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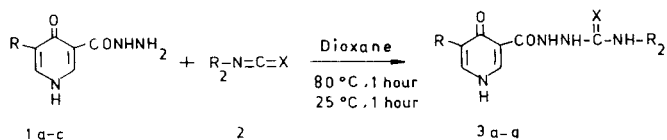
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1,4-Disubstituted-semicarbazide and thiosemicarbazide derivatives were synthesized from 5-substituted-4-oxo-1,4-dihydro-3-pyridinecarbohydrazides and cyclized to 3-mercapto-4*H*-1,2,4-triazoles. The obtained compounds could be *S*-methylated with methyl iodide in methanol. The new compounds were tested for antibacterial and antifungal activities.

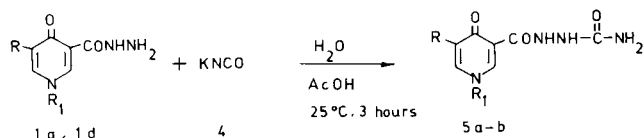
*J. Heterocyclic Chem.*, **17**, 175 (1980).

In our earlier papers the synthesis and antimicrobial testing of 1-alkyl-5-substituted-4-oxo-1,4-dihydro-3-pyridinecarboxylic acids (1), further of the corresponding carbohydrazides and their condensation products (2) had been described. In the present paper we report on the synthesis of  $\gamma$ -pyridone derivatives wearing a 1,2,4-triazolyl group in position 3 *via* semicarbazide and thiosemicarbazide derivatives.

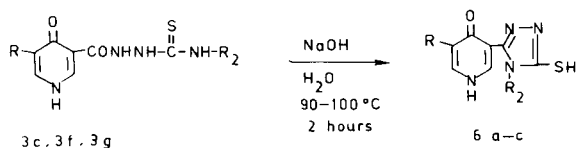
4-Oxo-1,4-dihydro-3-pyridinecarbohydrazides (**1a-c**) (2) react with isocyanates and isothiocyanates (**2**) in dioxane under mild conditions to afford 1,4-disubstituted semicarbazide and thiosemicarbazide derivatives (**3a-g**) in 80-90% yields.



The reaction of the carbohydrazides (**1a, 1d**) with potassium cyanate (**4**) in aqueous acetic acid at room temperature leads to 1-substituted semicarbazides (**5a-b**) with excellent yields.

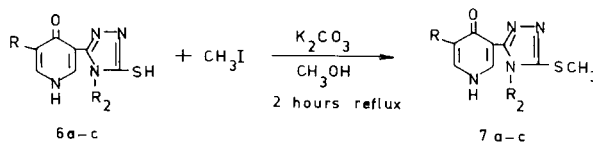


As it is known from the literature, 1-acyl-4-substituted thiosemicarbazides can be cyclized with base-catalysts to give 3-mercapto-4*H*-1,2,4-triazoles (**3**).



The 4-substituted-1-/5-substituted-4-oxo-1,4-dihydro-3-pyridinecarbonyl-/thiosemicarbazides (**3c, 3f, 3g**) were transformed into compounds **6a-c** by heating with dilute sodium hydroxide solution at 90-95° for 2 hours. In all cases the yield was 80-90%.

The 5-*R*-3-(4-*R*<sub>2</sub>-3-mercapto-4*H*-1,2,4-triazol-5-yl)-4-oxo-1,4-dihydropyridines (**6a-c**) could be *S*-methylated with methyl iodide in methanol, in the presence of anhydrous potassium carbonate.



The *S*-methylation is confirmed by the singlet at  $\delta = 2.66$  ppm in the nmr spectra of compounds **7a-c**.

The tautomerism of compounds **6a-c** can be studied by spectroscopic methods. In solid state compounds **6a** and **6b** exist predominantly in the thio form as it is shown by the  $\nu C=S$  band at 1250  $cm^{-1}$  in the ir spectra of these compounds. As for 5-heptyl-3-(3-mercapto-4-methyl-4*H*-1,2,4-triazol-5-yl)-4-oxo-1,4-dihydropyridine (**6c**) the thiol form is present even in solid state ( $\nu SH = 2605$   $cm^{-1}$ ).

