On the Mechanism of Thermal Decomposition of 4-Alkyl-5-sulfonylimino-Δ^2-1,2,3,4-thiatriazolines

Gerrit L'abbé* and Joris Bosman

Department of Chemistry, University of Leuven,
Celestijnenlaan 200F, B-3001 Heverlee, Belgium

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The kinetics of the thermal decomposition of several sulfonyl substituted thiatriazolinimines **1a-g** were investigated in different solvents both in the presence and in the absence of trapping reagents. The first-order rate constants observed in all cases, are dependent on the inductive effect of the sulfonyl substituent (R), as well as on solvent polarity, but independent on the nature and concentration of the co-reagent. These results, and the low activation energy, are rationalized by assuming an anchimeric assistance of the sulfonyl group during thermolysis. This would give the intermediate **7**, which collapses to the thiaziridinimine **2** before being trapped by the co-reagent.

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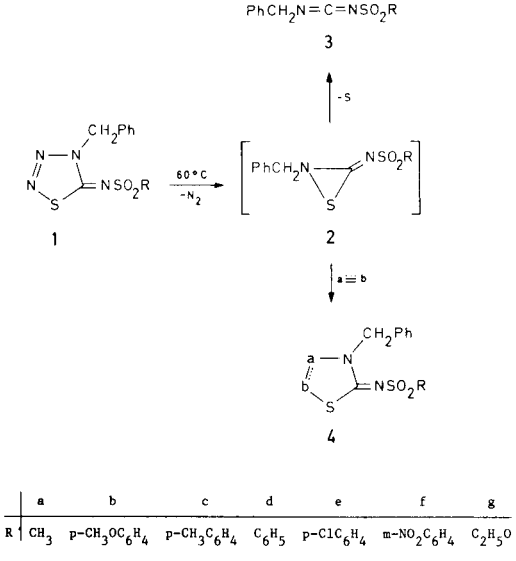
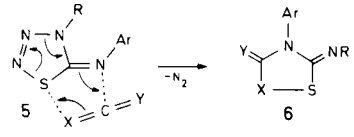
Some years ago we reported that the title compounds **1** decompose at 60° to yield carbodiimides **3** by loss of nitrogen and sulfur [1]. A thiaziridinimine **2** was postulated as an intermediate since it could be trapped by a large variety of unsaturated systems (**2** → **4**), including heterocumulenes (Scheme 1) [2,3].

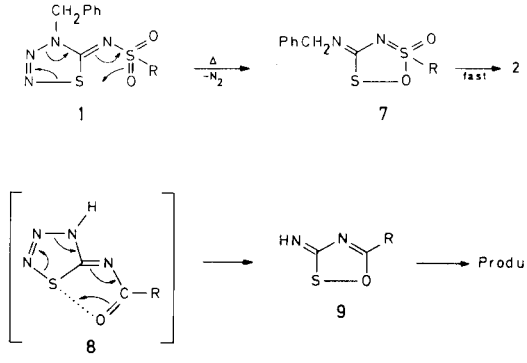
Scheme 1



4-Alkyl-5-arylimino-1,2,3,4-thiatriazolines **5**, on the contrary, proved to be more stable thermally and reacted with heterocumulenes by a bimolecular mechanism (**5** → **6**), not involving a three-membered ring as intermediate [4]. Moreover, the introduction of strong electron-withdrawing substituents on the aryl group (*i.e.* picryl) did not change the mechanism of the cycloaddition-elimination reactions of **5** [5].



What makes the sulfonyl derivatives **1** so peculiar that they can react by first-order kinetics and *via* thiaziridinimines **2**? A plausible explanation would be anchimeric assistance by the S=O bond (**1** → **7** → **2**), analogous to the elusive acylaminothiatriazoles which are assumed to decompose according to **8** → **9** [3]. This consideration prompted us to investigate the influence of different sulfonyl substituents (R) and of the solvent polarity on the thermal reactivity of **1** under a variety of conditions.



