Cycloaddition-Elimination Reactions of 4-Methyl-5-(substituted)-imino-$\triangle^2$-1,2,3,4-thiatriazolines with Isocyanates

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4-Methyl-5-(substituted)imino-1,2,3,4-thiatriazolines **1** ($R^2 \neq Me$) undergo cycloaddition-elimination reactions with isocyanates to yield 4-methyl-5-(substituted)imino-1,2,4-thiadiazolidine-3-ones **5** *via* the thermodynamically less stable isomers **4**. The latter have not been isolated, except for **4q** which was shown to isomerize rapidly into **5q** with phenylsulfonyl isocyanate. The reactions of **1** are accelerated by using less bulky R^2 substituents and more electrophilic isocyanates, in accordance with the viewpoint that **1** reacts as a masked 1,3-dipole. The products **4i-n** (= **5i-n**), derived from **1b**, add isocyanates reversibly to give 2,3,4,5-tetrahydro-6aλ^4-thia-1,3,4,6-tetraazapentalene-2,5-diones **9i-n**, which have been isolated and characterized spectroscopically. Such compounds with a hypervalent sulfur atom thus occur as intermediates during the isomerization of **4** to **5** under the influence of isocyanates.

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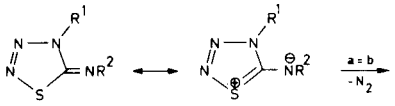
Thiatriazolines **1** belong to a general class of heterocyclic masked 1,3-dipoles (see resonance structure) which undergo cycloaddition-elimination reactions with electrophilic a=b systems [1]. Since the resulting products of type **2** also possess a thioimidate structural unit, further reactions with the reagent a=b are possible with elimination of the first a=b molecule added and formation of the isomeric compounds **3**. The occurrence of the second reaction depends on the relative thermodynamic stabilities of **2** and **3**, and consequently on the nature of the R substituents. This sequence has been established for the reactions of 4-methyl-5-phenyliminothiatriazoline (**1**, R^1 = Me, R^2 = Ph) with isothiocyanates [2], and the present investigation was undertaken to clear up the situation with isocyanates.



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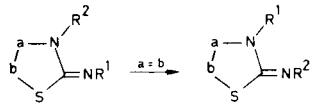


2 3

In a previous communication [3] we have reported that **1a** reacts with *n*-butyl isocyanate to yield **5b** as the sole reaction product according to a bimolecular mechanism. In the absence of direct evidence to the contrary, we had assumed that **5b** results directly from addition of the isocyanate C=N bond onto the S-1 and N-4 atoms of **1a** with elimination of nitrogen (see Figure 1). This reaction path is questionable since it has been refuted already for isothiocyanates [2].

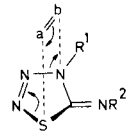


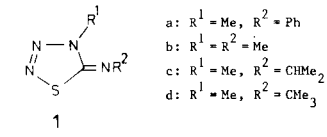
Figure 1

In this paper we will demonstrate that Figure 1 is untenable for isocyanates, but that the sequence **1** → **4** → **5** represents the correct reaction course. Furthermore, evidence will be given that the isomerization of **4** into **5** is not simply a Dimroth rearrangement [4].

Results and Discussion.

The reactions of 4-methyl-5-phenyliminothiatriazoline **1a** with isocyanates (1.0-1.1 equivalents) in chloroform solution at room temperature furnished **5a-g** as the sole reaction products. When these were monitored by ^{1}H nmr spectroscopy, no evidence was found for the presence of **4a-g**, and the following reactivity order was noticed: *t*-BuNCO < *n*-BuNCO < $PhCH_2NCO$ < PhNCO < *p*-$NO_2C_6H_4NCO$.

