

# 5-Imino- $\Delta^3$ -1,2,4-thiadiazoline Derivatives with a Linear N-S...O Grouping. Synthesis and Crystal Structures

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Received February 25, 1981

A series of carbonyl derivatives of 5-imino- $\Delta^3$ -1,2,4-thiadiazolines has been prepared and shown by X-ray analysis of a selected example to have a trithiapentalene-like structure. When diphenylketene was used as acylating reagent, the primary product (**14**), obtained at room temperature, rearranged on heating in a polar solvent into a  $\Delta^2$ -thiazolin-4-one (**15**). The structure of **15** has been confirmed by X-ray analysis, and shown to be a zwitterion. Rearranged products (i.e., **16** and **20-22**) were also obtained when **3** was reacted with dimethyl acetylenedicarboxylate or methanesulfonyl chloride, whereas tosyl chloride gave normal tosylated derivatives (**17-19**). The latter have also a nearly linear N-S...O arrangement, but the interaction between S and O is weak.

*J. Heterocyclic Chem.*, **18**, 1309 (1981).

A number of trithiapentalene analogues of types **1** and **2** have been reported which exhibit single-bond/no-bond resonance properties (1).



**1** (X = S, O, NR)



**2** (X = S, O, NR)

The best known representatives are the  $\alpha$ -(1,2-dithiol-3-ylidene) carbonyl compounds **1** (X = S). Some examples of **1** and **2** with X other than S are also known (2,3). For instance, the symmetrical 1,6-dioxo-6a $\lambda^4$ -thia-3,4-diazapentalenes **2** (X = O) were recently obtained by reacting 5-amino-1,2,3,4-thiaziazole with acyl chlorides (3). When imidoyl chlorides were used instead of acyl chlorides, the salts of 5-(unsubstituted)imino- $\Delta^3$ -1,2,4-thiadiazolines **3** were formed. This has led to the present synthesis of a number of carbonyl derivatives of type **2** (X = NR) as well as sulfonyl derivatives and to examine their N-S...O bonding nature.

From **3a-c** we have prepared compounds **4-14** by treatment with a variety of acylating reagents. These include acyl chlorides (derivatives **4-7**, **11**), isocyanates (derivatives **12**, **13**), diphenylketene (derivative **14**) and even carbonyl isothiocyanates (derivatives **8-10**) which eliminate HNCS during the substitutions. The reactions occurred in the presence of triethylamine or pyridine as base, and could be carried out equally well with the salts **3** or the free bases derived from them. For instance, compounds **4**, **5**, **13** and **14** were isolated from the corresponding free bases in yields of 99, 77, 63 and 47% respectively.

### Reaction products



	R <sup>1</sup>	R <sup>2</sup>		R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>
<b>a</b>	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	<b>4</b>	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>
<b>b</b>	p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	(CH <sub>3</sub> ) <sub>2</sub> CH	<b>5</b>	p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	(CH <sub>3</sub> ) <sub>2</sub> CH	C <sub>6</sub> H <sub>5</sub>
<b>c</b>	CH <sub>3</sub>	p-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	<b>6</b>	p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	(CH <sub>3</sub> ) <sub>2</sub> CH	CH <sub>3</sub>
			<b>7</b>	p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	(CH <sub>3</sub> ) <sub>2</sub> CH	(CH <sub>3</sub> ) <sub>2</sub> CH
			<b>8</b>	p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	(CH <sub>3</sub> ) <sub>2</sub> CH	OC <sub>2</sub> H <sub>5</sub>
			<b>9</b>	CH <sub>3</sub>	p-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	p-ClC <sub>6</sub> H <sub>4</sub>
			<b>10</b>	CH <sub>3</sub>	p-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	OC <sub>2</sub> H <sub>5</sub>
			<b>11</b>	CH <sub>3</sub>	p-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>
			<b>12</b>	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub> NH
			<b>13</b>	CH <sub>3</sub>	p-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>5</sub> NH
			<b>14</b>	CH <sub>3</sub>	p-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CH

The results obtained when using the salts are listed in Table 1. The lower yields obtained in some cases result from competitive base-induced decomposition of **3** into *N*-cyanoamidines (R<sup>1</sup>NH-(R<sup>2</sup>)C=N-CN and sulfur (3) as well as from loss of material during the isolation procedure. The solid state ir spectra of **4-14** are devoid of normal C=O stretching vibrations above 1630 cm<sup>-1</sup>. Instead, strong absorptions are observed at 1510-1540 cm<sup>-1</sup> for **4-7** and at 1585-1610 cm<sup>-1</sup> for **8-14**. This indicates that the geometry of the side chain backbone is the same as found in  $\alpha$ -(1,2-dithiol-3-ylidene) carbonyl compounds **1** (X = S) and that some kind of interaction exists between oxygen and sulfur (1). The pertinent <sup>13</sup>C nmr data are summarized in Table 1 and the other spectral data are recorded in the Experimental.

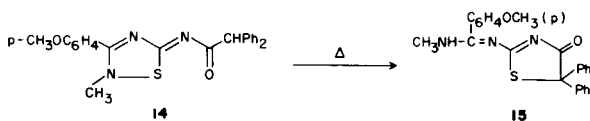
The reaction of **3c** with diphenylketene is of particular interest since it yields **14** under mild conditions (room temperature) and the thiazolinone **15** under more drastic conditions (refluxing pyridine). We have verified that the kinetic product **14** isomerizes into the thermodynamically

Table I  
Characterization of the Thiadiazoline Derivatives (a)

Compound	Yield %	Mp °C	<sup>13</sup> C NMR (b)			
			C3	C5	C=O	Other shift values
<b>4</b>	84	204-205	163.9	181.7	179	
<b>5</b>	63	235-236				
<b>6</b>	31	105-107	173.7	181.5	184.5	(CH <sub>3</sub> ) <sub>2</sub> C at 21 and 28.8, CH <sub>3</sub> CO at 24
<b>7</b>	80	114-115	173.6	181.8	191	(CH <sub>3</sub> ) <sub>2</sub> C at 21 and 28.8, (CH <sub>3</sub> ) <sub>2</sub> CHCO at 19.6 and 36.3
<b>8</b>	68	103-105				
<b>9</b>	97	211-214	165.5	180.3	177.4	CH <sub>3</sub> N at 34.8 ( <sup>1</sup> J <sub>CH</sub> = 142.3 Hz), CH <sub>3</sub> O at 55.6
<b>10</b>	42	137-139				
<b>11</b>	93	174-176				
<b>12</b>	96	247-249				
<b>13</b>	92	218-221	166.2	(c)	165	CH <sub>3</sub> N at 34.7 (or 34.2), CH <sub>3</sub> CH <sub>2</sub> N at 14.9 and 34.2 (or 34.7)
<b>14</b>	65-78	176-177	165.3	179.9	185.3	CH <sub>3</sub> N at 34.6 ( <sup>1</sup> J <sub>CH</sub> = 141.9 Hz), CH <sub>3</sub> O at 55.7, CHPh <sub>2</sub> at 60.1 ( <sup>1</sup> J <sub>CH</sub> = 130 Hz)
<b>17</b>	89	197-200	166	177.2		
<b>18</b>	54	170-172	175.8	177.9		(CH <sub>3</sub> ) <sub>2</sub> C at 20.8 and 28.4
<b>19</b>	50	134-136	167.7	176.5		CH <sub>3</sub> N at 36.4 ( <sup>1</sup> J <sub>CH</sub> = 143.9 Hz)

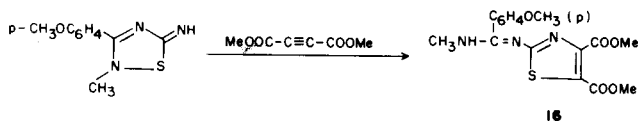
(a) The numbering system is in accordance with the monocyclic representation of the compounds. (b) All the spectra ( $\delta$  values in ppm from TMS) were recorded in deuteriochloroform except that of **13** (Me<sub>2</sub>SO-d<sub>6</sub>). (c) Not observed.

more stable **15** when heated in a polar solvent such as pyridine or acetonitrile. The proposed structure of **15**

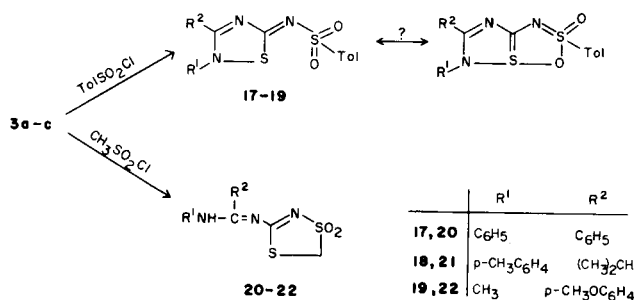


is strongly supported by the characteristic N-CH<sub>3</sub> doublet resonance at  $\delta$  3.2 in the <sup>1</sup>H nmr spectrum, and by the mass spectrum which shows significant fragment peaks at m/e 217 and 198 attributable to M<sup>+</sup>-Ph<sub>2</sub>C=S and Ph<sub>2</sub>C=S<sup>+</sup> respectively.