The rates of decomposition of **1a-g** were measured spectroscopically by integration of the benzyl methylene signals in the δ 4-6 region of the ^{1}H nmr spectra. The experiments were carried out in deuterated chloroform at 60° both in the presence and in the absence of a co-reagent, and the results are summarized in Table 1. The first-order kinetics observed in all cases indicate that the co-reagent does not alter the mechanism of decomposition of **1**. Furthermore, when different heterocumulenes were added to the chloroform solutions of **1a-g**, the rates were almost unaffected and the observed small variations are attributable to the polarity effect and/or experimental error.

The methylsulfonyl and arylsulfonyl substituted thiatriazolinimines **1a-f** have similar decomposition rates, whereas the ethoxysulfonyl derivative **1g** is much more resistant towards thermolysis. This is understandable if we assume

Table 1
Kinetics of the Thermal Decomposition of **1a-g** in Deuteriochloroform at 60°

Compound	Co-reagent (equivalents)	10^5 k_1 (s^{-1})
1a	–	18.6
	RN=C=NR (1) [a]	18.1
	PhN=C=S (1)	16.0
	PhN=C=S (5)	16.9
	p-$NO_2C_6H_4$N=C=S (1)	16.8
	PhN=C=O (1)	18.0
1b	–	19.9
	RN=C=NR (1) [a]	23.5
	PhN=C=S (1)	19.1
	PhN=C=S (5)	19.1
1c	–	20.6
	RN=C=NR (1) [a]	21.6
	PhN=C=S (1)	20.0
	PhN=C=S (5)	19.7
1d	–	18.9
	RN=C=NR (1) [a]	19.3
	RN=C=NR (5) [a]	19.2
	PhN=C=S (1)	17.8
	PhN=C=S (5)	18.5
1e	–	15.6
	RN=C=NR (1) [a]	16.6
	PhN=C=S (1)	16.6
	PhN=C=S (5)	15.8
1f	RN=C=NR (1) [a]	14.8
	PhN=C=S (1)	14.1
	PhN=C=S (5)	14.4
1g	–	3.9
	RN=C=NR (1) [a]	4.4
	PhN=C=S (1)	4.2
	PhN=C=S (5)	3.9

[a] R = c-C_6H_{11}.

that the sulfonyl group participates during thermolysis (**1** → **7** → **2**). Indeed, the ethoxy group decreases the electron density at the S=O bond by its strong electron-withdrawing inductive effect, thereby retarding the decomposition. On the contrary, the conjugative effect of the aryl substituents cannot be transmitted directly to the S=O bond, and consequently, only a modest rate-decrease is observed for the chlorophenyl and nitrophenyl substituents (**1e,f**).

The polarity of the solvent has a significant effect on the rates of decomposition as illustrated in Table 2. Thus, **1a** thermolyzes about 6.5 times faster in carbon tetrachloride than in acetonitrile, and low reaction rates were also observed when the other thiatriazolinimines **1b-g** were decomposed in acetonitrile (Table 3). We explain these results by assuming that **7** is indeed an intermediate, since its dipole moment is expected to be smaller than that of **1** by analogy to similar systems [6].

Finally, the energy of activation for the thermolysis of **1a** in deuterated toluene was found to be 25.1 kcal/mol (Table 4) which is much lower than that of the phenylimino analogue (**5**, R = Me, Ar = Ph), E_a = 31.4 kcal/mol, ΔS^* = +3 e.u. [7]. This corresponds to a rate enhancement (k_{MeSO_2}/k_{Ph}) of 526 at 90°. The low activation energy and the concomitant rate accelerating effect are best explained by a process in which the sulfonyl group assists in the decomposition.

Table 2
Influence of Solvent Polarity on the Thermolysis of **1a** at 60°

Solvent	10^5 k_1 (s^{-1})
CCl_4	45.3 [a]
C_6D_6	24.4
$CDCl_3$	18.6
CD_3CN	6.9
$(CD_3)_2SO$	6.5

[a] In the presence of one equivalent of dicyclohexylcarbodiimide.

