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Cycloaddition of *N*-(2,2,2-Trichloroethylidene)-Substituted Carboxamides and Carbamates to 1,2,4-Thiadiazol-5(2*H*)-imines

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ABSTRACT: *1,2,4-Thiadiazol-5(2H)-imines* **4** *react with N-(2,2,2-trichloroethylidene)-substituted amides* **5** *to form [3 + 2]-cycloaddition products* **6** *featured by an extra coordination of the ring sulfur atom to the terminal nitrogen atom of the side 1,3-diazapropenylidene group, as established by X-ray diffraction investigation. This coordination evidently plays an important role in the alkylation of compounds* **6** *into* **8** *at the oxygen atom under mild conditions. The S—N bond "switch-over" restoring the original 1,2,4-thiadiazole ring occurs therewith.* © 2003 Wiley Periodicals, Inc. Heteroatom Chem 14:474–480, 2003; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.10182

INTRODUCTION

Substituted 1,2,4-thiadiazol-5(2*H*)-imines **4** became accessible in the 1970s when Barnikow [1] and, at a later date, Goerdeler [2] had proposed a simple method for preparation of these compounds from imidoyl chlorides **1**, through their derivatives **2** and **3** (Scheme 1). Nucleophilic agents **4** have already found application in fine organic synthesis. The most interesting of their properties is the ability to take part in [3 + 2]-cycloaddition reactions as 1,3-dipoles [2–6]. In particular, much has been studied about their interaction with isocyanates, isothiocyanates, and carbodiimides [2]. Here we report the cycloaddition, to agents **4**, of *N*-(2,2,2-trichloroethylidene)-substituted carboxamides and carbamates **5**, in which the electrophilicity of the C=N bonds is especially pronounced [7].

RESULTS AND DISCUSSION

By using the standard method, we synthesized a series of substituted 1,2,4-thiadiazol-5(2*H*)-imine hydrobromides **3** and the corresponding free bases **4**, which react under mild conditions with *N*-acyl- or *N*-alkoxycarbonylimines **5**, as shown in Scheme 1. It is more convenient to prepare the cycloaddition products **6** by treatment of a mixture of the appropriate salt **3** and *N*-substituted amide **7** with triethylamine. The structure of compound **6** incorporating the 1,2,4-thiadiazolidine ring was confirmed by IR and NMR (^{1}H, ^{13}C) spectra (Table 1) and by X-ray crystallographic data for **6h** (Fig. 1, Table 2).

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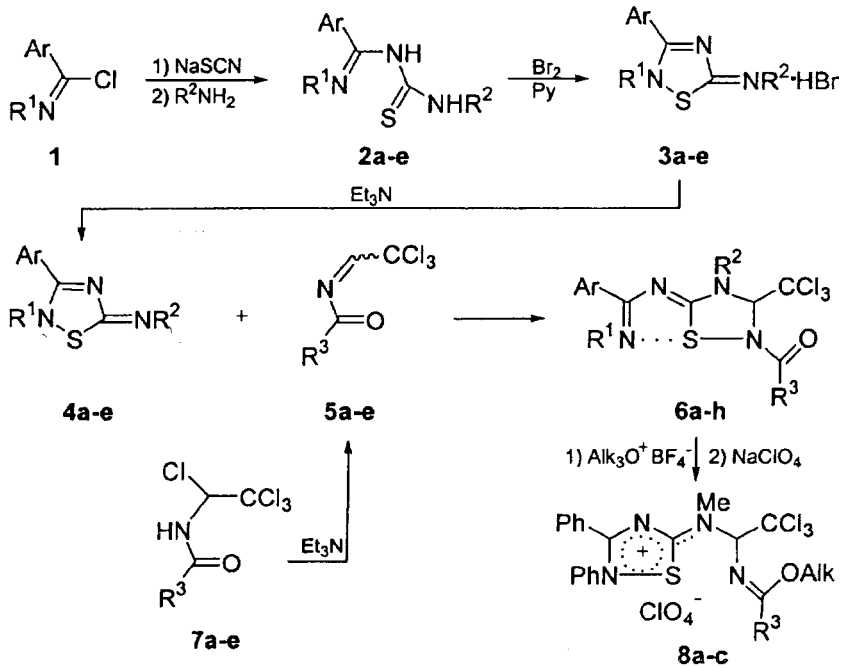


