Heterocycles. CXXVII. Action of Sulfur on Some Heterocyclic Compounds. Formation of Thioamides, Oxidative Cyclization and Thiation.

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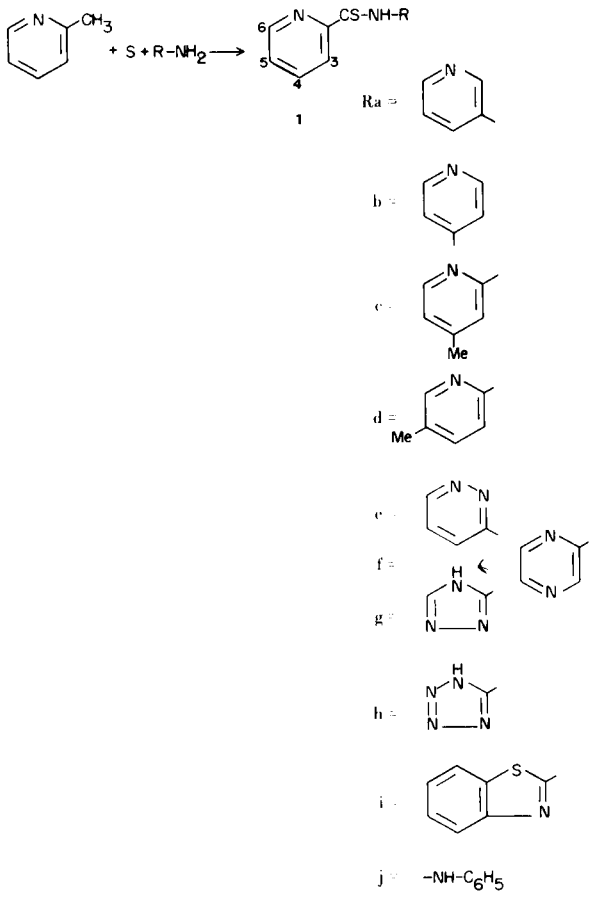
The formation of heterocyclic thioamides from alkylpyridines, heteroaromatic amines and sulfur was investigated. Oxidative cyclization of these thioamides afforded the corresponding thiazoloazines. Attempted thiation of some hydrazones gave triazolopyridines and some examples of direct thiation of heterocycles are given.

Reactions between heterocyclic compounds and sulfur have been little investigated (1). Although pyridine does not react, 2-methylpyridine is claimed to give a pyrrolopyridine derivative (2) and 4-methylpyridine or 2-methylquinoline undergo oxidative coupling (3,4). There are also some reports on the formation of thioamides from alkylpyridines and sulfur in the presence of aliphatic or aromatic amines (5-11). Syntheses of thioamides have received widespread attention and methods of their preparation have been reviewed (12,13). However, there are few studies concerning the synthesis from compounds with reactive methyl or methylene groups and sulfur in the presence of an amine (14). This reaction is usually referred to as Willgerodt or Willgerodt-Kindler reaction, although both type of reactions use ketones as starting material. It is, however, possible that mechanistic aspects of all these reactions may be related. Our interest in heterocycles with a thioamide side chain (15-17) prompted us to investigate some synthetic aspects of this system.



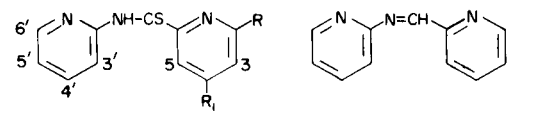
There are few examples of conversion of alkylpyridines with sulfur in the presence of a heterocyclic amine into the corresponding thioamides (11,18-20). Usually high temperatures and long reaction time were required for these transformations. It is well known that reactions of organic compounds with sulfur are frequently promoted, either thermally or by base catalysis (21-23). For example, reaction between methylarenes, sulfur and anhydrous ammonia begins at about 230°, but reasonable rates were attained in the range of 300-350° (24).

