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Thiatriazoline **4a** decomposes in acetone and yields a thermolabile crystalline material, identified as the 1,2,4-oxathiazole derivative **6a** on the basis of ir, ^1H and ^{13}C nmr spectroscopy. It degrades to **7a** in the crystalline state as well as in solution. Cycloaddition-elimination reactions of **6a** with isothiocyanates proceed rapidly and furnish the same products as previously obtained from **4a**. Some other reactions of **4** with carbonyl compounds were briefly investigated and provide evidence for the formation of unstable 1,2,4-oxathiazolidines.

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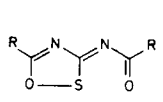
The 1,2,4-oxathiazole ring system is scarcely encountered in the literature. It constitutes the framework of the molecules **1** [1], **2** and **3** [2] which are more or less stabilized by single bond-no bond resonance [3], resulting in an elongation of the S-O distance. For example, the two S-O bonds in **1** are equal (1.88 Å) [4] and longer than the normal S-O single bond (1.60 Å) [5]. Whereas **1** is stabilized by the aromatic thiapentalene resonance, **2** and **3** are thermolabile due to the weakness of their S-O bonds. Thus, any synthetic pathway to the title compounds should require mild conditions, and the present report describes such an approach.



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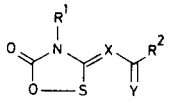
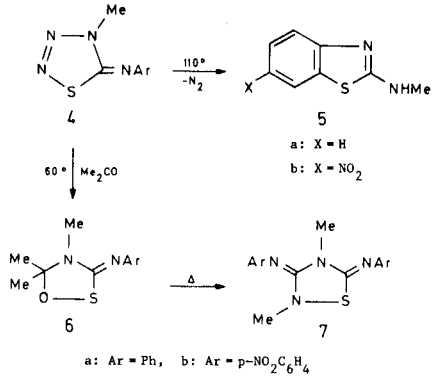


2 : X = CH, Y = NR

3 : X = N, Y = S or NR

It is known that 4-methyl-5-phenylimino-1,2,3,4-thiatriazoline **4a** decomposes in toluene at 110° to give the benzothiazole **5a** [6]. In acetone, however, decomposition already occurs at room temperature, and at 60° is complete within 2 hours. After evaporation of the solvent and trituration of the resulting oil with *n*-hexane, white crystals (mp 65-67°) were isolated corresponding to structure **6a** on the basis of spectral data. Thus, the ^1H nmr spectrum in deuteriochloroform exhibits singlets at δ 1.55 (6H) and 3.0 (3H) and a multiplet for the phenyl protons at δ 6.9-7.3, while the ^{13}C nmr spectrum shows methyl carbon signals at δ 22.6 and 30.1 ($^1J_{CH}$ = 138.5 Hz), ring carbon resonances at δ 100.4 (C-5) and 159.8 (C-3), and phenyl carbon absorptions at δ 121.1 (C_o), 123.9 (C_p), 129.3 (C_m) and 151.3 (C_i). The shielding of the *ortho* and *para* carbons, and the deshielding of the *ipso* carbon are diagnostic for an *N*-phenylimino substituent [7]. These data, as well as the ir C=N stretching vibration at 1640 cm^{-1}, led us to assign unambiguously structure **6a** to the reaction product. Further information (ms, microanalysis) was not available since the product deteriorates on standing, even when dissolved in acetone for a prolonged period of time (24 hours). The thermolysis product, identified as **7a**, probably results from fragmentation of **6a** into acetone, sulfur and *N*-methyl-*N'*-phenylcarbodiimide, followed by addition of the latter to **6a** with elimination of acetone.



4 5 6 7

a: X = H
b: X = NO_2

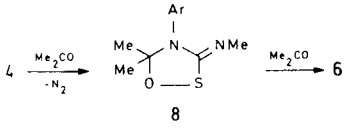
a: Ar = Ph, b: Ar = p-$NO_2C_6H_4$

The more thermostable thiatriazoline **4b** yields **5b** in refluxing toluene and **7b** when heated in acetone at 60° for 60 hours. When the latter reaction was monitored by ^1H nmr spectroscopy, a singlet resonance attributable to **6b** was observed at δ 3.0, which constituted the major product peak in the early period with a maximum concentration of 36% after 9 hours. It then decreased in intensity in favor of singlet resonances at δ 2.8 and 3.5 for **7b**, as well as several minor peaks from unidentified products.