A similar ring transformation was observed when the free base of **3c** was treated with dimethyl acetylenedicarboxylate, yielding **16**.



In order to examine the ability of the sulfonyl group to engage in bonding interaction with the sulfur atom, we have also converted **3a-c** into the tosylated derivatives **17-19** (Table 1). Methanesulfonyl chloride and **3a-c** reacted by a different path to give the 1,4,3-dithiazoline 4,4-dioxides **20-22**. This is not unexpected in view of the



acidity of the methyl group in the  $\alpha$ -position of the sulfonyl function. Whether these reactions proceed in a similar manner to the sequence **3c**  $\rightarrow$  **14**  $\rightarrow$  **15** or directly via a sulfene intermediate (**4**) has not been established.

The compounds **20-22** manifest a series of broad strong absorptions in the region 1500-1600 cm<sup>-1</sup> in the solid state ir spectra. The <sup>1</sup>H nmr spectrum of **22** exhibits a doublet absorption at  $\delta$  2.90 for the NCH<sub>3</sub> protons, thus contributing to its structure elucidation. The <sup>13</sup>C nmr data (Table 2) and other spectral data (Experimental) are also in agreement with the structure assignment.

#### Crystal Structure Analyses.

Confirmation of structure **15** was obtained by a single crystal X-ray analysis (Fig 1). The thiazoline ring adopts an envelope conformation with C<sub>5</sub> located 0.39 Å out of

Table 2  
Characterization of the Rearranged Products

Compound	Yield %	Mp °C	<sup>13</sup> C NMR (a)				Other shift values
			C2	C4	C5		
<b>15</b>	64	232-233	184.1	189.1	77.5	CH <sub>3</sub> NHC=N at 30 and 166.8	
<b>16</b>	34	144-146		147.2 (b) 147.9	118.9 (b) 120.5	CH <sub>3</sub> NHC=N (b) at 29.3/33 and 161.7/164/7	
<b>20</b>	47	197-199	170.7		51.6	NHC=N at 161.8	
<b>21</b>	33	163-166	171.7		49.5	(CH <sub>3</sub> ) <sub>2</sub> C at 20.4 and 31.0, NHC=N at 176.2	
<b>22</b>	20	218-220	168.3		51.5	CH <sub>3</sub> O at 55.4; CH <sub>3</sub> NHC=N at 29.7 and 162.3 or 166.2	

(a) The spectra ( $\delta$  values in ppm) were recorded in deuteriochloroform (**16**, **21**) or DMSO-*d*<sub>6</sub> (**15**, **20**, **22**). (b) Signals dedoubled at  $-40^\circ$  probably due to conformational isomerism.

the plane defined by the four other atoms. An examination of the bond lengths N<sub>3</sub>-C<sub>2</sub> (1.34 Å), C<sub>2</sub>-N<sub>6</sub> (1.30 Å), N<sub>6</sub>-C<sub>7</sub> (1.36 Å) and C<sub>7</sub>-N<sub>8</sub> (1.31 Å), as well as the dihedral angle C<sub>2</sub>-N<sub>6</sub>-C<sub>7</sub>-N<sub>8</sub> ( $-128^\circ$ ), clearly indicates the presence of a zwitterionic structure (**5**) as shown below.

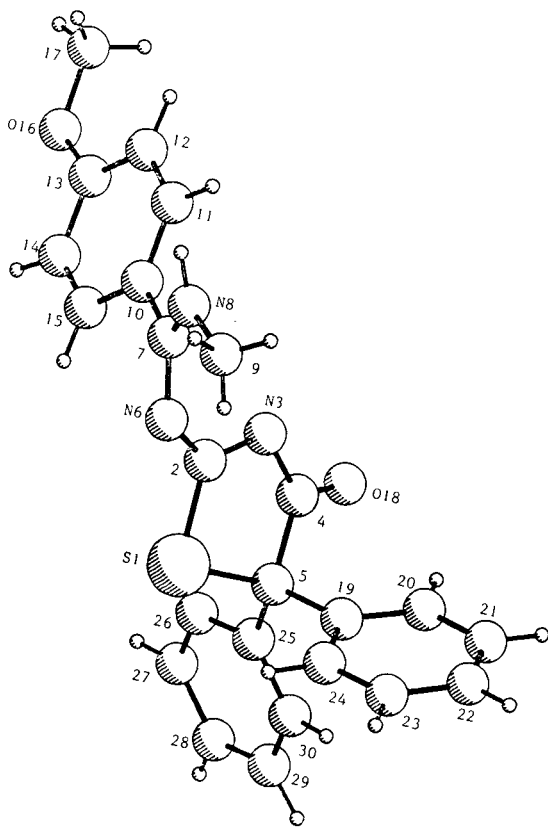
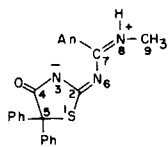


Figure 1. Molecular structure of **15** with numbering scheme



The exocyclic C=O bond length (1.22 Å) is normal. The molecules in the crystal are linked by N<sub>8</sub>'-H...N<sub>3</sub> hydrogen bonds: N<sub>3</sub>-N<sub>8</sub>' = 2.87 Å, N<sub>3</sub>-H<sub>8</sub>' = 1.99 Å, N<sub>3</sub>-H<sub>8</sub>'-N<sub>8</sub>' =  $168^\circ$ .

We have also determined the crystal structures of the two thiadiazolinimine derivatives **13** and **19** (Figures 2 and 3) in order to study the bonding interaction between oxygen and sulfur. For structure **13**, the thiadiazoliniminocarbonyl system is almost planar (see Table 3), while the benene ring is twisted  $37^\circ$  out of this plane. The short S...O contact distance (2.29 Å), together with the long N-S (1.74 Å) and C=O (1.26 Å) bonds indicate a fairly strong S...O bonding interaction, analogous to that in similar systems (2). The angle N<sub>2</sub>-S<sub>1</sub>...O<sub>20</sub> is  $166^\circ$ . The molecules are linked in pairs across a center of symmetry by hydrogen bonds from N<sub>17</sub> to N<sub>15</sub>': N<sub>17</sub>-N<sub>15</sub>' = 2.97 Å, H<sub>17</sub>-N<sub>15</sub>' = 2.08 Å.

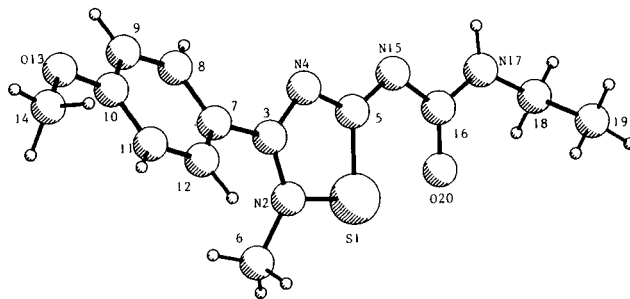


Figure 2. Molecular structure of **13** with numbering scheme

In compound **19**, the N<sub>2</sub>-S<sub>2</sub>...O<sub>17</sub> atoms are located in a nearly linear arrangement ( $168^\circ$ ). However, the deviations from planarity of the thiadiazoliniminosulfonyl system are larger than in **13** (see Table 3). The S...O contact distance (2.51 Å) is larger than in **13** and is only slightly less than the Huggins constant energy distance of 2.58 Å (6), suggesting little bonding interaction between S<sub>1</sub> and O<sub>17</sub> (7).