In the case of azines with an alkyl group attached at an activated position (ortho or para to the ring nitrogen) and heteroaromatic amines one can anticipate that these compounds can assist the formation of the initial sulfur-containing reactive intermediates from which the final products are formed (5,25,26). In this manner, heteroaromatic amines reacted with sulfur in the presence of excess 2-methylpyridine to give the corresponding thio-

Table I

Compound No.	M.p. °C	Yield %	Solvent for crystallization	Formula	Mass spectrum M^+	Analysis Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N	Nmr data
1a	94	21 (72) (a)	sublimed	$C_{11}H_9N_3S$	215	61.39	4.22	19.53	61.30	4.30	19.53	(DMSO-d_6): τ = 1.05 (m, H_2'), 1.65 (m, H_4'), 2.50 (m, H_5'), 1.40 (m, H_6'), 1.35 (m, H_3), 2.0 (m, H_4), 2.40 (m, H_5), 1.40 (m, H_6), -2.4 (broad, NH).
1b	130-131	14 (57) (a)	ethanol	$C_{11}H_9N_3S$	215	61.39	4.22	19.53	61.58	4.56	19.56	(DMSO-d_6): τ = 1.45 (m, H_2' and H_6'), 1.9 (m, H_3' and H_5'), 1.4 (m, H_3), 2.10 (m, H_4), 2.45 (m, H_5), 1.4 (m, H_6), -3.3 (broad, NH).
1c	113	15	ethanol	$C_{12}H_{11}N_3S$	229	62.87	4.84	18.33	62.92	4.83	18.15	(deuteriochloroform): τ = 0.70 (m, H_3'), 1.11 (m, H_3), 1.32 (m, H_6), 1.65 (dd, H_6'), 2.05 (m, H_4), 2.49 (m, H_5), 2.93 (m, H_5'), 7.52 (s, Me), -2.65 (broad s, NH), $J_{5',6'}$ = 4.8 Hz.
1d	138-139	13	ethanol	$C_{12}H_{11}N_3S$	229	62.87	4.84	18.33	62.99	4.78	18.10	(deuteriochloroform): τ = 0.71 (dd, H_3'), 1.15 (m, H_3), 1.36 (m. H_6), 1.63 (m, H_6'), 2.07 (m, H_4), 2.31 (m, H_4'), 2.50 (m, H_5), 7.62 (s, Me), -2.60 (broad s, NH), $J_{3',4'}$ = 7.5 Hz.
1e	147	5 (b)	petrolether and CCl_4	$C_{10}H_8N_4S$	216	55.55	3.73	25.92	55.75	3.75	25.76	(deuteriochloroform): τ = 0.45 (dd, H_4'), 2.55 (dd, H_5'), 0.90 (dd, H_6'), $J_{4',5'}$ = 9.0, $J_{5',6'}$ = 4.8, $J_{4',6'}$ = 1.5 Hz; τ = 1.40 (m, H_3), 2.15 (m, H_4), 2.50 (m, H_5), 1.40 (m, H_6), -2.0 (broad, NH).
1f	151-153	27	ethanol/DMF or CCl_4	$C_{10}H_8N_4S$	216	55.55	3.73	25.92	55.75	3.85	25.67	(DMSO-d_6): τ = -0.50 (d, H_3'), 2.5 (d, H_5' and H_6'), $J_{3',5'}$ = 1.0 Hz; τ 1.30 (m, H_3), 2.15 (m, H_4), 2.5 (m, H_5), 1.25 (m, H_6), -2.7 (broad, NH).
1g	193-195 (c)	29	ethanol/DMF	$C_8H_7N_5S$	205	46.83	3.44	34.12	47.08	3.81	34.45	(DMSO-d_6): τ = 1.42 (m, H_6), 1.57 (m, H_3), 1.63 (s, H_5'), 2.06 (m, H_4), 2.45 (m, H_5), -2.90 (broad s, NH).
1h	174-175	86	ethanol	$C_7H_6N_6S$	206	40.78	2.93	40.77	40.92	3.15	40.98	(DMSO-d_6): τ = 1.35 (m, H_6), 1.51 (m, H_3), 2.00 (m, H_4), 2.37 (m, H_5), -1.0 (broad s, NH).
1i	176-177	4 (d)	ethanol/DMF	$C_{13}H_9N_3S_2$	271	57.56	3.34	15.49	57.13	3.34	15.17	
2 (R = R_1 = Me)	98-100	16	ethanol/H_2O	$C_{13}H_{13}N_3S$	243	64.18	5.39	17.28	64.32	5.50	17.27	(deuteriochloroform): τ = 0.37 (d, H_3), 2.10 (ddd, H_4), 1.4 (m, H_5 and H_6), 7.4 (s, 6'-Me), 7.55 (s, 4'-Me), 2.75 (broad s, H_3' and H_5'), $J_{3,4}$ = 8.5, $J_{4,5}$ = 7.8, $J_{4,6}$ = 1.6, $J_{3,5} \cong$ 1.5 Hz.

