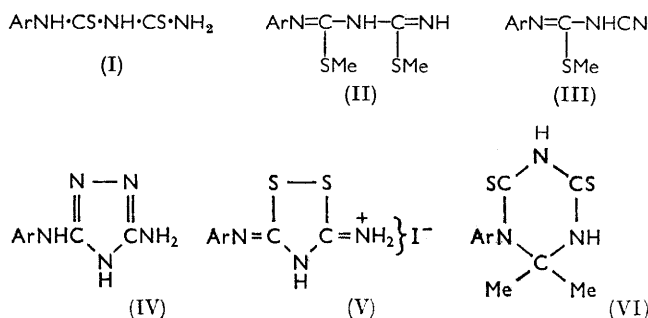


## Some 1-Aryldi-isodithiobiurets and 3-Amino-5-anilino-1,2,4-triazoles

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Some new 3-amino-5-anilino-1,2,4-triazoles have been prepared for biological study.

WHEN a 1-aryldithiobiuret (I) is dissolved in sodium hydroxide solution and shaken with methyl iodide a 1-aryl-SS-dimethyldi-isodithiobiuret (II) separates. Some *N*-aryl-*N'*-cyano-*S*-methylisothioureia (III) is also formed.<sup>1</sup> Both the di-isodithiobiuret (II) (*cf.* refs. 2 and 3) and the isothioureia (III)<sup>4</sup> (*cf.* ref. 5) react with hydrazine hydrate to give a 3-amino-5-anilino-1,2,4-triazole (IV) and methanethiol. In view of the effects of 3-amino-5-*p*-toluidino-1,2,4-triazole (IV; Ar = *p*-tolyl) on plant growth,<sup>6</sup> a number of 3-amino-5-anilino-1,2,4-triazoles (IV) have been prepared<sup>4</sup> for further study. Some dithiazoles (V) and 1-aryl-5,6-dihydro-6,6-dimethyl-1,3,5-triazine-2,4-dithiones (VI)<sup>7</sup> have also been obtained.



### EXPERIMENTAL

**1-Aryl-SS-dimethyldi-isodithiobiurets.**— 1-Phenyldithiobiuret (5.3 g., 0.025 mole) was dissolved in a solution of sodium hydroxide (2.3 g., 0.058 mole) in water (100 ml.). Methyl iodide (3.3 ml., 0.053 mole) was added, the mixture was shaken for 75 min., and the excess of methyl iodide was taken off under vacuum. The solid SS-dimethyl-1-phenyldi-isodithiobiuret was filtered off (filtrate A) and washed with dilute sodium hydroxide solution and then water (4.65 g., 78%), and gave needles, m.p. 121–122° (from ethanol)\* (Found: C, 50.3; H, 5.75; N, 17.55; S,

26.3. Calc. for C<sub>10</sub>H<sub>13</sub>N<sub>3</sub>S<sub>2</sub>: C, 50.2; H, 5.45; N, 17.6; S, 26.7%) (Table 2).

Acidification of filtrate A yielded *N*-cyano-*N'*-phenyl-*S*-methylisothioureia (0.66 g., 14%) as needles, m.p. 192–193° (from ethanol) (Found: C, 56.3; H, 4.8; N, 21.85; S, 16.8. Calc. for C<sub>9</sub>H<sub>9</sub>N<sub>3</sub>S: C, 56.5; H, 4.7; N, 22.0; S, 16.8%) (Table 3).

The *N*-aryl-*N'*-cyano-*S*-methylisothioureas all showed characteristic i.r. absorption at 2160 cm.<sup>-1</sup>.

**3-Amino-5-anilino-1,2,4-triazole from 1-Aryl-SS-dimethyldi-isodithiobiurets and Hydrazine Hydrate.**—SS-Dimethyl-1-phenyldi-isodithiobiuret (4.8 g., 0.02 mole) was dissolved in ethanol (50 ml.). Hydrazine hydrate (60%; 5 ml.) was added, the mixture was heated under reflux for 30 min., the excess of ethanol was distilled off, water (2 vols.) was added, the mixture was cooled, and the triazole was filtered off (2.7 g., 77%) and gave plates, m.p. 163–164° (from water), (Table 4).

**3-Amino-5-anilino-1,2,4-triazole from *N*-Cyano-*S*-methyl-*N'*-phenylisothioureia.**—A solution of *N*-cyano-*S*-methyl-*N'*-phenylisothioureia (1.91 g., 0.01 mole) in aqueous ethanol was heated under reflux with hydrazine hydrate (60%; 2 ml.) for 75 min. then cooled. The triazole (1.37 g., 78%) separated as shining plates, m.p. 162–163°.

