

Isolation of Stable Monoadducts

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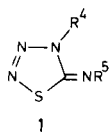
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Picryl isothiocyanate (**4**), prepared in a two-step sequence from picryl chloride (**2**), reacts smoothly with alkyl azides to yield 4-alkyl-5-picrylimino-1,2,3,4-thiazolines **5** which are stable below 100°. These adducts combine with isocyanates in a bimolecular process with loss of nitrogen, similar to the formation of phenylimino derivatives but different from that of sulfonyliminothiazolines.

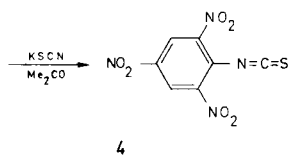
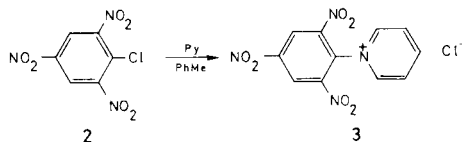
J. Heterocyclic Chem., **27**, 1059 (1990).

Some years ago we reported that sulfonyl isothiocyanates react with alkyl azides to give isolable thiazolone-5-imines **1a**, which can be used as synthons for the preparation of a large variety of other heterocycles [1,2]. The reactions of aryl and acyl isothiocyanates with alkyl azides were also investigated, but yielded thiazolone-5-imines, **1b** and **1c**, only as elusive intermediates which were transformed *in situ* into a series of bisadducts after loss of nitrogen [3,4].

a: $R^5 = ArSO_2$ b: $R^5 = p-XC_6H_4$ (X = H, CH₃, Cl, NO₂)c: $R^5 = p-XC_6H_4CO$ (X = H, Cl, NO₂)

In view of the complexity of the reactions with aryl isothiocyanates [3], we have searched for an aromatic isothiocyanate which would have similar reactivity towards azides as sulfonyl isothiocyanates, and prevent the formation of bisadducts. Picryl isothiocyanate proved to be a suitable candidate.

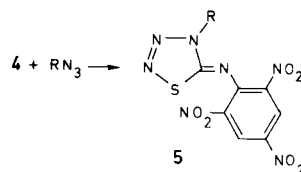
To our knowledge, there is only one reference on the synthesis of picryl isothiocyanate published by Giles and Parker [5]. In their study on the mechanism of aromatic nucleophilic substitution by the ambident thiocyanate ion, these authors mentioned the synthesis of **4** from picryl fluoride and potassium thiocyanate. We have developed a more convenient method starting from picryl chloride **2**,



which is first converted into picrylpyridinium chloride **3** and then treated with potassium thiocyanate to give **4** in *ca* 50% overall yield. This compound is extremely sensitive to moisture and care must be taken to work under dry conditions.

The N=C=S function of **4** exhibits a diagnostic broad and strong stretching vibration at 2080 cm⁻¹ in the ir spectrum, and a carbon resonance at δ 143 in the ¹³C nmr spectrum. The latter is shifted downfield compared with phenyl isothiocyanate (δ 135) and *p*-nitrophenyl isothiocyanate (δ 140) [6].

Picryl isothiocyanate **4** reacted with a number of alkyl azides at room temperature, or even better at 55° in an inert solvent (carbon tetrachloride), to give the thiazolone-5-imines **5a-h** in excellent yields. The less nucleophilic phenyl azide and the sterically hindered *t*-butyl azide and diphenylmethyl azide did not react. The isolation of the monoadducts **5a-h** contrasts with the behavior of the other aryl isothiocyanates towards azides where 2:1 adducts were obtained [3]. However, it parallels the chemistry of sulfonyl isothiocyanates [1].

a: $R = C_6H_5CH_2$ b: $R = p-CH_2OC_6H_4CH_2$ c: $R = p-(CH_2)_3C-C_6H_4CH_2$ d: $R = n-C_4H_9$ e: $R = (CH_3)_2CH$ f: $R = CH_3OCOCH_2$ g: $R = (CH_2)_3SiCH_2$ h: $R = ClCH_2CH_2$

The cycloaddition rates of picryl isothiocyanate with benzyl azide (concentration 0.25 M each) at 55° were followed by nmr (methylene singlets), and furnished the following relative rate constants in four different solvents:

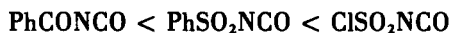
	CDCl ₃	C ₆ D ₆	C ₆ D ₅ NO ₂	CD ₃ CN
k/k _{CD₃CN}	1.8	1.5	1.2	1

These values are based on the half-life times measured from the second-order diagrams ($t_{1/2} = 370$ minutes in acetonitrile, corresponding to a rate constant of $18 \times 10^{-5} \text{ s}^{-1} \text{ M}^{-1}$). Since no significant solvent effect is observed, the involvement of a zwitterionic intermediate during the cycloaddition step appears unlikely, and the reaction is considered to be concerted.