(a) At 200°. (b) At 175-180 after 8 hours compound **7** and 3-aminopyridazine-5(2*H*)thione were obtained. (c) At 183° new crystals with m.p. 228-229° began to separate. (d) After 8 hours under reflux.



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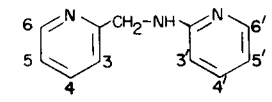

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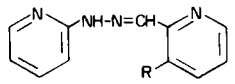

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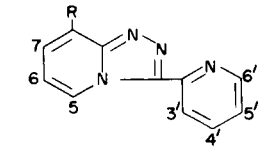

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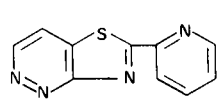

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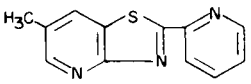

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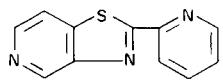

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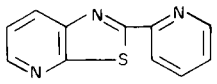

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amides (**1**) in moderate yields (Table I). 2,4,6-Trimethylpyridine reacted only with one of its three methyl groups to give **2** (R = R_1 = Me), even with excess of sulfur and amine. The participation of the 2-methyl group in the thioamide group formation is evident from the nmr spectrum of the product since the signals for the methyl groups at position 4 and 6 appear in a ratio of 1:1. It is well known, that in certain ionic reactions 4-methylpyridines revealed greater reactivity than the ortho isomers and the enhanced reactivity has been attributed to participation of *p*-quinonoid resonance stabilized structures. Since in the described reactions of methylpyridines with sulfur ionic mechanism is improbable, it is understandable that a changed reactivity pattern is observed (18,20).

In addition to methylpyridines, some other functionalized heterocycles were investigated as model compounds for thioamide group formation. Pyridyl-2-aldehyde was readily transformed into the corresponding thioamide (**2**, R = R_1 = H) in the presence of 2-aminopyridine and sulfur. In fact, the reacting species is the Schiff base (**3**) since, contrary to a previous report that the Schiff base is formed after a long reaction time (29), aminopyridine reacts immediately with pyridyl-2-aldehyde. The thioamide (**2**, R = R_1 = H) is formed from **3** either in diethylene glycol as high boiling solvent or, in a better yield, using 2-methylpyridine as solvent. Although *N,N*-dimethylformamide was recently claimed to be advantageous as solvent for thiations (27) in our hands inferior yields were obtained. Also other promotors, such as diethylamine or indene proved to be ineffective. The thioamide is formed even with an equimolar amount of sulfur, contrary to claims that great excess of sulfur is necessary when Schiff bases from aromatic aldehydes are used as starting material (28).

One can also postulate that the transformation of Schiff bases into the corresponding thioamides may involve hydrogen sulfide addition to the formimido double bond with subsequent dehydrogenation. We could establish that this reaction takes place, but only to a minor extent. The main reaction is thus a direct attack of the sulfur, in its activated form, on the formimido group. If this group is reduced, such as in **4**, the reaction proceeds smoothly and a better yield of the thioamide is obtained.

The reaction was extended also to hydrazones of heterocyclic aldehydes (**5**, R = H or NO_2), but instead of the anticipated formation of thiohydrazides oxidative cyclization took place and derivatives of *s*-triazolo[4,3-*a*]pyridine (**6**, R = H or NO_2) were formed. However, if the possibility of such cyclization involving the pyridine ring nitrogen was excluded, as in the case of pyridyl-2-aldehyde phenylhydrazone, the corresponding thiohydrazide (**1j**) was formed.