Table 3
Kinetics of the Thermolysis of **1a-f** in deuterioacetonitrile at 60°

Compound	10^5 k_1 (s^{-1})
1a	6.9
1b	6.6
1c	6.5
1d	6.0
1e	4.5
1f	3.6
1g	1.3

Table 4
Kinetics of the Thermolysis of **1a** in Toluene-d_8 (0.125 *M*) in the Presence of one Equivalent of Dicyclohexylcarbodiimide

T(°C)	50°	60°	65°	70°	80°	90°
10^5 k_1 (s^{-1})	6.0	29.9	35.2	67.8	202.2	494.8

E_a = 25.1 kcal/mol
ΔS^* (60°) = -1 e.u.

If **7** occurs as intermediate in the thermolysis of **1**, it must collapse to **2** before reacting with the heterocumulenes or with acetonitrile. Indeed, the amount of cycload-

Scheme 2

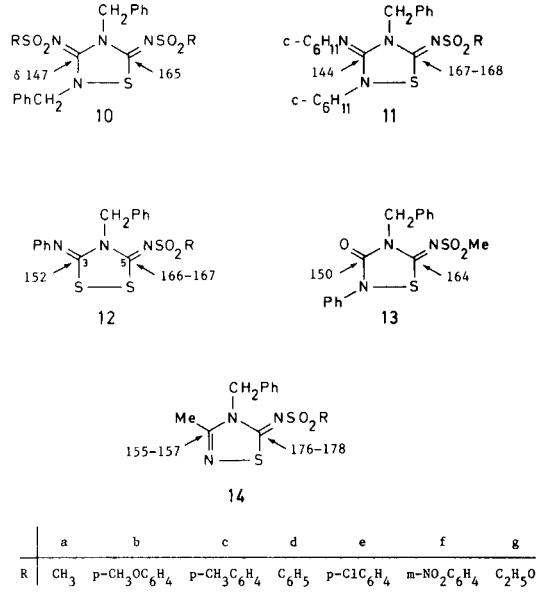


Table 5
Characterization of the New Heterocycles [a]

Compound	IR	^{1}H NMR	^{13}C NMR			Molecular Formula	Analysis %	
	C=N	CH_2	CH_2	C-3	C-5	($M^{+\cdot}$)	Calcd./Found	
							C	H
1a	1540	5.60	52.8	–	165.5	$C_9H_{10}N_4O_2S_2$ (270)	40.00	3.70
							40.00	3.61
1b	1530	5.53	52.7	–	165.2	$C_{15}H_{14}N_4O_3S_2$ (362)	49.71	3.89
							49.63	3.90
1f	1520	5.62	52.5	–	167.7	$C_{14}H_{11}N_5O_4S_2$ (377)	44.56	2.94
							44.70	3.03
1g	1545	5.59	52.9	–	167.6	$C_{10}H_{12}N_4O_3S_2$ (300)	39.99	4.03
							40.15	3.92
10a	1545	5.09	49.3	147.3	165.0	$C_{18}H_{20}N_4O_4S_3$ (452)	47.77	4.45
		5.34	53.3				47.62	4.36
11a	1540	5.00	48.3	144.0	166.7	$C_{22}H_{32}N_4O_2S_2$ (448)	58.90	7.19
	1680						59.03	7.17
11b	1530	4.98	48.3	144.1	166.5	$C_{28}H_{36}N_4O_3S_2$ (540)	62.20	6.71
	1675						62.35	6.58
11d	1525	4.95	48.3	144.0	167.0	$C_{27}H_{34}N_4O_2S_2$ (510)	63.50	6.71
	1670						63.33	6.57
11e	1535	4.95	48.4	143.8	167.2	$C_{27}H_{33}ClN_4O_2S_2$ (544)	59.49	6.10
	1675						59.35	5.94
11f	1530	5.05	48.6	143.6	168.0	$C_{27}H_{33}N_5O_4S_2$ (555)	58.36	5.99
	1680						58.40	6.02
11g	1540	5.05	48.5	144.2	168.2	$C_{23}H_{34}N_4O_3S_2$ (478)	57.71	7.16
	1680						57.70	7.08
12a	1520	5.40	52.2	152.1	166.1	$C_{16}H_{15}N_3O_2S_3$ (377)	50.91	4.00
	1650						50.93	4.01
12b	1510	5.33	52.2	152.1	165.6	$C_{22}H_{19}N_3O_3S_3$ (469)	56.27	4.08
	1620						56.27	4.09
12d	1520	5.34	52.2	152.1	166.2	$C_{21}H_{17}N_3O_2S_3$ (439)	57.38	3.90
	1645						57.22	3.88
12e	1490	5.35	52.3	152.0	166.5	$C_{21}H_{16}ClN_3O_2S_3$ (473)	53.21	3.40
	1620						53.09	3.34
12f	1500	5.37	52.5	151.9	167.5	$C_{21}H_{16}N_4O_4S_3$ (484)	52.05	3.33
	1625						51.91	3.24
12g	1500	5.41	52.3	152.3	167.1	$C_{17}H_{17}N_3O_3S_3$ (407)	50.10	4.20
	1620						49.91	4.19
13	1550	5.10	48.6	150.4	164.0	$C_{16}H_{15}N_3O_3S_2$ (361)	53.17	4.18
							53.01	4.20
14a	1525	5.18	49.3	154.7	176.3	$C_{11}H_{13}N_3O_2S_2$ (283)	46.63	4.62
							46.48	4.46
14b	1500	5.14	49.3	154.8	176.2	$C_{17}H_{17}N_3O_3S_2$ (375)	54.38	4.56
							54.29	4.61
14d	1520	5.18	49.4	154.8	176.6	$C_{16}H_{15}N_3O_2S_2$ (345)	55.63	4.38
							55.54	4.38
14e	1500	5.14	49.5	154.9	176.8	$C_{16}H_{14}ClN_3O_2S_2$ (379)	50.59	3.71
							50.73	3.65
14f	1525	5.23	49.2	156.9	177.1	$C_{16}H_{14}N_4O_4S_2$ (390)	49.22	3.61
							49.15	3.49
14g	1530	5.22	49.5	155.1	178.0	$C_{12}H_{15}N_3O_3S_2$ (313)	45.99	4.82
							46.13	4.96