In 96% ethanolic solutions all the three compounds (**6a-c**) can be characterized by the thiol form, their uv spectra resemble to those of the *S*-methyl derivatives (**7a-c**).

1-(5-Butyl-4-oxo-1,4-dihydro-3-pyridinecarbonyl)-semicarbazide (**5a**) was cyclized by heating with a 10% sodium hydroxide solution for 10 hours to 5-butyl-4-oxo-3-(5-oxo-4,5-dihydro-1*H*-1,2,4-triazol-3-yl)-1,4-dihydropyridine (**8**) with 85.5% yield.

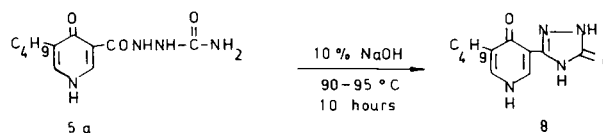
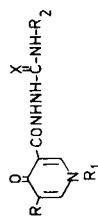
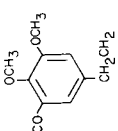
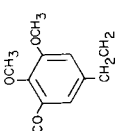


Table 1  
1,4-Disubstituted-Semicarbazide and Thiosemicarbazide Derivatives and their UV and IR Data

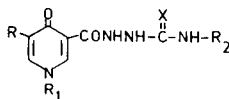


Starting Material	RNCO or RNCS	Product	R	R <sub>1</sub>	X	R <sub>2</sub>	Yield %	M.p. °C	Appearance, Solvent of Recrystallization	Formula M.W.	Analysis Calcd./Found %	C	H	N	S	λ max nm	log ε	IR (Potassium bromide) cm <sup>-1</sup> ν C=O ν C=N ν C=O ν C=S amide ring NHCONH	
<b>1a</b>	C <sub>6</sub> H <sub>5</sub> NCO	<b>3a</b>	C <sub>6</sub> H <sub>5</sub>	H	O	C <sub>6</sub> H <sub>5</sub>	95.9	236-237	white	C <sub>17</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub> 328.373	62.18 62.11	6.14 6.13	17.07 17.05			284 3.88	241 4.29	1700 i 1635 1660 i	
<b>1a</b>	C <sub>6</sub> H <sub>5</sub> NCO	<b>3b</b>	C <sub>6</sub> H <sub>5</sub>	H	O	C <sub>6</sub> H <sub>5</sub>	89.2	218	white	C <sub>17</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub> 308.363	58.42 58.57	7.84 7.47	18.17 18.00			286 3.78	254 3.91	1700 1635 1640	
<b>1a</b>	C <sub>6</sub> H <sub>5</sub> NCS	<b>3c</b>	C <sub>6</sub> H <sub>5</sub>	H	S	C <sub>6</sub> H <sub>5</sub>	91.5	226-227 dec.	Ethanol	C <sub>17</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> S 344.437	59.28 59.14	5.85 5.76	16.27 16.36	9.31			258 4.26	1695 1635	1280
<b>1a</b>	CH <sub>3</sub> NCS	<b>3d</b>	C <sub>6</sub> H <sub>5</sub>	H	S	CH <sub>3</sub>	95.7	190-191	white	C <sub>17</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> S 282.366	51.05 51.03	6.43 6.33	19.84 19.99	11.35 11.31			287 3.85	245 4.20	1680 1650 1270
<b>1a</b>	H <sub>3</sub> CO-  NCS	<b>3e</b>	C <sub>6</sub> H <sub>5</sub>	H	S	H <sub>3</sub> CO- 	76.5	195-196	white	C <sub>21</sub> H <sub>20</sub> N <sub>2</sub> O <sub>5</sub> S 432.546	58.31 58.25	6.52 6.82	12.95 12.87	7.41 7.53			281 3.97	250 4.25	1645 1645
<b>1b</b>	C <sub>6</sub> H <sub>5</sub> NCS	<b>3f</b>	C <sub>6</sub> H <sub>13</sub>	H	S	C <sub>6</sub> H <sub>5</sub>	80.6	222-224 dec.	white	C <sub>21</sub> H <sub>20</sub> N <sub>2</sub> O <sub>2</sub> S 372.492	61.27 61.05	6.49 6.71	15.04 15.07	8.61 8.62			257 4.07	1670 1650	1270
<b>1c</b>	CH <sub>3</sub> NCS	<b>3g</b>	C <sub>6</sub> H <sub>13</sub>	H	S	CH <sub>3</sub>	96.0	193 dec.	Methanol pale yellow	C <sub>17</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> S 324.447	55.53 55.16	7.46 7.51	17.27 17.23	9.88 9.74			288 3.85	245 4.24	1680 1650
<b>1a</b>	KNCO	<b>5a</b>	C <sub>6</sub> H <sub>5</sub>	H	O	H	78.2	230-231	white	C <sub>11</sub> H <sub>10</sub> N <sub>2</sub> O 252.275	52.37 52.17	6.39 6.56	22.21 21.96				287 3.79	254 3.93	1680 1650 i 1670
<b>1d</b>	KNCO	<b>5b</b>	H <sub>11</sub> NCONH- -NHCO	CH <sub>2</sub> =CH-CH <sub>2</sub>	O	H	97.9	283 dec.	white	C <sub>13</sub> H <sub>16</sub> N <sub>2</sub> O 242.286	42.73 42.64	4.48 4.54	29.07 29.17					1700 1700	1650