A few other carbonyl compounds were briefly examined. Solutions of **4a** (0.5 *M*) with four equivalents of acetophenone or benzophenone in deuteriochloroform at 60° showed ^1H nmr absorptions corresponding to **7a**, unreacted **4a** and a small amount of the presumed oxathiazolidine (δ 3.0) (reaction time 2 hours). With benzaldehyde, the reaction was followed at room temperature, but only **7a** was observed as reaction product.

Mechanistically, the ring transformation **4** → **6** is assumed to proceed by a cycloaddition-elimination process involving S_1 and the exocyclic imine nitrogen atom of **4** [8]. This would yield the intermediate **8** which, due to its pronounced nucleophilic *N*-methylimine function, is ex-

cepted to undergo a second, fast cycloaddition-elimination reaction with acetone. We have searched for the presence of **8** during the decomposition of **4a** in deuterated acetone, and found and nmr resonance at δ 2.85 which first appeared and later disappeared as the reaction progressed (maximum 5% at room temperature and 10% at 60°). This resonance may be tentatively ascribed to the exocyclic *N*-methyl protons of **8a** since it lies at the expected position.



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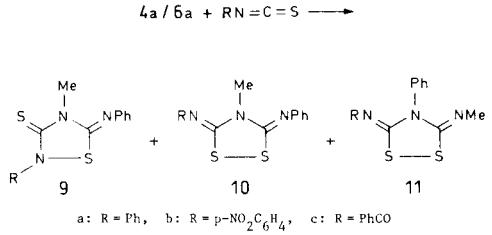
The novel 1,2,4-oxathiazolidin-3-imine **6a** possesses a thioimidate structural unit similar to **4a**, and is capable of undergoing cycloaddition-elimination reactions with isothiocyanates. Previous studies have shown that thiadiazolidines **9** and isomeric dithiazolidines **10** and **11** are formed from **4a** in ratios depending on the nature of the isothiocyanate [7-9]. Analogous results were obtained with **6a**, but at much higher rates (see Experimental). Hence, acetone can be used as solvent to catalyze the cycloaddition-elimination reactions of **4**.



EXPERIMENTAL

4-Methyl-5-phenylimino-1,2,3,4-thiatriazoline (**4a**).

This compound (mp 68°) was obtained by methylation of 5-anilinothiatriazole with trimethyloxonium tetrafluoroborate according to the procedure of Toubro and Holm [10].

4-Methyl-5-(*p*-nitrophenyl)imino-1,2,3,4-thiatriazoline (**4b**).

Sodium azide (7.8 g, 120 mmoles) was suspended in ethanol (60 ml) at 0°, and a solution of *p*-nitrophenyl isothiocyanate (7.2 g, 40 mmoles) in acetone (100 ml) was added dropwise with stirring while a continuous flow of carbon dioxide was bubbled through the reacting solution. Then, water (100 ml) was added and the whole was stirred for another 15 minutes. The precipitated 5-(*p*-nitroanilino)thiatriazole was filtered off, dried and crystallized from ethanol-acetone (9:1), yield 83% (7.37 g), mp 169° (lit [11] 152°).

This compound (2.85 g, 12.7 mmoles) was suspended in a mixture of ether (12 ml) and methanol-water (12 ml, 9:1), and a solution of diazomethane (2 equivalents) in ether was added dropwise. The solution was stirred for 24 hours and then evaporated to give a crude mixture of **4b** (54%) and the isomeric *N*-methyl-*N*-(*p*-nitrophenyl)amino-1,2,3,4-thiatriazole (46%) according to ^{1}H nmr spectroscopy. These were separated by flash chromatography on silica gel with *n*-hexane-ether (4:6) as the eluent.

4-Methyl-5-(*p*-nitrophenyl)imino-1,2,3,4-thiatriazoline (**4b**).