[a] The ir spectra (cm^{-1}) were taken in potassium bromide discs. The nmr spectra (δ-values in ppm from tetramethylsilane) were recorded in deuteriochloroform, except those of **1f**, **14f** (^{13}C) and **10a** (^{1}H and ^{13}C) which were recorded in dimethyl sulfoxide-d_6.

duct formed with heterocumulenes decreases in the order: RN=C=NR > PhN=C=S > *p*-$NO_2C_6H_4N$=C=S and PhN=C=O, thus following the nucleophilicity of the reagents. For instance, when **1a** (0.5 *M*) was heated at 60° with one equivalent of each of the above trapping reagents in chloroform, the nmr spectra shows yields of 69, 29, 9

and 10% respectively. Compound **7**, however, would be expected to react preferentially with electrophilic partners [8], but this is not the case. The structures of the adducts are shown in Scheme 2 and their attributions were based on criteria discussed previously (see also Table 5) [2,9].

In conclusion, the kinetic data support rather than exclude the intermediacy of **7** during the thermolysis of **1**. This intermediate first isomerizes to **2** before being trapped by the co-reagent.

EXPERIMENTAL

4-Benzyl-5-methylsulfonylimino-1,2,3,4-thiatriazoline (**1a**).

This compound was obtained by reacting methylsulfonyl isothiocyanate [10] (27.4 g, 200 mmoles) with benzyl azide (26.6 g, 200 mmoles) in dry carbon tetrachloride (100 ml) for 20 hours. The precipitate was collected and washed with carbon tetrachloride and ether, yield 61%, mp 104-107° dec (chloroform).

4-Benzyl-5-(*p*-methoxyphenyl)sulfonylimino-1,2,3,4-thiatriazoline (**1b**).

This compound was obtained by reacting *p*-anisylsulfonyl isothiocyanate (2.2 g, 9.6 mmoles) with benzyl azide (1.28 g, 9.6 mmoles) in dry dichloromethane (5 ml) at room temperature for 12 hours, followed by column chromatography on silcia gel with ether-petroleum ether (1:1) as the eluent; yield 32%, mp 108° dec (ether).

