the mercapto-group in 2-mercaptoglyoxalines. The same workers also investigated the use of benzylation and acetylation as protecting groups.

The effect of acylation on the 2-mercaptoglyoxaline structure has been investigated by using 2-mercapto-4(5)-methylglyoxaline [2] (I). With ethyl chloroformate in pyridine this gave an ethoxycarbonyl derivative for which the structures (II) and (III) (or tautomers thereof) are possible. The ultraviolet spectrum did not show the characteristic peak at 2600 Å and thus, according to the interpretation of Heath *et al.*,[1] structure (II) seemed indicated.

The formation of 2-ethylthio-4(5)-methylglyoxaline when this substance was heated did not provide evidence of structure, for, although Jones [3] reports ethylation of the sulphur

* Part IX, *J.*, 1955, 1695.

[1] Heath, Lawson, and Rimington, *J.*, 1951, 2215.
[2] Bullerwell and Lawson, *J.*, 1951, 3030.
[3] Jones, *J. Amer. Chem. Soc.*, 1952, **74**, 1084.

atom on heating 4(5)-ethoxycarbonyl-2-mercaptoglyoxaline, Dixon [4] showed that *S*-ethoxycarbonylthiuronium chlorides also give *S*-alkyl derivatives when heated.

It is known that under certain conditions oxidation of 2-mercaptoglyoxalines leads to disulphides.[5] Oxidation of the compound (II or III) with nitric acid gave a crystalline disulphide, $C_{14}H_{18}O_4N_4S_2$ (IV), which could have been produced only from structure (III). The disulphide on hydrolysis lost the ethoxycarbonyl groups and gave an amorphous basic substance (V) (probably polymeric) having the composition of a disulphoxide.

The correctness of the structure 1-ethoxycarbonyl-2-mercapto-4- or -5-methylglyoxaline (III) was confirmed by methylation, followed by hydrolysis to remove the ethoxycarbonyl group. The basic product (VI) was identical with that obtained by the direct methylation of 2-mercapto-4(5)-methylglyoxaline (I) which according to Marckwald [6] would be expected to give an *S*-methyl derivative. The *S*-alkyl structure was confirmed by the preparation from the corresponding ethylthio-derivative of a bromo- and an iodo-derivative with no sign of disulphide formation.

From the above results it is clear that failure to show absorption in the 2600 Å region is not sufficient evidence for deciding between *N*- and *S*-acylation in 2-mercaptoglyoxalines.

It seems probable that 1-ethoxycarbonyl-2-mercapto-4- or -5-methylglyoxaline (III) arises by migration of the acyl group from the sulphur to the nitrogen atom. Such a rearrangement would account for the same substance's being obtained from the mercaptoglyoxaline and ethyl chloroformate in sodium hydroxide solution, *i.e.*, under conditions which would favour *S*-substitution. Moreover, when the ethoxycarbonylation is done at room temperature in a non-basic medium, a hydrochloride of a base giving a picrate is obtained. This base must be the *S*-ethoxycarbonyl isomer (II) since the known *N*-ethoxycarbonyl derivative (III) is non-basic and does not give a picrate. The above hydrochloride on treatment with pyridine yields the *N*-ethoxycarbonyl derivative. Such a rearrangement of an acyl group from a sulphur to a nitrogen atom is well established for thioureas.[7]

2-Mercaptoglyoxaline on treatment with formaldehyde gave 1-hydroxymethyl-2-mercaptoglyoxaline.[8] 2-Mercapto-1-methylglyoxaline likewise gives a hydroxymethyl derivative which from chemical considerations would be expected to be 3(1)-hydroxymethyl-1(3)-methyl-2-thioglyoxalone. The spectrum of this compound shows strong absorption at 2630 Å which is explicable only in terms of the thione formula since the isomeric sulphide would be expected to show absorption typical of the *S*-alkylglyoxalines (cf. Table). It must therefore be concluded that the thione group in this particular environment is capable of absorbing strongly in the 2600 Å region.

Whether the absorption maximum at *ca.* 2600 Å (in ethanol) shown by non-acylated 2-mercaptoglyoxalines is due to the auxochromic effect of a thiol group on the glyoxaline chromophore thus appears to be questionable and the probability of its being due to the thione form emerges (cf. Koch [9]).