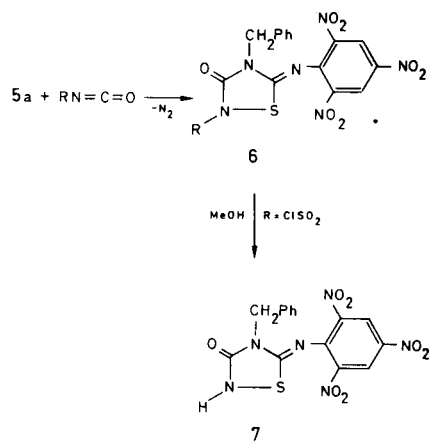
The thiatriazoline-5-imines **5a-h** were characterized by spectral methods (see Experimental). Noteworthy are the C-5 absorptions (δ 161-162) in the ^{13}C nmr spectra which lie between those of the phenylimino (δ 156) and tosylimino derivatives (δ 166) [7].

Whereas **1a** decomposed at 60-80° to carbodiimides *via* thiaziridinimine intermediates [1], the 5-picryliminothiatriazolines **5** were found to be exceptionally thermostable. For instance, **5a** and **5e** did not thermolyze at 90° in chlorobenzene or toluene; decomposition started only after prolonged heating at 105° and was complete after 3-5 days. The resulting intractable mixtures showed no ir spectroscopic evidence of carbodiimide formation.

Another striking difference between **1a** and **5** lies in their reactivity towards isocyanates; the former reacting by first order kinetics [2,8], whereas the latter follow second order kinetics. The approximate rate constants of **5a** with benzyl isocyanate and phenyl isocyanate (concentration 0.074 *M* each) in deuteriochloroform at 60° were 0.43×10^{-3} and $1.5 \times 10^{-3} \text{ s}^{-1} \text{ M}^{-1}$ respectively, based on the half-life times in the second-order diagrams (525 and 150 minutes). Acyl and sulfonyl isocyanates reacted at room temperature according to the following reactivity sequence:



Thus, **5a**, does not parallel the chemistry of 5-sulfonyliminothiatriazolines **1a**, but reacts similarly to the other aryliminothiatriazolines **1b** [9], although at much lower rate. The reaction products were characterized as 5-picrylimino-1,2,4-thiadiazolidin-3-ones, **6a-e** and **7**, the



6	a	b	c	d	e	f
R	$\text{C}_6\text{H}_5\text{CH}_2$	$\text{C}(\text{CH}_3)_3$	C_6H_5	$\text{C}_6\text{H}_5\text{CO}$	$\text{C}_6\text{H}_5\text{SO}_2$	ClSO_2

latter resulting from methanolysis of **6f** during the work-up procedure. The spectral analyses are given in the Experimental.

No reaction was observed when **5a** was heated with phenyl isothiocyanate, benzoyl isothiocyanate, *N,N'*-dicyclohexylcarbodiimide, diphenylketene, ethyl cyanofornate and trichloroacetonitrile in chloroform at 60° for several days.

EXPERIMENTAL

Synthesis of Picryl Isothiocyanate (4).

Freshly distilled pyridine (4 ml, 51 mmoles) in dry toluene (25 ml, dried over sodium) was added dropwise (over a period of 10 minutes) and with stirring to a solution of picryl chloride [10] (12.4 g, 50 mmoles) in dry toluene (125 ml) at 60°, and the mixture was stirred at 60° for 30 minutes and then at room temperature for another 12 hours. After cooling, the precipitated pyridinium salt **3** was filtered off, washed with toluene (100 ml) and with dry ether (100 ml), and dried *in vacuo* at 50°; yield 92%, mp 130-135°.