i = inflexion. (a) **5b** insoluble in Ethanol.

Table 2

Nmr Data for 1,4- Disubstituted Semicarbazide and Thiosemicarbazide Derivatives



Compound No.	Solvent	C <sub>2</sub> -H	C <sub>6</sub> -H	C <sub>5</sub> -(CH <sub>2</sub> ) <sub>3</sub> -CH <sub>3</sub>	C <sub>5</sub> -CH <sub>2</sub> -(CH <sub>2</sub> ) <sub>2</sub> -CH <sub>3</sub>		δ ppm
<b>3a</b>	Trifluoroacetic acid	9.21 s	8.43 s	0.80-1.25 m	1.25-2.10 m	C <sub>5</sub> -CH <sub>2</sub> -(CH <sub>2</sub> ) <sub>2</sub> -CH <sub>3</sub> -NH-C <sub>6</sub> H <sub>5</sub>	2.65-3.20 m 7.41 s
<b>3b</b>	Trifluoroacetic acid	9.28 s	8.51 s	0.80-1.17 m	1.20-2.00 m	-NH-(CH <sub>2</sub> ) <sub>3</sub> -CH <sub>3</sub> -NH-CH <sub>2</sub> -(CH <sub>2</sub> ) <sub>2</sub> -CH <sub>3</sub> C <sub>5</sub> -CH <sub>2</sub> -(CH <sub>2</sub> ) <sub>2</sub> -CH <sub>3</sub> -NH-CH <sub>2</sub> -(CH <sub>2</sub> ) <sub>2</sub> -CH <sub>3</sub>	0.80-1.17 m 1.20-2.00 m 2.60-3.10 m 3.20-3.65 m
<b>3c</b>	DMSO-d <sub>6</sub>	8.59 d J = 2 Hz	7.20-7.90 m	0.80-1.20 m	1.20-1.90 m	C <sub>5</sub> -CH <sub>2</sub> -(CH <sub>2</sub> ) <sub>2</sub> -CH <sub>3</sub> CSNH <sub>6</sub> H <sub>5</sub> CSNH <sub>6</sub> H <sub>5</sub> CONHNHCS CONHNHCS	2.30-2.80 m 3.20-3.70 bs 7.20-7.90 m 10.08 s 12.85 s
<b>3d</b>	Trifluoroacetic acid	9.30 s	8.50 s	0.75-1.15 m	1.25-2.00 m	C <sub>5</sub> -CH <sub>2</sub> -(CH <sub>2</sub> ) <sub>2</sub> -CH <sub>3</sub> -NH-CH <sub>3</sub>	2.88 t J = 7 Hz 3.30 s
<b>3e</b>	DMSO-d <sub>6</sub>	8.53 bs	7.84 bs	0.75-1.10 m	1.20-1.80 m	C <sub>5</sub> -CH <sub>2</sub> -(CH <sub>2</sub> ) <sub>2</sub> -CH <sub>3</sub> -NH-CH <sub>2</sub> -CH <sub>3</sub> 3,4-(CH <sub>3</sub> O) <sub>2</sub> -C <sub>6</sub> H <sub>3</sub> 3,4-(CH <sub>3</sub> O) <sub>2</sub> -C <sub>6</sub> H <sub>3</sub> CSNH-CH <sub>2</sub> -CH <sub>2</sub> - CONHNHCS CONHNHCS	2.30-3.10 m 3.77 s 3.80 s 6.89 s 8.05 bs 9.68 bs 12.22 bs