Phenylsulfonyl isocyanate also combined with **1a** in deuteriochloroform solution at room temperature within 4 minutes, but the methyl singlet of **5h** at δ 3.29 then decreased in intensity in favor of a singlet at δ 3.45 during a period of *ca* 4 days. This process occurred rapidly at 60° and addition of deuterium chloride to the solution converted both signals into a third one at δ 3.1. The reactions were performed on a preparative scale and the products identified as **6** (δ 3.45) and **7** (δ 3.1) on the basis of spectral analyses (see Experimental) and independent synthesis. Thus, thermolysis of **1a** in refluxing toluene yielded 2-methylaminobenzothiazole **8** [5], which was converted into **6** with phenylsulfonyl isocyanate, and into **7** with hydrochloric acid. Furthermore, **6** was easily hydrolyzed to **7**



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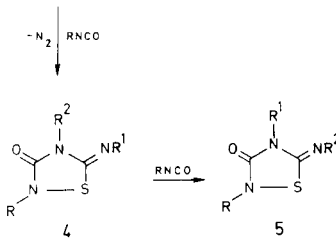
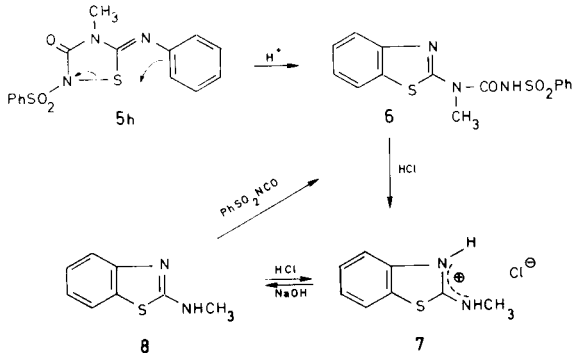


4 5

4/5	R^1	R^2	R
a	Me	Ph	Et
b	Me	Ph	n-Bu
c	Me	Ph	t-Bu
d	Me	Ph	$PhCH_2$
e	Me	Ph	Ph
f	Me	Ph	p-ClC_6H_4
g	Me	Ph	p-$NO_2C_6H_4$
h	Me	Ph	$PhSO_2$
i	Me	Me	$PhCH_2$
j	Me	Me	Ph
k	Me	Me	p-$MeOC_6H_4$
m	Me	Me	p-ClC_6H_4
n	Me	Me	$PhSO_2$
p	Me	$CHMe_2$	Ph
q	Me	$CHMe_2$	$PhSO_2$
r	Me	CMe_3	Ph
s	Me	CMe_3	$PhSO_2$

and then converted back to **8** with a solution of sodium hydroxide. From these experiments, we conclude that the acid present in chloroform catalyzes the isomerization of **5h** to **6** and its further hydrolysis to **7**. A similar rearrangement has already been reported [6].



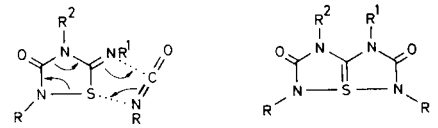
5h 6 8 7

The aforementioned reactivity sequence of isocyanates towards **1a** already militates against Figure 1, where **1a** is expected to react preferentially with nucleophilic partners. Since the reverse is observed, we assume that the reactions occur at the nucleophilic imine function of **1a**, although the resulting primary products **4a-h** have not been detected by nmr. Further evidence against Figure 1 was obtained by varying the bulk of the R^2 substituent. Thus, **1b** reacted with phenyl isocyanate (concentration 0.5 *M* each) at room temperature, whereas **1c** required heating at 60°, and **1d** reacted only very sluggishly at 100° with the formation of many side products. This dramatic steric effect of the R^2 substituent on the rate is not reconcilable with Figure 1, but is in accord with the viewpoint that **1** reacts as a masked 1,3-dipole.

The thiatriazolines **1c,d**, having a bulky R^2 substituent, again led to the thermodynamically more stable products **5p-s**. In one case, however, we were able to isolate the two isomers, **4q** and **5q**. They precipitated as a 1:1 mixture when phenylsulfonyl isocyanate was added to a toluene solution of **1c**. Compound **4q** was purified chromatographically and shown to isomerize instantaneously into **5q** upon addition of phenylsulfonyl isocyanate in chloroform solution.

