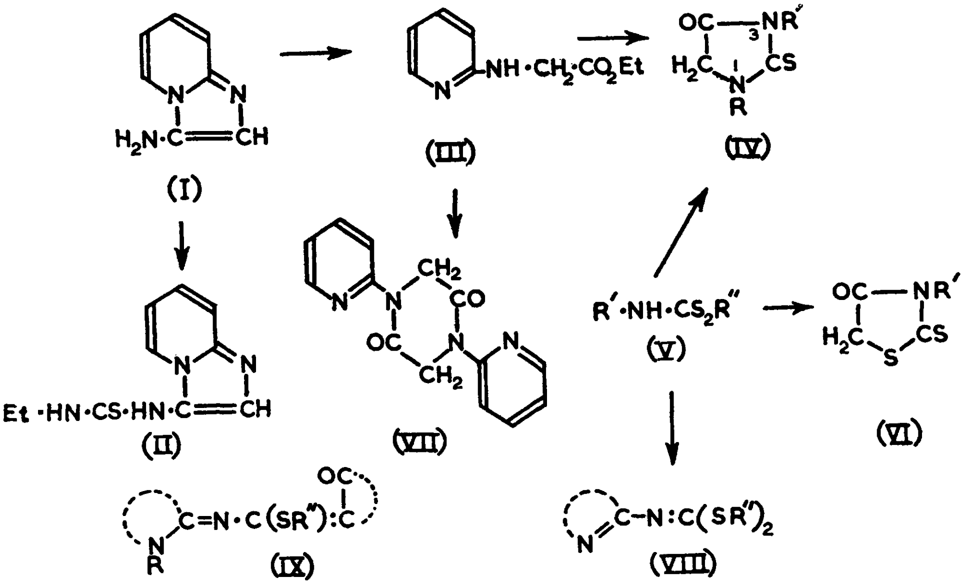
326. *Heterocyclyl-rhodanines and -2-thiohydantoins.*

By Edward B. Knott.

Ethyl *N*-2-pyridylaminoacetate has been converted into a series of 3-substituted 1-2′-pyridyl-2-thiohydantoins. *N*-Pyridyl-, *N*-quinolyl-, and *N*-thiazolyl-dithiocarbamic esters have been condensed with *N*-substituted glycines, glycine esters, or glycine nitriles to give 3-pyridyl-, 3-quinolyl-, and 3-thiazolyl-2-thiohydantoins, or have been cyclized to the 3-substituted rhodanines.

The formation of 1 : 3-disubstituted 2-thiohydantoins (IV) is usually brought about by the condensation of an *iso*thiocyanate [1] or a *N*-substituted dithiocarbamic ester [2] with a *N*-substituted glycine, glycine ester, or glycine nitrile.[3] Substituted rhodanines (VI) are usually obtained by cyclizing the carboxymethyl ester of a *N*-substituted dithiocarbamic acid.[4]

The difficulty of obtaining glycines, dithiocarbamates, or *iso*thiocyanates carrying heterocyclic residues on the nitrogen atom no doubt accounts for the absence in the literature of preparations of 2-thiohydantoins or rhodanines derivable from them. Tien and Hunsberger [5] recently reported the preparation of *N*-3-pyridylglycine, and Bristow, Charlton, Peak, and Short [6] described the synthesis of *N*-2-pyridylglycine nitrile. The latter, unlike *N*-alkylglycine nitriles, is unsuitable for the preparation of 2-thiohydantoins since, as found by Bristow *et al.*,[6] it behaves like the isomeric glyoxaline (I), reacting with ethyl *iso*thiocyanate to give what is probably the thiourea (II). It is readily hydrolyzed to ethyl *N*-2-pyridylaminoacetate (III) which, on distillation, is partly converted into the diketopiperazine (VII). The aminoacetate (III) condenses normally with *iso*thiocyanates or dithiocarbamic esters to give 3-substituted 1-2′-pyridyl-2-thiohydantoins (IV; R = 2-C_5H_4N). In a similar manner ethyl *N*-(6-methyl-2-pyridyl)-aminoacetate was prepared and converted into 3-substituted 1-(6-methyl-2-pyridyl)-2-thiohydantoins.



It was then found that 2-, 3-, and 4-aminopyridines, 3-aminoquinoline (but not the

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[1] Neumark and Stelzner, *Ber.*, 1891, **24**, 3285.

[2] Wheeler, Nicolet, and Johnson, *Amer. Chem. J.*, 1911, **46**, 456.

[3] Delépine, *Bull. Soc. chim. France*, 1903, **29**, 1198; Cook and Cox, *J.*, 1949, 2343.