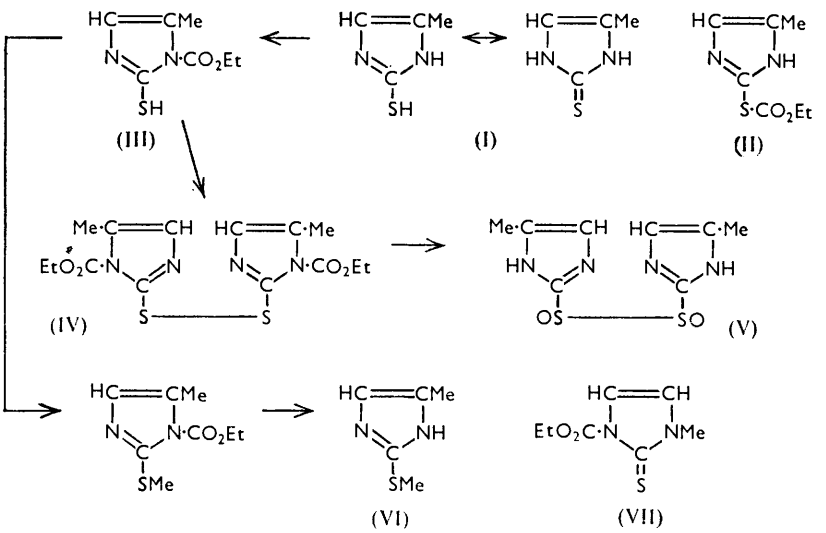
Spectroscopic investigation [10] of the thiol–thione tautomerism of 2-mercaptobenzothiazole and its derivatives [10] indicated that the thione form predominated in alcoholic solution since the *N*-methyl derivatives differed but little from the parent compound in their absorption, whereas the *S*-methyl derivatives absorbed at a lower wavelength with a great reduction in intensity. In alkaline solution the thione–thiol equilibrium was altered in favour of the " acidic " thiol form since the *S*-sodio-derivatives showed the absorption typical of the *S*-alkyl derivatives.

Analogous behaviour of the methyl derivatives of the 2-mercaptoglyoxalines has been observed (Table), *i.e.*, the absorption of the *S*-methyl derivative occurs at a slightly lower wavelength and with a much reduced intensity. It therefore appears that the absorption at 2600 Å in the 2-mercaptoglyoxalines is due mainly to contributions from the thione

[4] Dixon, *J.*, 1907, 912.
[5] Anschutz and Schwickerath, *Annalen*, 1895, **284**, 99; Biltz and Krebs, *ibid.*, 1912, **391**, 203; Balaban and King, *J.*, 1927, 1858.
[6] Marckwald, *Ber.*, 1892, **25**, 2360.
[7] Dixon and co-workers, *J.*, 1920, **117**, 80, 720.
[8] Heath, Lawson, and Rimington, *J.*, 1951, 2218.
[9] Koch, *J.*, 1949, 401.
[10] Morton and Stubbs, *J.*, 1939, 1321; Hassan and Hunter, *J.*, 1936, 1672.

form. This is supported by the work of Ettlinger [11] who on the basis of infrared absorption data considers that 2-mercapto-1-methylglyoxaline exists mainly in the thione form.

Accepting the view of Ettlinger and by analogy with 2-mercapto-4(5)-methylglyoxaline one would expect that acylation of 2-mercapto-1-methylglyoxaline would also take place at the nitrogen atom. The correctness of this view is shown in that the substance (VII), obtained by the action of ethyl chloroformate on the latter compound in pyridine, is non-basic and is also obtained by the action of pyridine on the hygroscopic *S*-ethoxycarbonyl-hydrochloride resulting from ethoxycarbonylation in non-basic media, as in the case of the 4(5)-methyl derivative above.



Grote's reagent,[12] used to distinguish between $\geq$C·SH and $>$C:S in organic sulphur compounds, gives a green colour with all mercaptoglyoxalines examined which have a potential thiol group and gives no colour with the sulphides. With the ethoxycarbonyl derivative of 2-mercapto-1-methylglyoxaline the colour produced is indigo, indicating the thione structure (VII). A number of other acylated derivatives of 2-mercapto-1-methylglyoxaline have been prepared with a view to their use as antithyroid substances. These, by analogy, have been designated as *N*-acyl derivatives.