Synthesis of the Thiatriazolinimines **1c,d,e**.

These compounds were prepared by reacting benzyl azide with the appropriate sulfonyl isothiocyanates according to our earlier procedure [1]. Compound **1d** was purified by column chromatography on silica gel with ether-petroleum ether (1:1) as the eluent, giving crystals (mp 68°, dec) instead of an oil as previously reported.

4-Benzyl-5-(*m*-nitrophenyl)sulfonylimino-1,2,3,4-thiatriazoline (**1f**).

This compound was obtained by reacting *m*-nitrophenylsulfonyl isothiocyanate (2.7 g, 10.5 mmoles) with benzyl azide (1.4 g, 10.5 mmoles) in dry carbon tetrachloride (15 ml) at room temperature for 3 hours, followed by crystallization of the precipitate from ethanol, yield 51%, mp 132° dec.

4-Benzyl-5-ethoxysulfonylimino-1,2,3,4-thiatriazoline (**1g**).

A suspension of ethoxysulfonyl chloride (2.4 g, 16.7 mmoles) and lead thiocyanate (2.7 g, 8.35 mmoles) in benzene (15 ml) was refluxed for 5 hours. After filtration, benzyl azide (2.2 g, 16.7 mmoles) was added and the solution was stirred at room temperature for 10 hours. The solvent was removed and the residue was chromatographed on silica gel with ether-petroleum ether (1:1) as the eluent, giving **1g** as a viscous oil which was crystallized from ether-pentane (1:1), yield 13%, mp 54°.

2,4-Dibenzyl-3,5-bis(methylsulfonylimino)-1,2,4-thiadiazolidine (**10a**).

This compound was obtained by heating **1a** (4.35 g, 16 mmoles) in chloroform (16 ml) for 2 hours, followed by column chromatography on silica gel with petroleum ether and methanol as the eluents; yield 9%, mp 206° (methanol). **Note:** The ir spectrum of the crude reaction mixture showed a strong absorption at 2195 cm^{-1}, corresponding to **3a**.

4-Benzyl-2-cyclohexyl-3-cyclohexylimino-5-methylsulfonylimino-1,2,4-thiadiazolidine (**11a**).

This compound was obtained by heating **1a** (4.35 g, 16 mmoles) with *N,N'*-dicyclohexylcarbodiimide (3.30 g, 16 mmoles) in chloroform (16 ml) for 2 hours, followed by column chromatography on silica gel with petroleum ether-ether (1:1) as the eluent, yield 45%, mp 115° (ether).

4-Benzyl-2-cyclohexyl-3-cyclohexylimino-5-(*p*-methoxyphenyl)sulfonylimino-1,2,4-thiadiazolidine (**11b**).

This compound was obtained by heating **1b** (2 g, 5.6 mmoles) with *N,N'*-dicyclohexylcarbodiimide (11.5 g, 56 mmoles) in chloroform (20 ml) for 2 hours. The excess of carbodiimide was distilled off *in vacuo* and the residue was chromatographed on silica gel with petroleum ether-ether (1:1) as the eluent, yield 31%, mp 117° (petroleum ether-ether).

4-Benzyl-2-cyclohexyl-3-cyclohexylimino-5-phenylsulfonylimino-1,2,4-thiadiazolidine (**11d**).

This compound was obtained by heating **1d** (0.5 g, 1.5 mmoles) with *N,N'*-dicyclohexylcarbodiimide (1.5 g, 7.5 mmoles) in chloroform (8 ml) for 2 hours, followed by crystallization of the reaction mixture after addition of ether-petroleum ether (10 ml, 4:1), yield 33%, mp 132° (ether).

4-Benzyl-5-(*p*-chlorophenyl)sulfonylimino-2-cyclohexyl-3-cyclohexylimino-1,2,4-thiadiazolidine (**11e**).

This compound was obtained by heating **1e** (1 g, 2.7 mmoles) with *N,N'*-dicyclohexylcarbodiimide (2.75 g, 5 equivalents) in carbon tetrachloride (10 ml) for 2 hours. The excess of carbodiimide was distilled off *in vacuo* and the residue was crystallized from ether, yield 42%, mp 131°.