Similarly *N*-benzyl-*S*-methyl-*N'*-cyanoisothioureia<sup>10</sup> afforded 3-amino-5-benzylamino-1,2,4-triazole (83%) as plates, m.p. 150–151° (from water) (Found: C, 57.0; H, 6.15; N, 36.8. C<sub>9</sub>H<sub>11</sub>N<sub>3</sub> requires C, 57.15; H, 5.8; N, 37.0%). When an ethanolic solution of 1-*m*-methoxyphenyldithiobiuret was treated with sodium hydroxide solution and benzyl chloride (*cf.* ref. 9), *S*-benzyl-*N*-cyano-*N'*-*m*-methoxyphenylisothioureia (56%), m.p. 144–145°, was obtained (Found: C, 64.95; H, 4.85; N, 13.95; S, 11.2. C<sub>16</sub>H<sub>15</sub>N<sub>3</sub>OS requires C, 64.6; H, 5.05; N, 14.15; S, 10.8%). On hydrazinolysis this gave 3-amino-5-*m*-methoxyanilino-1,2,4-triazole (93%) as needles, m.p. 144–145° (from water) (Found: C, 52.65; H, 5.25; N, 34.3; C<sub>9</sub>H<sub>11</sub>N<sub>3</sub>O requires C, 52.6; H, 5.4; N, 34.2%).

Hydrazinolysis of 1-*p*-bromophenyl-4-methyl-4-isodithiobiuret (m.p. 139–141°) yielded 3-amino-5-*p*-bromophenyl-

<sup>3</sup> F. H. S. Curd, D. G. Davey, D. N. Richardson, and R. B. Ashworth, *J. Chem. Soc.*, 1949, 1739.

<sup>4</sup> J. S. Davidson, *J. Chem. Soc. (C)*, 1967, 2471.

<sup>5</sup> E. Fromm and R. Kapeller-Adler, *Annalen*, 1928, **467**, 266.

<sup>6</sup> J. Roberts, *Weed Research*, 1968, **8**, 151.

<sup>7</sup> A. E. S. Fairfull and D. A. Peak, *J. Chem. Soc.*, 1955, 803.

<sup>8</sup> S. Swaminathan and P. C. Guha, *J. Indian Chem. Soc.*, 1946, **23**, 324.

<sup>9</sup> E. Fromm and K. Schneider, *Annalen*, 1906, **348**, 172.

<sup>10</sup> J. S. Davidson, *Chem. and Ind.*, 1965, 1977.

\* The same compound was obtained from *S*(4)-methyl-1-phenyl-4-isodithiobiuret and methyl sulphate as described by Underwood and Dains.<sup>2</sup> The compound, m.p. 195°, isolated by Swaminathan and Guha<sup>8</sup> must have been *N*-cyano-*S*-methyl-*N'*-phenylisothioureia.

<sup>1</sup> A. E. S. Fairfull and D. A. Peak, *J. Chem. Soc.*, 1955, 796.

<sup>2</sup> H. G. Underwood and F. B. Dains, *Univ. Kansas Sci. Bulletin*, 1936, **24**, 5.

TABLE I

Dithiobiurets (I) from the amine and isoperthiocyanic acid

Ar	Yield (%)	M.p.	Found (%)		Required (%)	
			C	H	C	H
1-(2,6-Diethyl-phenyl)	37	177—178°	54.05	6.5	54.0	6.15
1-(2,3-Xylyl)	56	179—180	50.5	5.4	50.2	5.45
1-(2,4-Xylyl)	32	152—153*	50.4	5.4	50.2	5.45
1-(2,5-Xylyl)	74	137—138	N, 17.9		N, 17.6	
1-(3,4-Xylyl)	53	151—152	50.3	4.9	50.2	5.45
1-(2,4-Dimethoxy-phenyl)	35	149—150	43.75	5.05	44.3	4.8
1- <i>p</i> -Methylthio-phenyl	35	170—171	41.95	4.1	42.0	4.3
1-Methyl-1- <i>m</i> -tolyl	48	131—132	50.2	5.6	50.2	5.45
1-Methyl-1- <i>o</i> -tolyl	42	185—187	50.15	5.4	50.2	5.45
1- <i>m</i> -Methoxyphenyl	50	179—180				
1- <i>m</i> -Tolyl	71	163				

\* Lit. (E. W. Bousquet and H. G. Guy, U.S.P. 2,410,862 (*Chem. Abs.*, 1947, **41**, 1806a), m.p. 138—139°, lit.<sup>9</sup>, 129° (Found: N, 17.3; S, 26.5.  $C_{10}H_{13}N_3S_2$  requires N, 17.6; S, 26.7%).