In the case of 1(3)-ethoxycarbonyl-3(1)-methyl-2-thioglyoxalone (VII) the bathochromic shift in the absorption (Table) accompanying the introduction of the ethoxycarbonyl group may be attributed to the effect of this group on the absorption of the parent substance acting as the thione tautomer. For 1-ethoxycarbonyl-2-mercapto-4- or -5-methylglyoxaline (III) however a second explanation may be advanced. An examination of the infrared spectrum of 1-ethoxycarbonyl-2-mercapto-4- or -5-methylglyoxaline (III) in chloroform or Nujol shows that chelation of the mercapto- and ethoxycarbonyl groups takes place, since a splitting of the CO absorption band to give peaks at 5·65 and 5·74 μ is observed. The bathochromic shift from the 2600 to the 3050 Å region which occurs on the introduction of the *N*-ethoxycarbonyl group may, in this case, be alternatively attributed to this intramolecular hydrogen bonding (cf. Wiegand and Merkel;[13] Ferguson and Kelly [14]).

The acetyl derivative of 2-mercapto-4(5)methylglyoxaline (I) (Heath *et al.*[8]) was assigned the acetylthio-structure mainly on the basis of the lack of absorption in the 2600 Å region. Cook, Downer, and Heilbron,[15] however, tentatively assigned an *N*-acetyl structure to the monoacetyl derivative of 5-benzamido-2-mercaptoglyoxaline although again no

[11] Ettlinger, *J. Amer. Chem. Soc.*, 1950, **72**, 4699.
[12] Grote, *J. Biol. Chem.*, 1931, **93**, 25.
[13] Wiegand and Merkel, *Annalen*, 1947, **557**, 242.
[14] Ferguson and Kelly, *J. Amer. Chem. Soc.*, 1951, **73**, 3707.
[15] Cook, Downer, and Heilbron, *J.*, 1948, 1262.

absorption on the 2600 Å region was shown. In view of these conflicting conclusions, a dilute solution of the acetyl derivative of 2-mercapto-4(5)-methylglyoxaline in chloroform was titrated with iodine in the same solvent according to the procedure used by Werner [16] for thioureas. The rapid uptake of 1 equivalent of iodine, followed by a further slow uptake, presumably due to iodination of the ring, indicates the presence of a free thiol group. The compound in question must therefore be regarded as having the *N*-acetyl structure. The infrared spectrum of this compound substantiated such a formulation, the following bands being present : 2·9 μ (N–H monomeric), 3·12 μ (N–H associated), 6·02 μ (CH:CMe), 5·81 μ (CH_3·CO), 6·71 μ (NH·CS·N) and 3·70 μ (?) (trace of SH).

Light absorption of 2-mercaptoglyoxalines.

	$\lambda_{max.}$ (Å)	ε	Solvent
2-Mercapto-4(5)-methylglyoxaline (I)	2570	15,000	H_2O
	2630	14,700	EtOH
	2710	13,700	$CHCl_3$
2-Mercapto-1-methylglyoxaline	2510	14,400	H_2O
	2600	13,600	EtOH
	2670	17,000	$CHCl_3$
2-Methylthioglyoxaline	2500	4,720	EtOH
4(5)-Methyl-2-methylthioglyoxaline (VI)	2500	3,400	EtOH
1-Ethoxycarbonyl-2-mercapto-4(5)-methylglyoxaline (III)	3090	15,600	$CHCl_3$
1(3)-Ethoxycarbonyl-3(1)-methyl-2-thioglyoxalone (VII)	3040	12,700	$CHCl_3$
1(3)-Benzyloxycarbonyl-3(1)-methyl-2-thioglyoxalone	3040	12,000	$CHCl_3$
Di-(1-ethoxycarbonyl-4- or -5-methyl-2-glyoxalinyl) disulphide (IV)	2750	12,200	$CHCl_3$
2-Benzylthio-4(5)-methylglyoxaline	2510	5,020	EtOH
1(3)-Hydroxymethyl-3(1)-methyl-2-thioglyoxalone	2630	14,400	EtOH
1 : 3-Di(hydroxymethyl)-2-thioglyoxalone	2670	13,600	EtOH

Experimental

1-*Ethoxycarbonyl-2-mercapto-4- or -5-methylglyoxaline* (III).—2-Mercapto-4(5)-methylglyoxaline (5·7 g., 0·05 mol.) in pyridine (20 ml.) was cooled in ice, and ethyl chloroformate (6 g., 0·055 mol.) added dropwise with stirring during 10 min. After 20 minutes, sodium hydrogen carbonate (4·2 g.) in water (30 ml.) was added, and the precipitate removed and recrystallised from water (7·2 g.). 1-*Ethoxycarbonyl-2-mercapto-4- or -5-methylglyoxaline* had m. p. 121° (Found : C, 45·2; H, 5·5. $C_7H_{10}O_2N_2S$ requires C, 45·2; H, 5·4%). The product, sparingly soluble in water and dilute hydrochloric acid, dissolved readily in alkali. The introduction of a second ethoxycarbonyl group into 2-mercapto-4(5)-methylglyoxaline could not be effected by using excess of ethyl chloroformate.