4-Benzyl-2-cyclohexyl-3-cyclohexylimino-5-(*m*-nitrophenyl)sulfonylimino-1,2,4-thiadiazolidine (**11f**).

This compound was obtained by heating **1f** (0.5 g, 1.32 mmoles) with *N,N'*-dicyclohexylcarbodiimide (2.7 g, 13.2 mmoles) at 60° for 6 hours. The excess of carbodiimide was distilled off *in vacuo* and the residue was subjected to thin-layer chromatography on silica gel with petroleum ether-ether (1:1) as the development solvent, yield 10% after crystallization from ether-petroleum ether (1:1), mp 93°.

4-Benzyl-2-cyclohexyl-3-cyclohexylimino-5-ethoxysulfonylimino-1,2,4-thiadiazolidine (**11g**).

This compound was obtained by heating **1g** (0.6 g, 2 mmoles) with *N,N'*-dicyclohexylcarbodiimide (4.24 g, 20 mmoles) in chloroform (10 ml) at 60° for 6 hours. The excess of carbodiimide was distilled off *in vacuo* and the residue was chromatographed on silica gel with petroleum ether-ether (2:1) as the eluent. After crystallization from ether-petroleum ether **11g** was obtained in 26% yield, mp 98°.

4-Benzyl-5-methylsulfonylimino-3-phenylimino-1,2,4-dithiazolidine (**12a**).

This compound was obtained by heating **1a** (4.35 g, 16 mmoles) with phenyl isothiocyanate (12.75 g, 160 mmoles) in chloroform

(16 ml) for 2 hours, followed by column chromatography on silica gel with ether-petroleum ether (1:1) as the eluent, yield 25% after crystallization from ether-petroleum ether (1:1), mp 125°.

4-Benzyl-5-(*p*-methoxyphenyl)sulfonylimino-3-phenylimino-1,2,4-dithiazolidine (**12b**).

This compound was obtained by heating **1b** (1 g, 2.8 mmoles) with phenyl isothiocyanate (3.7 g, 28 mmoles) at 60° for 5 hours. The excess of isothiocyanate was distilled off and the residue was crystallized from ethanol, yield 36% (480 mg), mp 133°.

4-Benzyl-3-phenylimino-5-phenylsulfonylimino-1,2,4-dithiazolidine (**12d**).

This compound was obtained by heating **1d** (0.6 g, 1.8 mmoles) with phenyl isothiocyanate (2.43 g, 18.0 mmoles) in chloroform (5 ml) for 2 hours. The excess of isothiocyanate was distilled off and the residue was chromatographed on silica gel with ether-petroleum ether (1:1) as the eluent, yield 10% after crystallization from ether-petroleum ether, mp 108°. **Note**: When the reaction was carried out in the absence of solvent **12d** was isolated in 20% yield.

4-Benzyl-5-(*p*-chlorophenyl)sulfonylimino-3-phenylimino-1,2,4-dithiazolidine (**12e**).

This compound was obtained by heating **1e** (1.8 g, 4.9 mmoles) with phenyl isothiocyanate (6.64 g, 49 mmoles) in chloroform (10 ml) for 2 hours. The excess of isothiocyanate was distilled off and the residue was crystallized from ether, yield 47%, mp 115°.

4-Benzyl-5-(*m*-nitrophenyl)sulfonylimino-3-phenylimino-1,2,4-dithiazolidine (**12f**).

This compound was obtained by heating **1f** (0.7 g, 1.86 mmoles) with phenyl isothiocyanate (2.6 g, 18.6 mmoles) in chloroform (5 ml) for 2 hours. The excess of isothiocyanate was distilled off and the resulting oil was triturated with cold dichloromethane-ether (1:1) to give crystals, yield 45%, mp 131° (dichloromethane-ether, 1:1).

4-Benzyl-5-ethoxysulfonylimino-3-phenylimino-1,2,4-dithiazolidine (**12g**).