Further information was obtained when the reaction of **1c** with phenyl isocyanate in deuterated acetonitrile (concentration 0.5 *M* each) was monitored by ^1H nmr spectroscopy. A singlet resonance appeared at δ 3.0 which constituted the major product peak at the early stage of the reaction (25% after 10 minutes), but then decreased in intensity as the reaction progressed. We confidently attribute this signal to the exocyclic methyl protons of **4p** since it lies at the expected position. This observation, and the isolation of **4q**, constitute convincing evidence that **4** is an intermediate in the conversion of **1** to **5**.

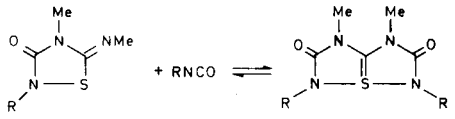
What is the mechanism of the isomerization process **4** → **5**? Is it concerted as shown in Figure 2, or does the reaction proceed *via* a thiapentalene intermediate **9** [7]?



9

Figure 2

This problem was solved when we discovered that **4i-m** (= **5i-m**) equilibrated with **9i-m** in the presence of an excess of isocyanate. Thus, when a chloroform solution of **4i** (= **5i**) (0.25 *M*) was treated with a fivefold excess of benzyl isocyanate, the methyl signals of **4i** at δ 2.9 (R^1) and 3.25 (R^2) decreased in intensity in favor of a singlet absorption at δ 3.7 for **9i**, until an equilibrium concentration of *ca* 25% was reached. Addition of more benzyl isocyanate to the solution further increased the amount of **9i**.



4/5 9 i-n

4/5/9	i	j	k	m	n
R	$PhCH_2$	Ph	p-$MeOC_6H_4$	p-ClC_6H_4	$PhSO_2$

When R = aryl, the presence of a fivefold excess of isocyanate shifted the equilibrium towards **9j-m**, which then partially precipitated from the chloroform or tetrahydrofuran solutions. These thiapentalenes were also observed in the ^{1}H nmr spectra during the reactions of **1b** with equimolar amounts of aryl isocyanates (0.5 *M*) in deuteriochloroform. Their maximum concentration occurred at the early period when a considerable amount of isocyanate was still present. Then, they dissociated as the isocyanate was being consumed. Figure 3 illustrates a typical reaction profile. Thiapentalene **9n** precipitated directly from solution by mixing **1b** with phenylsulfonyl isocyanate in toluene, but it dissociated into **4n** (= **5n**) when dissolved in dimethyl sulfoxide.

Spectral Analysis.

Distinction between the structures **4** and **5** was essentially based on the ^{13}C nmr absorptions of the R^1 and R^2 substituents (Table 1). Thus, a methyl substituent at the N-4 position absorbs at $\delta \sim 30$ with a typical $^1J_{CH}$ coupling constant of 141-142 Hz. When the methyl is attached to the exocyclic imine function, absorptions are found at δ 38-39 with a $^1J_{CH}$ coupling constant of 135-136 Hz. In the ^{1}H nmr spectra, the proton resonances of an endocyclic methyl (usually δ 3.3-3.4) are deshielded compared with those of methylimino protons (δ 2.9-3.05), and this effect is even more pronounced for isopropyl CH proton absorptions (δ 4.55 for **4q** and δ 3.1 for **5q**).

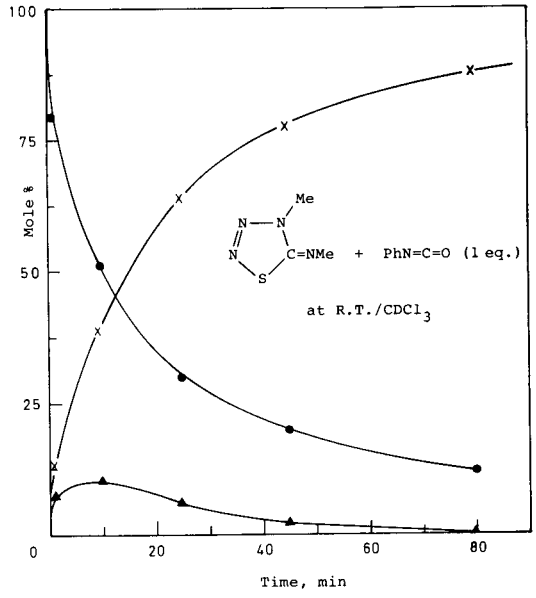


Figure 3. Reaction of **1b** (0.5 *M*) with one equivalent of phenyl isocyanate in deuteriochloroform at room temperature. Relative concentrations of **1b** (●), **4j** (x) and **9j** (▲).