2-4	R^1	Ar	R^2
a	Ph	Ph	Me
b	Ph	Ph	*c*-C_6H_{11}
c	$PhCH_2$	Ph	Ph
d	Ph	4-$MeOC_6H_4$	Ph
e	4-MeC_6H_4	Ph	4-$MeOC_6H_4$

5, 7	R^3
a	H
b	Me
c	Ph
d	MeO
e	EtO

6	R^1	Ar	R^2	R^3
a	Ph	Ph	Me	H
b	Ph	Ph	Me	Me
c	Ph	Ph	Me	MeO
d	Ph	Ph	Me	EtO
e	Ph	Ph	*c*-C_6H_{11}	Ph
f	$PhCH_2$	Ph	Ph	MeO
g	Ph	4-$MeOC_6H_4$	Ph	Ph
h	4-MeC_6H_4	Ph	4-$MeOC_6H_4$	MeO

8	R^3	Alk
a	Me	Me
b	MeO	Me
c	EtO	Et

SCHEME 1

The sulfur atom in compound **6h**, as established, is additionally coordinated by the terminal nitrogen atom of the side 1,3-diazapropenylidene group. The distances S···N(1) (1.960 Å) and S···N(4) (1.916 Å), though noticeably elongated as compared to S—N bonds in bivalent sulfur compounds (1.707 Å) [8], are nevertheless significantly shorter than the sum of the van der Waals radii (3.35 Å) [9]. The bond system SN(1)C(8)N(2)C(15)N(3)N(4) is planar, and the maximum deviation of the atoms from the least-squares plane does not exceed 0.061 Å. The triad N(3)C(23)N(4) forms with this plane a dihedral angle of 15.1°. The bonds N(1)—C(8) (1.303 Å) and N(2)—C(15) (1.312 Å) are longer than the standard C=N double bond (1.27 Å). At the same time the distances N(2)—C(8) (1.365 Å) and N(3)—C(15) (1.351 Å) are substantially shortened in comparison with the value of 1.45 Å characteristic of a single bond N(sp^2)—C(sp^2) [10]. It should be noted also the shortening of the bond N(4)—C(25) (1.358 Å) evidently caused by the n–π interaction of the N(4) atom with the C=O group. Thus the structure of **6h** can be represented as a superimposition of three forms, monocyclic neutral A, monocyclic bipolar B, and bicyclic C (Scheme 2). A significant contribution of the bipolar forms of type B to the ground state of compounds **6e,g** is evident from their IR spectra (Table 1). The $\nu_{C=O}$ of these compounds is shifted 30–50 cm^{-1} to lower frequencies relative to the $\nu_{C=O}$ of disubstituted carboxamides.

