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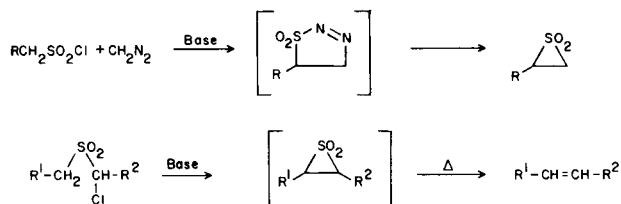
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Received February 29, 1980

Thermal extrusion of sulfur dioxide from 1-methyl-3-(5-chlorosulfonyl-1,3,4-thiadiazol-2-yl)urea (**1**) provides 1-methyl-3-(5-chloro-1,3,4-thiadiazol-2-yl)urea in quantitative yield.

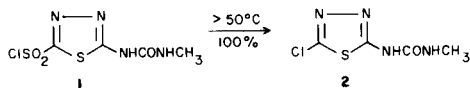
*J. Heterocyclic Chem.*, **17**, 1311 (1980).

Extrusion of sulfur dioxide with concomitant carbon-carbon bond formation is a basic theme of heterocyclic chemistry (2,3), and constitutes a technique of fundamental importance in synthetic organic methodology (equations 1 and 2) (4,5). However, extension of this method to the formation of carbon-heteroatom bonds has proceeded

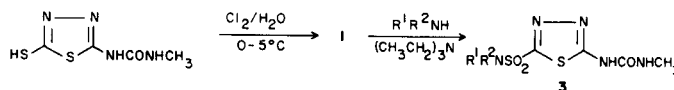


tentatively. Relatively unreactive substrates, which require Group VIII metal catalysis for acceptable conversions to desired products, exemplify limitations of heteroatomic bond formation by this technique (6).

We wish to report that 1-methyl-3-(5-chlorosulfonyl-1,3,4-thiadiazol-2-yl)urea **1** is rapidly converted to 1-methyl-3-(5-chloro-1,3,4-thiadiazol-2-yl)urea **2** in essentially quantitative yield under mild conditions (equation 3, see Table, example 1).



As part of a program to improve the efficiency of preparation of the proven herbicides 1-alkyl-3-(5-sulfa-moyl-1,3,4-thiadiazol-2-yl)ureas **3** (equation 4), we investigated the synthesis of **1** and its subsequent conversion



to the sulfonamides **3** under a range of conditions. At or below 20°, treatment of 1-methyl-3-(5-chlorosulfonyl-1,3,4-thiadiazol-2-yl)urea with a primary or secondary amine in the presence of triethylamine routinely provides the expected sulfonamide (see Table, examples 2-4). However, at temperatures in excess of 50°, sulfonamide formation is preempted by rapid extrusion of sulfur dioxide and generation of 1-methyl-3-(5-chloro-1,3,4-thiadiazol-2-yl)urea (Table, example 5). Interestingly, the pendant urea functionality of the heterocycle, in addition to any included amines, are recovered unchanged from thermolysis.

Extrusion of sulfur dioxide and ring chlorination may proceed *via* radical or ionic intermediates. However, the failure to isolate substituted urea or amine products, in conjunction with the facile, regiospecific nature of the conversion, suggest operation of a concerted mechanism for elimination of sulfur dioxide and formation of the carbon-chloride bond.

Table

Thermal Dependence of Reactions of 1-Methyl-3-(5-chlorosulfonyl-1,3,4-thiadiazol-2-yl)urea (a)

Example	Amine	Reaction Temperature (°C)	Solvent	Product (%) (b)	M.p. (°C)	Lit. M.p. (°C)
1	—	77	ethyl acetate	<b>2</b> (99)	216-217	217-218 (c)
2	Allylamine	0-2	tetrahydrofuran	<b>3</b> , R <sup>1</sup> = H R <sup>2</sup> = alkyl (89)	235	(d)
3	Ammonia	5-10	aqueous ammonia	<b>3</b> , R <sup>1</sup> = R <sup>2</sup> = H (98)	243-245	(e)
4	Morpholine	0-2	tetrahydrofuran	<b>3</b> , R <sup>1</sup> R <sup>2</sup> = morpholino (93)	293-295	(f)
5	Allylamine	50-60	ethyl acetate	<b>2</b> (87)	216-218	217-218 (c)