Additional evidence for structures **5a-h** is provided by the phenyl C-resonances at δ 147-149 (C_i), 120-121 (C_o) and 124-125 (C_p) which are diagnostic for a phenylimino substituent [2].

Table 1

Selected NMR Data of the 1,2,4-Thiadiazolidines [a]

Compound	CH_3	$CHMe_2$	CH_3	$CHMe_2$	CMe_3	*N*-phenylimino C_i	C_o	C_p	C-3	C-5
5a	3.35		30.1			148.8	120.9	124.8	154.6	151.5
5b	3.30		30.1			148.9	120.9	124.8	154.8	151.6
5c	3.32		29.5			148.8	121.1	124.5	154.1	151.3
5d	3.40		30.2			148.6	120.8	124.8	154.9	151.1
5e	3.42		30.2			148.5	120.8	125.1	152.5	150.3
5f	3.45		30.3			148.3	120.8	125.2	152.2	149.7
5g	3.45		30.4			148.0	120.7	125.6	152.0	148.3
5h	3.29		30.2			147.2	120.5	125.7	150.6	148.5
5i = 4i	3.25		29.8						155.6	150.5
	2.90		38.7							
5j = 4j	3.35		29.9						153.2	149.3
	3.05		38.7							
5k = 4k	3.30		29.9						153.6	149.7
	3.00		38.7							
5n = 4n	3.10		29.8						151.0	146.8
	3.00		38.3							
5p	3.30	3.1	30.1	55.6					153.1	145.2
4q	2.95	4.55	38.6	48.7					150.9	146.2
5q	3.10	3.10	30.1	55.5					151.0	143.2
5r	3.20		30.0		54.3				152.6	139.3
5s	3.00		29.9		54.8				150.5	137.1

[a] All the spectra (δ-values in ppm from TMS) were recorded in deuteriochloroform. The phenylimino C_m-reonances lie at δ 129.6-129.9.