TABLE 1 Yields and Characteristics of Compounds **6, 8**, and **11**

Compd	Yield (%)	mp (°C)	Formula	Found (Calcd) (%)			IR (cm^{-1})[a]	^1H NMR (δ)[b]
				Cl	N	S		
6a	56	158 dec. (MeCN)	$C_{18}H_{15}Cl_3N_4OS$	24.15 (24.07)	12.59 (12.68)	7.22 (7.26)	1650 ($\nu_{C=O}$)	A mixture of stereoisomers. 3.70, 3.73 (s, CH_3N); 5.30, 6.09 (s, 1:5, CCl_3CH); 7.03–7.59 (m, $2C_6H_5$); 8.32, 8.58 (s, 5:1, HCO)
6b[c]	73	164 dec. (MeCN)	$C_{19}H_{17}Cl_3N_4OS$	23.54 (23.33)	12.36 (12.29)	7.10 (7.03)	1640 ($\nu_{C=O}$)	2.18 (s, CH_3C), 3.69 (s, CH_3N), 6.26 (s, CCl_3CH), 7.02–7.59 (m, $2C_6H_5$)
6c	64	144 (EtOH)	$C_{19}H_{17}Cl_3N_4O_2S$	22.40 (22.54)	12.02 (11.88)	6.71 (6.80)	1670 ($\nu_{C=O}$)	3.69 (s, CH_3N), 3.74 (s, CH_3O), 5.91 (s, CCl_3CH), 7.03–7.56 (m, $2C_6H_5$)
6d	76	146–147 (AcOEt)	$C_{20}H_{19}Cl_3N_4O_2S$	21.74 (21.89)	11.63 (11.53)	6.63 (6.60)	1680 ($\nu_{C=O}$)	1.27 (t, CH_3CH_2), 3.69 (s, CH_3N), 4.19 (q, CH_3CH_2), 5.90 (s, CCl_3CH), 7.03–7.57 (m, $2C_6H_5$)
6e	81	174 dec. (AcOEt)	$C_{29}H_{27}Cl_3N_4OS$	18.27 (18.15)	9.69 (9.56)	5.53 (5.47)	1620 ($\nu_{C=O}$)	1.19–3.04 (m, 5 CH_2), 3.97 (m, CH_2CHCH_2), 6.55 (s, CCl_3CH), 6.70–7.86 (m, 3 C_6H_5)
6f	76	148 dec. (AcOEt)	$C_{25}H_{21}Cl_3N_4O_2S$	19.23 (19.41)	10.37 (10.23)	5.82 (5.85)	1670 ($\nu_{C=O}$)	3.79 (s, CH_3), 5.02 (s, CH_2), 6.49 (s, CCl_3CH), 7.23–7.60 (m, 3 C_6H_5)
6g	77	168 dec. (MeCN)	$C_{30}H_{23}Cl_3N_4O_2S$	17.17 (17.44)	9.14 (9.19)	5.30 (5.26)	1600 ($\nu_{C=O}$)	3.75 (s, CH_3O), 6.69–6.79 (m, 4 Har.), 7.16 (s, CCl_3CH), 7.26–7.93 (m, 15 Har.)
6h	70	179 dec. (C_6H_6)	$C_{26}H_{23}Cl_3N_4O_3S$	18.25 (18.40)	9.60 (9.69)	5.51 (5.55)	1670 ($\nu_{C=O}$)	2.38 (s, $CH_3C_6H_4$); 3.80, 3.86 (s, 2 CH_3O); 6.45 (s, CCl_3CH); 6.96–7.52 (m, C_6H_5, $2C_6H_4$)
8a[d]	66	182 dec. (MeOH)	$C_{20}H_{20}Cl_4N_4O_5S$	24.64 (24.87)	9.73 (9.82)	5.65 (5.62)	1620	A mixture of stereoisomers. 2.43 (s, CH_3C); 3.80, 3.93 (s, 2.5:1, CH_3N); 4.05, 4.10 (s, 1:2.5 CH_3O); 5.58, 5.99 (s, 1:2.5 CCl_3CH); 7.30–7.55 (m, $2C_6H_5$)
8b	22	168 dec. (MeOH)	$C_{20}H_{20}Cl_4N_4O_6S$	24.34 (24.19)	9.82 (9.56)	5.50 (5.47)	1610	3.85 (s, CH_3N); 4.02, 4.21 (s, $2CH_3O$); 5.79 (s, CCl_3CH); 7.28–7.58 (m, $2C_6H_5$)
8c	57	167 dec. (MeOH)	$C_{22}H_{24}Cl_4N_4O_6S$	22.50 (23.08)	9.18 (9.12)	5.18 (5.22)	1600	1.40 (m, 2 CH_3CH_2), 3.85 (s, CH_3N); 4.42, 4.64 (m, 2 CH_3CH_2); 5.79 (s, CCl_3CH); 7.30–7.58 (m, $2C_6H_5$)
11	73	200 dec.	$C_{24}H_{19}Cl_3{}^{15}N^{14}N_3OS$	20.44 (20.50)	11.06 (10.99)	6.22 (6.18)	1650 ($\nu_{C=O}$)	A mixture of stereoisomers. 2.27 (s, CH_3); 5.71, 6.33 (d, 8:1, $^3J_{HH} = 8$ Hz, CCl_3CH); 6.68–7.95 (m, $2C_6H_5$, C_6H_4); 8.98, 9.19 (dd, 1:8, $^1J_{^{15}NH} = 93$ Hz, $^3J_{HH} = 8$ Hz, NH)