1-*Ethoxycarbonyl-2-mercaptoglyoxaline.*—This *compound* prepared as above from 2-mercaptoglyoxaline (75% yield) had m. p. 119—20° (from ethyl acetate) (Found : C, 42·0; H, 4·8. $C_6H_8O_2N_2S$ requires C, 41·9; H, 4·7%).

2-*Ethoxycarbonylthio-4(5)-methylglyoxaline Picrate.*—To finely ground 2-mercapto-4(5)-methylglyoxaline (5·7 g.) in ethanol (100 ml.) was added ethyl chloroformate (6·0 g.), and the resulting suspension left overnight. Removal of the ethanol at room temperature gave a water-soluble, acidic yellow oil, which on addition of aqueous picric acid gave 2-*ethoxycarbonylthio-4(5)-methylglyoxaline picrate* (3·0 g., 14·5%), m. p. 89—92° (Found : C, 37·9; H, 3·2. $C_{13}H_{13}O_9N_5S$ requires C, 37·6; H, 3·1%).

Addition of pyridine to an aqueous solution of the above oil gave 1-ethoxycarbonyl-2-mercapto-4- or 5-methylglyoxaline.

Di-(1-ethoxycarbonyl-4- or -5-methyl-2-glyoxalinyl) Disulphide (IV).—1-Ethoxycarbonyl-2-mercapto-4- or -5-methylglyoxaline (3·36 g., 0·018 mol.) was dissolved in acetic acid (40 ml.) and cooled to 0°. Concentrated nitric acid (2 ml.) was added with stirring during 30 min., followed by water (30 ml.) and then solid sodium carbonate to pH 7. The disulphide was filtered off and crystallised from aqueous ethanol to give yellow plates (3 g.), m. p. 138—139°. (Found : C, 45·4; H, 4·8; N, 15·1; S, 17·3%; *M*, 376. $C_{14}H_{18}O_4N_4S_2$ requires C, 45·4; H, 4·9; N, 15·2; S, 17·3%; *M*, 370).

Di-(1-ethoxycarbonyl-2-glyoxalinyl) disulphide, yellow plates, m. p. 153° (from aqueous ethanol) (Found : C, 42·6; H, 4·1. $C_{12}H_{14}O_4N_4S_2$ requires C, 42·1; H, 4·1%), was similarly prepared.

[16] Werner, *J.*, 1912, 2168.

Di-[4(5)-*methyl*-2-*glyoxalinyl*] *Disulphoxide* (V).—Di-(1-ethoxycarbonyl-4- or -5-methyl-2-glyoxalinyl) disulphide (1·1 g., 0·0045 mol.) was added to 6N-sodium hydroxide (12 ml.) and left overnight. On neutralisation of the solution with 6N-hydrochloric acid a light yellow amorphous powder (0·8 g.), m. p. 250—254°, was precipitated. The product was initially soluble in ethanol but when kept it became insoluble in the usual organic solvents. Purification of the *disulphoxide* was effected by dissolving it in hydrochloric acid and reprecipitating it with sodium carbonate (Found: C, 37·1; H, 3·8. $C_8H_{10}O_2N_4S_2$ requires C, 37·2; H, 3·9%).

2-*Methylthio*-4(5)-*methylglyoxaline* (VI).—2-Mercapto-4(5)-methylglyoxaline (5·7 g., 0·05 mol.) was dissolved in ethanol, and methyl iodide (3·2 ml., 0·05 mol.) added. After 2 hr., the ethanol was removed under reduced pressure and aqueous potassium carbonate added to pH 10. The oil which separated slowly solidified at 0° and after recrystallisation from water the 2-*methylthio*-4(5)-*methylglyoxaline* (3·3 g.) had m. p. 82—83° (Found: C, 47·0; H, 6·4. $C_5H_6N_2S$ requires C, 46·9; H, 6·3%).