[4] Holmberg, *J. prakt. Chem.*, 1910, **81**, 455.

[5] Tien and Hunsberger, *Chem. and Ind.*, 1955, 119.

[6] Bristow, Charlton, Peak, and Short, *J.*, 1954, 616.

2-isomer), and 2-aminothiazole (but not 2-aminobenzothiazole) condensed readily with carbon disulphide and triethylamine at room temperature to give high yields of the corresponding 1-substituted triethylammonium dithiocarbamates (V; $R'' = Et_3NH$). This reaction has recently been published by Fairfull and Peak.[7] The alkyl, preferably methyl, esters of these dithiocarbamic acids (V; $R'' = Me$), with *N*-substituted glycines, glycine esters, or glycine nitriles, readily yielded 1-substituted 2-thiohydantoins with the heterocyclic residue at position 3. Fusion of the dithiocarbamate (V; $R'' = Me$, $R' =$ 2- or 3-pyridyl) at 140° caused the evolution of methanethiol and the formation of a tar from the 2-isomer, but of 3-pyridyl *iso*thiocyanate from the 3-isomer. This *iso*thiocyanate is a high-boiling liquid (cf. Fairfull *et al.*[7]) and it therefore seems likely that the 2-pyridyl analogue obtained by the latter authors as a brick-red solid with m. p. 110—111° is a polymer.

Condensation of sodium chloroacetate with triethylammonium dithiocarbamates from heterocyclic compounds, followed by acidification of the solution of the salt of the carboxymethyl ester (V; $R'' = CH_2{\cdot}CO_2H$) so formed, leads in some cases directly to the rhodanine derivatives (VI). In other cases the carboxymethyl ester was isolated and subsequently cyclized to these products (VI), either by fusion or by treatment with acetic anhydride.

These methyl dithiocarbamates are, like thioamides, soluble in sodium hydroxide and on treatment with methyl iodide in alcoholic sodium ethoxide give the dimethyl dithiocarbimidates (VIII). These bases are then readily quaternized and converted into azadimethin*mero*cyanines (IX) substituted in the chain by methylthio-groups.

EXPERIMENTAL

Ethyl N-2-*Pyridylaminoacetate* (III).—*N*-2-Pyridylaminoacetonitrile (20 g.) (Bristow *et al.*[6]) was added to a cooled solution of concentrated sulphuric acid (20 c.c.) in ethanol (100 c.c.). The sulphate, which was precipitated, gradually dissolved under reflux. After 2 hours' boiling the solution was poured on ice (200 g.), the acid was neutralized with solid sodium hydrogen carbonate, and the oil extracted with ether. The dried ethereal solution gave 20·8 g. (82%) of *ester*, b. p. 156—160°/13·5 mm., on distillation (Found: C, 59·7; H, 6·6; N, 15·6. $C_9H_{12}O_2N_2$ requires C, 60·0; H, 6·65; N, 15·55%), which solidified to asbestos-like needles at 5°. The residue from the distillation (1·8 g.; soft yellow needles, m. p. 252°, from acetic acid) is believed to be 2 : 5-*dioxo*-1 : 4-*di*-2′-*pyridylpiperazine* (VII) (Found: C, 63·0; H, 4·65; N, 20·7. $C_{14}H_{12}O_2N_4$ requires C, 62·7; H, 4·5; N, 20·9%).

Ethyl N-6-*methyl*-2-*pyridylaminoacetate* was obtained similarly in 48% yield based on 2-amino-6-methylpyridine, as a colourless oil, b. p. 158—162°/12 mm. (Found: C, 62·0; H, 7·3; N, 14·6. $C_{10}H_{14}O_2N_2$ requires C, 61·85; H, 7·2; N, 14·45%).

N-*Ethyl*-N′-[*pyridino*(1 : 2-*a*)*glyoxalin*-5-*yl*]*thiourea* (II).—*N*-2-Pyridylaminoacetonitrile (13·3 g.) and ethyl *iso*thiocyanate (8·8 c.c.) were fused together on a steam-bath for 5 min. The melt had then solidified. It (12·2 g., 55%) formed colourless needles, m. p. 206°, from ethanol (Found: C, 54·5; H, 5·1; N, 25·4; S, 14·7. $C_{10}H_{12}N_4S$ requires C, 54·5; H, 5·45; N, 25·5; S, 14·55%).