[a] IR spectra were taken on a Specord 71IR spectrophotometer in a CH_2Cl_2 solution (**6a–h, 8a–c**) and on a UR 20 spectrophotometer in a KBr disk (**11**). Only bands in the region of 1600–1700 cm^{-1} are indicated.

[b] ^1H NMR spectra were recorded on the following spectrometers: Varian VXR 300 (**6a–g, 8a,c, 11**), Varian Mercury 400 (**6h**), and Varian Gemini 200 (**8b**). Most of the compounds were dissolved in $CDCl_3$ and compound **11** was dissolved in DMSO-d_6.

[c] ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 22.22$ (CH_3C), 39.17 (CH_3N), 78.87 ($CHCCl_3$), 102.35 (CCl_3); 124.45, 126.80, 128.32, 129.49, 129.55, 130.65, 131.17, 138.59 ($2C_6H_5$); 159.79, 170.54 (2C=N); 173.57 (C=O).

[d] ^{13}C NMR (75 MHz, $CDCl_3$, a mixture of stereoisomers) $\delta = 17.09$, 18.82 (CH_3C); 42.64, 44.18 (CH_3N); 57.51, 58.24 (CH_3O); 79.60, 85.52 ($CHCCl_3$); 100.47, 102.00 (CCl_3); 126.42, 127.01, 127.08, 128.68, 128.77, 130.31, 130.40, 130.54, 130.64, 131.06, 132.74, 133.03, 133.78, 134.04 ($2C_6H_5$); 163.65, 164.44, 171.90, 173.81, 174.07, 175.20 (3C=N).