This compound was obtained in 28% yield (836 mg), mp 75° dec; ^{1}H nmr (250 MHz, deuteriochloroform): δ 4.0 (s, 3H, CH_3), 7.1 and 8.25 (two d, 4H, aryl); ^{13}C nmr (deuteriochloroform): δ 34.7 (CH_3, $^1J_{CH}$ = 143 Hz), 120.7, 125.6, 144.1 and 156.7 (Ar), 157.5 (C-5).

Anal. Calcd. for $C_8H_7N_5SO_2$ (mol wt 237): C, 40.51; H, 2.95. Found: C, 40.73; H, 3.07.

N-Methyl-*N*-(*p*-nitrophenyl)amino-1,2,3,4-thiatriazole.

This compound was obtained in 27% yield (820 mg), mp 100° dec; ^{1}H nmr (deuteriochloroform): δ 3.8 (s, 3H, CH_3), 7.7 and 8.4 (two d, 4H, Ar); ^{13}C nmr (deuteriochloroform): δ 42.9 (CH_3, $^1J_{CH}$ = 141 Hz), 123.2, 125.8, 146.0 and 151.1 (Ar), 179.0 (C-5).

Anal. Calcd. for $C_8H_7N_5SO_2$ (mol wt 237): C, 40.51; H, 2.95. Found: C, 40.73; H, 3.09.

Thermolysis of **4b**.

a) In Toluene.

A solution of **4b** (0.5 g, 2.1 mmoles) in toluene (5 ml) was heated at 110° for 4 days. The precipitated **5b** was collected by filtration, and the filtrate was evaporated and analyzed by ^{1}H nmr spectroscopy, indicating the presence of much starting material (δ 4.0) and a small amount of **7b** (δ 2.8 and 3.5).

2-Methylamino-6-nitrobenzothiazole **5b**.

This compound was obtained in 39% yield (161 mg), mp 285°; ^{1}H nmr (250 MHz, dimethyl sulfoxide-d_6): δ 3.0 (d, 3H, CH_3), 7.5 (d, 1H, H-4), 8.1 (dd, 1H, H-5), 8.6 (br, 1H, NH), 8.7 (d, 1H, H-7); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 30.6 (CH_3), 117.0 and 117.7 (C-4 and/or C-7), 122.0 (C-5), 131.0 (C-7a), 140.6 (C-6), 158.3 (C-3a), 171.5 (C-2).

Anal. Calcd. for $C_8H_7N_3O_2S$ (mol wt 209): C, 45.93; H, 3.34. Found: C, 46.06; H, 3.39.

b) In Acetone.

Compound **4b** (1.0 g, 4.2 mmoles) was heated in acetone (10 ml) at 60° for 5 days (complete reaction by ^{1}H nmr analysis). The yellow precipitate was filtered off and recrystallized from toluene.

3,5-bis(*p*-nitrophenylimino)-2,4-dimethyl-1,2,4-thiadiazolidine (**7b**).

This compound was obtained in 39% yield (319 mg), mp 195°; ir (potassium bromide): 1610 (s), 1560 and 1330 cm^{-1} (s); ^{1}H nmr (250 MHz, deuteriochloroform): δ 2.8 (s, 3H, CH_3 at position 2), 3.5 (s, 3H, CH_3 at position 4), 7.0, 7.1, 8.15 and 8.25 (four d, 8 aromatic H); ^{13}C nmr (deuteriochloroform): δ 32.1 (CH_3 at position 4, $^1J_{CH}$ = 142 Hz), 39.8 (CH_3 at position 2, $^1J_{CH}$ = 141.5 Hz), 149.4 (C-3), 153.8 (C-5), 121.5, 121.6, 125.2, 125.5, 142.3, 144.6, 154.0 and 154.8 (aromatic C-atoms).

Anal. Calcd. for $C_{16}H_{14}N_6O_4S$ (mol wt 386): C, 49.74; H, 3.62. Found: C, 49.94; H, 3.64.