Triethylammonium N-2-*Pyridyldithiocarbamate* (V; $R' = 2\text{-}C_5H_4N$, $R'' = NEt_3$).—2-Aminopyridine (18·8 g.), carbon disulphide (12 c.c.), and triethylamine (30 c.c.) were warmed to give a clear solution. Two phases separated rapidly and the whole was shaken at room temperature for 1½ hr. The whole had then solidified. The mass was ground with ether, washed with ether, and air-dried. It (49·0 g., 90·5%) formed lemon-yellow plates, m. p. 84—85° (Fairfull *et al.*[7] give 82% yield and m. p. 88—89°) (Found: C, 53·2; H, 7·6; N, 15·2; S, 23·7. Calc. for $C_{12}H_{21}N_3S_2$: C, 53·1; H, 7·75; N, 15·5; S, 23·6%).

It afforded the *ethoxycarbonylmethyl ester* (V; $R' = 2\text{-}C_5H_4N$, $R'' = EtO_2C{\cdot}CH_2$), pale yellow aggregates, m. p. 88—89°, from methanol (Found: C, 46·6; H, 4·7; N, 11·1; S, 25·2. $C_{10}H_{12}O_2N_2S_2$ requires C, 46·9; H, 4·7; N, 10·95; S, 25·0%), and the methyl ester (V; $R' = 2\text{-}C_5H_4N$, $R'' = Me$), pale lemon spears, m. p. 91°, from ethanol (lit., m. p. 88—89°) (Found: C, 45·9; H, 4·2; N, 14·9; S, 34·7. Calc. for $C_7H_8N_2S_2$: C, 45·7; H, 4·35; N, 15·2; S, 34·8%). The latter ester, on fusion at 145°, evolved methanethiol smoothly but the residue, an orange-coloured tar with the odour of benzothiazole and a sharp tang, could not be distilled without decomposition. The *ethyl ester* (V; $R' = 2\text{-}C_5H_4N$, $R'' = Et$), obtained in 71% yield, formed lemon-yellow needles, m. p. 64°, from propan-2-ol (Found: N, 14·0; S, 32·3. $C_8H_{10}N_2S_2$ requires N, 14·15; S, 32·3%). 1-(N-2-*Pyridylthiocarbamoyl*)*piperidine* was obtained

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[7] Fairfull and Peak, *J.*, 1955, 796.

in 96% yield by keeping the methyl ester (9·2 g.) and piperidine (5 c.c.) in methanol (20 c.c.) for 15 hr. and then refluxing the mixture for 1 hr. It formed white flakes, m. p. 112—113°, from *cyclo*hexane (Found: C, 59·9; H, 6·95; N, 18·9; S, 14·7. $C_{11}H_{15}N_3S$ requires C, 59·7; H, 6·8; N, 19·0; S, 14·5%).

Triethylammonium *N*-3-pyridyldithiocarbamate, obtained as for the 2-isomer in 42% yield, formed yellow prisms, m. p. 87° (effervescence), from ether (lit.[7] 92% yield, m. p. 85—86°) (Found: C, 52·9; H, 7·5; N, 15·4; S, 23·6. Calc. for $C_{12}H_{21}N_3S_2$: C, 53·1; H, 7·75; N, 15·5; S, 23·6%). The derived methyl ester, white flakes, m. p. 135—136° (lit.,[7] m. p. 133—135°) (Found: N, 15·2; S, 34·7. Calc. for $C_7H_8N_2S_2$: N, 15·2; S, 34·8%) (5·0 g.), was fused at 145°/14 mm. Methanethiol was evolved, and then 3-pyridyl *iso*thiocyanate (3·3 g., 89·2%) distilled at 104°. The almost colourless oil, with the odour of benzothiazole and a sharp tang, had b. p. 228°/765 mm. (lit.,[7] b. p. 231—233°) (Found: C, 52·8; H, 3·1; N, 20·4; S, 23·7. Calc. for $C_6H_4N_2S$: C, 52·95; H, 2·95; N, 20·6; S, 23·55%).

Triethylammonium N-4-*Pyridyldithiocarbamate.*—4-Aminopyridine (4·8 g.) was dissolved in hot pyridine (30 c.c.), then cooled to room temperature, and carbon disulphide (3·3 c.c.) and triethylamine (8 c.c.) were added. After 3—4 hr. crystals separated and next morning ether (100 c.c.) was added and the solid was washed with cold ethanol. The *salt* (6·9 g., 51%) formed orange flakes, m. p. 141°, from methanol–ether (Found: C, 53·3; H, 7·9; N, 15·2; S, 23·8%), and afforded the *methyl ester* in 74% yield as pale yellow prisms, m. p. 142—144°, from ethanol (Found: C, 46·0; H, 4·65; N, 15·0; S, 34·95. $C_7H_8N_2S_2$ requires C, 45·7; H, 4·35; N, 15·2; S, 34·8%).