Table 2
Reaction Conditions and Characterization of the 1,2,4-Thiadiazolidines

Compound	Reaction Temp (°C)	Conditions Time	Yield %	Mp °C	Crystallization Solvent	IR (KBr) C=O	IR (KBr) C=N	Molecular formula	Analysis (Calcd./Found) %C	Analysis (Calcd./Found) %H
5a	20	30 h	61	(oil)	–	1720	1635	$C_{11}H_{13}N_3OS$ (235)	56.15/56.01	557/5.48
5b	20	50 h	95	(oil)	–	1720	1640	$C_{13}H_{17}N_3OS$ (263)	59.29/59.23	6.51/6.48
5c	20	60 h	84	103	chloroform-*n*-hexane	1710	1630	$C_{13}H_{17}N_3OS$ (263)	59.29/59.17	6.51/6.40
5d	20	4 h	75	79	*n*-hexane	1710	1630	$C_{16}H_{15}N_3OS$ (297)	64.62/64.56	5.08/5.13
5e	20	30 min	94	80	chloroform-*n*-hexane	1710	1630	$C_{15}H_{13}N_3OS$ (283)	63.58/63.73	4.62/4.67
5f	0	30 min	71	102	chloroform-*n*-hexane (1:1)	1720	1640	$C_{15}H_{12}ClN_3OS$ (318)	56.69/56.58	3.81/3.69
5g	0	30 min	65	174	chloroform-*n*-hexane (3:1)	1728	1650	$C_{15}H_{12}N_4O_3S$ (328)	54.92/54.71	3.69/3.83
5h	0	< 5 min	40	162	–	1745	1645	$C_{15}H_{13}N_3O_3S_2$ (347)	51.86/51.60	3.77/3.83
5i = 4i	20	overnight	52	57	ether-hexane (6:4)	1710	1650	$C_{11}H_{13}N_3OS$ (235)	56.15/56.24	5.57/5.50
5j = 4j	20	4 h	39	63	ether	1720	1660	$C_{10}H_{11}N_3OS$ (221)	54.28/54.41	5.02/5.06
5k = 4k	20	overnight	38	102	chloroform-ether (1:1)	1715	1655	$C_{11}H_{13}N_3O_2S$ (251)	52.57/52.61	5.22/5.13
5m = 4m	20	6 h	46	114	methanol	1720	1670	$C_{10}H_{10}ClN_3OS$ (255)	47.05/46.87	3.95/3.85
5p	55	10 h	49	59	*n*-hexane-chloroform (4:1)	1725	1655	$C_{12}H_{15}N_3OS$ (249)	57.81/57.74	6.06/6.14
4q	0	< 5 min	15	55	*n*-hexane-ether (8:2)	1750	1660	$C_{12}H_{15}N_3O_3S_2$ (313)	46.00/46.04	4.83/4.82
5q	0	< 5 min	17	63	*n*-hexane-ether (8:2)	1745	1670	$C_{12}H_{15}N_3O_3S_2$ (313)	46.00/45.81	4.83/4.82
5r	100	4 h	7	62	ether-*n*-hexane (1:1)	1720	1650	$C_{13}H_{17}N_3OS$ (263)	59.29/59.23	6.51/6.42
5s	0	15 min	24	74	–	1740	1650	$C_{13}H_{17}N_3O_3S_2$ (327)	47.70/47.70	5.24/5.35

The nmr spectra of **9j-n** were taken from freshly prepared solutions before any appreciable decomposition had occurred. The methyl singlets at δ 3.6-3.9 in the ^1H nmr spectra are deshielded compared with those of **4j-n**. A ^{13}C nmr spectrum of **9m** was recorded in deuterated tetrahydrofuran at $-70°$ and indicated a symmetrical structure with low field absorptions at δ 150.5 (C-2 and C-5) and 166.4 (C-3a), aromatic peaks at δ 124.2, 129.8 (x2) and 138.7, and a methyl resonance at δ 33.0. When this solution, containing 70-75% of **9m** and 25-30% of **4m**, was brought to room temperature, further dissociation happened until **9m** reached an equilibrium concentration of 25-30%. Dissociation of **9** proceeds rapidly in polar solvents such as dimethyl sulfoxide, particularly for **9n** where the resulting phenylsulfonyl isocyanate is removed from the equilibrium by reacting with dimethyl sulfoxide [8].

The mass spectra (EI) of **9j-m** are devoid of molecular ion peaks and show fragmentation patterns corresponding to those of **4j-m**, with this significant difference that the $(RNCO)^{+\cdot}$ fragment peaks are much more intense for **9j-m** (77, 44 and 72%) than for **4j-m** (4, 16 and 7%). In all these spectra, important peaks are found for the radical ions of **4j-m**, and the parent peaks have m/z values attributable to $(RNS)^{+\cdot}$.

EXPERIMENTAL

The thiatriazolines **1a-d** used in this work were prepared by methylation of the corresponding 5-(substituted)aminothiatriazoles with trimethyloxonium tetrafluoroborate according to the procedure of Toubro and Holm [9].

Synthesis of the 1,2,4-thiadiazolidines **5**.

General Procedure.

The thiatriazolines **1a-d** (10 mmoles) were allowed to react with 1.0-1.1 equivalents of isocyanate in 20 ml solvent (chloroform for **5a-g**, ether for **5h**, toluene for **5i-s** and benzene for **5p**) under the conditions given in Table 2. Compounds **5h,k,m**, which precipitated from the reaction mixture, and **5c,d,e,f,i,p**, which were obtained after removal of the solvent, were crystallized from the appropriate solvents (see Table 2). Compound **5k** was first dissolved in dry methanol and filtered to remove impurities, and then crystallized from chloroform-*n*-hexane. The other products were obtained after column chromatography of the crude reaction mixtures on silica gel with chloroform (**5a,s**), chloroform-*n*-hexane (**5b,g**) or chloroform-ethyl acetate (**5j**) as the eluents.