During the preparation of the corresponding thioamide (**1e**) from 3-aminopyridazine we could observe that raising reaction temperature to 175-180° and prolonged reaction time caused the formation of two different products. From the crude reaction mixture after extraction with ethyl acetate a thiazolopyridazine (**7**) was isolated and the residue yielded after extraction with water almost the same amount of 3-aminopyridazine-5(2*H*)thione. This finding prompted us to investigate the possibility of converting heterocyclic thioamides into thiazoloazines as well as the direct thionation of some heterocycles.

In fact, with an alkaline solution of potassium ferricyanide heterocyclic thioamides were oxidatively cyclized and derivatives of thiazolo[4,5-*b*]pyridine (**8**), thiazolo[5,4-*c*]pyridine (**9**), thiazolo[5,4-*b*]pyridine (**10**) and thiazolo[4,5-*c*]pyridazine (**7**) were obtained. Interestingly, *N*-2-pyridylthiopicolinamide (**2**, R = R_1 = H) afforded under the same reaction conditions only the desulfurated product, *N*-2-pyridylpicolinamide.

Experiments with the purpose of direct thionation of different heterocycles or thier amino derivatives were performed, but with limited success. Nevertheless, 3-aminopyridazine when heated with sulfur and in the presence of catalytic amount of 2-methylpyridine or diethyl malonate at 160-170° for 6 hours afforded in moderate yield the

so far unknown 3-aminopyridazine-5(2*H*)thione. In the same manner *s*-triazolo[4,3-*b*]pyridazine afforded the corresponding 3-thione, whereas imidazo[1,2-*b*]pyridazine was transformed into a mixture of 8-thione and 3,8-dithione as evidenced from nmr spectrum. Finally, quinoline could be transformed into 2(1*H*)quinolinethione, but only at 250°.

EXPERIMENTAL

Melting points were taken on a Kofler micro hot stage. All nmr spectra were obtained on a JEOL JNM C60-HL spectrometer and mass spectra were recorded on a Hitachi-Perkin-Elmer RMU-6L instrument.

All preparations of intermediates were conducted with adherence to published techniques. Contrary to the report describing the preparation of 2-(*N*-2-pyridylformimidoyl)pyridine (**3**) (29) we found that the product is formed quickly after few minutes. Upon scratching the reaction mixture the product crystallized, m.p. 120°. Prepared were also pyridyl-2-aldehyde 2-pyridylhydrazone, m.p. 185-186° (lit. (30) gives m.p. 179-180°) and pyridyl-2-aldehyde phenylhydrazone, m.p. 183° (lit. (31) gives m.p. 180-182°).

Pyridyl-2-aldehyde 3-Nitro-2-pyridylhydrazone (**5**, R = NO_2).

The compound was obtained from 2-hydrazino-3-nitropyridine and pyridyl-2-aldehyde in an ethanolic solution after 5 hours under reflux. M.p. 132-135° dec., (from aqueous ethanol): mass spectrum: M^+ = 243.

Anal. Calcd. for $C_{11}H_9N_5O_2$: C, 54.32; H, 3.73; N, 28.80. Found: C, 54.55; H, 3.98; N, 28.66.

2,2'-(Iminomethylene)dipyridine (**4**).

A solution of 2-(*N*-2-pyridylformimidoyl)pyridine (0.9 g.) in ehtanol (200 ml.) was treated with palladized charcoal (0.15 g. of 5%) and the mixture was shaken in a pressure bottle in an atmosphere of hydrogen at 45 psi at room temperature for 2 hours. Upon filtration and evaporation of the solvent the residue was distilled *in vacuo* and the fraction at 120°/1 mm was used for further reactions; nmr (deuteriochloroform): τ = 1.50 (m, H_6), 1.90 (m, H_6'), 2.75 (m, H_4', covered with $H_3H_4H_5$), 3.5 (m, H_3, and H_5'), 5.40 (d, CH_2), 3.95 (broad, t, NH), J_{CH_2NH} = 6 Hz.