3-Amino-1,2,4-dithiazole hydrioides (V) from the dithiobiuret and iodine

ArNH	M.p.	Found (%)		Required (%)	
		I	S	I	S
5-(2,4-Dimethoxyanilino)	228—229°	32.75	15.9	32.0	16.1
5-(2,5-Dimethoxyanilino)	164—166	31.5	15.8	32.0	16.1
5-(2,5-Xylidino)	185—186	35.2	17.3	34.8	17.5
5-(3,4-Xylidino)	203	34.9	17.6	34.8	17.5

1-Aryl-5,6-dihydro-6,6-dimethyl-1,3,5-triazine-2,4-dithiones (VI)

Ar	Yield (%)	M.p. (decomp.)	Found (%)		Required (%)	
			C	H	C	H
1-(2,4-Dimethoxy-phenyl)		262—263°	49.9	5.5	50.2	5.45
1- <i>m</i> -Methoxyphenyl	90	228—229	51.05	5.4	51.3	5.3
1-(2,3-Xylyl)	98	252—253	56.2	6.2	55.9	6.1
1-(2,5-Xylyl)		240—241	55.4	6.1	55.9	6.1
1-(3,4-Xylyl)	96	264—265	55.55	6.25	55.9	6.1

1,2,4-triazole (80%), m.p. 243—245° (Found: Br, 31.75; N, 27.65.  $C_8H_8BrN_3$  requires Br, 31.5; N, 27.6%).

3-Amino-5-methylanilino-1,2,4-triazole.—A solution of 1-methyl-1-phenyldithiobiuret (20.1 g.) in 2N-sodium hydroxide solution (100 ml.) was shaken with an excess of methyl iodide. The semisolid obtained was separated, washed with water, dissolved in ethanol, and heated under reflux with hydrazine hydrate (0.2 mole). The mixture was diluted with water and cooled to give the triazole (7.7 g.,

TABLE 2

1-Aryl-SS-dimethyldi-isodithiobiurets (II)

Ar		Yield (%)	M.p.	Found (%)		Required (%)	
				C	H	C	H
1-Phenyl	Needles	78	121— 122°	50.3	5.75	50.2	5.45
1- <i>m</i> -Tolyl	Needles	31	73	52.1	5.9	52.1	5.9
1- <i>o</i> -Methoxyphenyl	Prisms	52	116— 117	48.8	5.4	49.0	5.6
1- <i>p</i> -Ethoxyphenyl	Needles	48	97— 98	51.2	5.8	50.9	6.0
1-(2,4-Dimethoxy-phenyl)	Prisms	18	106— 107 *				

\* (Found: N, 14.55; S, 21.65.  $C_{12}H_{17}N_3O_2S_2$  requires N, 14.05; S, 21.4%).

TABLE 3

N-Aryl-S-methyl-N'-cyanoisothioureas (III)

Ar		Yield (%)	M.p.	Found (%)		Required (%)	
				C	H	C	H
Phenyl	Needles	14	192— 193°	56.3	4.8	56.5	4.7
<i>m</i> -Tolyl		34	154— 155	57.5	5.55	57.6	5.4
<i>o</i> -Methoxyphenyl	Plates	5.5	144— 145	54.15	5.0	54.3	5.0
<i>m</i> -Methoxyphenyl	Needles	12	162— 163	54.3	5.0	54.3	5.0
<i>p</i> -Ethoxyphenyl	Needles	2.4	165	56.3	5.6	56.1	5.5

TABLE 4

3-Amino-5-anilino-1,2,4-triazoles (IV) from 1-aryldi-isodithiobiurets (II)

ArNH		Yield (%)	M.p.	Found (%)		Required (%)	
				C	H	C	H
5-Anilino	Plates	77	163— 164°				
5- <i>m</i> -Toluidino	Plates *	92	141— 142	57.5	5.7	57.15	5.8
5- <i>o</i> -Anisidino	Needles †	99	183	52.8	5.6	52.6	5.4
5- <i>p</i> -Phenetidino	Needles †		198— 199				
5-(2,4-Dimethoxy- anilino)			233— 235	N, 29.35		N, 29.8	

\* From ethanol-petroleum. † From ethanol.

46%) as needles, m.p. 181—182° (from ethanol) (Found: C, 57.2; H, 5.95; N, 36.9.  $C_9H_{11}N_3$  requires C, 57.2; H, 5.8; N, 37.0%).

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