A solution of **3** (4 g, 12 mmoles) and dry potassium thiocyanate (1.2 g, 12 mmoles, recrystallized from methanol) in dry acetone (100 ml) was stirred at 0° for 30 minutes. After removal of the solvent at 0°, the residue was washed with cold heptane (50 ml) and then extracted three times with carbon tetrachloride (150 ml) at 45°. The combined extracts were concentrated, giving yellow crystals of pure **4** in 50-60% yield, mp 95° (carbon tetrachloride) (lit [5] 95°); ir (potassium bromide) 3110 (m, C-H), 2080 (broad s, NCS), 1625 and 1610 (s), 1550 and 1345 cm^{-1} (s, NO_2); ^1H nmr (deuteriochloroform): δ 9.1 (s); ^{13}C nmr (deuteriochloroform): δ 124.5, 125.8, 142.5 and 145.8 ($\text{C}_m, \text{C}_i, \text{C}_p$ and C_o aryl; the positions are denoted with respect to the NCS function), 143.2 (NCS).

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

A suspension of picryl isothiocyanate (1.08 g, 4 mmoles) and two equivalents of benzyl azide (1.064 g) in dry carbon tetrachloride (25 ml) was heated at 55° for 24 hours. After cooling to 0°, the precipitate was filtered off, washed with carbon tetrachloride (10 ml) and dried to give **5a** in 90% yield (1.45 g), mp 147° dec (acetonitrile); ir (potassium bromide): 3110 (m), 1640 (s), 1610 (s), 1540 and 1340 cm^{-1} ; ^1H nmr (dimethyl sulfoxide- d_6): δ 5.6 (s, 2H, CH_2), 7.4 (s, 5H, Ph), 9.1 (s, 2H, picryl); ^{13}C nmr (dimethyl sulfoxide- d_6): δ 51.0 (CH_2), 128.0, 128.4, 128.7 and 134.1 (Ph), 124.6, 142.7, 142.9 and 141.4 (picryl), 161.6 (C-5).

Anal. Calcd. for $\text{C}_{14}\text{H}_9\text{N}_7\text{O}_6\text{S}$ (mol wt 403): C, 41.69; H, 2.23. Found: C, 41.67; H, 2.32.

4-(*p*-Methoxybenzyl)-5-picrylimino-1,2,3,4-thiatriazoline (5b).

This compound was similarly prepared from picryl isothiocyanate and two equivalents of *p*-methoxybenzyl azide (reaction time 6 hours at 55°), yield 89%, mp 152° dec (acetonitrile); ir (potassium bromide): 3100 (m), 1630 (s), 1605 (s, br), 1545 and 1340 cm^{-1} (s); ^1H nmr (dimethyl sulfoxide- d_6): δ 3.8 (s, 3H, OCH_3), 5.5 (s, 2H, CH_2), 6.9 and 7.3 (two d, 4 anisyl H), 9.1 (s, 2H, picryl); ^{13}C nmr (dimethyl sulfoxide- d_6): δ 50.6 (CH_2), 55.1 (OCH_3), 114.1, 126.1, 129.8 and 159.3 (anisyl), 124.6, 141.3, 142.6 and 142.9 (picryl), 161.5 (C-5).

Anal. Calcd. for $\text{C}_{15}\text{H}_{11}\text{N}_7\text{O}_7\text{S}$ (mol wt 433): C, 41.57; H, 2.54. Found: C, 41.58; H, 2.53.

4-(*t*-Butylbenzyl)-5-picrylimino-1,2,3,4-thiaziazoline (**5c**).

This compound was prepared from picryl isothiocyanate (1.08 g, 4 mmoles) and two equivalents of *p*-(*t*-butyl)benzyl azide (1.51 g) in carbon tetrachloride (25 ml), reaction time 18 hours at 55°. The reaction mixture was worked up by filtration of the hot solution, concentration of the filtrate to 1/4th of its original volume, addition of a mixture of ether/petroleum ether (25 ml, 2:1) and cooling, yield 75% (1.375 g). A second crop (150 mg) can be obtained by addition of more petroleum ether to the mother liquor and cooling, overall yield 83%, mp 134° (ether/petroleum ether/dichloromethane, 6:3:1); ir (potassium bromide): 3100 (m), 2970 (m), 1630 (s), 1610 (s, br), 1535 and 1345 cm⁻¹ (s, br); ¹H nmr (dimethyl sulfoxide-*d*₆): δ 1.3 (s, 9H, *t*-Bu), 5.6 (s, 2H, CH₂), 7.3 and 7.4 (two d, 4 phenyl H), 9.1 (s, 2H, picryl); ¹³C nmr (dimethyl sulfoxide-*d*₆): δ 31.0 and 34.3 (*t*-Bu), 50.6 (CH₂), 125.6, 127.9, 131.1 and 150.9 (phenyl), 124.5, 141.3, 142.6 and 142.8 (picryl), 161.5 (C-5).