Triethylammonium N-6-*methyl*-2-*pyridyldithiocarbamate* (85%) was obtained as for the above but 24 hours' shaking was necessary for solidification. It formed lemon-yellow aggregates, m. p. 76°, from methanol–ether (Found: N, 14·45; S, 22·55. $C_{13}H_{23}N_3S_2$ requires N, 14·75; S, 22·5%). The *methyl ester*, obtained in 71% yield, formed pale yellow plates, m. p. 89—90°, from methanol (Found: N, 14·1; S, 32·45. $C_8H_{10}N_2S_2$ requires N, 14·15; S, 32·35%).

Methyl N-4-*Methyl*-2-*pyridyldithiocarbamate.*—2-Amino-4-methylpyridine (54·0 g.), carbon disulphide (33 c.c.), triethylamine (80 c.c.), and dioxan (20 c.c.) were refluxed together to dissolve the amine. Two phases then separated and the whole was shaken at room temperature for 24 hr. The orange tar was washed with ether, and methanol (100 c.c.) was added followed by methyl iodide (30 c.c.). An exothermic reaction set in which was controlled by cooling. After 1 hr. water was run into the solution, to give 75·6 g. (76%) of the ester, which formed pale yellow needles, m. p. 101—102°, from methanol (Found: N, 14·3; S, 32·0%).

Bistriethylammonium Salt of 2 : 6-*Bis*(*dithiocarboxyamino*)*pyridine.*—2 : 6-Diaminopyridine (10·9 g.) was dissolved in pyridine (40 c.c.), and triethylamine (33 c.c.) and carbon disulphide (14 c.c.) were added. Two phases separated after 5 min. and the whole was then shaken at room temperature for 16 hr. The solid was washed with ether, and then ethanol. The *bis-dithiocarbamate* (39·7 g., 86%) formed orange crystals, m. p. 112°, from methanol–ether (Found: N, 14·95; S, 27·8. $C_{19}H_{37}N_5S_4$ requires N, 15·1; S, 27·65%). The derived *dimethyl ester* (78% yield) formed buff crystals, m. p. 132—133°, from ethanol (Found: N, 14·5; S, 44·6. $C_9H_{11}N_3S_4$ requires N, 14·5; S, 44·3%).

Triethylammonium N-3-*Quinolyldithiocarbamate.*—3-Aminoquinoline (5·0 g.), carbon disulphide (2·2 c.c.), and triethylamine (5·5 c.c.) were kept in dioxan (10 c.c.) at room temperature for 20 hr. The solid cake of *salt* (98%) formed pale yellow prisms, m. p. 89°, from ethanol–ether (Found: N, 12·95; S, 19·65. $C_{16}H_{23}N_3S_2$ requires N, 13·1; S, 19·95%) and gave a *methyl ester* (87%), pale yellow needles, m. p. 137—138° (from ethanol) (Found: C, 56·2; H, 4·3; N, 11·85; S, 27·3. $C_{11}H_{10}N_2S_2$ requires C, 56·4; H, 4·3; N, 11·95; S, 27·35%).

Triethylammonium N-2-*thiazolyldithiocarbamate*, with pyridine as solvent, was obtained in 60% yield as yellow flakes, m. p. 142° (lit.,[7] m. p. 141—142°). The *methyl ester* formed straw-coloured needles, m. p. 175—176°, from ethanol (lit.,[7] m. p. 184—185°) (Found: C, 31·35; H, 3·2; N, 14·75; S, 50·0. Calc. for $C_5H_6N_2S_3$: C, 31·6; H, 3·2; N, 14·75; S, 50·5%).

2-Aminobenzothiazole, 2-aminoquinoline, and 2-amino-4 : 6-dimethylpyrimidine could not be brought into reaction with carbon disulphide and triethylamine.

3-*Ethyl*-1-2′-*pyridyl*-2-*thiohydantoin* (IV; $R = 2\text{-}C_5H_4N$; $R' = Et$).—Ethyl *N*-2-pyridylaminoacetate (18·0 g.) and ethyl *iso*thiocyanate (13·3 g.) were fused together at 135° for 5 hr. The melt solidified when chilled. The solid *thiohydantoin* (14·6 g., 44%) formed greenish flakes, m. p. 107°, from propan-2-ol or *cyclo*hexane (Found: C, 54·3; H, 5·15; N, 18·85; S, 14·75. $C_{10}H_{11}ON_3S$ requires C, 54·3; H, 4·95; N, 19·0; S, 14·45%).