1-*Ethoxycarbonyl*-2-*methylthio*-4- *or* -5-*methylglyoxaline*.—1-Ethoxycarbonyl-2-mercapto-4- or -5-methylglyoxaline (4·65 g., 0·025 mol.) was dissolved in ethanol (30 ml.), and methyl iodide (3·1 ml., 0·025 mol.) added. After 12 hr. aqueous potassium carbonate was added to pH 7 and the solutions evaporated under reduced pressure. The oily residue taken up in warm aqueous ethanol gave 1-*ethoxycarbonyl*-2-*methylthio*-4- or -5-*methylglyoxaline*, needles, m. p. 46° (2·5 g.) (Found: C, 48·1; H, 5·8. $C_8H_{12}O_2N_2S$ requires C, 48·0; H, 5·9%). This substance (1·5 g.) was hydrolysed with 6N-sodium hydroxide (10 ml.) at room temperature (12 hr.). On acidification followed by addition of sodium carbonate to pH 9, 2-methylthio-4(5)-methylglyoxaline (above) separated as an oil which later solidified.

2-*Ethylthio*-4(5)-*methylglyoxaline*.—1-Ethoxycarbonyl-2-mercapto-4- or -5-methylglyoxaline (1 g.) was heated in a stream of nitrogen at 140° till carbon dioxide evolution ceased (0·5 hr.). Extraction with ether left a residue of 2-mercapto-4(5)-methylglyoxaline, m. p. 244—245° (45 mg.). Evaporation of the ether left an oil (500 mg.) which gave 2-ethylthio-4(5)-methylglyoxaline picrate, m. p. 135—136° (Balaban and King [5] give m. p. 136—137°).

Halogenation of 2-*Ethylthio*-4(5)-*methylglyoxaline*.—2-Ethylthio-4(5)-methylglyoxaline (2·8 g.) in chloroform (10 ml.) was treated with iodine (5 g.) for 0·5 hr. at room temperature. After being washed with water, the chloroform solution was evaporated and left 2-*ethylthio*-5(4)-*iodo*-4(5)-*methylglyoxaline* (1 g., 19%), white needles (from aqueous ethanol), m. p. 166—167° (decomp.) (Found: C, 27·1; H, 3·6; N, 10·6. $C_6H_9N_2SI$ requires C, 26·9; H, 3·4; N, 10·5%). Substitution of bromine for iodine in the above reaction gave 5(4)-*bromo*-2-*ethylthio*-4(5)-*methylglyoxaline*, m. p. 181—182° (decomp.) (Found: C, 32·8; H, 4·2; N, 12·7. $C_6H_9N_2SBr$ requires C, 32·6; H, 4·1; N, 12·7%).

Acylation of 2-*Mercapto*-1-*methylglyoxaline with Chloroformic Esters*.—2-Mercapto-1-methylglyoxaline, treated in pyridine with ethyl chloroformate as described above for 2-mercapto-4(5)-methylglyoxaline, gave 1(3)-*ethoxycarbonyl*-3(1)-*methyl*-2-*thioglyoxaline*, m. p. 121—122° (from ethanol) (95% yield) (Found: C, 45·7; H, 5·4. $C_7H_{10}O_2N_2S$ requires C, 45·2; H, 5·4%). 2-*Ethoxycarbonylthio*-1-*methylglyoxaline picrate*, m. p. 94—96° (decomp.), was obtained when the reaction was carried out in non-basic medium as for the 4(5)-methyl derivative (above) (Found: C, 37·4; H, 3·0. $C_{13}H_{13}O_9N_5S$ requires C, 37·6; H, 3·1%). Using methyl chloroformate in pyridine gave 1(3)-*methoxycarbonyl*-3(1)-*methyl*-2-*thioglyoxalone*, m. p. 135° (from ethanol) (90% yield) (Found: C, 41·8; H, 4·4. $C_6H_8O_2N_2S$ requires C, 41·9; H, 4·7%). Benzyl chloroformate likewise gave 1(3)-*benzyloxycarbonyl*-3(1)-*methyl*-2-*thioglyoxaline* (yield 10%), needles, m. p. 91—92°, from benzene–light petroleum, but a better yield (40%) was obtained by adding the benzyl chloroformate to a solution of the mercaptoglyoxaline in 4N-sodium hydroxide at 0° (Found: C, 58·3; H, 5·0. $C_{12}H_{12}O_2N_2S$ requires C, 58·1; H, 4·8%).

