

Table II

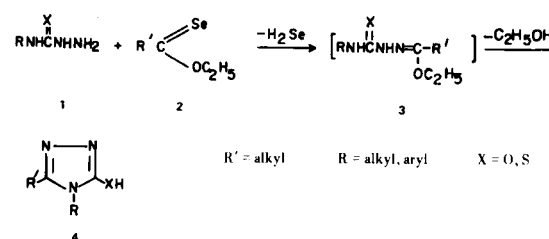
Mass Spectral Data of 3-Hydroxy- and 3-Mercapto-1,2,5-triazoles

Compound No.	Derivatives		Molecular Formula m/e
	MS; m/e (%)	Structure	
1	32 (11), 42 (17), 57 (13), 59 (30), 60 (21), 74 (100), 115 (66)		C ₃ H ₅ N ₃ S (115)
2	27 (15), 29 (10), 39 (14), 41 (29), 42 (9), 43 (8), 45 (7), 55 (14), 56 (18), 59 (6), 60 (7), 70 (45), 74 (10), 114 (6), 128 (44), 129 (100), 130 (7)		C ₄ H ₇ N ₃ S (129)
3	27 (11), 39 (10), 51 (31), 56 (36), 77 (45), 91 (11), 118 (12), 149 (24), 190 (80), 191 (100)		C ₉ H ₉ N ₃ S (191)
4	39 (9), 41 (9), 51 (15), 70 (14), 77 (25), 91 (21), 149 (14), 204 (80), 205 (100)		C ₁₀ H ₁₁ N ₃ S (205)
5	39 (10), 41 (10), 51 (17), 55 (11), 77 (30), 105 (24), 118 (12), 149 (12), 150 (12), 189 (13), 190 (38), 204 (36), 218 (37), 219 (100), 220 (16)		C ₁₁ H ₁₃ N ₃ S (219)
6	41 (12), 51 (13), 77 (27), 91 (13), 118 (17), 149 (11), 190 (21), 191 (53), 204 (39), 232 (24), 233 (100)		C ₁₂ H ₁₅ N ₃ S (233)
7	32 (8), 41 (9), 42 (23), 43 (24), 55 (25), 56 (41), 60 (21), 129 (100)		C ₄ H ₇ N ₃ S (129)
8	32 (19), 39 (10), 41 (15), 42 (16), 55 (21), 56 (29), 60 (10), 74 (17), 105 (18), 129 (100), 142 (21), 170 (28), 185 (54)		C ₈ H ₁₅ N ₃ S (185)
9	29 (17), 41 (13), 56 (15), 60 (12), 69 (20), 70 (24), 128 (32), 129 (31), 156 (40), 157 (100)		C ₆ H ₁₁ N ₃ S (157)
10	27 (48), 29 (55), 41 (32), 42 (27), 48 (59), 44 (68), 55 (24), 60 (70), 69 (28), 74 (22), 84 (27), 88 (29), 102 (50), 119 (14), 128 (24), 143 (41), 156 (100), 159 (24), 170 (22), 171 (94)		C ₇ H ₁₃ N ₃ S (171)
11	27 (29), 29 (32.5), 30 (20), 32 (7), 39 (10), 41 (20.5), 42 (10), 43 (20), 44 (20.5), 55 (11.5), 59 (13), 60 (20.5), 69 (8.5), 71 (10), 74 (10), 88 (8), 102 (6.5), 115 (9), 128 (4.5), 142 (8), 143 (100), 144 (8), 156 (15.5), 170 (7.5), 185 (15)		C ₈ H ₁₅ N ₃ S (185)
12	32 (29), 39 (21), 42 (23), 56 (20), 65 (25), 66 (26), 77 (22), 92 (21), 93 (100), 114 (93), 119 (30), 175 (16)		C ₉ H ₉ N ₃ O (175)
13	39 (20), 41 (30), 51 (32), 70 (79), 77 (40), 91 (73), 104 (13), 118 (11), 132 (11), 188 (36), 189 (100), 190 (14)		C ₁₀ H ₁₁ N ₃ O (189)

Table II (Continued)

Compound No.	MS; m/e (%)	Molecular Formula m/e
14	39 (23), 41 (20), 43 (25), 51 (27), 55 (19), 65 (12), 69 (11), 77 (33), 84 (32), 91 (39), 99 (7), 104 (12), 105 (37), 112 (14), 118 (13), 146 (3), 173 (6), 175 (5), 188 (43), 202 (29), 203 (100), 204 (13)	C ₁₁ H ₁₃ N ₃ O (203)
15	39 (8), 41 (11), 51 (11), 77 (18), 91 (12), 174 (33), 175 (100), 188 (10), 217 (34)	C ₁₂ H ₁₅ N ₃ O (217)

semicarbazides (1). The reaction takes place through a stage involving the formation of the hydrazones **3**, which eliminate a molecule of hydrogen selenide under the reaction conditions and are converted into the derivatives **4**. In fact, we were able to isolate such a hydrazone **3** during brief heating of compound **1** with **2**.



