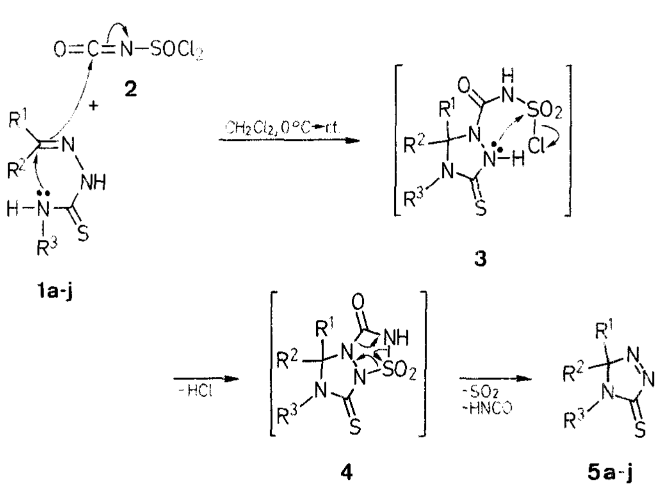
Reaction of 4-Arylthiosemicarbazones with Chlorosulfonyl Isocyanate. A Novel Synthesis of Δ^1-[1,2,4]-Triazoline-5-thiones

Manisha Tripathi, Durga Nath Dhar*

Department of Chemistry, Indian Institute of Technology, Kanpur 208016, India

A novel synthesis of Δ^1-[1,2,4]triazoline-5-thiones by the reaction of 4-arylthiosemicarbazones with chlorosulfonyl isocyanate is described.

Chlorosulfonyl isocyanate, ClO_2S-NCO, (CSI) has received considerable attention[1], owing to its reactivity as a 'uniparticulate' electrophile[2] and as a heterocumulene in cycloaddition reactions with olefins, acetylenes and bicyclic strained hydrocarbons[3]. Our continued interest in the addition reactions of CSI[4] has led us to explore its reactivity towards various 4-arylthiosemicarbazones. We have found that these reactions constitute a facile method for the synthesis of the novel heterocyclic system, Δ^1-[1,2,4]triazoline-5-thiones. There is only one method reported[5] for the synthesis of these heterocyclic systems, and it involves the oxidative cyclization of 4-substituted thiosemicarbazones with basic alumina as a catalyst. Our method is superior, however, due to the milder reaction conditions employed. These reactions take place in a relatively shorter time and afford the products in a high degree of purity and in a very good yield. The reactions are carried out by adding one equivalent of CSI to a stirred solution of 4-arylthiosemicarbazone (**1**) at 0°, followed by work-up to give the pure products (**5**). A possible pathway for the formation of **5** is depicted in the scheme. The intermediate compound, **4**, could not be isolated, but its formation was confirmed by infrared spectroscopic analysis, [bands at 1740 (ν_{CO}), 1380, 1180 cm^{-1} (ν_{SO_2})]. Subsequently, **4** undergoes an elimination reaction (loss of SO_2) leading to the formation of **5**. The evolution of SO_2 has been confirmed by its reaction on acidified dichromate paper (orange → green). The structures of the products were confirmed by comparison with authentic samples (m.p., IR, ^{1}H-NMR and mass spectra), prepared according to Ref. 5.



1, 5	R^1	R^2	R^3
a	CH_3	CH_3	C_6H_5
b	CH_3	C_2H_5	C_6H_5
c		$-(CH_2)_5-$	C_6H_5
d		$-(CH_2)_4-$	C_6H_5
e	C_2H_5	C_2H_5	C_6H_5
f	CH_3	CH_3	p-$Cl-C_6H_4$
g	CH_3	C_2H_5	p-$Cl-C_6H_4$
h		$-(CH_2)_5-$	p-$Cl-C_6H_4$
i		$-(CH_2)_4-$	p-$Cl-C_6H_4$
j	C_2H_5	C_2H_5	p-$Cl-C_6H_4$

5a–j; General Procedure:

To a stirred solution of **1** (0.002 mol), in dry dichloromethane (5 ml), is added chlorosulfonyl isocyanate (0.002 mol) at 0–5 °C. Stirring is continued for 15 min, and the reaction mixture is allowed to attain the room temperature (ca. 24°), followed by stirring for additional 3 h. The solvent is removed under vacuum, and the residue obtained is column chromatographed (silica gel, with benzene as eluent). Evaporation of the solvent afforded the pure compounds **5**.

Table. Δ^1-[1,2,4]-Triazoline-5-thiones **5**

Product **5**	Yield [%]	m.p. [°C]	Molecular Formula[a] or Lit. m.p. [°C]	IR (KBr)[b] ν[cm^{-1}] $\nu_{C=S}$	^{1}H-NMR ($CDCl_3$/TMS)[c] δ[ppm]	MS (70 eV)[d] m/e (M^+)
a	95	175	172–174[5]	1300	1.6 (s); 7.0–8.0 (m)	205
b	92	125	$C_{11}H_{13}N_3S$ (219.3)	1290	1.6 (s); 1.8 (t); 2.4 (q); 6.8–7.5 (m)	219
c	89	200	$C_{13}H_{15}N_3S$ (245.3)	1300	1.7 (m); 6.8–7.5 (m)	245
d	87	178	$C_{12}H_{13}N_3S$ (231.3)	1280	1.6 (m); 7.0–7.6 (m)	231
e	85	150	$C_{12}H_{15}N_3S$ (233.3)	1295	1.8 (t); 2.3 (q); 7.0–7.6 (m)	233
f	93	137	136[5]	1280	1.8 (s); 7.2–7.8 (m)	239
g	91	86	$C_{11}H_{12}ClN_3S$ (253.8)	1300	1.6 (s); 1.8 (t); 2.3 (q); 7.2–8.0 (m)	253
h	92	208	$C_{13}H_{14}ClN_3S$ (279.8)	1290	1.6 (m); 7.4–8.0 (m)	279
i	90	170	$C_{12}H_{12}ClN_3S$ (265.8)	1295	1.7 (m); 7.2–7.8 (m)	265
j	87	125	$C_{12}H_{14}ClN_3S$ (267.8)	1300	1.8 (t); 2.2 (q); 6.9–7.5 (m)	267

[a] Satisfactory microanalyses obtained: C ±0.18, H ±0.33, N ±0.23; except **5i**: N −0.41.
[b] Recorded on a Perkin Elmer Model 580 Infrared spectrophotometer.
[c] Recorded on a Varian EM-390 (90 MHz) NMR spectrometer.
[d] Recorded on a Jeol JMS-300 D Mass spectrometer.

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