Anal. Calcd. for $C_{11}H_{11}N_3$: N, 22.69. Found: N, 22.81.

General Procedure for the Preparation of Thioamides from Aminoheterocycles.

A mixture of 0.01 mole of the aminoheterocycle, 0.01 mole of sulfur and 10 ml. of 2-methylpyridine was heated under reflux for 4 hours. Excess of the solvent was evaporated *in vacuo* and the residue was treated with a 5% aqueous solution of sodium hydroxide. Upon filtration, the filtrate was acidified and the separated product dried and crystallized. Compounds are presented in Table I.

N-2-Pyridylthiopicolinamide (**2**, R = R_1 = H).

A.

2-(*N*-2-Pyridylformimidoyl)pyridine (0.5 g.) was heated on an oil bath and in the melt a slow stream of hydrogen sulfide was introduced for 1 hour. Upon cooling the orange reaction mixture was treated with 5% aqueous solution of sodium hydroxide, filtered and filtrate acidified with hydrochloric acid. The separated product had m.p. 78-82° (yield 20 mg., 3.4%) and was identified as the thioamide (lit. (18) gives m.p. 82°); nmr (deuteriochloroform): τ = 1.31 (m, H_3), 0.70 (m, H_3'), 1.54 (m, H_6 and H_6'), 2.24 (m, H_4 and H_4'), 2.68 and 2.90 (m, H_5 and H_5'), -2.55 (broad s, NH); mass spectrum: M^+ = 215.

Anal. Calcd. for $C_{11}H_9N_3S$: C, 61.39; H, 4.22; N, 19.53. Found: C, 61.19; H, 4.20; N, 19.67.

B.

A mixture of **3** (0.91 g.), sulfur (0.6 g.) and diethyleneglycol dimethylether (10 ml.) was heated at 140-150° for 4 hours. The solvent was evaporated *in vacuo*, the residue treated with 5% aqueous solution of sodium hydroxide, filtered and after acidification the product separated. It was crystallized from ethanol, m.p. 81-83° (yield 0.245 g., 23%). The product was found to be identical with that prepared as described under A.

If the same reaction was conducted in the presence of diethyl malonate (0.2 g.) yield was 12%, in the presence of 2-methylpyridine (10 ml.) the yield was 37% and in *N,N*-dimethylformamide as solvent (10 ml.) at 90-100° the product was obtained in 15% yield.

C.

A mixture of **4** (0.93 g.), sulfur (0.6 g.) and 2-methylpyridine (10 ml.) was heated under reflux for 4 hours. The solvent was evaporated *in vacuo* and the residue treated as described under B. The thioamide was obtained in 49% yield.

3-(Pyridyl-2')-*s*-triazolo[4,3-*a*]pyridine (**6**, R = H).

A.

A mixture of **5** (R = H) (0.991 g.) and sulfur (0.16 g.) was heated in a sealed tube at 130-140° for 7 hours. The reaction mixture was then treated with dilute aqueous sodium hydroxide and a dark oil separated. The alkaline solution was decanted and the oily residue sublimed and thereafter crystallized from *n*-heptane, m.p. 124° (yield 13%) and identical with the compound prepared as described under B; mass spectrum: M^+ = 196; nmr (deuteriochloroform): τ = 0.27 (m, H_5), 2.20 (m, H_6 and H_7), 1.5 (m, H_8), 2.70 (m, H_3' and H_4'), 3.15 (m, H_5'), 1.4 (m, H_6').

B.

A solution of **5** (R = H) (0.99 g.) in dry methylene chloride (30 ml.) was treated with lead tetraacetate (2.44 g.) and the solution left at room temperature for 12 hours. The solution was decanted from the precipitate, evaporated to dryness and the residue extracted with chloroform. Upon evaporation of the solvent a dark oil remained and after some time crystals separated. After sublimation at 100-110°/0.1 mm and crystallization from *n*-heptane the product had m.p. 127° (lit. (32) gives m.p. 127-128°) (yield 0.28 g., 29%).