1(3)-*Hippuroyl*-3(1)-*methyl*-2-*thioglyoxaline*.—To 2-mercapto-1-methylglyoxaline (0·01 mol.), dissolved in 2-picoline (10 ml.), 2-phenyloxazol-5-one (0·01 mol.) was slowly added. After 24 hr. the solution was poured into ice-water; the precipitated 1(3)-*hippuroyl*-3(1)-*methyl*-2-*thioglyoxalone*, purified by recrystallisation from ethyl acetate, had m. p. 175° (Found: C, 56·4; H, 5·0; N, 15·3. $C_{13}H_{13}O_2N_3S$ requires C, 56·9; H, 4·7; N, 15·3%).

2-*Benzoylthio*-1-*methylglyoxaline Hydrochloride*.—2-Mercapto-1-methylglyoxaline (0·01 mol.) was heated in benzene (25 ml.) with benzoyl chloride (0·01 mol.) at 100°. The precipitated *hydrochloride*, recrystallised from ethanol, had m. p. 183° (Found: C, 51·7; H, 4·1. $C_{11}H_{11}ON_2SCl$ requires C, 51·9; H, 4·3%).

3(1)-*Benzoyl*-1(3)-*methyl*-2-*thioglyoxalone*.—When the benzoylation of 1-methyl-2-mercaptoglyoxaline was carried out in pyridine and a few drops of ethanol were added, yellow needles of the *glyoxalone*, m. p. 102° (from ethanol), were obtained (Found: C, 59·7; H, 4·4. $C_{11}H_{10}ON_2S$

requires C, 60·5; H, 4·6%). This was also obtained by treatment of the above hydrochloride with aqueous sodium hydrogen carbonate.

2-*Ethoxycarbonylmethylthio*-1-*methylglyoxaline Hydrochloride*.—Ethyl chloroacetate (0·01 mol.) was heated with 2-mercapto-1-methylglyoxaline (0·01 mol.) in ethanol (10 ml.) at 100° for 30 min. The hydrochloride was precipitated by ether, and recrystallised from ethanol–ether as prisms, m. p. 99° (Found: C, 40·8; H, 5·6. $C_8H_{13}O_2N_2SCl$ requires C, 40·6; H, 5·5%). Using chloroacetic acid instead of the ester (above) gave 2-*carboxymethylthio*-1-*methylglyoxaline hydrochloride*, m. p. 162° (from ethanol) (Found: C, 35·1; H, 4·6. $C_6H_9O_2N_2SCl$ requires C, 34·5; H, 4·3%).

1(3)-*Hydroxymethyl*-3(1)-*methyl*-2-*mercaptoglyoxaline*.—2-Mercapto-1-methylglyoxaline (1 g.) and neutralised formaldehyde solution (6 ml. of 40%) were heated together on the water-bath for 1 hr. Ethanol (20 ml.) was then added and heating continued for a further 1 hr. The deposited crystals (0·6 g.) of the *hydroxymethyl derivative*, recrystallised from alcohol, had m. p. 115—118° (Found: C, 41·9; H, 5·7; N, 19·7. $C_5H_8ON_2S$ requires C, 41·7; H, 5·6; N, 19·4%).

4- *or* 5-*Ethoxycarbonyl*-1-*hydroxymethyl*-2-*mercaptoglyoxaline*.—4(5)-Ethoxycarbonyl-2-mercaptoglyoxaline was treated with formaldehyde as above, to give 4- or 5-*ethoxycarbonyl*-1-*hydroxymethyl*-2-*mercaptoglyoxaline* (1·8 g., 73%), m. p. 138—139° (from water) (Found: C, 41·5; H, 5·0; N, 13·9. $C_7H_{10}O_3N_2S$ requires C, 41·6; H, 5·0; N, 13·9%).

1 : 3-*Di*(*hydroxymethyl*)-2-*thioglyoxalone*.—2-Mercaptoglyoxaline (0·5 g.) was heated on the steam-bath with neutralised aqueous formaldehyde (5 ml. of 40%) for 0·5 hr. The solution was then evaporated under reduced pressure and the remaining *glyoxalone* crystallised from ethanol as prisms, m. p. 129° (Found: C, 37·5; H, 4·7; N, 17·4. $C_5H_8O_2N_2S$ requires C, 37·5; H, 5·0; N, 17·5%).

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ROYAL FREE HOSPITAL SCHOOL OF MEDICINE,
8, HUNTER STREET, LONDON, W.C.1.

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