<b>3f</b>	Trifluoroacetic acid	9.32 s	8.48 s			C <sub>5</sub> -(CH <sub>2</sub> ) <sub>3</sub> -CH <sub>3</sub> C <sub>5</sub> -CH <sub>2</sub> -(CH <sub>2</sub> ) <sub>4</sub> -CH <sub>3</sub> C <sub>5</sub> -CH <sub>2</sub> -(CH <sub>2</sub> ) <sub>4</sub> -CH <sub>3</sub> -NH-C <sub>6</sub> H <sub>5</sub>	0.70-1.10 m 1.20-2.10 m 2.70-3.30 m 7.30-7.80 m
<b>3g</b>	DMSO-d <sub>6</sub>	8.48 bs	7.80 bs			C <sub>5</sub> -(CH <sub>2</sub> ) <sub>6</sub> -CH <sub>3</sub> C <sub>5</sub> -CH <sub>2</sub> -(CH <sub>2</sub> ) <sub>5</sub> -CH <sub>3</sub> C <sub>5</sub> -CH <sub>2</sub> -(CH <sub>2</sub> ) <sub>5</sub> -CH <sub>3</sub> -NH-CH <sub>3</sub> CSNHCH <sub>3</sub> CONHNHCS CONHNHCS	0.70-1.05 m 1.10-2.70 m 2.33-2.60 m 2.92 d J = 5 Hz 7.99 d J = 5 Hz 9.45 bs 12.35 s
<b>5a</b>	Trifluoroacetic acid	9.30 bs	8.52 bs			C <sub>5</sub> -(CH <sub>2</sub> ) <sub>3</sub> -CH <sub>3</sub> C <sub>5</sub> -CH <sub>2</sub> -(CH <sub>2</sub> ) <sub>2</sub> -CH <sub>3</sub> C <sub>5</sub> -CH <sub>2</sub> -(CH <sub>2</sub> ) <sub>2</sub> -CH <sub>3</sub>	0.80-1.16 m 1.25-2.00 m 2.91 t J = 7 Hz
<b>5b</b>	Trifluoroacetic acid	9.01 s (a)				N-CH <sub>2</sub> -CH=CH <sub>2</sub> N-CH <sub>2</sub> -CH=CH <sub>2</sub> N-CH <sub>2</sub> -CH=CH <sub>2</sub>	4.75-5.05 m 5.30-5.80 m 5.80-6.45 m

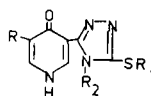
s = singlet, bs = broad singlet, d = doublet, t = triplet, m = multiplet. (a) C<sub>2</sub>-H and C<sub>6</sub>-H appears at the same chemical shift.

The obtained new compounds (**3a-g**, **5a-b**, **6a-c**, **7a-c**, **8**) were tested for antibacterial and antifungal activities. Only compounds **5a** and **8** exhibited a weak activity against microspores, while the rest of the compounds showed no significant activity.

#### EXPERIMENTAL

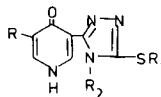
All melting points are uncorrected. The uv spectra were taken in ethanol with a Unicam SP 800 spectrophotometer, the ir spectra were recorded on a Zeiss UR 20 spectrophotometer, nmr spectra were measured with a Perkin-Elmer R-12 spectrometer using tetramethyl silane as an internal standard.