Note: When this reaction in deuterated acetone (0.5 *M*) was followed by ^{1}H nmr spectroscopy, **7b** only appeared after 9 hours when **6b** had attained its maximum concentration of 36%.

3-Phenylimino-4,5,5-trimethyl-1,2,4-oxathiazolidine (**6a**).

A solution of **4a** (1 g, 5.2 mmoles) in acetone (20 ml) was reflux-

ed for 2 hours. The solvent was removed under reduced pressure, and the resulting oil was triturated with *n*-hexane to give white crystals which were washed with *n*-pentane, yield 34% (450 mg), mp 65-67°; for spectral data, see text. This compound deteriorates rapidly upon standing (1 hour), preventing its elements analysis!

3,5-Bis(phenylimino)-2,4-dimethyl-1,2,4-thiadiazolidine (**7a**).

This compound was obtained when **6a** (300 mg) was allowed to stand in chloroform solution (10 ml) at room temperature for 3 days. After evaporation of the solvent, the resulting oil was crystallized from ether-*n*-hexane, yield 65% (249 mg), mp 123-125° (lit [12] 124°); ir (potassium bromide): 1660 and 1630 cm^{-1} (s); ^1H nmr (deuteriochloroform): δ 2.65 (s, 3H, CH_3 at N-2), 3.45 (s, 3H, CH_3 at N-4), 6.85-7.5 (m, 10 aromatic H); ^{13}C nmr (deuteriochloroform): δ 31.8 (CH_3 at N-4, $^1J_{CH}$ = 142 Hz), 40.2 (CH_3 at N-2, $^1J_{CH}$ = 141.5 Hz), 121.1 and 121.3 (Ph C_o), 122.3 and 124.9 (Ph C_p), 147.8 and 149.9 (Ph C_i), 149.6 (C-3), 154.0 (C-5).

Reaction of **6a** with Phenyl Isothiocyanate.

To a solution of **4a** (1 g, 5.2 mmoles) in acetone (21 ml), preheated at 60° for 2 hours, was added two equivalents of phenyl isothiocyanate (1.4 g) and the whole was stirred at room temperature for 1 day. The ^1H nmr spectrum of the reaction mixture showed the presence of **7a** (23%), **9a** (32%), **10a** (4%), **11a** (10%) and other unidentified products (8%). After flash chromatography on silica gel using an elution gradient from *n*-hexane to ether, pure samples of **9a** (252 mg) and **11a** (45 mg) were obtained, identical with authentic specimen [8].

Note: When the reactions of **4a** (0.5 *M*) with two equivalents of phenyl isothiocyanate in three different solvents at room temperature were analyzed by ^1H nmr spectroscopy after three days, the following results were obtained: in deuteriochloroform: 82% of **4a**, 16% of **9a** and 2% of **10a**; in deuterated acetonitrile: 57% of **4a**, 34% of **9a** and 9% of **10a**; in deuterated acetone: 78% of **9a**, 11% of **10a**, 6% of **11a** and 5% of presumably **8** (δ 2.85).

Reaction of **6a** with *p*-Nitrophenyl Isothiocyanate.

To a solution of **4a** (0.25 *M*) in deuterated acetone, preheated at 60° for 2 hours, was added two equivalents of *p*-nitrophenyl isothiocyanate. The reaction mixture was analyzed by ^1H nmr spectroscopy after 21 hours at room temperature, giving **7a** (5%), **9b** (5%), **10b** (47%), **11b** (29%) and presumably **8** (9%, δ 2.85). The resonances attributed to **9b**, **10b** and **11b** were checked by addition of authentic samples [8] to the nmr tube.

3-Benzoylimino-5-methylimino-4-phenyl-1,2,4-dithiazolidine (**11c**).

To a solution of **4a** (0.5 g, 2.6 mmoles) in acetone (10 ml), preheated at 60° for 2 hours, was added two equivalents of benzoyl isothiocyanate (848 mg) and the whole was stirred at room temperature for 20 hours. The precipitate (162 mg) was filtered off and the filtrate was treated with ether to give a second crop of product (112 mg) overall yield of **11c**, 30%, mp 205°. This compound was identical in all respects with an authentic sample [7].

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