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Reactions of Hydrazinium Thiocyanate with Aldehydes and Ketones

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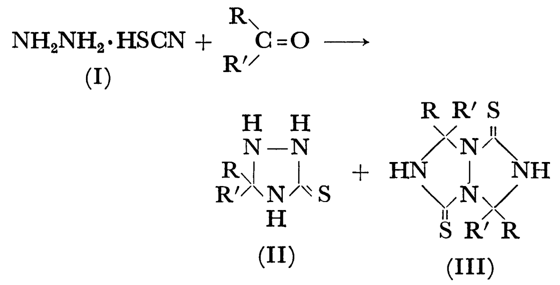
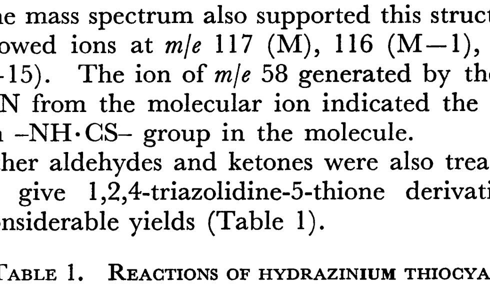
In a previous paper,[1] we reported on the reactions of hydrazinium thiocyanate (I) with alcohols to give 1,2,4-triazolidine-5-thione derivatives (II). These reaction mechanisms were not clear but the structure of II suggested that II can also be prepared from the reactions of I with aldehydes and ketones. Sunner[2] and Futaki and Tosa[3] studied these reactions and obtained triazolo-triazole derivatives III, but they did not isolate II. We have reinvestigated these reactions and have found that fairly large quantity of II is obtained together with III. Formation of II is easily overlooked because II is not stable to heat, light and moisture, and readily hydrolyzes or decomposes by ring opening. In this paper, we report on preparation of II and its structure.



When an aqueous solution of (I) and acetaldehyde was allowed to stand at room temperature, white needles (IIa), mp 122°C (decomp.), were obtained together with 1,5-dimethyl-*s*-triazolidino [1,2-*a*]-*s*-triazolidine-3,7-dithione (triazolo-triazole compound (IIIa)[4]). The elemental analysis (Table 2) and MS spectral data of (IIa) gave a molecular formula $C_3H_7N_3S$. The IR spectrum showed absorption bands for NH, CH_3, and C=S groups; and the NMR spectrum indicated the presence of ethylidene group at τ 8.61 (3H, d, J=6.0 Hz) and 5.00 (1H, q, J=6.0 Hz). Thermolysis of IIa gave acetaldehyde thiosemicarbazone (IVa) and oxidation gave 3-methyl-5-mercapto-1,2,4-triazole (Va).

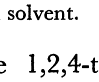
The following structure was deduced for IIa.



The mass spectrum also supported this structure *viz.*, it showed ions at *m/e* 117 (M), 116 (M−1), and 102 (M−15). The ion of *m/e* 58 generated by the loss of HSCN from the molecular ion indicated the presence of an –NH·CS– group in the molecule.

Other aldehydes and ketones were also treated with I to give 1,2,4-triazolidine-5-thione derivatives (II) in considerable yields (Table 1).

Table 1. Reactions of hydrazinium thiocyanate (I) with aldehydes and ketones[a)]

Aldehyde	Yield (%) of II	Ketone	Yield (%) of II
CH_3CHO	34.36	CH_3COCH_3	6.85
C_2H_5CHO	40.76	$C_2H_5COCH_3$	26.62
n-C_3H_7CHO	32.21	*n*-$C_3H_7COCH_3$	49.28
		$C_2H_5COC_2H_5$	56.18
			72.18

a) Water (ketone) or 50% aqueous methanol (aldehyde) was used as reaction solvent.

We considered that the 1,2,4-triazolidine-5-thione derivatives (II) was produced by the cycloaddition of thiocyanic acid to the hydrazones formed from aldehydes and ketones with hydrazine.

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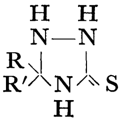
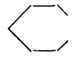
1) I. Arai, Y. Satoh, I. Muramatu, and A. Hagitani, This Bulletin, **42**, 2739 (1969).

2) S. Sunner, *Svensk Kem. Tidskr.*, **64**, 121 (1952).

3) K. Futaki and N. Tosa, *Chem. Pharm. Bull.*, (Tokyo), **6**, 58 (1958).

