

1-Oxo-1,2,3,5-thiatriazolidin-4-one

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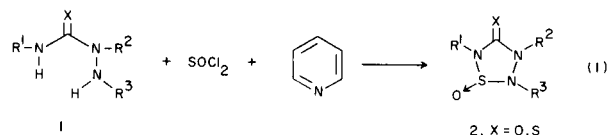
Reaction of thionyl chloride and semicarbazides or thiosemicarbazides produces the novel 1-oxo-1,2,3,5-thiatriazolidin-4-one or 4-thione ring system.

J. Heterocyclic Chem., **16**, 895 (1979).

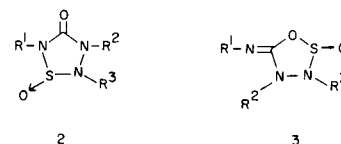
Recently, both Deyrup (1,2) and Chupp (3) have reported that thionyl chloride can be used to generate novel heterocycles when reacted with 2-amino amides or 2-hydroxy aryl amides. We would like to report the synthesis of another novel heterocycle, the 1-oxo-1,2,3,5-thiatriazolidin-4-one or 4-thione system, which results from reaction of thionyl chloride with substituted semicarbazides or thiosemicarbazides.

Results and Discussion.

A series of 1,2,4-trisubstituted semicarbazides and thiosemicarbazides were reacted with one equivalent of thionyl chloride in the presence of two equivalents of pyridine to yield the 1-oxo-1,2,3,5-thiatriazolidin-4-ones and thiones. These are shown in Table I.



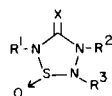
By analogy to Deyrup's original work (1), the products of the cyclization could either be the thiatriazolidinone **2** (X = O) or the corresponding 5-imino oxathiadiazolidine **3**.



However, the imino structure could be ruled out on the basis of spectral data. In the infrared, no imino band is

Table I

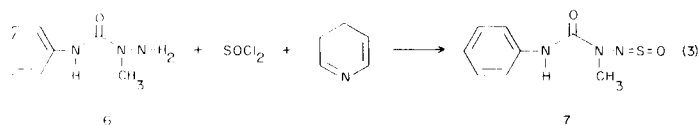
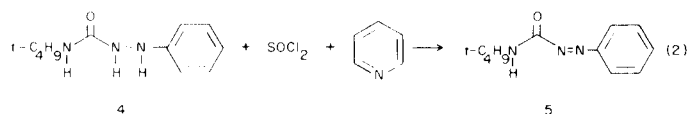
1-Oxo-1,2,3,5-Thiatriazolidin-4-ones and 4-Thiones



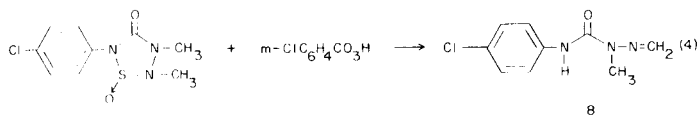
Compound No.	R ¹	R ²	R ³	X	Nmr (ppm)	Ir (cm ⁻¹)		Elemental Analysis			% Yield (a)
						CO	Melting Point °C	Calculated/Found	C	H	
9	<i>i</i> -C ₆ H ₅	CH ₃	CH ₃	O	1.57 (S, 9H), 2.64 (S, 3H), 3.13 (S, 3H)	1700	46.5-48	40.97 40.83	7.32 7.24	20.49 20.37	65
10	C ₆ H ₅	CH ₃	CH ₃	O	3.00 (S, 3H), 3.26 (S, 3H), 7.40 (S, 5H)	1725	77-79	48.00 48.30	4.49 4.85	18.66 18.46	82
11	3,4-Cl ₂ C ₆ H ₃	CH ₃	CH ₃	O	3.04 (S, 3H), 3.26 (S, 3H), 7.23-7.77 (m, 3H)	1720	108-110	36.73 37.22	3.06 3.19	14.28 14.52	52
12	4-ClC ₆ H ₄	CH ₃	CH ₃	O	3.00 (S, 3H), 3.26 (S, 3H), 7.47 (S, 4H)	1710	83-84	41.16 41.32	3.85 3.80	16.18 16.25	83
13	2,4,5-Cl ₃ C ₆ H ₂	CH ₃	CH ₃	O	3.10 (S, 3H), 3.29 (S, 3H), 7.56 (S, 1H), 7.63 (S, 1H)	1722	150.5-152	32.87 32.96	2.43 2.52	12.78 12.67	44
14	3,4-Cl ₂ C ₆ H ₃	CH ₃	<i>i</i> -C ₃ H ₇	O	2.21 and 1.33 (overlapping doublet, J = 6 Hz, 3H), 3.26 (S, 3H), 3.66 (Sept., J = 6 Hz, 1H), 7.13-7.66 (m, 3H)	1700	74-75.5	40.99 41.37	4.03 4.00	13.04 13.16	25
15	C ₆ H ₅	CH ₃	CH ₃	S	2.93 (S, 3H), 3.33 (S, 3H), 7.56 (S, 5H)	—	119-120	44.81 44.76	4.56 4.56	17.42 17.43	49
16	4-FC ₆ H ₄	CH ₃	CH ₃	S	3.10 (S, 3H), 3.60 (S, 3H), 7.23 (A ₂ B ₂ , J = 5 Hz, 4H)	—	86-88	41.70 41.65	3.86 3.82	16.21 16.30	85