This compound was obtained by heating **1g** (175 mg, 0.58 mmole) with phenyl isothiocyanate (0.79 g, 5.8 mmoles) at 60° for 5 hours. The excess of isothiocyanate was distilled off and the residue was purified by thin layer chromatography on silica gel with ether-petroleum ether (1:1) as the development solvent, yield 45% after crystallization from ethanol, mp 71°.

4-Benzyl-5-methylsulfonylimino-2-phenyl-1,2,4-thiadiazolidine-3-one (**13**).

This compound was obtained by heating **1a** (0.3 g, 1.1 mmoles) in phenyl isocyanate (1.31 g, 11 mmoles) at 80° for 2 hours. The excess of phenyl isocyanate was distilled off and the residue was crystallized from ether, yield 65%, mp 135°.

4-Benzyl-3-methyl-5-methylsulfonylimino-1,2,4-thiadiazoline (**14a**).

This compound was obtained by heating **1a** (0.5 g, 1.85 mmoles) in acetonitrile (8 ml) for 7 hours, followed by thin-layer chromatography on silica gel with ether as development solvent, yield 6% after crystallization from chloroform, mp 120°.

4-Benzyl-5-(*p*-methoxyphenyl)sulfonylimino-3-methyl-1,2,4-thiadiazoline (**14b**).

This compound was obtained by heating **1b** (1.7 g, 4.7 mmoles) in dry acetonitrile (15 ml) at 60° for 24 hours. After removal of the solvent, the residue was crystallized from ether to give **14b** in 45% yield, mp 136°.

4-Benzyl-3-methyl-5-phenylsulfonylimino-1,2,4-thiadiazoline (**14d**).

This compound was obtained by heating **1d** (1.14 g, 3.4 mmoles) overnight in acetonitrile (20 ml), followed by column chromatography on silca gel with ether as the eluent, yield 34%, mp 122° (ethyl acetate).

4-Benzyl-5-(*p*-chlorophenyl)sulfonylimino-3-methyl-1,2,4-thiadiazoline (**14e**).

This compound was obtained by heating **1e** (0.9 g, 2.5 mmoles) overnight in acetonitrile (20 ml). After removal of *N*-benzyl-*N'*-(*p*-chlorophenyl)sulfonylurea (150 mg, 20%) by crystallization from ether at −80°, the residue was subjected to preparative tlc with ether-petroleum ether (1:1) as development solvent, giving **14e** in 4% yield after two crystallizations from dichloromethane, mp 138°.

4-Benzyl-3-methyl-5-(*m*-nitrophenyl)sulfonylimino-1,2,4-thiadiazoline (**14f**).

This compound was obtained by heating **1f** (0.3 g, 0.8 mmole) in acetonitrile (10 ml) for 15 hours, followed by thin-layer chromatography on silica gel with ether as development solvent; yield 18% after crystallization from methanol, mp 101°.

4-Benzyl-5-ethoxysulfonylimino-3-methyl-1,2,4-thiadiazoline (**14g**).

This compound was obtained by heating **1g** (0.5 g, 1.7 mmoles) in acetonitrile (10 ml) at 60° for 4 days. After removal of the solvent, the residue was crystallized from ether to give **14g** in 40% yield, mp 94°.

Kinetic Measurements.

Solutions of **1a-g** (0.063-0.5 *M*) both in the presence and in the absence of a co-reagent were placed in nmr tubes at 60° (± 0.1) for decomposition. At several time intervals, the tubes were cooled to 0° and analyzed by ^{1}H nmr spectroscopy (90 MHz). The rates of decomposition were followed by integration of the benzyl methylene signals in the spectra (δ 4-6). First-order rates were observed for two half-lives. By plotting log concentration (%) *vs* time, linear plots were obtained, all having a correlation coefficient better than 0.998. The first-order rate constants were determined from the slopes of the linear plots and the results are summarized in Tables 1-3. Control experiments were carried out by continuous measurements on a 250 MHz instrument, giving overlapping results. Measurements for **1a** were made in deuterated toluene at several temperatures and the activation parameters were calculated by using the Eyring equation. The results are summarized in Table 4.

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