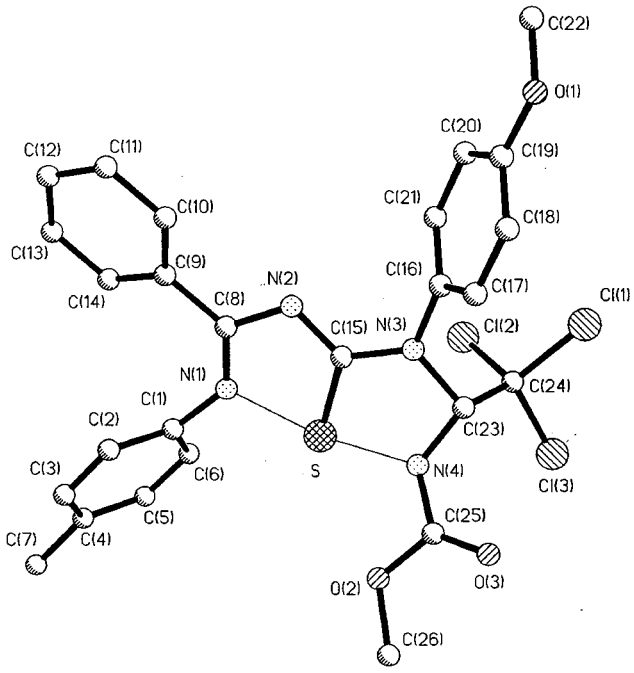


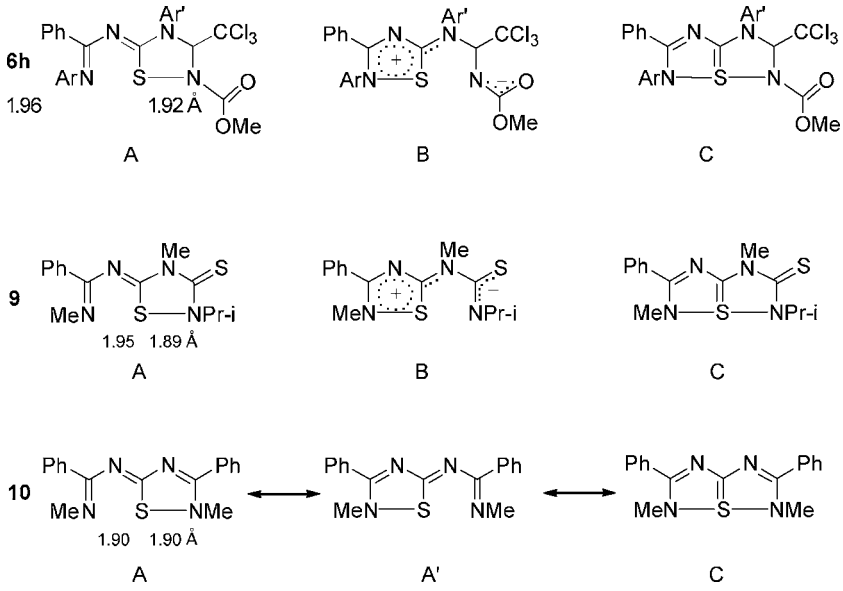
FIGURE 1 Molecular structure of compound **6h**.

It is of interest to compare the structures **6h** (A–C) with similar structures **9** (A–C) [2] and **10** (A, A′, C) [11]. It may be considered that the charge delocalization over the S—N bond in **6h** is more significant than in **9** despite the higher "bipolarity" of **6h** (B) compared to **9** (B). The equalization of the bond lengths in the triad N···S···N of compound **6h** approaches the ideal state found in **10**, which is an example of the classical "bond–no-bond" resonance system.

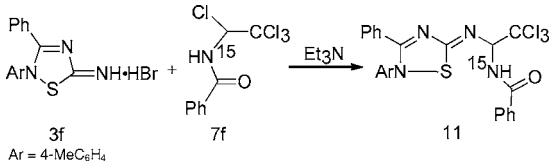
TABLE 2 Selected Geometrical Parameters of **6h**

Bond Length (Å)		*Angle (°)*	
S–N(1)	1.960(2)	N(1)–S–N(4)	166.12(9)
S–N(4)	1.916(2)	N(1)–S–C(15)	81.14(11)
S–C(15)	1.733(3)	N(4)–S–C(15)	85.36(11)
N(1)–C(1)	1.419(3)	S–N(1)–C(1)	115.6(2)
N(1)–C(8)	1.303(3)	S–N(1)–C(8)	110.9(2)
N(2)–C(8)	1.365(3)	C(1)–N(1)–C(8)	132.9(2)
N(2)–C(15)	1.312(3)	C(8)–N(2)–C(15)	111.7(2)
N(3)–C(15)	1.351(3)	C(15)–N(3)–C(16)	122.6(2)
N(3)–C(16)	1.439(3)	C(15)–N(3)–C(23)	116.6(2)
N(3)–C(23)	1.466(3)	C(16)–N(3)–C(23)	120.8(2)
N(4)–C(23)	1.421(3)	S–N(4)–C(23)	113.0(2)
N(4)–C(25)	1.358(3)	S–N(4)–C(25)	121.0(2)
O(3)–C(25)	1.202(3)	C(23)–N(4)–C(25)	108.2(2)
		O(3)–C(25)–N(4)	126.9(3)
		S–C(15)–N(2)	120.8(2)
		S–C(15)–N(3)	116.6(2)
		N(2)–C(15)–N(3)	122.6(2)

The marked structural bipolarity is likely to play a large role in the alkylation of compounds **6** into **8**. The alkylation proceeds at the oxygen atom under mild conditions and in most cases rather selectively as can be seen from the comparison of IR spectra of the related compounds **6** and **8** (Table 1). Furthermore, the signals at 164 and 172 ppm in the ^{13}C NMR spectrum of **8a** (see footnote *d* in Table 1) correspond to those of atoms C(3) and C(5) in 1,2,4-thiadiazolium cation with a disubstituted amine group in the 5-position [12]. These findings indicate that in the process of the alkylation the "switch-over" of the S—N bond and the reestablishment of the heterocycle initially present in reagents **3** and **4** do occur.