1-*Phenyl*-3-2′-*pyridyl*-2-*thiohydantoin* (IV; $R = Ph$, $R' = 2\text{-}C_5H_4N$).—Ethyl *N*-phenylaminoacetate (1·0 g.) and methyl *N*-2-pyridyldithiocarbamate (1·0 g.) were fused together at

150° for 15 min. The melt solidified and the *product* (0·7 g., 47%) formed cream-coloured needles, m. p. 190°, from ethanol (Found : C, 62·3; H, 4·3; N, 15·55; S, 12·1. $C_{14}H_{11}ON_3S$ requires C, 62·5; H, 4·1; N, 15·65; S, 11·9%).

1 : 3-*Di*-(6-*methyl*-2-*pyridyl*)-2-*thiohydantoin*.—Ethyl *N*-(6-methyl-2-pyridyl)aminoacetate (10·0 g.) and methyl *N*-(6-methyl-2-pyridyl)dithiocarbamate (10·2 g.) were fused together at 145° for 2 hr. The melt solidified after 1½ hr. The cooled solid was ground under ethanol to give 11·85 g. (77·0%) of yellow crystals. It was extracted with boiling ethanol (5 × 50 c.c.), leaving 9·3 g. of undissolved residue, which formed white crystals, m. p. 220—222° from benzene in which it was sparingly soluble (Found : C, 60·25; H, 4·65; N, 18·6; S, 10·8. $C_{16}H_{14}ON_4S$ requires C, 60·45; H, 4·7; N, 18·8; S, 10·75%). The ethanol extract, on concentration to 100 c.c., gave yellow flakes (2·0 g.) when chilled, m. p. 189—190°, after a further recrystallization from benzene (Found : C, 60·75; H, 4·9; N, 19·0; S, 11·05%). Both *compounds* behave as 2-*thiohydantoins* in dye condensations. The nature of the isomerism has not been investigated. The thiohydantoins given in the Table were obtained by similar methods.

1 : 3-*Disubstituted* 2-*thiohydantoins* (IV).

R'	Time (hr.) *	Yield (%) (solvent) †	M. p.	Formula	Required (%)				Found (%)			
					C	H	N	S	C	H	N	S
				R = 2-pyridyl								
Me	7	47 (E)	141°	$C_9H_9ON_3S$	52·7	4·3	20·1	15·5	52·2	4·35	20·3	15·45
Ph	7	56 (A) [a]	186	$C_{14}H_{11}ON_3S$	62·3	4·2	15·85	11·1	62·5	4·1	15·65	11·9
Allyl	2	39 (M) [b]	62	$C_{11}H_{11}ON_3S$	57·0	4·8	17·8	13·8	56·6	4·7	18·0	13·75
*cyclo*Hexyl	7	40 (E)	174	$C_{14}H_{17}ON_3S$	60·8	6·25	14·9	11·8	61·0	6·2	15·25	11·65
Benzyl	5	63 (M) [c]	115	$C_{15}H_{13}ON_3S$	63·8	5·0	15·1	11·2	63·6	4·6	14·85	11·3
n-Heptyl	7 [f]	70 (E) [d]	70	$C_{15}H_{21}ON_3S$	61·5	7·3	14·45	11·2	61·8	7·2	14·45	11·0
2-Pyridyl	2 [g]	67 (E) [e]	173	$C_{13}H_{10}ON_4S$	58·0	3·9	20·65	11·9	57·8	3·7	20·75	11·85
3-Pyridyl	2 [h]	72 (E) [e]	170—171	$C_{13}H_{10}ON_4S$	—	—	20·55	12·05	—	—	20·75	11·85
6-Methyl-2-pyridyl	2 [h]	73 (E)	146—147	$C_{14}H_{12}ON_4S$	59·4	4·35	19·65	11·4	59·2	4·25	19·85	11·25
4-Methyl-2-pyridyl	1½	57 (E) [f]	151	$C_{14}H_{12}ON_4S$	59·5	4·5	19·65	11·25	59·2	4·25	19·85	11·25
3-Quinolyl	½	62 (E) [b, c]	204	$C_{17}H_{12}ON_4S$	63·6	3·95	17·1	10·2	63·75	3·75	17·5	10·0
				R = 6-methyl-2-pyridyl								
Et	6	29 (P)	85	$C_{11}H_{13}ON_3S$	56·3	5·7	17·9	13·7	56·15	5·5	17·85	13·6

* At 150° unless otherwise stated.

† E = ethanol, A = acetic acid, M = methanol, P = propan-2-ol. The products are white needles unless otherwise stated.