Table 3

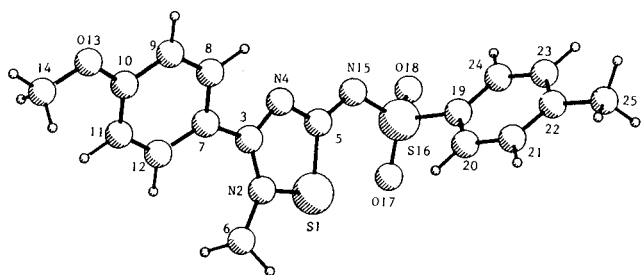
Deviations from the Least-squares Plane Through the Atoms Marked\*  
(The equation of the planes are for **13**:  $-8.6170x + 2.7247y + 9.2825z = 0.0956$ ; for **19**:  $8.5287x + 0.5757y + 7.6415z = 2.9759$ )

Compound <b>13</b>		Compound <b>19</b>	
Atom	Distance (Å)	Atom	Distance (Å)
*S1	-0.004	*S1	-0.021
*N2	0.006	*N2	0.020
*C3	-0.007	*C3	-0.008
*N4	0.002	*N4	-0.013
*C5	0.002	*C5	0.022
N15	0.003	N15	0.036
C16	-0.015	S16	0.159
O20	-0.029	O17	-0.073

Table 4

## Crystal Data

	C <sub>15</sub> H <sub>16</sub> N <sub>4</sub> O <sub>2</sub> S Compound <b>13</b>	C <sub>22</sub> H <sub>21</sub> N <sub>3</sub> O <sub>2</sub> S Compound <b>15</b>	C <sub>17</sub> H <sub>17</sub> N <sub>3</sub> O <sub>3</sub> S <sub>2</sub> Compound <b>19</b>
M	292.36	415.52	375.47
a	14.115(5) Å	21.077(7) Å	14.316(3) Å
b	10.530(5) Å	7.642(2) Å	12.303(2) Å
c	10.252(4) Å	13.906(3) Å	10.090(2) Å
β	108.82(3)°	105.85(2)°	94.09(2)°
V	1442.3(16) Å <sup>3</sup>	2154.6(10) Å <sup>3</sup>	1772.7(6) Å <sup>3</sup>
Z	4	4	4
F(000)	616	872	784
D <sub>m</sub>	1.32(2) g cm <sup>-3</sup>	1.28(1) g cm <sup>-3</sup>	1.41(1) g cm <sup>-3</sup>
D <sub>c</sub>	1.346 g cm <sup>-3</sup>	1.281 g cm <sup>-3</sup>	1.407 g cm <sup>-3</sup>
μ (MoKα)	2.32 cm <sup>-1</sup>	1.77 cm <sup>-1</sup>	3.18 cm <sup>-1</sup>
Space group	P 2 <sub>1</sub> /a	P 2 <sub>1</sub> /a	P 2 <sub>1</sub> /c

Figure 3. Molecular structure of **19** with numbering scheme

In addition, no difference in bond lengths is found between S<sub>16</sub>-O<sub>17</sub> and S<sub>16</sub>-O<sub>18</sub> (1.45 Å). In the crystal, the anisyl and tolyl rings are twisted 24° and 82° respectively out of the plane of the thiadiazoliniminosulfonyl system.

## EXPERIMENTAL

Reactions of **3** with Acyl Chlorides and Acyl Isothiocyanates.

Triethylamine (1-2 equivalents) was added dropwise with stirring to an ice-cooled suspension of **3** (2.5 mmoles) and acyl chloride (2.5 mmoles) in acetonitrile or tetrahydrofuran (20 ml). After being refluxed for 1 hour,

the solution was poured into ice-water and the precipitate (or oil) was collected. It was dissolved in chloroform, in some cases washed with an aqueous NaOH solution, dried over sodium sulfate (or magnesium sulfate) and evaporated.

For the synthesis of **4**, **6** and **11** the reaction was carried out with 10-15 ml of pyridine as base and in the absence of solvent. Compounds **8**, **9** and **10** were similarly obtained from **3b,c** and the corresponding acyl isothiocyanate in pyridine (10-15 ml) at room temperature for 1 week.

5-Benzoylimino-2,3-diphenyl-Δ<sup>3</sup>-1,2,4-thiadiazoline (**4**).

This compound was crystallized from carbon tetrachloride-hexane; ir (potassium bromide): 1525 (s); 1330 cm<sup>-1</sup> (s); <sup>1</sup>H nmr (deuteriochloroform): δ 7.16-7.72 (m, 13H), 8.32-8.52 (m, 2H); ms: m/e (relative intensity) 357 (29, M<sup>+</sup>), 180 (9, PhC≡N<sup>+</sup>Ph), 119 (22, PhNCO<sup>+</sup>), 117 (24, PhNCN<sup>+</sup>), 105 (100, PhCO<sup>+</sup>).

Anal. Calcd. for C<sub>21</sub>H<sub>15</sub>N<sub>3</sub>OS (357): C, 70.57; H, 4.23. Found: C, 70.44; H, 4.26.

5-Benzoylimino-3-isopropyl-2-(p-tolyl)-Δ<sup>3</sup>-1,2,4-thiadiazoline (**5**).

This compound was crystallized from chloroform-methanol; ir (potassium bromide): 1510 (s br), 1340 cm<sup>-1</sup> (s br); <sup>1</sup>H nmr (deuteriochloroform): δ 1.25 (d, 6H), 2.25 (s, 3H), 3.04 (sept, 1H), 7.1-7.6 and 8.3-8.5 (two m, 9H); ms m/e (relative intensity) 337 (46, M<sup>+</sup>), 294 (11, M<sup>+</sup>-Me<sub>2</sub>CH), 260 (20, M<sup>+</sup>-Ph), 105 (100, PhCO<sup>+</sup>), 77 (33, Ph<sup>+</sup>).

Anal. Calcd. for C<sub>19</sub>H<sub>19</sub>N<sub>3</sub>OS (337): C, 67.63; H, 5.68. Found: C, 67.64; H, 5.64.

5-Acetylimino-3-isopropyl-2-(p-tolyl)-Δ<sup>3</sup>-1,2,4-thiadiazoline (**6**).

This compound was purified by column chromatography on silica gel with carbon tetrachloride-ethyl acetate as the eluent and crystallized from hexane; ir (potassium bromide): 1540 (m), 1330 and 1320 cm<sup>-1</sup> (s); <sup>1</sup>H nmr (deuteriochloroform): δ 1.30 (d, 6H), 2.43 (s, 6H), 2.98 (sept, 1H), 7.1-7.4 (m, 4H); ms: m/e (relative intensity) 275 (94, M<sup>+</sup>), 260 (100, M<sup>+</sup>-Me), 233 (13, M<sup>+</sup>-MeCH=CH<sub>2</sub>), 158 (10, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>N=C=N-C≡NH<sup>+</sup>), 138 (67, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>NSH<sup>+</sup>), 118 (10, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>NCH<sup>+</sup>), 106 (10, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>NH<sup>+</sup>), 91 (10, C<sub>7</sub>H<sub>7</sub><sup>+</sup>).

Anal. Calcd. for C<sub>14</sub>H<sub>17</sub>N<sub>3</sub>OS (275): C, 61.06; H, 6.22. Found: C, 61.22; H, 6.38.

5-Isobutyrylimino-3-isopropyl-2-(p-tolyl)-Δ<sup>3</sup>-1,2,4-thiadiazoline (**7**).

This compound was crystallized from hexane; ir (potassium bromide): 1530 (s), 1360 cm<sup>-1</sup> (s br); <sup>1</sup>H nmr (deuteriochloroform): δ 1.32 (d, 12H), 2.45 (s, 3H), 2.97-3.01 (m, 2H), 7.1-7.5 (m, 4H); ms: m/e (relative intensity) 303 (15, M<sup>+</sup>), 260 (100, M<sup>+</sup>-Me<sub>2</sub>CH), 137 (8, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>NS<sup>+</sup>) 91 (8, C<sub>7</sub>H<sub>7</sub><sup>+</sup>).