Table 3

5-*R*-3-(4-*R*<sub>1</sub>-3-*SR*<sub>1</sub>-4*H*-1,2,4-triazol-5-yl)-4-oxo-1,4-dihydropyridines and their Uv and Ir Data

Starting Material	Product	R	R <sub>1</sub>	R <sub>2</sub>	Yield %	M.p. °C	Appearance, Solvent of Recrystallization	Formula M.W.	Analysis Calcd./Found %				λ max nm log ε	Ir (Potassium bromide) cm <sup>-1</sup>		
									C	H	N	S		ν C=O	ν C=S	ν SH ring
3c	6a	C <sub>4</sub> H <sub>6</sub>	H	C <sub>6</sub> H <sub>5</sub>	89.9	315	white DMF	C <sub>17</sub> H <sub>18</sub> N <sub>4</sub> OS 326.422	62.55	5.56	17.16	9.82	261	1650	1250	
									62.36	5.79	17.25	10.04	4.23			
3f	6b	C <sub>6</sub> H <sub>13</sub>	H	C <sub>6</sub> H <sub>5</sub>	90.5	315 dec.	white Methanol	C <sub>18</sub> H <sub>22</sub> N <sub>4</sub> OS 354.477	64.38	6.26	15.81	9.04	260	1650	1250	
									63.96	6.01	15.75	8.96	4.23			
3g	6c	C <sub>7</sub> H <sub>15</sub>	H	CH <sub>3</sub>	82.8	264	white Methanol	C <sub>15</sub> H <sub>22</sub> N <sub>4</sub> OS 306.432	58.80	7.24	18.28	10.46	254	1660	2605	
									59.02	7.35	18.33	10.59	3.31			
6a	7a	C <sub>4</sub> H <sub>6</sub>	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	70.3	114-115	white Ethanol-water	C <sub>18</sub> H <sub>20</sub> N <sub>4</sub> OS·H <sub>2</sub> O 358.465	60.31	6.19	15.63	8.94	260	1660		
									60.28	6.25	15.48	8.85	4.00			
6b	7b	C <sub>6</sub> H <sub>13</sub>	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	79.7	164	white Benzene-ethyl acetate	C <sub>20</sub> H <sub>24</sub> N <sub>4</sub> OS 368.504	65.19	6.56	15.20	8.70	260	1655		
									65.42	6.80	15.22	8.58	4.02			
6c	7c	C <sub>7</sub> H <sub>15</sub>	CH <sub>3</sub>	CH <sub>3</sub>	50.1	125	white Ethyl acetate	C <sub>18</sub> H <sub>24</sub> N <sub>4</sub> OS 320.459	59.97	7.55	17.48	10.01	264	1660		
									59.70	7.75	17.09	9.82	3.99			

Table 4

Nmr Data for 5-*R*-3-(4-*R*<sub>2</sub>-3-*SR*<sub>1</sub>-4*H*-1,2,4-triazol-5-yl)-4-oxo-1,4-dihydropyridines