[a] Black. [b] Straw-coloured. [c] Pale green. [d] Flakes. [e] Buff-coloured. [f] 135°. [g] 145°. [h] 140°.

1-*Ethyl*-3-2'-*pyridyl*-2-*thiohydantoin* (IV; R = Et, R' = $2\text{-}C_5H_4N$).—Ethylaminoacetonitrile (4·2 g.) and methyl *N*-2-pyridyldithiocarbamate (9·2 g.) were heated together on a steam-bath for 1 hr. Methanethiol was evolved and an orange-coloured tar remained. 5N-Hydrochloric acid (30 c.c.) was added and the clear orange-coloured solution was heated for a further 30 min. Water (100 c.c.) was added and the solution was basified with ammonia, to give orange-coloured grains (10·2 g.) which were ground in a little ethanol and filtered (5·6 g.). The product was dissolved in benzene (50 c.c.) and chilled overnight. The white needles, m. p. 135—136°, which separated were discarded and the benzene solution was concentrated to 25 c.c. The addition of light petroleum (b. p. 60—80°) gave a gummy *thiohydantoin* which yielded 2·2 g. (20%) of flat, buff needles, m. p. 132°, after crystallization from ethanol and then from benzene (Found : C, 54·5; H, 4·95; N, 18·8; S, 14·7. $C_{10}H_{11}ON_3S$ requires C, 54·3; H, 4·95; N, 19·0; S, 14·4%).

1-*Methyl*-3-2'-*thiazolyl*-2-*thiohydantoin* (IV; R = Me, R' = $2\text{-}C_3H_2NS$).—To a solution of potassium hydroxide (5·6 g.) in water (25 c.c.) was added sarcosine hydrochloride (6·3 g.), followed by methyl *N*-2-thiazolyldithiocarbamate (9·5 g.) and ethanol (50 c.c.). The mixture was heated for 20 hr. Water (100 c.c.) was added and the solid filtered off. The filtrate was acidified with dilute acetic acid, the small amount of tar was filtered off, and the filtrate was concentrated to 100 c.c. An orange-coloured tar separated on chilling, which crystallized completely in 3 days. From ethanol the *thiohydantoin* (1·9 g., 18%) formed pink needles, m. p. 133° (Found : C, 39·55; H, 3·45; N, 19·7; S, 30·25. $C_7H_7ON_3S_2$ requires C, 39·4; H, 3·3; N, 19·7; S, 30·1%).

1-*Ethyl*-3-2'-*thiazolyl*-2-*thiohydantoin* was obtained similarly in 28% yield from *N*-ethylglycine hydrochloride, and formed pink needles, m. p. 176—177°, from ethanol (Found : C, 41·95; H, 4·1; N, 18·5; S, 28·25. $C_8H_9ON_3S_2$ requires C, 42·25; H, 4·0; N, 18·5; S, 28·45%).

3-2'-*Pyridyl*-2-*thiothiazolid*-4-*one* (VI, R' = 2-C_5H_4N).—Triethylammonium *N*-2-pyridyldithiocarbamate (5·4 g.) was dissolved in water (30 c.c.), and a solution of sodium chloroacetate (2·4 g.) in water (10 c.c.) was added at 20°. The solution was kept for 20 hr. and acidified with acetic acid. The resulting solid (3·2 g., 70%) formed orange-coloured aggregates, m. p. 133° (effervescence), from ethanol. It is *carboxymethyl* N-2'-*pyridyldithiocarbamate* (V; R' = 2-C_5H_4N, R'' = $HO_2C{\cdot}CH_2$) (Found: C, 42·1; H, 3·75; N, 12·05; S, 28·3. $C_8H_8O_2N_2S_2$ requires C, 42·1; H, 3·5; N, 12·3; S, 28·1%). The ester (4·6 g.) and acetic anhydride (40 c.c.) were heated together for 1 hr. on a steam-bath, and the solvent was removed. The reddish tar was dissolved in propan-2-ol (25 c.c.) and kept for several weeks. The pale yellow *thiazolidone* (1·2 g., 28·5%) which had then separated formed rosettes of straw-coloured needles, m. p. 77°, from propan-2-ol (Found: N, 13·1; S, 30·35. $C_8H_6ON_2S_2$ requires N, 13·35; S, 30·5%).