Anal. Calcd. for C<sub>16</sub>H<sub>21</sub>N<sub>3</sub>OS (303): C, 63.33; H, 6.97. Found: C, 63.26; H, 6.82.

5-Carboxyimino-3-isopropyl-2-(p-tolyl)-Δ<sup>3</sup>-1,2,4-thiadiazoline (**8**).

This compound had ir (potassium bromide): 1595 (s), 1315 cm<sup>-1</sup> (s br); <sup>1</sup>H nmr (deuteriochloroform): δ 1.2-1.5 (m, 9H), 2.54 (s, 3H), 3.0 (sept, 1H), 4.52 (q, 2H), 7.3-7.6 (m, 4H); ms: m/e (relative intensity) 305 (44, M<sup>+</sup>), 260 (25, M<sup>+</sup>-OEt), 233 (59, M<sup>+</sup>-COOEt), 164 (14, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>NHSCN<sup>+</sup>), 160 (40, Me<sub>2</sub>CHC≡NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 137 (100, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>NS<sup>+</sup>), 118 (10, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>NCH<sup>+</sup>), 106 (11, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>NH<sup>+</sup>), 91 (41, C<sub>7</sub>H<sub>7</sub><sup>+</sup>).

Anal. Calcd. for C<sub>15</sub>H<sub>19</sub>N<sub>3</sub>O<sub>2</sub>S (305): C, 58.99; H, 6.27. Found: C, 58.89; H, 6.19.

5-(p-Chlorobenzoylimino)-3-(p-methoxyphenyl)-2-methyl-Δ<sup>3</sup>-1,2,4-thiadiazoline (**9**).

This compound had ir (potassium bromide): 1610 (s), 1340 cm<sup>-1</sup> (s br); <sup>1</sup>H nmr (deuteriochloroform): δ 3.71 (s, 3H, CH<sub>3</sub>), 3.82 (s, 3H, OCH<sub>3</sub>), 6.97, 7.40, 7.78, 8.31 (four d, 8H); ms: m/e (relative intensity) 359 (35, M<sup>+</sup>), 248 (10, M<sup>+</sup>-ClC<sub>6</sub>H<sub>4</sub>), 148 (10, CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>C≡NC<sub>6</sub>H<sub>4</sub>), 141 (35), 139 (100, ClC<sub>6</sub>H<sub>4</sub>CO<sup>+</sup>), 111 (20, ClC<sub>6</sub>H<sub>4</sub><sup>+</sup>).

Anal. Calcd. for C<sub>17</sub>H<sub>14</sub>ClN<sub>3</sub>O<sub>2</sub>S (360): C, 56.74; H, 3.92. Found: C, 56.59; H, 3.89.

Table 5

## Structure Determination Parameters

Compound	C <sub>13</sub> H <sub>16</sub> N <sub>4</sub> O <sub>2</sub> S	C <sub>24</sub> H <sub>21</sub> N <sub>3</sub> O <sub>2</sub> S	C <sub>17</sub> H <sub>17</sub> N <sub>3</sub> O <sub>3</sub> S <sub>2</sub>
Crystal size	0.20 × 0.16 × 0.22 mm	0.25 × 0.40 × 0.30 mm	0.40 × 0.27 × 0.18 mm
Independent reflexions	2703	3785	2320
Threshold for "less than"	3.0	2.0	3.0
Observed reflexions	1138	2773	1618
Structure solved using	MULTAN (9)	SINGEN & PHASE	SINGEN & PHASE (8)
Hydrogens	refined	refined	included but not refined
Final R (observed only)	0.038	0.041	0.053
Final R (all reflexions)	0.103	0.067	0.078

Table 6

Atomic Coordinates (x 10<sup>4</sup>) of Non-hydrogen Atoms with Standard Deviations in Parentheses

Atom	Compound 13			Atom	Compound 15			Atom	Compound 19		
	x	y	z		x	y	z		x	y	z
S1	4779(1)	3927(1)	3383(1)	S1	6826(0)	-55(1)	1481(0)	S1	1714(1)	1862(2)	1814(2)
N2	3626(2)	4327(3)	2205(3)	C2	6977(1)	-26(3)	2797(1)	N2	851(4)	1624(5)	2847(6)
C3	2995(3)	3335(4)	1899(4)	N3	6801(1)	1444(2)	3182(1)	C3	436(5)	2550(7)	3206(8)
N4	3346(2)	2250(3)	2551(3)	C4	6561(1)	2693(3)	2470(1)	N4	799(4)	3468(5)	2724(6)
C5	4303(3)	2384(4)	3400(4)	C5	6691(1)	2322(2)	1432(1)	C5	1516(5)	3278(6)	1984(8)
C6	3449(4)	5671(5)	1823(7)	N6	7266(1)	-1401(2)	3274(1)	C6	712(6)	496(6)	3307(8)
C7	1967(3)	3407(4)	949(4)	C7	7309(1)	-1724(2)	4248(1)	C7	-355(6)	2611(6)	4057(8)
C8	1223(3)	2694(4)	1218(5)	N8	7893(1)	-2060(2)	4849(1)	C8	-466(6)	3582(6)	4768(8)
C9	251(3)	2726(4)	332(5)	C9	8502(1)	-1838(5)	4568(3)	C9	-1209(6)	3724(7)	5552(8)
C10	14(3)	3431(4)	-867(4)	C10	6724(1)	-1876(3)	4625(1)	C10	-1861(6)	2899(7)	5678(8)
C11	744(4)	4130(4)	-1165(5)	C11	6760(1)	-1541(3)	5620(2)	C11	-1768(6)	1942(7)	4988(9)
C12	1718(3)	4110(4)	-255(4)	C12	6216(1)	-1704(3)	5981(2)	C12	-1039(6)	1788(6)	4192(8)
O13	-962(2)	3390(3)	-1696(3)	C13	5618(1)	-2206(3)	5343(2)	O13	-2551(4)	3127(5)	6488(6)
C14	-1211(4)	4088(6)	-2958(6)	C14	5576(1)	-2535(4)	4343(2)	C14	-3218(8)	2316(9)	6706(12)
N15	4823(2)	1458(3)	4155(3)	C15	6116(1)	-2368(3)	3988(2)	N15	1972(4)	4076(5)	1433(6)
C16	5780(3)	1802(4)	4924(4)	O16	5053(1)	-2419(3)	5619(1)	S16	2857(2)	3791(2)	628(2)
N17	6324(3)	873(4)	5688(4)	C17	5071(2)	-2115(9)	6641(3)	O17	2905(4)	2634(5)	358(6)
C18	7366(3)	1018(5)	6533(5)	O18	6296(1)	4042(2)	2625(1)	O18	2868(4)	4515(5)	-501(5)
C19	8078(4)	1041(7)	5709(7)	C19	7327(1)	3296(3)	1410(1)	C19	3846(5)	4123(6)	1701(8)
O20	6114(2)	2903(2)	4896(3)	C20	7433(1)	5014(3)	1750(2)	C20	4110(6)	3452(7)	2761(10)
				C21	7997(1)	5895(4)	1714(2)	C21	4903(6)	3715(8)	3559(9)
				C22	8468(1)	5106(4)	1346(2)	C22	5446(6)	4593(8)	3322(11)
				C23	8363(1)	3418(4)	991(2)	C23	5165(8)	5243(8)	2266(12)
				C24	7800(1)	2528(3)	1021(2)	C24	4382(7)	5015(7)	1457(10)
				C25	6098(1)	2790(3)	553(1)	C25	6325(7)	4838(8)	4155(12)
				C26	5484(1)	2108(3)	516(2)				
				C27	4944(1)	2474(4)	-297(2)				
				C28	5015(2)	3520(4)	-1061(2)				
				C29	5616(2)	4190(4)	-1022(2)				
				C30	6159(1)	3842(3)	-219(2)				

5-Carbethoxyimino-3-(*p*-methoxyphenyl)-2-methyl- $\Delta^3$ -1,2,4-thiadiazoline (10).