Compound No.	Solvent	C <sub>2</sub> -H	C <sub>6</sub> -H	N-C <sub>6</sub> H <sub>5</sub>	N-CH <sub>3</sub>	S-CH <sub>3</sub>	δ ppm
6a	Trifluoroacetic acid	8.40 bs	7.40-8.00 (a) m	—	—	—	C <sub>5</sub> -(CH <sub>2</sub> ) <sub>5</sub> -CH <sub>3</sub> 0.80-1.20 m
							C <sub>5</sub> -CH <sub>2</sub> -(CH <sub>2</sub> ) <sub>2</sub> -CH <sub>3</sub> 1.20-2.00 m
							C <sub>5</sub> -CH <sub>2</sub> -(CH <sub>2</sub> ) <sub>2</sub> -CH <sub>3</sub> 2.92 t J = 7 Hz
7a	Deuteriochloroform	7.78 s	7.25-7.65 (a) m	—	2.66 s	—	C <sub>5</sub> -(CH <sub>2</sub> ) <sub>5</sub> -CH <sub>3</sub> 0.70-1.05 m
							C <sub>5</sub> -CH <sub>2</sub> -(CH <sub>2</sub> ) <sub>2</sub> -CH <sub>3</sub> 1.15-1.60 m
							C <sub>5</sub> -CH <sub>2</sub> -(CH <sub>2</sub> ) <sub>2</sub> -CH <sub>3</sub> 2.30-2.70 m
6b	DMSO-d <sub>6</sub>	8.05 s	7.61 s	7.46 s	—	—	C <sub>5</sub> -(CH <sub>2</sub> ) <sub>5</sub> -CH <sub>3</sub> 0.75-1.05 m
							C <sub>5</sub> -CH <sub>2</sub> -(CH <sub>2</sub> ) <sub>4</sub> -CH <sub>3</sub> 1.05-1.45 m
							C <sub>5</sub> -CH <sub>2</sub> -(CH <sub>2</sub> ) <sub>4</sub> -CH <sub>3</sub> 2.00-2.40 m
7b	Deuteriochloroform	7.81 s	7.25-7.70 (a) m	—	2.66 s	—	C <sub>5</sub> -(CH <sub>2</sub> ) <sub>5</sub> -CH <sub>3</sub> 0.70-1.04 m
							C <sub>5</sub> -CH <sub>2</sub> -(CH <sub>2</sub> ) <sub>4</sub> -CH <sub>3</sub> 1.10-1.65 m
							C <sub>5</sub> -CH <sub>2</sub> -(CH <sub>2</sub> ) <sub>4</sub> -CH <sub>3</sub> 2.15-2.65 m
6c	DMSO-d <sub>6</sub>	8.10 d J = 2.7 Hz	7.82 s	—	3.40 s	—	ring-NH 10.95 bs
							C <sub>5</sub> -(CH <sub>2</sub> ) <sub>5</sub> -CH <sub>3</sub> 0.75-1.10 m
							C <sub>5</sub> -CH <sub>2</sub> -(CH <sub>2</sub> ) <sub>5</sub> -CH <sub>3</sub> 1.15-1.75 m
7c	Deuteriochloroform	7.93 s	7.59 s	—	3.57 s	2.64 s	C <sub>5</sub> -CH <sub>2</sub> -(CH <sub>2</sub> ) <sub>5</sub> -CH <sub>3</sub> 2.48 t J = 7.5 Hz
							C <sub>5</sub> -(CH <sub>2</sub> ) <sub>5</sub> -CH <sub>3</sub> 0.65-1.05 m
							C <sub>5</sub> -CH <sub>2</sub> -(CH <sub>2</sub> ) <sub>5</sub> -CH <sub>3</sub> 1.10-1.80 m
							C <sub>5</sub> -CH <sub>2</sub> -(CH <sub>2</sub> ) <sub>5</sub> -CH <sub>3</sub> 2.30-2.80 m
							ring-NH 8.82 s

(a) The C<sub>6</sub>-H and N-C<sub>6</sub>H<sub>5</sub> protons appear together.

General Procedure for the Synthesis of 1-(5-Alkyl-4-oxo-1,4-dihydro-3-pyridinecarbonyl)-4-substituted-semicarbazides and Thiosemicarbazides (**3a-g**).

To a suspension of the 5-alkyl-4-oxo-1,4-dihydro-3-pyridinecarbohydrazide (**1a-c**) (2) (0.01 mole in dioxane (50 ml.)) the appropriate isocyanate or isothiocyanate (0.01 mole) was added at 80°. The reaction mixture was stirred at 80° for one hour (after a few minutes crystals began to separate) and then at 25° for one hour. After a few hours the separated crystals were filtered off, and washed with dioxane and ethanol. For the yields, m.p., solvents used for recrystallization and analytical data of compounds **3a-g** see Table 1, and for their spectroscopic characteristics Tables 1 and 2.

General Procedure for the Synthesis of 1-(5-Butyl-4-oxo-1,4-dihydro-3-pyridinecarbonyl)-semicarbazide (**5a**) and 1,1'-(1-Allyl-4-oxo-1,4-dihydro-3,5-pyridinedicarbonyl)-disemicarbazide (**5b**).