For the synthesis of **5r**, three equivalents of isocyanate were used and the crude reaction mixture was twice chromatographed on silica gel, first with *n*-hexane-chloroform (7:3) and then with carbon tetrachloride-ethyl acetate (9:1) as the eluents.

In the case of **5q**, benzenesulfonyl isocyanate (1.27 g, 6.9 mmoles) was added to a solution of **1c** (1 g, 6.3 mmoles) in dry toluene (13 ml). The precipitate was collected and shown by ^1H nmr to consist of a 1:1 mixture of **4q** and **5q**. These products were separated by column chromatography on silica gel with chloroform-ethyl acetate (95:5) as the eluent.

N-(Benzothiazol-2-yl)-*N*-methyl-*N'*-phenylsulfonylurea (**6**).

This compound was obtained by adding two drops of concentrated hydrochloric acid to a solution of **5h** (0.5 g, 1.44 mmoles) in methanol-chloroform (30 ml, 1:1) at room temperature. After 5 hours, the precipitate was filtered off in 56% yield (0.278 g), mp 162-168°.

This compound was also obtained by reacting **8** (0.2 g, 1.2 mmoles) with phenylsulfonyl isocyanate (0.22 g, 1.2 mmoles) in dry toluene (5 ml) at room temperature. After 15 minutes, the white precipitate was collected in 81% yield (0.35 g); spectral

data: ir (potassium bromide): 2400-3150 (br, NH), 1703 cm^{-1} (s, CO); ^1H nmr (deuteriochloroform): δ 3.45 (s, 3H, CH_3), 7.2-8.3 (m, 10H, ArH + NH); ^{13}C nmr (deuteriochloroform): δ 34.6 (CH_3), 121.1, 121.4, 124.6, 127.3 (benzothiazole CH), 130.5 (C-7a), 128.7, 128.9, 133.8, 139.2 (Ph C-atoms), 149.2, 149.6 (C=O and/or C-3a), 164.6 (C-2).

Anal. Calcd. for $C_{15}H_{13}N_3O_3S_2$ (mol wt 347): C, 51.86; H, 3.77. Found: C, 51.96; H, 3.77.

2-Methylaminobenzothiazole Hydrochloride (**7**).

A solution of **5h** (0.296 g, 0.85 mmole) in chloroform (10 ml), containing a drop of concentrated hydrochloric acid, was heated at 60° for 24 hours. After cooling, the precipitate was filtered off in 66% yield (189 mg).

This compound was also obtained when **6** (0.2 g, 0.6 mmole) in chloroform (20 ml), containing a drop of hydrochloric acid, was stirred at room temperature for 4 hours. The white precipitate was collected in 42% yield (50 mg), mp 180-182°; spectral data: ir (potassium bromide): 2200-3400 (br, NH), 1645 cm^{-1} (s); ^1H nmr (dimethyl sulfoxide-d_6, 250 MHz): δ 3.1 (3H, CH_3), 7.2-8.0 (four m, 4 aromatic H), 10.9 (br, NH); ^{13}C nmr (dimethyl sulfoxide-d_6) δ 32.0 (CH_3), 114.4 (C-4), 122.8 and 123.9 (C-6 and/or C-7), 124.2 (C-7a), 127.2 (C-5), 139.8 (C-3a), 167.4 (C-2). An identical spectrum was obtained when **8** was treated with deuterium chloride.

This compound was further characterized by treatment with an aqueous sodium hydroxide solution, giving **8** in 73% yield.

2,3,4,5-Tetrahydro-6aλ^4-thia-1,3,4,6-tetraazapentalene-2,5-diones **9j-m**.

A solution of **4j-m** (= **5j-m**) (0.8 mmole) and 5 equivalents of isocyanate in dry tetrahydrofuran (5 ml) was stirred at room temperature for 1-4 hours. The white precipitate was collected and analyzed (yields not optimized).