The nmr and mass spectral fragmentation of the aforementioned compounds are listed in Tables I and II.

EXPERIMENTAL

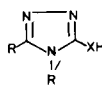
The nmr spectra were obtained on a Varian EM-360 spectrometer. Mass spectra were taken on a Varian CH7A Mass spectrometer. The elemental analyses were performed by Dornis und Kolbe Mikroanalytisches Laboratorium, Hohenweg 17, West Germany and Service Central de Microanalyses (C.N.R.S.) 2, Rue Henry Dunant-94320 Thiais, France. Melting points were measured on a Kofler hot bench apparatus. All of the semicarbazide and thiosemicarbazide derivatives were purchased from commercial sources. Aliphatic selenone esters were prepared from the corresponding iminoester (6).

Propyl Selenoester-4-phenylsemicarbazone.

4-Phenylsemicarbazide (1.51 g., 0.01 mole) was dissolved in anhydrous methanol and propyl selenoester (1.79 g., 0.01 mole) in 10 ml. of methanol was added. The mixture was heated under reflux for 1 hour and allowed to stand at room temperature for 1 day then the suspension which resulted was filtered. Evaporation of the solvent leaves 2 g. of semicarbazone (80%); m.p. (after two recrystallizations from anhydrous ethanol) 120°; ir (tablet with potassium bromide): 1675 cm⁻¹ (C=N); ms: 249 (85), 204 (8), 130 (42), 102 (50), 93 (100), 77 (30), 74 (28), 71 (50), 70 (32), 43 (63); ¹H nmr: 0.90 δ (3H, t), 1.25 (3H, t), 1.62 (2H, m), 2.40 (2H, t), 4.16 (2H, q), 7.32 (5H, m), 8.30 (1H, s?), 9.11 (1H, s?) (In DMSO-d₆ with TMS as the internal reference).

Anal. Calcd. for C₁₃H₁₉N₃O₂: C, 62.25; H, 7.63; N, 16.86. Found: C, 62.50; H, 7.66; N, 16.95.

Table III
Physical Properties of 3-Hydroxy- and 3-Mercapto-1,2,4-triazoles Derivatives



Compound No.	R	R'	X	Reaction Solvent	Time of Reflux	B.p. °C (mm) (M.p. °C)	Crystallization Solvent	Yield %
1	CH ₃	H	S	1-Butanol	48	(216)	Ethanol-Petroleum ether	70
2	CH ₃ CH ₂	H	S	1-Butanol	35	(174)	1-Butanol-Petroleum ether	74
3	CH ₃	C ₆ H ₅	S	Methanol	50	(222)	<i>n</i> -Butyl acetate	87
4	CH ₃ CH ₂	C ₆ H ₅	S	Methanol	50	(171)	<i>n</i> -Butyl acetate	75
5	CH ₃ (CH ₂) ₂	C ₆ H ₅	S	Methanol	50	(148)	<i>n</i> -Butyl acetate	65
6	CH ₃ (CH ₂) ₃	C ₆ H ₅	S	Methanol	50	(121)	Benzene	82
7	CH ₃	CH ₃	S	Methanol	50	(209)	<i>n</i> -Butyl acetate	68
8	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{-CH}(\text{CH}_2)_2 \end{array}$	CH ₃	S	Methanol	50	(104)	<i>n</i> -Butyl acetate-Petroleum ether	52
9	CH ₃ CH ₂	CH ₃ CH ₂	S	Methanol	50	(144)	<i>n</i> -Butyl acetate-Petroleum ether	45
10	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{-CH} \end{array}$	CH ₃ CH ₂	S	Methanol	50	148 (1)	--	62
11	CH ₃ (CH ₂) ₃	CH ₃ CH ₂	S	Methanol	3	204 (1)	--	72
12	CH ₃	C ₆ H ₅	O	Methanol	25	(233)	Pyridine-Ethyl ether	80
13	CH ₃ CH ₂	C ₆ H ₅	O	Methanol	50	(127)	<i>n</i> -Butyl acetate-Petroleum ether	71
14	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{-CH} \end{array}$	C ₆ H ₅	O	Methanol	50	(156)	<i>n</i> -Butyl acetate-Petroleum ether	68
15	CH ₃ (CH ₂) ₃	C ₆ H ₅	O	Methanol	50	(124)	<i>n</i> -Butyl acetate-Petroleum ether	78