(a) After recrystallization

observed, but only a strong carbonyl bond at 1710-1720 cm^{-1} , which is consistent with a five membered cyclic urea (4). Furthermore, when R_1 is an aryl group such as phenyl or 4-chlorophenyl, the aryl protons appear as a singlet, which is also consistent with structure 2, rather than an imino aryl grouping. While this reaction appears to be a general one, cyclization can be achieved only if certain substituent requirements are fulfilled. In the semicarbazide and semithiocarbazide cases, both the 1- and 2-nitrogen atoms must have an alkyl or aryl substituent. If this is not observed, then acyclic products are formed, as illustrated by the following examples (Equations 2 and 3) (5).



It is also of interest to point out that of the three possible reagents which would lead to the 1,2,3,5-thiazotriazolidine system, only thionyl chloride will form a cyclic product. Reaction of semicarbazides with either sulfur dichloride or sulfuryl chloride, in presence of a base, fail to form five membered rings. Also, attempts to oxidize the 1-oxo-1,2,3,5-thiazotriazolidin-4-one to the 1,1-dioxo compound failed, and only the imine 8 (6) was recovered (Equation 4).



EXPERIMENTAL

General

Nmr were taken on a Varian T-60 Nmr Spectrophotometer in deuteriochloroform with TMS as an internal standard. Infrared spectra were taken on a Beckmann Acculab 2 Spectrophotometer. Melting points are uncorrected. All new compounds gave satisfactory elemental analysis. Semicarbazides and semithiocarbazides were prepared from the corresponding isocyanates or isothiocyanates and hydrazines.

Preparation of the 1-oxo-1,2,3,5-thiazotriazolidin-4-ones or 4-thiones is illustrated by the following example.

Preparation of 1-Oxo-2,3-dimethyl-5-(4-chlorophenyl)-1,2,3,5-thiazotriazolidin-4-one (14).

A solution of 8.13 g. (0.068 mole) of thionyl chloride in 50 ml. of dichloromethane was slowly added to cooled (5°) solution of 14.6 g. (0.068 mole) of 2,3-dimethyl-4-(4-chlorophenyl)semicarbazide and 10.8 g. (0.136 mole) of pyridine in 250 ml. of dichloromethane. The resulting mixture was allowed to warm to ambient temperature and stirred overnight. It was washed with 2 x 100 ml. water, dried over magnesium sulfate and the solvent evaporated under reduced pressure. The liquid slowly crystallized. Recrystallization (1:1 hexane/benzene) gave 14.7 g. of product, m.p. $83-84^\circ$.

REFERENCES AND NOTES

- (1) J. A. Deyrup, J. C. Gill, T. LeBlanc and H. L. Gingrich, *J. Org. Chem.*, **38**, 1645 (1973).
- (2) J. A. Deyrup and H. L. Gingrich *ibid.*, **42**, 1015 (1977).
- (3) J. P. Chupp, *J. Heterocyclic Chem.*, **11**, 1 (1974); U. S. Patent 3,900,484.
- (4) J. P. Chupp and D. J. Dahm, *ibid.*, **12**, 393 (1975).
- (5) These reactions were run under the same conditions as given in the experimental section. The structures of compounds 5 and 6 were consistent with spectral and elemental analyses.
- (6) Compound 8 was shown to be identical to an authentic sample provided by Dr. D. C. K. Chan of the laboratory.