SCHEME 2



SCHEME 3

It should be noted that analogs of compounds **3a–e**, bearing no substituent at the exocyclic nitrogen atom, interact with reagents **7** in the presence of triethylamine in a different way, without ring-opening. An example of such a reaction involving salt **3f** and ^{15}N-labeled amide **7f** is shown in Scheme 3. The structure of product **11** was easily deduced from the ^{1}H NMR spectrum (Table 1).

CONCLUSION

The investigation into the structure and properties of the cycloaddition products of *N*-acylated imino derivatives of chloral and substituted 1,2,4-thiadiazol-5(2*H*)-imines has widened the knowledge of heterocycles with a hypervalent sulfur atom, the chemistry of which is being studied intensively in recent years [13].

EXPERIMENTAL

General

All the reagents and solvents were commercial products and were used as received unless otherwise indicated. Melting points were determined on a capillary tube apparatus and were corrected. ^{1}H NMR spectra were recorded on a Varian Mercury 400 (400 MHz), a Varian VXR 300 (300 MHz), a Bruker AC 300 (300 MHz), or a Varian Gemini 200 (200 MHz) spectrometer. ^{13}C NMR spectra were obtained on a Varian VXR 300 (75 MHz) spectrometer. TMS was used as the internal standard.

Synthesis of N-Imidoylthioureas **2a–e**

To a stirred solution or a suspension of the appropriate imidoyl chloride **1** (50 mmol) in anhydrous MeCN (20 ml), preliminarily dried NaSCN (50 mmol) dissolved in MeCN (30 ml) was added in 0.5 h at 15–20°C. The mixture was stirred for a further 0.5 h and then a 35% aqueous solution of methylamine (10 ml) or a solution of cyclohexylamine or of the appropriate aniline (50 mmol) in MeCN (10 ml) was added dropwise in 0.5 h at 10–12°C. After the addition was complete, the reaction mixture was stirred at room temperature for 2 h, diluted with water (30 ml), stirred for 0.5 h, and filtered to separate the product.

Compound **2a**: 73% yield, mp 135°C (MeOH) (lit. 140°C) [3]. ^{1}H NMR (300 MHz, DMSO-d_6, a mixture of tautomers and stereoisomers) $\delta = 2.78$, 3.11 (d, 3.5:1, CH_3); 6.68–7.66 (m, $2C_6H_5$); 8.56, 8.86, 9.59, 9.85, 10.36, 11.82 (s and br s, 2NH). Found: N, 15.54; S, 11.74%. Calcd for $C_{15}H_{15}N_3S$: N, 15.60; S, 11.90%.

Compound **2b**: 92% yield, mp 159°C (AcOEt) (lit. 184°C) [14]. ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 1.30$–2.09 (m, 5 CH_2), 4.33 (m, CH_2CHCH_2), 6.66–7.38 (m, $2C_6H_5$), 7.93 (s, NH), 12.08 (d, NH). Found: C, 71.06; H, 6.90; N, 12.27; S, 9.36%. Calcd for $C_{20}H_{23}N_3S$: C, 71.18; H, 6.87; N, 12.45; S, 9.50%.

Compound **2c**: 87% yield, mp 133–134°C (MeCN) (lit. 95°C) [5]. ^{1}H NMR (300 MHz, DMSO-d_6/CCl_4) $\delta = 4.63$ (d, CH_2), 6.92–7.48 (m, $3C_6H_5$), 8.90 (br s, NH), 10.20 (s, NH) [15]. Found: C, 73.10; H, 5.58; N, 12.08; S, 9.14%. Calcd for $C_{21}H_{19}N_3S$: C, 73.01; H, 5.54; N, 12.16; S, 9.28%.