5-1'-*Ethoxyethylidene*-3-2'-*pyridyl*-2-*thiothiazolid*-4-*one*.—By the same procedure as for the above cyclization, but in the presence of ethyl orthoacetate (10 c.c.), the required *rhodanine* was obtained in 49% yield as rose-coloured flakes, m. p. 137—138°, from *cyclo*hexane, then from benzene (Found: C, 51·1; H, 4·6; N, 9·95; S, 23·05. $C_{12}H_{12}O_2N_2S_2$ requires C, 51·4; H, 4·3; N, 10·0; S, 22·9%).

3-(6-*Methyl*-2-*pyridyl*)-2-*thiothiazolid*-4-*one* (VI; R' = 6-Me-2-C_5H_3N).—Triethylammonium *N*-(6-methyl-2-pyridyl)dithiocarbamate (28·5 g.) and sodium chloroacetate (13·0 g.) were dissolved in water (100 c.c.) at 35°. When the solution was allowed to cool some solid separated. After 2 hr. the solution was filtered and acidified with dilute acetic acid. The thick, yellow meal was washed with water and air-dried. The product (22·5 g., 93%), forming fawn needles, m. p. 125° (effervescence), from ethanol, was *carboxymethyl* N-(6-*methyl*-2-*pyridyl*)*dithiocarbamate* (Found: N, 11·4; S, 26·5. $C_9H_{10}O_2N_2S_2$ requires N, 11·55; S, 26·45%). It was finely ground and heated at 125°/12 mm. The solid slowly fused, with effervescence, to give an orange-coloured tar which then crystallized. This was boiled with methanol (15 c.c.) and chilled, to give 4·8 g. (52%) of the *rhodanine* as pink flakes, m. p. 146—148°, after recrystallization from benzene then from propan-2-ol (Found: C, 48·3; H, 3·65; N, 12·55; S, 28·85. $C_9H_8ON_2S_2$ requires C, 48·25; H, 3·55; N, 12·5; S, 28·55%). The 5-1'-*ethoxyethylidene derivative* formed orange-coloured prisms, m. p. 165—166°, from ethanol (Found: C, 52·8; H, 4·85; N, 9·3; S, 21·7. $C_{13}H_{14}O_2N_2S_2$ requires C, 53·0; H, 4·75; N, 9·55; S, 21·8%).

3-3'-*Pyridyl*-2-*thiothiazolid*-4-*one*.—3-Aminopyridine (5·0 g.), dioxan (5 c.c.) and triethylamine (8 c.c.) were heated together to give a clear solution. Carbon disulphide (3·2 c.c.) was added and the whole was shaken for 2 hr. A solution of sodium chloroacetate (7·0 g.) in water (50 c.c.) was added, the whole was then heated for 10 min. on a steam-bath, and cooled, water (50 c.c.) was added, and the solution was acidified with dilute acetic acid. A tar was deposited which crystallized after several hours. The *rhodanine* (5·2 g., 46%) formed brown needles, m. p. 156—157°, from ethanol (Found: C, 46·1; H, 3·05; N, 13·25; S, 30·45. $C_8H_6ON_2S_2$ require C, 45·7; H, 2·85; N, 13·35; S, 30·5%).

3-4'-*Pyridyl*-2-*thiothiazolid*-4-*one*.—The above procedure, with the 4-pyridyl isomer as starting point, gave an 81% yield, on acidification of the reaction mixture, of *carboxymethyl* N-4'-*pyridyldithiocarbamate*, orange-coloured prisms, m. p. 152—153° (from aqueous acetic acid) (Found: N, 12·3; S, 28·2. $C_8H_8O_2N_2S_2$ requires N, 12·3; S, 28·1%). This cyclized readily in hot acetic anhydride (10 min. on a steam-bath). Decomposition of the reaction mixture with water gave a little tar, the filtrate from which on treatment with solid sodium hydrogen carbonate gave a 65% yield of the *rhodanine*, reddish prisms, m. p. 162—164° (from ethanol) (Found: N, 13·1; S, 30·2. $C_8H_6ON_2S_2$ requires N, 13·35; S, 30·5%).