A solution of potassium cyanate (0.022 mole) in water (10 ml.) was added dropwise, within 15 minutes, under stirring, at 0° to a solution of the carbohydrazide (**1a, 1d**) (0.02 mole) in a mixture of acetic acid (40 ml.) and water (40 ml.). After about 10 minutes white crystals began to separate from the solution. The reaction mixture was stirred at 20-25° for 3 hours, chilled and the precipitate was filtered off, and washed with water and ethanol.

For the physical data and analytical results of the semicarbazides **5a** and **5b** see Table 1, for their spectroscopic data Tables 1 and 2.

Cyclization of the Thiosemicarbazide Derivatives in Alkaline Medium. Preparation of 5-Alkyl-3-(4-substituted-3-mercapto-4*H*-1,2,4-triazol-5-yl)-4-oxo-1,4-dihydropyridines (**6a-c**).

A solution of 1-(5-alkyl-4-oxo-1,4-dihydro-3-pyridinecarbonyl)-4-substituted thiosemicarbazide (**3c, 3f, 3g**) (0.01 mole) and sodium hydroxide (0.012 mole) in water (50 ml.) was stirred at 90-95° for two hours, then the light yellow solution was filtered and acidified with 1:1 hydrochloric acid to pH = 4-5. After chilling the separated white crystalline material was filtered and washed with water.

For the physical data of the obtained compounds (**6a-c**) see Table 3, for their spectroscopic data Tables 3 and 4.

Preparation of 5-Alkyl-3-(4-substituted-3-methylmercapto-4*H*-1,2,4-triazol-5-yl)-4-oxo-1,4-dihydropyridines (**7a-c**).

A mixture of 5-alkyl-3-(4-substituted-3-mercapto-4*H*-1,2,4-triazol-5-yl)-4-oxo-1,4-dihydropyridine (**6a-c**) (0.01 mole), methyl iodide (0.011 mole),

anhydrous potassium carbonate (0.011 mole) and methanol (100 ml.) was stirred on a steam bath for two hours. The solution was filtered and evaporated to dryness under vacuum. The residue was dissolved in water (100 ml.), and extracted with three 50 ml. portions of methylene chloride. The organic extracts were dried over sodium sulfate, and evaporated. The viscous, resinous, colourless residue was crystallized from the solvent given in Table 3. For the yields, m.p. and analytical data of the S-methyl derivatives (**7a-c**) see Table 4.

The results of the uv, ir and nmr studies are summarized in Tables 5 and 6.

Preparation of 5-Butyl-4-oxo-3-(5-oxo-4,5-dihydro-1*H*-1,2,4-triazol-3-yl)-1,4-dihydropyridine (**8**).

A mixture of 1-(5-butyl-4-oxo-1,4-dihydro-3-pyridinecarbonyl)-semicarbazide (**5a**) (0.01 mole) and 10% sodium hydroxide solution (40 ml.) was stirred at 90-95° for 10 hours. The yellow solution was filtered and acidified with 1:1 hydrochloric acid under cooling to pH = 3. After dilution with water (60 ml.) the mixture was allowed to stand at 4° overnight, then the separated yellow crystals were filtered off and washed with water. In this manner 2.0 g. (yield, 85.5%) of the cyclized product (**8**) melting above 300° was obtained, and recrystallized from dimethyl formamide; uv (96% ethanol):  $\lambda$  max (log  $\epsilon$ ) 303 (3.89) 231 (4.02); ir (potassium bromide):  $\nu$  C=O (ring) 1750, 1655  $\text{cm}^{-1}$ ; nmr (trifluoroacetic acid): 9.13 (C<sub>2</sub>-H, bs), 8.54 (C<sub>6</sub>-H, bs), 0.75-1.20 (C<sub>2</sub>-(CH<sub>2</sub>)<sub>3</sub>-CH<sub>3</sub>, m), 1.25-2.05 (C<sub>5</sub>-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>2</sub>-CH<sub>3</sub>, m), 2.95 (C<sub>5</sub>-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>2</sub>-CH<sub>3</sub>, t, J = 7.5 Hz). Anal. Calcd. for C<sub>11</sub>H<sub>14</sub>N<sub>4</sub>O<sub>2</sub> (234.259): C, 56.40; H, 6.02; N, 23.92. Found: C, 56.25; H, 5.98; N, 23.73.

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