Table IV
Microanalytical Data of the Compounds Listed In Table III

Compound No.	Empirical Formula	Elemental Analysis (%)				
		C	H	N	S	
1	C ₃ H ₅ N ₃ S	Calcd.	31.30	4.34	36.52	27.82
		Found	31.43	4.54	36.19	27.57
2	C ₄ H ₇ N ₃ S	Calcd.	37.22	5.42	32.55	24.80
		Found	37.14	5.38	32.59	25.04
3	C ₉ H ₉ N ₃ S	Calcd.	56.54	4.71	21.98	16.75
		Found	56.32	4.78	21.80	17.04
4	C ₁₀ H ₁₁ N ₃ S	Calcd.	58.53	5.36	20.48	15.60
		Found	58.70	5.37	20.55	15.90
5	C ₁₁ H ₁₃ N ₃ S	Calcd.	60.27	5.93	19.17	14.61
		Found	60.04	5.93	19.32	14.87
6	C ₁₂ H ₁₅ N ₃ S	Calcd.	61.82	6.43	18.02	13.73
		Found	61.78	6.42	17.96	14.01
7	C ₄ H ₇ N ₃ S	Calcd.	37.22	5.42	32.55	24.80

Table IV (continued)

Microanalytical Data of the Compounds Listed in Table III

Compound No.	Empirical Formula	Elemental Analysis (%)				
			C	H	N	S
8	C ₈ H ₁₅ N ₃ S	Found	37.18	5.46	32.52	24.89
		Calcd.	51.89	8.10	22.70	17.29
9	C ₆ H ₁₁ N ₃ S	Found	51.86	8.17	22.68	17.35
		Calcd.	45.85	7.00	26.75	20.38
10	C ₇ H ₁₃ N ₃ S	Found	45.75	7.08	26.78	20.39
		Calcd.	49.12	7.60	24.56	18.71
11	C ₈ H ₁₅ N ₃ S	Found	49.10	7.63	24.63	18.70
		Calcd.	51.89	8.10	22.70	17.29
12	C ₉ H ₉ N ₃ O	Found	51.76	8.26	22.80	17.20
		Calcd.	61.71	5.14	24.00	
13	C ₁₀ H ₁₁ N ₃ O	Found	61.60	5.35	24.00	
		Calcd.	63.49	5.82	22.22	
14	C ₁₁ H ₁₃ N ₃ O	Found	63.44	5.88	22.38	
		Calcd.	65.02	6.40	20.68	
15	C ₁₂ H ₁₅ N ₃ O	Found	64.89	6.44	20.81	
		Calcd.	66.35	6.91	19.35	
		Found	65.64	6.91	19.48	

REFERENCES AND NOTES

General Synthesis of 3-Hydroxy- and 3-Mercapto-1,2,4-triazoles.

The following preparation of 3-mercapto-5-methyl-1,2,4-triazole (Table III, Experiment No. 1) will serve as an example of the procedure used to prepare compounds listed in Table III. In this case thiosemicarbazide (0.91 g., 0.01 mole) was dissolved in anhydrous methanol and 1.51 g. (0.01 mole) of methyl selenonester in 10 ml. of anhydrous methanol was added. The mixture was heated under reflux for 48 hours, then the suspension which resulted was filtered. The filtrate was evaporated leaving 0.8 g. (70%) of product, m.p. 216°.

- (1) M. Pesson, S. Dupin and M. Antoine, *Compt. Rend.*, **253**, 992 (1961).
- (2) M. Pesson and S. Dupin, *ibid.*, **252**, 3830 (1961).
- (3) S. A. Greenfield, M. C. Seidel and W. C. von Meyer, German Offen. 1,943,915 (Cl.C.07d), 12 Mar 1970.
- (4) M. Pesson, G. Polmans and S. Dupin, *Compt. Rend.*, **248**, 1677 (1959).
- (5) R. Ohi, H. Iwano, T. Shishido and I. Shimamura, German Offen. 1,935,310 (Cl.G. 03c), 19 Feb 1970.
- (6) V. I. Cohen, *J. Org. Chem.*, **42**, 2645 (1977).