Compound **2d**: 80% yield, mp 126°C (MeCN). ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 3.79$ (s, CH_3), 6.74–7.74 (m, $2C_6H_5$, C_6H_4), 8.16 (s, NH), 14.15 (s, NH). Found: N, 11.74; S, 8.82%. Calcd for $C_{21}H_{19}N_3OS$: N, 11.63; S, 8.87%.

Compound **2e**: 97% yield, mp 133–134°C (MeCN). ^{1}H NMR (300 MHz, DMSO-d_6/CCl_4, a mixture of tautomers and stereoisomers) $\delta = 2.21$, 2.35 (s, 1:6, CH_3C); 3.72, 3.80 (s, 6:1 CH_3O); 6.59–7.63 (m, C_6H_5, $2C_6H_4$); 9.82, 10.01, 10.15, 10.28, 10.44, 14.20 (s, 2NH). Found: N, 11.25; S, 8.56%. Calcd for $C_{22}H_{21}N_3OS$: N, 11.19; S, 8.54%.

Synthesis of 1,2,4-Thiadiazol-5(2H)-imine Hydrobromides **3a–f**

To a stirred solution (**2a,d**) or a suspension (**2b,c,e**) of the appropriate **2** (50 mmol) in $CHCl_3$ (50 ml), pyridine (50 mmol) was added in one portion followed by a solution of bromine (50 mmol) in $CHCl_3$ (25 ml) added dropwise in 40 min. The mixture was stirred for 1 h and precipitated **3a–e** was filtered off and washed with MeOH. The filtrate was concentrated in vacuum and the residue was washed with MeOH to give an additional amount of the product.

Compound **3a**: 95% yield, mp 229°C dec. Found: Br, 23.15; N, 12.13; S, 9.25%. Calcd for $C_{15}H_{13}N_3S$·HBr: Br, 22.94; N, 12.07; S, 9.21%.

Compound **3b**: 92% yield, mp 235°C dec. Found: Br, 19.26; N, 10.16; S, 7.73%. Calcd for $C_{20}H_{21}N_3S$·HBr: Br, 19.19; N, 10.09; S, 7.70%.

Compound **3c**: 92% yield, mp 172°C ($ClCH_2CH_2$-Cl). Found: Br, 18.31; N, 9.97; S, 7.54%. Calcd for $C_{21}H_{17}N_3S$·HBr: Br, 18.23; N, 9.90; S, 7.56%.

Compound **3d**: 95% yield, mp 218°C dec. ($ClCH_2$-CH_2Cl). Found: Br, 18.03; N, 9.63; S, 7.24%. Calcd for $C_{21}H_{17}N_3OS{\cdot}HBr$: Br, 18.15; N, 9.54; S, 7.28%.

Compound **3e**: 88% yield, mp 216–218°C (AcOH). Found: Br, 17.37; N, 9.33; S, 6.98%. Calcd for $C_{22}H_{19}N_3OS{\cdot}HBr$: Br, 17.58; N, 9.25; S, 7.06%.

N-Imidoylthiourea of the formula 4-MeC_6H_4-N=C(Ph)NHC(S)NH_2 [12] was brominated as described above to give compound **3f** in 92% yield; mp 227–228°C dec. (EtOH). Found: Br, 22.78; N, 12.13; S, 9.12%. Calcd for $C_{15}H_{13}N_3S{\cdot}HBr$: Br, 22.94; N, 12.07; S, 9.21%.

Preparation of Free Base **4e**

To a suspension of salt **3e** (20 mmol) in EtOH (40 ml), triethylamine (22 mmol) was added. The mixture was stirred for 4 h and the product was filtered off; 96% yield, mp 136°C (EtOH). Found: C, 70.68; H, 5.16; N, 11.33; S, 8.51%. Calcd for $C_{22}H_{19}N_3OS$: C, 70.75; H, 5.13; N, 11.25; S, 8.59%.