(a) See Experimental for additional detail. (b) Isolated yield of pure material. (c) Swiss Patent 524,632; *Chem. Abstr.*, **77**, 126642 (1972). (d) Compound **3**; *Anal. Calcd.* for C<sub>7</sub>H<sub>11</sub>N<sub>3</sub>O<sub>3</sub>S<sub>2</sub>: C, 30.32; H, 4.00; N, 25.25. Found: C, 30.18; H, 3.95; N, 25.36. (e) Compound **3**; *Anal. Calcd.* for C<sub>4</sub>H<sub>7</sub>N<sub>3</sub>O<sub>3</sub>S<sub>2</sub>: C, 20.25; H, 2.97; N, 29.52. Found: C, 20.14; H, 3.02; N, 29.74. (f) Compound **3**; *Anal. Calcd.* for C<sub>8</sub>H<sub>13</sub>N<sub>3</sub>O<sub>4</sub>S<sub>2</sub>: C, 31.26; H, 4.26; N, 22.79. Found: C, 31.44; H, 4.15; N, 22.68.

## EXPERIMENTAL

Melting points were determined on a Thomas Hoover capillary melting point apparatus, and are uncorrected. Microanalyses were performed by the Analytical Services Department of Air Products and Chemicals. Where appropriate, identity of compounds was confirmed by comparison of infrared spectra, determined by the usual Nujol mull and liquid film techniques on a Perkin-Elmer Model 257 Grating Infrared Spectrophotometer, and nmr spectra, determined as solutions in deuteriochloroform or DMSO- $d_6$  on a Varian A60 MHz spectrometer, with TMS as internal standard.

Thermolysis of **1**.

A solution of **1** (6.0 g., 0.023 mole) in 100 ml. of ethyl acetate was heated under reflux with stirring for 1.0 hour. The reaction mixture was cooled to room temperature; evaporation of the solvent gave 4.4 g. (98%) of a colorless solid **2**, m.p. 216-217°, identical to authentic material, m.p. 217-218° (6). The infrared spectrum of the product did not contain the 1150-1160  $\text{cm}^{-1}$  and 1320-1330  $\text{cm}^{-1}$  ( $\text{SO}_2\text{N}$ ) bands.

General Procedure for the Preparation of Sulfonamides **3**.

A solution of **1** (10.0 g., 0.04 mole), triethylamine (4.48, 0.04 mole), and the desired amine in 100 ml. of the appropriate solvent (see Table) is cooled to 0-10° with stirring for 2.5 hours. The reaction mixture is then allowed to warm to room temperature and filtered. Evaporation of the solvent and crystallization of the residue from ethanol provide pure **3** (see Table).

Isolation of **2** from the Attempted Preparation of 1-Methyl-3-(5-Alkylsulfamoyl-1,3,4-thiadiazol-2-yl)urea.

A solution of **1** (10.0 g., 0.04 mole) triethylamine (4.4 g., 0.04 mole), and allylamine (2.4 g., 0.04 mole) in 100 ml. of ethyl acetate is heated at 50-60° with stirring for 1 hour. The reaction mixture is cooled to ambient temperature; no precipitate of triethylamine hydrochloride is evident. Evaporation yields ethyl acetate and essentially quantitative recovery of unchanged triethylamine and alkylamine. The residue, a colorless solid **2**, has m.p. 216-218°, identical to authentic material, m.p. 217-218° (7). The infrared spectrum of the product did not contain the 1150-1160  $\text{cm}^{-1}$  and 1320-1330  $\text{cm}^{-1}$  ( $\text{SO}_2\text{N}$ ) bands.

## REFERENCES AND NOTES

- (1) A portion of this work has appeared in patent form: T. Cebalo, U. S. Patent 3,726,892 (1973); *Chem. Abstr.*, **75**, 49094 (1971).
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- (4) L. A. Paquette, *Acc. Chem. Res.*, **1**, 209 (1968).
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