3-2'-*Thiazolyl*-2-*thiothiazolid*-4-*one*.—Triethylammonium *N*-2'-thiazolyldithiocarbamate (27·7 g.) and sodium chloroacetate (11·6 g.) were dissolved in water (100 c.c.) and ethanol (100 c.c.) at 55°. After 10 min. a mass of yellow needles separated. The solution was allowed to cool and after 1 hr. the sodium salt of carboxymethyl *N*-2-thiazolyldithiocarbamate (23·2 g., 91%) was collected and washed with ethanol. The salt was dissolved in warm water (500 c.c.), and the solution was filtered and acidified with a solution of acetic acid (6 c.c.) in water (50 c.c.). The free *acid* formed pale yellow crystals, m. p. 178—179° (effervesced, solidified, and then melted at 192°), from acetic acid (Found: N, 11·75; S, 41·1. $C_6H_6O_2N_2S_3$ requires N, 11·95; S, 41·0%). The crystals (18 g.) were dissolved in hot acetic anhydride (50 c.c.) during 15 min. on a steam-bath. After 30 min. acetic acid (10 c.c.) was added and water was added with shaking. A thick, pale yellow meal of crystals separated. The *rhodanine* (14·1 g., 85%) formed straw-coloured needles, m. p. 130°, from ethanol (Found: C, 33·2; H, 2·0; N, 12·85; S, 44·6. $C_6H_4ON_2S_3$ requires C, 33·35; H, 1·85; N, 12·95; S, 44·45%). The 5-1'-*ethoxyethylidene* *derivative* formed rust-coloured needles, m. p. 118°, from ethanol (Found: C, 41·8; H, 3·8; N, 9·7; S, 33·8. $C_{10}H_{10}O_2N_2S_3$ requires C, 42·0; H, 3·5; N, 9·8; S, 33·6%).

3-3′-*Quinolyl*-2-*thiothiazolid*-4-*one*, obtained in 86% yield by the same procedure as the 3-pyridyl analogue, formed brown needles, m. p. 228° (soft at 215°), from aqueous acetic acid (Found: C, 55·2; H, 3·15; N, 10·7; S, 24·8. $C_{12}H_8ON_2S_2$ requires C, 55·4; H, 3·1; N, 10·8; S, 24·65%).

Dimethyl N-(2-*Pyridyl*)*dithiocarbimidate* (cf. VIII).—Methyl *N*-2′-pyridyldithiocarbamate (18·4 g.) was dissolved in a solution of sodium (2·3 g.) in ethanol (50 c.c.) at 22°, then methyl iodide (6·5 c.c.) was added, causing the temperature to rise to 60°. After 20 hr. at 20° water (150 c.c.) was added, the precipitated oil was taken up in ether, and the solution was dried and distilled. The yellow oil (17·4 g., 88%) was collected at 186°/15 mm. (Found: N, 13·9; S, 32·3. $C_8H_{10}N_2S_2$ requires N, 14·1; S, 32·35%).

3-*Ethyl*-5-[α-(1-*ethyl*-1 : 2-*dihydropyrid*-2-*ylideneamino*)*methylthiomethylene*]-2-*thiothiazolid*-4-*one* (cf. IX).—Dimethyl *N*-2′-pyridyldithiocarbimidate (4·0 g.) and ethyl toluene-*p*-sulphonate (4·1 g.) were fused together on a steam-bath for 1 hr. 3-Ethylrhodanine (3·3 g.), ethanol (20 c.c.), and triethylamine (1·7 c.c.) were added and the whole was refluxed for 30 min. Water (50 c.c.) was added, the mixture was kept at 5° for 20 hr., the aqueous layer was decanted, and the tar was shaken with benzene (10 c.c.) until crystalline. The *dye* was precipitated fully by the addition of light petroleum (25 c.c.) and recrystallized from methanol. It (3·9 g., 57%) formed rust flakes, m. p. 137—138°, from ethanol (Found: N, 12·2; S, 28·2. $C_{14}H_{17}ON_3S_3$ requires N, 12·4; S, 28·3%).

Dimethyl N-(2-*thiazolyl*)*dithiocarbimidate* was obtained in 62% yield by the method used for the 2-pyridyl analogue. It could not be distilled without decomposition. It crystallized completely at 0° and formed pale yellow rods, m. p. 22—23°, from light petroleum (b. p. 60—80°) (Found: C, 35·6; H, 4·05; N, 13·5; S, 46·9. $C_6H_8N_2S_3$ requires C, 35·3; H, 3·9; N, 13·75; S, 47 1%). The *ethiodide* was obtained, by refluxing the base and excess of ethyl iodide for 6 hr., as yellow needles, m. p. 147° (from ethanol–ether) (Found: I, 35·2. $C_8H_{13}N_2IS_3$ requires I, 35·3%).

3-*Ethyl*-5-[α-(3-*ethylthiazolin*-2-*ylideneamino*)*methylthiomethylene*]-2-*thiothiazolid*-4-*one*, obtained as the above analogue in 73% yield, formed violet needles, m. p. 124—126°, from ethanol (Found: C, 41·7; H, 4·5; N, 11·85; S, 37·15. $C_{12}H_{15}ON_3S_4$ requires C, 41·75; H, 4·35; N, 12·15; S, 37·1%).

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