This compound was crystallized from chloroform-hexane; ir (potassium bromide): 1610 and 1600 (s), 1365 (s), 1315 cm<sup>-1</sup> (s br); <sup>1</sup>H nmr (deuteriochloroform):  $\delta$  1.37 (t, 3H), 3.75 (s, 3H), 3.89 (s, 3H, OCH<sub>3</sub>), 4.34 (q, CH<sub>2</sub>), 7.0 and 8.7 (two d, 4H); ms: m/e (relative intensity) 293 (80, M<sup>+</sup>),

248 (16, M<sup>+</sup> - OEt), 221 (90, M<sup>+</sup> - CH<sub>2</sub>=CH<sub>2</sub> - CO<sub>2</sub>), 165 (9, CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>CNS<sup>+</sup>), 159 (34, CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>C(NC)=N<sup>+</sup>), 148 (34, CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>C≡NCH<sub>3</sub>), 134 (100, CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>C≡N<sup>+</sup>), 133 (32, CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>CN<sup>+</sup>).

Anal. Calcd. for C<sub>13</sub>H<sub>15</sub>N<sub>3</sub>O<sub>3</sub>S (293): C, 53.23; H, 5.15. Found: C, 57.37; H, 5.16.

Table 7

Bond Lengths (Å) with Standard Deviations in Parentheses

Compound 13		Compound 15		Compound 19	
S1-N2	1.736(3)	S1-C2	1.770(2)	S1-N2	1.698(7)
S1-C5	1.760(4)	S1-C5	1.837(2)	N2-C3	1.347(10)
N2-C3	1.343(5)	C2-N3	1.339(3)	N2-C6	1.481(9)
N2-C6	1.468(6)	C2-N6	1.302(3)	C3-N4	1.348(10)
C3-N4	1.335(5)	N3-C4	1.370(2)	C3-C7	1.471(11)
C3-C7	1.466(5)	C4-C5	1.566(3)	N4-C5	1.333(10)
N4-C5	1.358(5)	C4-O18	1.220(3)	C5-S1	1.776(8)
C5-N15	1.312(5)	C5-C19	1.541(3)	C5-N15	1.323(10)
C7-C8	1.388(7)	C5-C25	1.532(3)	C7-C8	1.408(11)
C7-C12	1.384(6)	N6-C7	1.355(3)	C8-C9	1.381(12)
C8-C9	1.380(6)	C7-N8	1.310(3)	C9-C10	1.391(12)
C9-C10	1.381(6)	C7-C10	1.472(3)	C10-C11	1.379(12)
C10-C11	1.379(7)	N8-C9	1.450(4)	C10-O13	1.357(11)
C10-O13	1.366(5)	C10-C11	1.388(3)	C11-C12	1.374(12)
C11-C12	1.391(6)	C10-C15	1.397(3)	C12-C7	1.421(11)
O13-C14	1.430(6)	C11-C12	1.376(4)	O13-C14	1.409(13)
N15-C16	1.375(5)	C12-C13	1.383(3)	N15-S16	1.591(7)
C16-N17	1.331(5)	C13-C14	1.393(4)	S16-O17	1.452(6)
C16-O20	1.256(5)	C13-O16	1.357(3)	S16-O18	1.447(6)
N17-C18	1.454(5)	C14-C15	1.365(4)	S16-C19	1.767(8)
C18-C19	1.507(9)	O16-C17	1.431(5)	C19-C20	1.383(12)
S1-O20	2.288(3)	C19-C20	1.392(3)	C20-C21	1.382(13)
		C19-C24	1.388(4)	C21-C22	1.362(14)
		C20-C21	1.380(4)	C22-C23	1.369(15)
		C21-C22	1.375(4)	C22-C25	1.493(14)
		C22-C23	1.377(4)	C23-C24	1.368(15)
		C23-C24	1.378(4)	C24-C19	1.372(12)
		C25-C26	1.383(4)	S1-O17	2.514(6)
		C25-C30	1.375(3)		
		C26-C27	1.397(4)		
		C27-C28	1.371(5)		
		C28-C29	1.352(5)		
		C29-C30	1.390(4)		

5-Benzoylimino-3-(*p*-methoxyphenyl)-2-methyl- $\Delta^3$ -1,2,4-thiadiazoline (**11**).

This compound was crystallized from methanol; ir (potassium bromide): 1610 (s), 1340  $\text{cm}^{-1}$  (s br);  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  3.79 (s, 3H), 3.90 (s, 3H, OCH<sub>3</sub>), 6.9-8.4 (four m, 9H); ms: m/e (relative intensity) 325 (19, M<sup>+</sup>), 105 (100, PhCO<sup>+</sup>).

*Anal.* Calcd. for C<sub>17</sub>H<sub>15</sub>N<sub>3</sub>O<sub>2</sub>S (325): C, 62.75; H, 4.65. Found: C, 62.81; H, 4.75.

Reactions of **3** with Isocyanates.

One equivalent of triethylamine in 10 ml of dry acetonitrile was added dropwise to an equimolar mixture of **3a** and ethyl isocyanate (2 mmoles). The suspension was stirred at room temperature for three days and then poured into water. The precipitate **12** was filtered off and dried. In the case of **13**, the reaction was carried out in the absence of solvent and with 20 ml of dry pyridine at reflux temperature for 1 hour. Then, the mixture was poured into ice-water and the precipitate was filtered off and dried in chloroform solution over magnesium sulfate.

2,3-Diphenyl-5-ethylcarbamoylimino- $\Delta^3$ -1,2,4-thiadiazoline (**12**).

This compound was crystallized from methanol-acetone; ir (potassium bromide): 3220 (NH), 1580  $\text{cm}^{-1}$  (s br);  $^1\text{H}$  nmr (DMSO-*d*<sub>6</sub>):  $\delta$  1.09 (t, 3H, CH<sub>3</sub>), 3.20 (p, 2H, CH<sub>2</sub>), 7.28-7.60 (m, 10H), 7.88 (t, NH); ms: m/e (relative intensity) 324 (70, M<sup>+</sup>), 280 (78, M<sup>+</sup> - EtNH), 180 (74, PhC≡NPh), 150

(78, PhNHSCN<sup>+</sup>), 123 (100, PhNS<sup>+</sup>), 77 (100, Ph<sup>+</sup>).

*Anal.* Calcd. for C<sub>17</sub>H<sub>16</sub>N<sub>4</sub>OS (324): C, 62.94; H, 4.97. Found: C, 62.78; H, 4.85.

5-Ethylcarbamoylimino-3-(*p*-methoxyphenyl)-2-methyl- $\Delta^3$ -1,2,4-thiadiazoline (**13**).

This compound was crystallized from methanol-chloroform; ir (potassium bromide): 3212 (m, NH), 1588 (s, br), 1429  $\text{cm}^{-1}$  (s br);  $^1\text{H}$  nmr (DMSO-*d*<sub>6</sub>):  $\delta$  1.03 (t, 3H), 3.14 (p, CH<sub>2</sub>), 3.58 (s, 3H, NCH<sub>3</sub>), 3.84 (s, 3H, OCH<sub>3</sub>), 7.12 (d, 2H), 7.78 (d, 2H), 7.52 (t, NH); ms: m/e (relative intensity) 292 (71, M<sup>+</sup>), 248 (47, M<sup>+</sup> - EtNH), 221 (48, M<sup>+</sup> - EtNCO), 220 (32, M<sup>+</sup> - EtNHCO), 148 (24, CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>C≡NCH<sub>3</sub>), 134 (100, CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>C≡N), 133 (24, CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>CN<sup>+</sup>), 124 (10, EtNHCON=C≡N<sup>+</sup>).

*Anal.* Calcd. for C<sub>15</sub>H<sub>16</sub>N<sub>4</sub>O<sub>2</sub>S (292): C, 53.41; H, 5.52. Found: C, 53.25; H, 5.39.

Reaction of **3c** with Diphenylketene.