3-(Pyridyl-2')-8-nitro-*s*-triazolo[4,3-*a*]pyridine (**6**, R = NO_2).

A.

The same procedure as for **6** (R = H) under A was employed, but the crude reaction mixture was dissolved in water and extracted with chloroform. The solvent was evaporated and the residue was purified by tlc on silica (0.25 mm, for development petrolether: chloroform:methanol, 3:2:1). The product was found to be identical with that described under B; mass spectrum: M^+ = 241.

B.

A solution of the hydrazone **5** (R = NO_2) (0.102 g.) and lead tetraacetate (0.216 g.) in methylene chloride was left overnight at room temperature. Upon cooling with ice and salt, the product was filtered off and crystallized from ethanol and *N,N*-dimethylformamide, m.p. 248-250° (yield 28%); mass spectrum: M^+ = 241;

nmr (DMSO-d_6, 130°): τ = 0.21 (dd, H_5), 1.37 (m, H_6'), 1.72 (m, H_7 and H_3'), 2.10 (m, H_4'), 2.52 (m, H_5'), 2.84 (t, H_6), $J_{5,7}$ = 1.5, $J_{5,6}$ = $J_{6,7}$ = 7 Hz.

Anal. Calcd. for $C_{11}H_7H_5O_2$: C, 54.77; H, 2.93; N, 29.04. Found: C, 54.68; H, 2.98; N, 29.14.

N-2-Pyridylthiophenylhydrazide (**1j**).

The same procedure as described for the preparation of **6** (R = H) under A was employed, but starting with pyridyl-2-aldehyde phenylhydrazone. The obtained product was crystallized from ethanol and cyclohexane, m.p. 181° (yield 21%); mass spectrum: M^+ = 229; nmr (DMSO-d_6): τ = 1.57 (m, H_3 and H_6), 1.91 (m, H_4), 2.50 (m, H_5), 2.9 and 3.1 (m, C_6H_5).

Anal. Calcd. for $C_{12}H_{11}N_3S$: C, 62.87; H, 4.84; N, 18.33. Found: C, 62.90; H, 4.79; N, 18.43.

2-(Pyridyl-2′)-7-methylthiazolo[4,5-*b*]pyridine (**8**).

Into a stirred aqueous solution of potassium ferricyanide (3 g. in 5 ml. water) a solution of **1d** (0.458 g.) in aqueous sodium hydroxide (5 ml. of 10%) was added portionwise. After addition was complete, the reaction mixture was stirred at room temperature for 3 hours, filtered and the product was crystallized from ethanol and *N*,*N*-dimethylformamide, m.p. 127-129° (yield 32%); mass spectrum: M^+ = 227.

Anal. Calcd. for $C_{12}H_9N_3S$: C, 63.43; H, 3.99; N, 18.49. Found: C, 63.55; H, 4.12; N, 18.66.

In a similar manner were prepared:

2-(Pyridyl-2′)thiazolo[5,4-*c*]pyridine (**9**).

The compound was obtained in 56% yield, m.p. 121-122° from ethanol and *N*,*N*-dimethylformamide); mass spectrum: M^+ = 213.

Anal. Calcd. for $C_{11}H_7N_3S$: C, 61.97; H, 3.31; N, 19.71. Found: C, 61.88; H, 3.42; N, 19.90.

2-(Pyridyl-2′)thiazolo[5,4-*b*]pyridine (**10**).

It was obtained in 38% yield, m.p. 178° (from ethanol); mass spectrum: M^+ = 213; nmr (DMSO-d_6): τ = 1.35; (dd, H_5), 2.45 (dd, H_6), 1.65 (dd, H_7), 2.3 (m, H_3' and H_5'), 1.95 (m, H_4'), 1.20 (m, H_6'), $J_{5,6}$ = 4.5, $J_{6,7}$ = 8.0, $J_{5,7}$ = 1.5 Hz.

Anal. Calcd. for $C_{11}H_7N_3S$: C, 61.97; H, 3.31; N, 19.71. Found: C, 62.08; H, 3.52; N, 19.90.

2-(Pyridyl-2′)thiazolo[4,5-*c*]pyridazine (**7**).