4) J. R. Bailey and A. T. McPherson, *J. Amer. Chem. Soc.*, **39**, 1322 (1917).

Table 2. 1,2,4-Triazolidine-5-thione  (II)

II	R	R′	Mp (°C) (decomp.)	Formula	Analysis (%)							
					Calcd				Found			
					C	H	N	S	C	H	N	S
IIa	CH_3	H	122	$C_3H_7N_3S$	30.75	6.03	35.86	27.36	30.75	6.42	35.29	—
IIb	C_2H_5	H	110	$C_4H_9N_3S$	36.62	6.91	32.03	24.44	36.72	6.85	31.57	—
IIc	n-C_3H_7	H	118	$C_5H_{11}N_3S$	41.36	7.64	28.93	22.08	41.50	7.46	28.36	—
IId	CH_3	CH_3	105	$C_4H_9N_3S$	36.62	6.91	32.03	24.44	36.63	6.84	32.08	—
IIe	C_2H_5	CH_3	116	$C_5H_{11}N_3S$	41.36	7.64	28.93	22.08	41.00	7.60	29.40	21.60
IIf	n-C_3H_7	CH_3	119	$C_6H_{13}N_3S$	45.26	8.23	26.39	20.13	45.64	7.53	26.55	20.09
IIg	C_2H_5	C_2H_5	124	$C_6H_{13}N_3S$	45.26	8.23	26.39	20.13	44.92	7.80	26.54	20.32
IIh			144	$C_7H_{15}N_3S$	49.09	7.65	24.54	18.72	49.45	7.38	24.18	18.86

Experimental

All melting points are uncorrected. The IR spectra were recorded from KBr pellets using a Shimadzu model IR-27B infrared spectrometer, and the NMR spectra were measured in a solution of deuteriomethanol with a Varian A-60 spectrometer. The mass spectra were obtained on a CEC 21-110B spectrometer at 70 eV.

Reaction of Hydrazinium Thiocyanate (I) with Acetaldehyde. Freshly prepared acetaldehyde (4.41 g, 0.1 mol) was added dropwise to a cooled solution of hydrazine monohydrochloride (6.85 g, 0.1 mol) and sodium thiocyanate (8.10 g, 0.1 mol) in 50% aqueous methanol (100 ml) with stirring. The solution was then stirred at room temperature for 24 hr under shield from light. The white precipitate (2.03 g) was filtered and recrystallized from methanol to give 1,5-dimethyl-*s*-triazolidino [1,2-*a*]-*s*-triazolidine-3,7-dithione (IIIa), mp 169°C (decomp.), (lit,[2] 168°C (decomp.)). The filtrate was evaporated to dryness under reduced pressure and the residue was extracted with methylene chloride. This extract was evaporated and the residue (3.87 g) gave 3-methyl-1,2,4-triazolidine-5-thione (IIa), mp 122°C (decomp.), from chloroform.

IR of (IIa): 3175, 2975, 2850, 1510, 1465, 1405, 1375, 1210, 1070, 945, 885 cm^{-1}.

MS of (IIa): m/e 117 ($C_3H_7N_3S^+$), 116 ($C_3H_6N_3S^+$), 115 ($C_3H_5N_3S^+$), 102 ($C_2H_4N_3S^+$), 101 ($C_2H_3N_3S^+$), 58 ($C_2H_6N_2^+$).

Thermolysis of 3-Methyl-1,2,4-triazolidine-5-thione (IIa). A solution of 0.5 g of (IIa) in 2-butanol (25 ml) was refluxed for 3 hr and then evaporated. The residue (0.5 g) was recrystallized from ethanol to give acetaldehyde thiosemicarbazone (IVa), mp 140°C, (lit,[5] mp 140°C).

Oxidation of 3-Methyl-1,2,4-triazolidine-5-thione (IIa). Oxygen was passed into a solution of one gram of (IIa) in 1 N sodium hydroxide (50 ml) for 5 hr with stirring at room temperature. The solution was then acidified with 1 N hydrochloric acid and concentrated under reduced presure. The white precipitate (0.64 g) was filtered and recrystallized from water to give 3-methyl-5-mercapto-1,2,4-triazole (Va), mp 270°C, identified by comparison (mixed mp and IR spectra) with an authentic sample.[6]

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5) L. K. Evans and A. E. Gillam, *J. Chem. Soc.*, **1943**, 565.

6) R. G. Jones and Anisworth, *J. Amer. Chem. Soc.*, **77**, 1538 (1955).