A suspension of **3c** (3.5 mmoles) and two equivalents of diphenylketene in 20 ml of dry pyridine was stirred at room temperature for 1 hour. The solution was poured into ice-water and extracted with chloroform. The extracts were washed with water, dried over magnesium sulfate, and evaporated. The crude 5-diphenylacetylmino-3-(*p*-methoxyphenyl)-2-methyl- $\Delta^3$ -1,2,4-thiadiazoline (**14**) was crystallized from chloroform-methanol; ir (potassium bromide): 1605 (s), 1490 (s), 1340  $\text{cm}^{-1}$  (s br);  $^1\text{H}$

Table 8

Bond Angles ( $^\circ$ ) with Standard Deviations in Parentheses

Compound 13		Compound 15		Compound 19	
N2-S1-C5	87.5(2)	C2-S1-C5	90.5(1)	N2-S1-C5	88.9(3)
S1-N2-C3	112.1(3)	S1-C2-N3	115.6(1)	S1-N2-C3	112.0(5)
S1-N2-C6	117.4(3)	S1-C2-N6	116.3(2)	S1-N2-C6	118.3(5)
C3-N2-C6	130.1(3)	N3-C2-N6	128.0(2)	C3-N2-C6	129.5(7)
N2-C3-N4	115.9(3)	C2-N3-C4	112.6(2)	N2-C3-N4	115.0(7)
N2-C3-C7	123.8(4)	N3-C4-C5	114.7(2)	N2-C3-C7	125.0(7)
N4-C3-C7	120.3(4)	N3-C4-O18	123.9(2)	N4-C3-C7	120.1(7)
C3-N4-C5	111.3(3)	C5-C4-O18	121.3(2)	C3-N4-C5	112.8(6)
S1-C5-N4	113.2(3)	S1-C5-C4	102.1(1)	S1-C5-N4	111.2(5)
S1-C5-N15	123.3(3)	S1-C5-C19	110.6(1)	S1-C5-N15	126.9(6)
N4-C5-N15	123.5(3)	S1-C5-C25	110.1(1)	N4-C5-N15	121.9(7)
C3-C7-C8	119.4(4)	C4-C5-C19	107.6(1)	C3-C7-C8	117.4(7)
C3-C7-C12	122.1(4)	C4-C5-C25	112.5(2)	C3-C7-C12	125.7(7)
C8-C7-C12	118.4(4)	C19-C5-C25	113.3(2)	C8-C7-C12	116.9(7)
C7-C8-C9	120.8(4)	C2-N6-C7	123.4(2)	C7-C8-C9	121.2(7)
C8-C9-C10	120.2(4)	N6-C7-N8	118.0(2)	C8-C9-C10	120.6(8)
C9-C10-C11	120.0(4)	N6-C7-C10	122.5(2)	C9-C10-C11	119.2(8)
C9-C10-O13	116.4(4)	N8-C7-C10	119.3(2)	C9-C10-O13	115.3(8)
C11-C10-O13	123.7(4)	C7-N8-C9	123.4(2)	C11-C10-O13	125.6(8)
C10-C11-C12	119.4(4)	C7-C10-C11	121.2(2)	C10-C11-C12	121.1(8)
C7-C12-C11	121.2(4)	C7-C10-C15	120.5(2)	C7-C12-C11	121.0(7)
C10-O13-C14	116.8(4)	C11-C10-C15	118.2(2)	C10-O13-C14	118.5(7)
C5-N15-C16	113.7(3)	C10-C11-C12	121.5(2)	C5-N15-S16	119.1(5)
N15-C16-N17	114.7(4)	C11-C12-C13	119.7(2)	N15-S16-O17	111.2(3)
N15-C16-O20	122.5(3)	C12-C13-C14	119.3(2)	N15-S16-O18	108.7(3)
N17-C16-O20	122.8(4)	C12-C13-O16	124.7(2)	N15-S16-C19	105.6(4)
C16-N17-C18	123.6(4)	C14-C13-O16	116.0(2)	O17-S16-O18	116.9(4)
N17-C18-C19	113.4(4)	C13-C14-C15	120.8(2)	O17-S16-C19	107.1(3)
C5-S1...O20	78.0(1)	C10-C15-C14	120.5(2)	O18-S16-C19	106.7(3)
N2-S1...O20	165.5(1)	C13-O16-C17	118.3(2)	S16-C19-C20	119.9(6)
		C5-C19-C20	120.5(2)	S16-C19-C24	120.6(6)
		C5-C19-C24	121.6(2)	C20-C19-C24	119.4(7)
		C20-C19-C24	117.8(2)	C19-C20-C21	118.6(8)
		C19-C20-C21	120.5(2)	C20-C21-C22	122.6(9)
		C20-C21-C22	121.2(3)	C21-C22-C23	117.4(9)
		C21-C22-C23	118.8(3)	C21-C22-C25	122.0(9)
		C22-C23-C24	120.5(3)	C23-C22-C25	120.6(9)
		C19-C24-C23	121.3(2)	C22-C23-C24	121.9(9)
		C5-C25-C26	119.5(2)	C19-C24-C23	120.1(9)
		C5-C25-C30	122.0(2)	C5-S1...O17	78.8(3)
		C26-C25-C30	118.5(2)	N2-S1...O17	167.7(3)
		C25-C26-C27	120.2(3)		
		C26-C27-C28	120.4(3)		
		C27-C28-C29	119.3(3)		
		C28-C29-C30	121.1(3)		
		C25-C30-C29	120.5(3)		

nmr (deuteriochloroform):  $\delta$  3.56 (s, 3H, CH<sub>3</sub>), 382 (s, 3H, OCH<sub>3</sub>), 5.50 (s, 1H, CH), 6.9 and 7.7 (two d, 4H), 7.2-7.5 (m, 10H); ms: m/e (relative intensity) 415 (7, M<sup>+</sup>), 248 (100, M<sup>+</sup> - Ph<sub>2</sub>CH), 194 (5, Ph<sub>2</sub>C=C=O<sup>+</sup>), 167 (22, Ph<sub>2</sub>CH<sup>+</sup>), 165 (20, fluorenyl<sup>+</sup>), 148 (6, CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>C $\equiv$ NCH<sub>3</sub>).

Anal. Calcd. for C<sub>24</sub>H<sub>21</sub>N<sub>3</sub>O<sub>2</sub>S<sub>1</sub> (415): C, 69.38; H, 5.09. Found: C, 69.33; H, 5.04.

In another experiment **3c** (2 mmoles) and diphenylketene (4 mmoles) were heated in 10 ml of dry pyridine for 2 hours. After working up *N*'-(5,5-diphenyl-4-oxo- $\Delta^3$ -thiazolin-2-yl)-*N*<sup>2</sup>-methyl-*p*-methoxybenzamidine (**15**) was obtained and crystallized from methanol; ir (potassium bromide): 1685 (w), 1600 (s), 1530 and 1510 cm<sup>-1</sup> (s br); <sup>1</sup>H nmr (deuteriochloroform):  $\delta$  3.2 (d, 3H, NCH<sub>3</sub>), 3.86 (s, 3H, OCH<sub>3</sub>), 7.0 and 7.62 (two d,

4H), 7.2-7.6 (m, 10H), 11.6 (br NH); ms: m/e (relative intensity) 415 (100, M<sup>+</sup>), 217 (34, M<sup>+</sup> - Ph<sub>2</sub>C=S), 198 (34, Ph<sub>2</sub>CS<sup>+</sup>), 194 (29, Ph<sub>2</sub>C=C=O<sup>+</sup>), 189 (51, M<sup>+</sup> - Ph<sub>2</sub>C=C=O - S), 188 (80, M<sup>+</sup> - Ph<sub>2</sub>C=C=O - SH), 186 (60), 165 (80, fluorenyl<sup>+</sup>), 159 (9, CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>C $\equiv$ NCH<sub>3</sub>), 148 (47, CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>C $\equiv$ NCH<sub>3</sub>), 134 (63, CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>C $\equiv$ NH), 133 (29, CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>CN<sup>+</sup>).

Anal. Calcd. for C<sub>24</sub>H<sub>21</sub>N<sub>3</sub>O<sub>2</sub>S (415): C, 69.38; H, 5.09. Found: C, 69.22; H, 5.12.

Compound **14** isomerized into **15** when heated in pyridine for 2 hours (yield 58%) or in acetonitrile for 30 hours (yield 50%).