2,3,4,5-Tetrahydro-3,4-dimethyl-1,6-diphenyl-6aλ^4-thia-1,3,4,6-tetraazapentalene-2,5-dione (**9j**).

This compound was obtained in 24% yield (72 mg), mp 124-130°; ir (potassium bromide): 1700 cm^{-1} (br, CO); ^1H nmr (deuteriochloroform): δ 3.85 (s, CH_3); ms (%) m/z 221 (74, $M^{+\cdot}$ -PhNCO), 123 (100, $PhNS^{+\cdot}$), 119 (77, $PhNCO^{+\cdot}$). **Note**: No analytical sample could be obtained since the product dissociates in solution.

2,3,4,5-Tetrahydro-1,6-di(*p*-methoxyphenyl)-3,4-dimethyl-6aλ^4-thia-1,3,4,6-tetraazapentalene-2,5-dione (**9k**).

This compound was obtained in 34% yield (0.11 g), mp 123-127°; ir (potassium bromide): 1700 cm^{-1} (br, CO); ^1H nmr (deuteriochloroform): δ 3.9 (s, CH_3); ms (%) m/z 251 (87, $M^{+\cdot}$ -$MeOC_6H_4NCO$), 153 (100, $MeOC_6H_4NS^{+\cdot}$), 149 (44, $MeOC_6H_4NCO^{+\cdot}$). **Note**: No analytical sample could be obtained since the product dissociates in solution.

2,3,4,5-Tetrahydro-1,6-di(*p*-chlorophenyl)-3,4-dimethyl-6aλ^4-thia-1,3,4,6-tetraazapentalene-2,5-dione (**9m**).

This compound was obtained in 26% yield (95 mg), mp 108-114°; ir (potassium bromide) 1700 and 1720 cm^{-1} (s, CO); ^1H nmr (deuteriochloroform): δ 3.9 (s, CH_3); ms: (%) m/z 255 (67, $M^{+\cdot}$ -ClC_6H_4NCO), 157 (100, $ClC_6H_4NS^{+\cdot}$), 153 (7, $ClC_6H_4NCO^{+\cdot}$).

Anal. Calcd. for $C_{17}H_{14}Cl_2N_4O_2S$ (mol wt 408): C, 50.00; H, 3.46. Found: C, 49.77; H, 3.49.

2,3,4,5-Tetrahydro-3,4-dimethyl-1,6-di(phenylsulfonyl)-6aλ^4-thia-1,3,4,6-tetraazapentalene-2,5-dione (**9n**).

This compound was obtained by reacting **1b** (0.58 g, 5 mmoles) with phenylsulfonyl isocyanate (1.6 g, 10 mmoles) in dry toluene (10 ml) at room temperature. The precipitate was collected in 91% yield (1.2 g), mp 130-133°; ir (potassium bromide): 1720 cm^{-1} (br, CO); ^1H nmr (dimethyl sulfoxide-d_6): δ 3.6 (s, CH_3); ms: 285 (24, $M^{+\cdot}$ -$PhSO_2NCO$), 183 (14, $PhSO_2NCO^{+\cdot}$).

Anal. Calcd. for $C_{17}H_{16}N_4O_6S_3$ (mol wt 468): C, 43.59; H, 3.45. Found: C, 43.67; H, 3.41.

4-Methyl-5-methylimino-2-phenylsulfonyl-1,2,4-thiadiazolidin-3-one (**4n** = **5n**).

Compound **9n** (0.5 g, 1 mmole) was stirred in dimethyl sulfoxide (10 ml) at room temperature for 30 minutes. Upon addition of water (10 ml) **4n** (= **5n**) precipitated in 57% yield (0.16 g), mp 114-116° (dichloromethane-ether, 6:4); ir (potassium bromide): 1735 (s, CO), 1660 cm^{-1} (s, C=N); ^1H nmr and ^{13}C nmr: see Table 1.

Anal. Calcd. for $C_{10}H_{11}N_3O_3S_2$ (mol wt 285): C, 42.10; H, 3.89. Found: C, 42.01; H, 3.83.

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