Anal. Calcd. for C₁₈H₁₇N₇O₆S (mol wt 459): C, 47.06; H, 3.70. Found: C, 47.12; H, 3.70.

4-(*n*-Butyl)-5-picrylimino-1,2,3,4-thiaziazoline (**5d**).

This compound was obtained by reacting picryl isothiocyanate (0.80 g, 3 mmoles) with *n*-butyl azide (0.59 g, 6 mmoles) in carbon tetrachloride (10 ml) at room temperature for 3 days. After evaporation of the solvent, the residue was chromatographed on silica gel with dichloromethane as the eluent to give **5d** as a yellow oil in 82% yield (0.9 g); ir (carbon tetrachloride): 3100 (w), 1640 (s), 1610 (s), 1545 and 1340 cm⁻¹ (s); ¹H nmr (250 MHz, deuteriochloroform): δ 1.0 (t, 3H, CH₃), 1.45 (sextet, 2H, CH₂), 1.95 (quintet, 2H, CH₂), 4.4 (t, 2H, CH₂N), 9.0 (s, 2H, picryl); ¹³C nmr (deuteriochloroform): δ 13.4, 19.5, 29.8 and 48.5 (*n*-Bu), 124.3, 141.0, 143.2 and 144.6 (picryl), 161.8 (C-5).

Oil not analyzed; M⁺ Calcd: 369.0491. Found: 369.0484.

4-Isopropyl-5-picrylimino-1,2,3,4-thiaziazoline (**5e**).

This compound was prepared by reacting picryl isothiocyanate (1.08 g, 4 mmoles) with two equivalents of isopropyl azide (0.68 g) in carbon tetrachloride (30 ml) at 55° for 16 hours. The reaction was worked up by cooling the solution to -10°, removal of the unreacted isothiocyanate by filtration and evaporation of the filtrate; yield 92% (1.3 g), mp 108° (tetrahydrofuran/petroleum ether); ir (potassium bromide): 3090 (s), 1665 (s, br), 1620 and 1590 (s), 1530 and 1345 cm⁻¹ (s); ¹H nmr (dimethyl sulfoxide-*d*₆): δ 1.6 (d, 6H, two CH₃), 4.8 (septet, 1H, CH), 9.05 (s, 2H, picryl); ¹³C nmr (dimethyl sulfoxide-*d*₆): δ 20.8 and 52.3 (CHMe₂), 124.7, 141.2, 142.5 and 143.2 (picryl), 161.3 (C-5).

Anal. Calcd. for C₁₀H₉N₇O₆S (mol wt 355): C, 33.80; H, 2.54. Found: C, 33.86; H, 2.45.

4-Methoxycarbonylmethyl-5-picrylimino-1,2,3,4-thiaziazoline (**5f**).

This compound was prepared by reacting picryl isothiocyanate (1.08 g, 4 mmoles) with two equivalents of methyl azidoacetate (0.92 g) in carbon tetrachloride (25 ml) at 55° for 18 hours. The solution was cooled to -10°, the crystals were filtered off (1.25 g), the mother liquor was evaporated and the residue crystallized from tetrahydrofuran/petroleum ether to give a second crop of product (120 mg), overall yield 89% (1.37 g), mp 134°; ir (potassium bromide): 3095 (m), 1760 (s), 1630 (s), 1610 (s), 1530-1550 and 1345 cm⁻¹ (s); ¹H nmr (dimethyl sulfoxide-*d*₆): δ 3.75 (s, 3H, CH₃), 5.35 (s, 2H, CH₂), 9.1 (s, 2H, picryl); ¹³C nmr

(dimethyl sulfoxide-*d*₆): δ 48.5 (CH₃), 52.8 (OCH₃), 124.3, 141.6, 142.1 and 142.7 (picryl), 161.3 (C-5), 166.1 (CO).

Anal. Calcd. for C₁₀H₉N₇O₆S (mol wt 385): C, 31.17; N, 1.82. Found: C, 31.16; H, 1.80.