It was obtained in 36% yield, m.p. 245° (from ethanol); nmr (DMSO-d_6): τ = 0.90 (d, H_6), 1.65 (d, H_7), 1.65 (m, H_3'), 2.05 (m, H_4'), 2.50 (m, H_5'), 1.40 (m, H_6'), $J_{6,7}$ = 5 Hz.

Anal. Calcd. for $C_{10}H_6N_4S$: C, 56.07; H, 2.82; N, 26.16. Found: C, 56.22; H, 3.02; N, 26.33.

Alternatively, a mixture of 2-methylpyridine (0.7 g.), sulfur (0.4 g.), 3-aminopyridazine (0.49 g.) and diglyme (6 ml.) was heated at 175-180° for 3 hours. Excess of the solvent was evaporated *in vacuo* and the residue was extracted twice with hot ethyl acetate (each time with 40 ml.). The extracts were charcoaled and upon filtration and evaporation of the solvent to dryness the residue was treated with 3*N* sodium hydroxide (10 ml.), filtered and upon acidification compound **1e** was obtained. After crystallization from petrolether and carbon tetrachloride the compound melted at 147° (yield 50 mg.). The in sodium hydroxide insoluble part was washed with water and crystallized from ethanol. It was identified as compound **7**, m.p. 245° (yield 70 mg.). Mixed m.p. with a sample, obtained as described above, showed no depression.

3-Aminopyridazine-5(2*H*)thione.

A mixture of 3-aminopyridazine (0.38 g.), sulfur (0.128 g.) and few drops of 2-methylpyridine or diethyl malonate was heated in a sealed tube at 160-170° for 6 hours. The reaction product was treated with ethanol, filtered and crystallized from ethanol and water, m.p. 198-200° (yield 45%); mass spectrum: M^+ = 127; nmr (DMSO-d_6): τ = 3.37 (d, H_4), 2.35 (d, H_6), 3.3 (broad s, NH), $J_{4,6}$ = 2.1 Hz.

Anal. Calcd. for $C_4H_5N_3S$: C, 37.80; H, 3.97; N, 33.06. Found: C, 38.01; H, 4.06; N, 32.89.

The compound was transformed with methyl iodide in its 5-methylthio derivative in the usual way, m.p. 192-193° (from chloroform and *n*-hexane); mass spectrum: M^+ = 141; nmr (DMSO-d_6): τ = 3.45 (d, H_4), 1.70 (d, H_6), 3.76 (broad s, NH_2), 7.08 (s, Me), $J_{4,6}$ = 2.1 Hz.

Anal. Calcd. for $C_5H_7N_3S$: N, 29.78. Found: N, 30.02.

In a similar manner were prepared:

s-Triazolo[4,3-*b*]pyridazine-3(2*H*)thione.

The crude product was purified by dissolution in 5% sodium hydroxide, charcoaled and the filtrate acidified with acetic acid; m.p. 265-267° (yield 42%); mass spectrum: M^+ = 152; nmr (DMSO-d_6): τ = 1.45 (dd, H_6), 2.10 (dd, H_7), 1.90 (dd, H_8), -4.55 (broad s, NH), $J_{6,7}$ = 4.5; $J_{7,8}$ = 9.5; $J_{6,8}$ = 1.5 Hz.

Anal. Calcd. for $C_5H_4N_4S$: S, 21.04. Found: S, 20.90.

The compound formed a *S*-methyl derivative, m.p. 120-121° (from chloroform and *n*-hexane); nmr (DMSO-d_6): τ = 1.55 (dd, H_6), 1.90 (dd, H_7), 2.87 (dd, H_8), 7.10 (s, SMe), $J_{6,7}$ = 4.5; $J_{7,8}$ = 9.5; $J_{6,8}$ = 1.5 Hz.

Anal. Calcd. for $C_6H_6N_4S$: N, 33.73. Found: N, 33.55.

2(1*H*)Quinolinethione.

It was obtained after 7 hours at 250° in 26% yield, m.p. 174-175° (lit. (33) gives m.p. 174-175°); mass spectrum: M^+ = 161.

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