General Procedure for the Synthesis of 1,2,4-Thiadiazolidines **6a–h**

To a stirred mixture of the appropriate reagents **3a–e** (5 mmol) and **7a** [16], **7b,c** [17], or **7d,e** [18] (5 mmol) in anhydrous CH_2Cl_2 (10 ml), a solution of triethylamine (10 mmol) in CH_2Cl_2 (5 ml) was added dropwise in 20 min. The mixture was stirred for a further 4 h and diluted with water (15 ml). The organic layer was separated, concentrated in vacuum, and the residue was treated with EtOH (10 ml) to give crystalline **6a–h**. In the case of **6h** a portion of the precipitated product was filtered off before the addition of water. The title compounds are characterized in Table 1.

Alternative Method for Preparation of Compound **6h**

To a suspension of **4e** (5 mmol) in anhydrous dioxane (15 ml), compound **5d** [17] (5 mmol) was added. The mixture was stirred for 6 h and the precipitated product (77% yield) was separated by filtration.

X-Ray Crystallography of Compound **6h**

A single crystal of **6h** (0.18 × 0.26 × 0.61 mm) was grown from an acetonitrile solution. Crystal data: $C_{26}H_{23}Cl_3N_4O_3S$, M = 577.89, triclinic, $P\bar{1}$ (*N*2), a = 9.594(7), b = 10.915(3), c = 13.221(5) Å, α = 95.86(3), β = 93.19(6), γ = 104.27(6)°, V = 1330.1(12) Å^3, Z = 2, D_{calc} = 1.44 g·cm^{-3}, μ = 4.59 cm^{-1}. Measurements were performed at 18°C on an Enraf-Nonius CAD 4 diffractometer operating in the ω–2Θ scan mode (the ratio of the scanning rates $\omega/2\Theta = 1.2$). Intensity data were collected within the range $1 < \Theta < 24°$ using graphite monochromated Mo Kα radiation (λ = 0.71069 Å). Intensities of 4458 reflections (4261 unique reflections, $R_{int} = 0.014$) were measured. Data were corrected for Lorentz and polarization effects but not for absorption. The structure was solved by direct method [19] and refined by full-matrix least-squares technique in the anisotropic approximation [20]. In the refinement, 3091 reflections with $I > 2\sigma$ (I) were used. All hydrogen atoms were located in the difference Fourier maps and included in the final refinement with fixed positional and thermal parameters. Convergence was obtained at $R_1(F) = 0.035$, $R_w(F^2) = 0.090$, and GOF = 1.037 (334 refined parameters; obs/variable 9.3; the largest and minimal peaks in the final difference map, 0.25 and −0.24 e/Å^3). The weighting scheme $\omega = 1/[\sigma^2(Fo^2) + (0.047P)^2 + 0.585P]$ with $P = (Fo^2 + 2Fc^2)/3$ was used.

Full details of the crystal structure determination have been deposited at the Cambridge Crystallographic Data Centre under number CCDC 172355.

Preparation of 1,2,4-Thiadiazolium Salts **8a–c**

A mixture of **6b, 6c**, or **6d** (3 mmol), the appropriate trialkyloxonium tetrafluoroborate (3 mmol) and anhydrous CH_2Cl_2 (10 ml) was stirred at room temperature for 48 h, after which time the solvents were removed under a reduced pressure and the residue was triturated with AcOEt (5 ml) to give a solid which was filtered off and redissolved in MeOH (10 ml) at 40–50°C. A 3 M solution of $NaClO_4$ in MeOH (3 ml) was added to the resulting solution and, after standing for 48 h at room temperature, the precipitated product was filtered off. Compounds **8a–c** are characterized in Table 1.

Synthesis of Compound **11**

To a stirred mixture of reactants **3f** (5 mmol) and **7f** [21] (5 mmol) in anhydrous CH_2Cl_2 (10 ml), a solution of triethylamine (10 mmol) in CH_2Cl_2 (5 ml) was added dropwise in 20 min. The reaction mixture was stirred for a further 4 h and then the precipitated product was separated and washed with EtOH. Compound **11** is characterized in Table 1.

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