5-Picrylimino-4-trimethylsilylmethyl-1,2,3,4-thiaziazoline (**5g**).

This compound was prepared by reacting picryl isothiocyanate (1.08 g, 4 mmoles) with an excess of trimethylsilylmethyl azide (3 g) in carbon tetrachloride (25 ml) at 55° for 18 hours. The reaction mixture was filtered and the filtrate was evaporated and crystallized from ether/petroleum ether, yield 65% (1.04 g), mp 109°; ir (potassium bromide): 3100 (m), 1595 (s), 1535 and 1350 cm⁻¹ (s); ¹H nmr (deuteriochloroform): δ 0.3 (s, 9H, SiMe₃), 3.8 (s, 2H, CH₂), 8.95 (s, 2H, picryl); ¹³C nmr (deuteriochloroform): δ -2.2 (SiMe₃), 39.7 (CH₂), 124.4, 141.0, 143.5 and 144.9 (picryl), 162.6 (C-5).

Anal. Calcd. for C₁₁H₁₃N₇O₆Si (mol wt 399): C, 33.18; H, 3.26. Found: C, 33.14; H, 3.13.

4-(β-Chloroethyl)-5-picrylimino-1,2,3,4-thiaziazoline (**5h**).

This compound was prepared by reacting picryl isothiocyanate (1.08 g, 4 mmoles) with two equivalents of β-chloroethyl azide (0.85 g) in carbon tetrachloride (25 ml) at 55° for 18 hours. After evaporation of the solvent, the residue was crystallized from tetrahydrofuran/petroleum ether; yield 70% (1.05 g), mp 108° (carbon tetrachloride); ir (potassium bromide) 3100 (m), 1660 (s), 1615 (s), 1530 and 1345 cm⁻¹ (s); ¹H nmr (250 MHz, dimethylsulfoxide-*d*₆) δ 4.1 and 4.8 (two t, 4H, CH₂CH₂), 9.1 (s, 2H, picryl); ¹³C nmr (dimethylsulfoxide-*d*₆) δ 40.6 and 49.6 (ClCH₂CH₂N), 124.6, 141.5, 142.6 and 142.7 (picryl), 161.4 (C-5).

Anal. Calcd. for C₉H₈ClN₇O₆S (mol wt 375): C, 28.76; H, 1.60. Found: C, 28.86; H, 1.53.

2,4-Dibenzyl-5-picrylimino-1,2,4-thiadiazolidin-3-one (**6a**).

A solution of **5a** (0.2 g, 0.5 mmole) and benzyl isocyanate (133 mg, 1 mmole) in chloroform (7 ml) was heated at 60° for 24 hours. After removal of the solvent, the residue was crystallized from chloroform/ether to give **6a** in 86% yield (217 mg), mp 175°; ir (potassium bromide): 3095 (w), 1730 (s, C=O), 1630 (s, C=N), 1600 (s), 1545 and 1345 cm⁻¹ (s); ¹H nmr (deuteriochloroform): δ 4.76 and 5.02 (two s, 4H, CH₂ at N-2 and N-4), 7.2-7.5 (m, 10H, two Ph), 8.87 (s, 2H, picryl); ¹³C nmr (deuteriochloroform): δ 47.6 and 49.5 (CH₂ at N-4 and N-2, ¹J_{CH} = 142 Hz), 124.3, 141.2, 141.8 and 142.9 (picryl), 128.3-129.1, 133.6 and 134.2 (two Ph), 153.2 (C-3), 156.5 (C-5, ³J_{CH} = 4.5 Hz).

Anal. Calcd. for C₂₂H₁₆N₆O₇S (mol wt 508): C, 51.97; H, 3.15. Found: C, 51.82; H, 2.99.

4-Benzyl-2-(*t*-butyl)-5-picrylimino-1,2,4-thiadiazolidin-3-one (**6b**).