Reaction of **3c** with Dimethyl Acetylenedicarboxylate.

Three equivalents of dimethyl acetylenedicarboxylate in tetrahydro-

furan were added dropwise to an ice-cooled suspension of the free base of **3c** (0.75 g) in 15 ml of tetrahydrofuran. The reaction mixture was stirred at room temperature for 30 minutes and then refluxed for another 30 minutes. The solvent was removed and the residual oil was chromatographed on silica gel with carbon tetrachloride-ethyl acetate as the eluent. This furnished *N*<sup>1</sup>-(4,5-dicarbomethoxythiazol-2-yl)-*N*<sup>2</sup>-methyl-*p*-methoxybenzamide (**16**) which was crystallized from chloroform-cyclohexane; ir (potassium bromide): 3280 (br), 1740, 1710, 1585 (s), 1550, 1450 cm<sup>-1</sup> (s br); nmr (deuteriochloroform): δ 3.06 (d, 3H, NCH<sub>3</sub>), 3.82, 3.86 and 3.96 (three s, three CH<sub>3</sub>), 6.8-7.6 (two m, 4H), 9.6-10.8 (br, NH); mass spectrum, m/e (relative intensity) 363 (100, M<sup>+</sup>), 148 (95, CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>C≡NCH<sub>3</sub>), 147 (25), 133 (13, CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>CN<sup>+</sup>).

Anal. Calcd. for C<sub>16</sub>H<sub>17</sub>N<sub>3</sub>O<sub>5</sub>S (mol wt 363): C, 52.88; H, 4.72. Found: C, 52.71; H, 4.73.

#### Reactions of **3** with Tosyl Chloride.

A mixture of **3** (2.5 mmoles) and two equivalents of tosyl chloride in 10 ml of dry pyridine was refluxed for 10-15 minutes. The solution was poured into water (100 ml) and the precipitate was filtered off, washed with cold water and dried.

#### 2,3-Diphenyl-5-tosylimino-Δ<sup>3</sup>-1,2,4-thiadiazoline (**17**).

This compound was crystallized from chloroform-hexane; ir (potassium bromide): 1595 (w), 1460, 1440 and 1410 (s br), 1295 and 1280 (s br), 1130 cm<sup>-1</sup> (s); <sup>1</sup>H nmr (deuteriochloroform): δ 2.39 (s, 3H), 7.16-7.56 (m, 12H), 7.83 (d, 2H); ms: m/e (relative intensity) 407 (29, M<sup>+</sup>), 375 (49, M<sup>+</sup> - S), 310 (36, M<sup>+</sup> - SO<sub>2</sub> - SH), 285 (12, M<sup>+</sup> - SO<sub>2</sub> - S - CN), 194 (100, PhC≡N<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 180 (44, PhC≡NPh), 155 (51, Ts<sup>+</sup>), 129 (41, PhC≡N-CN), 123 (12, PhNS<sup>+</sup>), 91 (58, C<sub>7</sub>H<sub>7</sub><sup>+</sup>), 77 (33, Ph<sup>+</sup>).

Anal. Calcd. for C<sub>21</sub>H<sub>17</sub>N<sub>3</sub>O<sub>2</sub>S<sub>2</sub> (408): C, 61.90; H, 4.21. Found: C, 61.99; H, 4.31.

#### 3-Isopropyl-2-(*p*-tolyl)-5-tosylimino-Δ<sup>3</sup>-1,2,4-thiadiazoline (**18**).

This compound was purified by column chromatography on silica gel with carbon tetrachloride-ethyl acetate as the eluent and then crystallized from chloroform-hexane; ir (potassium bromide): 1445 (s br), 1280 (s), 1130 cm<sup>-1</sup> (s); <sup>1</sup>H nmr (deuteriochloroform): δ 1.25 (d, 6H), 2.40 and 2.45 (two s, 6H, 2 CH<sub>3</sub>), 2.9 (sept, 1H), 7.1-7.4 (m, 6H), 7.8 (d, 2H); ms: m/e (relative intensity) 387 (76, M<sup>+</sup>), 355 (10, M<sup>+</sup> - S), 323 (11, M<sup>+</sup> - SO<sub>2</sub>), 163, (69), 161 (13), 160 (100, Me<sub>2</sub>CHC≡N<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 155 (35, Ts<sup>+</sup>), 137 (35, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>NS<sup>+</sup>), 118 (16, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>NCH<sup>+</sup>), 95 (10, Me<sub>2</sub>CHC(NC)=N<sup>+</sup>), 91 (80, C<sub>7</sub>H<sub>7</sub><sup>+</sup>).

Anal. Calcd. for C<sub>19</sub>H<sub>21</sub>N<sub>3</sub>O<sub>2</sub>S<sub>2</sub> (388): C, 58.89; H, 5.46. Found: C, 58.94; H, 5.48.

#### 3-(*p*-Methoxyphenyl)-2-methyl-5-tosylimino-Δ<sup>3</sup>-1,2,4-thiadiazoline (**19**).

This compound was crystallized from chloroform-hexane; ir (potassium bromide): 1600 (s), 1480 (s br), 1430 (s br), 1380 (s), 1275 and 1260 (s br), 1130 cm<sup>-1</sup> (s); <sup>1</sup>H nmr (deuteriochloroform): δ 2.36 (s, 3H), 3.71 and 3.84 (two s, 6H, 2 CH<sub>3</sub>), 6.9-7.8 (four m, 8H); ms: m/e (relative intensity) 375 (29, M<sup>+</sup>), 311 (39, M<sup>+</sup> - SO<sub>2</sub>), 225 (15), 224 (100, CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>C≡N<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 189 (11, CH<sub>3</sub>N=C(C<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>)<sub>2</sub>N=C=NH<sup>+</sup>), 159 (57), 155 (37, Ts<sup>+</sup>), 148 (68, CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>C≡NCH<sub>3</sub>), 139 (22, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sup>+</sup>), 133 (16, CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>CN<sup>+</sup>), 91 (90, C<sub>7</sub>H<sub>7</sub><sup>+</sup>).

Anal. Calcd. for C<sub>17</sub>H<sub>17</sub>N<sub>3</sub>O<sub>3</sub>S<sub>2</sub> (375): C, 54.38; H, 4.56. Found: C, 54.48; H, 4.62.

#### Reactions of **3** with Methanesulfonyl Chloride.

A solution of triethylamine (2 equivalents) in 10 ml of tetrahydrofuran was added to an ice-cooled suspension of **3a,b** (3 mmoles) and 1 equivalent of methanesulfonyl chloride in 15 ml of tetrahydrofuran. After the reaction mixture had been stirred at room temperature for 30 minutes, the precipitate (triethylamine hydrochloride) was filtered off and the filtrate evaporated. The residue was treated with ether to remove the remaining triethylamine hydrochloride and crystallized from chloroform-cyclohexane. For the synthesis of **22** a mixture of **3c** (3.3 mmoles) and two equivalents of methanesulfonyl chloride was treated with 10 ml of pyridine at reflux temperature for 30 minutes. The reaction

mixture was poured into ice-water and the brown precipitate was dissolved in chloroform and dried over magnesium sulfate. After partial removal of the solvent, the solution was cooled to give **22**.

#### *N*<sup>1</sup>-(4,4-Dioxo-Δ<sup>2</sup>-1,4,3-dithiazolin-2-yl)-*N*<sup>2</sup>-phenylbenzamide (**20**).

This compound had ir (potassium bromide): 3320 (s, NH), 1500-1610 (s br), 1445 (m), 1360 (m), 1305 (s), 1185 cm<sup>-1</sup> (s); <sup>1</sup>H nmr (DMSO-*d*<sub>6</sub>): δ 4.64 (s, 2H, CH<sub>2</sub>), 7.0-7.8 (m, 10H), 11.9 (br NH); ms: m/e (relative intensity) 331 (100, M<sup>+</sup>), 222 (66), 221 (PhNH-C(Ph)=N-CN<sup>+</sup>), 220 (50, PhN=C(Ph)N=C=N<sup>+</sup>), 180 (61, PhC≡NPh), 129 (47, PhC≡N<sub>2</sub>CN), 118 (37, PhNHCN<sup>+</sup>), 113 (13), 104 (24, PhC≡N<sub>2</sub>H), 77 (67, Ph<sup>+</sup>).

Anal. Calcd. for C<sub>15</sub>H<sub>13</sub>N<sub>3</sub>O<sub>2</sub>S<sub>2</sub> (331): C, 54.36; H, 3.95. Found: C, 54.18; H, 3.89.

#### *N*<sup>1</sup>-(4,4-Dioxo-Δ<sup>2</sup>-1,4,3-dithiazolin-2-yl)-*N*<sup>2</sup>-(*p*-tolyl)isobutyramidine (**21**).

This compound was purified by column chromatography on silica gel with cyclohexane-ethyl acetate as the eluent and crystallized from chloroform-cyclohexane; ir (potassium bromide): 3180 (w, NH), 1560 and 1495 (s br), 1365 (s), 1325 and 1305 (s), 1215 (s), 1180 cm<sup>-1</sup> (s); <sup>1</sup>H nmr (deuteriochloroform): δ 1.16 (d, 6H), 2.43 (s, 3H, CH<sub>3</sub>), 2.6-3.0 (sept, 1H), 4.42 (s, 2H, CH<sub>2</sub>), 7.0-7.4 (m, 4H), 11.4 (br NH); ms: m/e (relative intensity) 311 (56, M<sup>+</sup>), 233 (7, M<sup>+</sup> - CH<sub>2</sub>SO<sub>2</sub>), 202 (50), 201 (78, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>NH-C(CHMe<sub>2</sub>)=N-CN<sup>+</sup>), 200 (42), 161 (19), 160 (11, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>N≡CCHMe<sub>2</sub>), 159 (19, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>N=C=CMe<sub>2</sub><sup>+</sup>), 132 (100, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>NHCN<sup>+</sup>), 118 (19, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>N≡CH), 106 (44, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>NH<sup>+</sup>), 95 (6, Me<sub>2</sub>CHC≡N-CN), 91 (67, C<sub>7</sub>H<sub>7</sub><sup>+</sup>).

Anal. Calcd. for C<sub>13</sub>H<sub>17</sub>N<sub>3</sub>O<sub>2</sub>S<sub>3</sub> (311): C, 50.14; H, 5.50. Found: C, 50.05; H, 5.47.

#### *N*<sup>1</sup>-(4,4-Dioxo-Δ<sup>2</sup>-1,4,3-dithiazolin-2-yl)-*N*<sup>2</sup>-methyl-*p*-methoxybenzamide (**22**).

This compound was recrystallized from chloroform; ir (potassium bromide): 3310 (s), 1590 (s), 1550 (s), 1500 (s), 1300 (s), 1255, 1190, 1120 cm<sup>-1</sup> (s); <sup>1</sup>H nmr (DMSO-*d*<sub>6</sub>): δ 2.90 (d, 3H, NCH<sub>3</sub>), 3.76 (s, 3H, CH<sub>3</sub>O), 4.52 (s, 2H, CH<sub>2</sub>), 6.9 and 7.3 (two d, 4H), 9.2-9.5 (br, NH); ms: m/e (relative intensity) 299 (31, M<sup>+</sup>), 298 (29), 235 (10, M<sup>+</sup> - SO<sub>2</sub>), 190 (100), 189 (58, CH<sub>3</sub>NH-C(C<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>)=N-CN<sup>+</sup>), 188 (96), 159 (30, C<sub>7</sub>H<sub>7</sub>O<sub>2</sub>C<sub>6</sub>H<sub>4</sub>C≡N<sup>+</sup>), 148 (28, CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>C≡N<sub>2</sub>CH<sub>3</sub>), 134 (61, CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>C≡NH), 133 (26, CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>CN).

Anal. Calcd. for C<sub>11</sub>H<sub>13</sub>N<sub>3</sub>O<sub>3</sub>S<sub>2</sub> (299): C, 44.13; H, 4.38. Found: C, 44.17; H, 4.37.

#### Crystal Structure Determinations of **13**, **15** and **19**.

Measurements were made on a Syntex P2<sub>1</sub> automatic diffractometer using graphite-monochromatized Mo Kα radiation (λ = 0.71069 Å). Densities were determined by flotation in aqueous cadmium chloride. Accurate cell parameters were obtained from a least-squares analysis of the reciprocal space coordinates of 24 reflections. Crystal data are given in Table 4.

Intensities of all reflections in a hemisphere of reciprocal space out to 2θ = 50° were collected by the omega-scan technique using a scan range of 0.5° either side of the calculated value. Intensity values for equivalent reflections were averaged to give a unique set of independent reflections. Reflections whose intensity (I) was greater than a threshold number of standard deviations (σ(I)) of the averaged value were considered as observed. The very large number of unobserved reflections for compound **13** is due to the small size of the crystal. Structure determination parameters are given in Table 5.

Lorentz and polarization corrections were applied assuming a 50% mosaic character for the monochromator crystal. No correction was made for absorption.

All structures were solved by direct methods and refined (observed reflections only) by full-matrix least-squares methods using the X-Ray 76 System (9). Structure determination parameters are given in Table 5.



Anisotropic temperature factors were refined to C, N, O and S for which the analytical scattering expressions of Cromer and Mann (10) were used. When hydrogen parameters were refined isotropic temperature factors were used. The hydrogen scattering factors used were those of Stewart *et al.*, (11). The atomic coordinates, bond lengths (in Å) and bond angles (in degrees) are listed in Tables 6, 7 and 8, respectively.

#### Acknowledgement.

We thank Dr. G. Verhelst for having carried out some preliminary experiments in this field. Financial support from the University (Research Grants), from the Ministerie voor Wetenschapsbeleid and from the Fonds voor Kollektief Fundamenteel Onderzoek, is gratefully acknowledged.

#### REFERENCES AND NOTES

- (1) For a recent review, see C. Th. Pedersen, *Sulfur Rep.*, **1**, 1 (1980).
- (2) R. Neidlein and H. Reuter, *Tetrahedron*, **27**, 4117 (1971); A. Kutoglu and H. Jepsen, *Chem. Ber.*, **105**, 125 (1972); I. Leban, *Acta Cryst.*, **B32**, 1601 (1976); R. D. Gilardi and I. L. Karle, *ibid.*, **B27**, 1073 (1971).
- (3) G. L'abbé, G. Verhelst and G. Vermeulen, *Angew. Chem.*, **89**, 420 (1977); *Angew. Chem., Int. Ed. Engl.*, **16**, 403 (1977); G. L'abbé and G. Vermeulen, *Bull. Soc. Chim. Belg.*, **90**, 89 (1981).
- (4) Reviews: G. Opitz, *Angew. Chem.*, **79**, 161 (1967); *Angew. Chem., Int. Ed. Engl.*, **6**, 107 (1967); J. F. King, *Acc. Chem. Res.*, **8**, 10 (1975).
- (5) A. zwitterionic structure for 2-amino- $\Delta^3$ -thiazolin-4-ones has already been reported: L. A. Plastas and J. M. Stewart, *Chem. Commun.*, 811 (1969); A. F. Cameron and N. J. Hair, *J. Chem. Soc. (B)*, 1733 (1971); V. Amirthalingam and K. V. Muralidharan, *Acta Cryst.*, **B28**, 2417 and 2421 (1972).
- (6) M. L. Huggins, *J. Am. Chem. Soc.*, **75**, 4126 (1953).
- (7) R. J. S. Beer, D. McMonagle, M. S. S. Siddiqui, A. Hordvik and K. Jynge, *Tetrahedron*, **35**, 1199 (1979).
- (8) J. M. Stewart, P. A. Machin, C. W. Dickinson, H. L. Ammon, H. Heck and H. Flack, The X-Ray System, Technical Report TR-446 of The Computer Science Center, University of Maryland, March 1976.
- (9) P. Main, L. Lessinger, M. M. Woolfson, G. Germain and J-P. Declercq, "MULTAN 73", York (U.K.) and Louvain-la-Neuve, Belgium, 1973.
- (10) D. T. Cromer and J. B. Mann, *Acta Cryst.*, **A24**, 321 (1968).
- (11) R. F. Stewart, E. R. Davidson and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).