A solution of **5a** (0.2 g, 0.5 mmole) and *t*-butyl isocyanate (147 mg, 1.5 mmoles) in chloroform (4 ml) was heated at 60° for 5 days. After removal of the solvent, the residue was crystallized from ether to give **6b** in 93% yield (219 mg), mp 125°; ir (potassium bromide): 3095 (w), 1730 (s, C=O), 1640 (s, C=N), 1600 (s), 1545 and 1345 cm⁻¹ (s); ¹H nmr (deuteriochloroform): δ 1.6 (s, 9H, *t*-Bu), 5.0 (s, 2H, CH₂), 7.4 (s, 5H, Ph), 9.0 (s, 2H, picryl); ¹³C nmr (deuteriochloroform): δ 28.3 and 60.0 (*t*-Bu), 47.1 (CH₂), 124.2, 141.0, 142.2 and 143.1 (picryl), 128.1, 128.3, 128.5 and 134.4 (Ph), 152.2 (C-3), 156.2 (C-5).

Anal. Calcd. for C₁₅H₁₈N₆O₇S (mol wt 474): C, 48.10; H, 3.80. Found: C, 48.25; H, 3.92.

4-Benzyl-2-phenyl-5-picrylimino-1,2,4-thiadiazolidin-3-one (**6c**).

A solution of **5a** (0.2 g, 0.5 mmole) and phenyl isocyanate (119 mg, 1 mmole) in chloroform (10 ml) was heated at 60° for 1 day. After removal of the solvent, the residue was crystallized from chloroform/*n*-hexane to give **6c** as yellow crystals in 89% yield (220 mg), mp 175°; ir (potassium bromide): 3090 (w), 1735 (s, C=O), 1630 (s, C=N), 1600 (s), 1535 and 1345 cm⁻¹ (s); ¹H nmr (deuteriochloroform): δ 5.1 (s, 2H, CH₂), 7.2-7.6 (m, 10H, two Ph), 8.9 (s, 2H, picryl); ¹³C nmr (deuteriochloroform): δ 47.8 (CH₂), 124.3, 141.5 (x2) and 143.0 (picryl), 123.3, 127.4, 128.4, 128.7, 128.8, 130.0, 134.0 and 135.2 (two Ph), 150.9 (C-3), 155.3 (C-5).

Anal. Calcd. for C₂₁H₁₄N₆O₇S (mol wt 494): C, 51.01; H, 2.83. Found: C, 50.93; H, 2.81.

2-Benzoyl-4-benzyl-5-picrylimino-1,2,4-thiadiazolidin-3-one (**6d**).

Compound **5a** (0.2 g, 0.5 mmole) was allowed to react with two equivalents of benzoyl isocyanate (146 mg) in chloroform (4 ml) at room temperature for 24 hours. After removal of the solvent, the residue was crystallized from chloroform/*n*-hexane to give **6d** in 96% yield (249 mg), mp 228°; ir (potassium bromide): 3095 (m), 1770 and 1690 (s, C=O), 1645 (s, C=N), 1605 (s), 1540 and 1345 cm⁻¹ (s); ¹H nmr (tetrahydrofuran-d₈): δ 5.05 (s, 2H, CH₂), 7.3-7.9 (two m, 10H, two Ph), 9.15 (s, 2H, picryl); ¹³C nmr (tetrahydrofuran-d₈): δ 48.0 (CH₂), 125.3, 141.1, 143.7 and 143.9 (picryl), 128.3, 128.8, 129.2, 129.6, 130.4, 132.9, 133.2, 135.5 (two Ph), 149.3 (C-3), 156.3 (C-5), 167.0 (CO).

Anal. Calcd. for C₂₂H₁₄N₆O₈S (mol wt 522): C, 50.57; H, 2.68. Found: C, 50.42; H, 2.60.

2-Benzenesulfonyl-4-benzyl-5-picrylimino-1,2,4-thiadiazolidin-3-one (**6e**).

This compound was obtained by reacting **5a** (0.2 g, 0.5 mmole) with benzenesulfonyl isocyanate (182 mg, 1 mmole) in chloroform (4 ml) at room temperature for 1 hour. The solvent was removed and the residue was crystallized from chloroform/*n*-hexane to give **6e** in 88% yield (245 mg); mp 196°; ir (potassium bromide): 3100 (m), 1750 (m, C=O), 1660 (s, C=N), 1610 (s), 1540 and 1345 cm⁻¹ (s); ¹H nmr (250 MHz, tetrahydrofuran-d₈): δ 4.85 (s, 2H, CH₂), 7.1-8.1 (five m, 10H, two Ph), 9.10 (s, 2H, picryl); ¹³C nmr (tetrahydrofuran-d₈): δ 48.2 (CH₂), 125.2, 140.4 and 143.8 (x2) (picryl), 128.7, 129.2, 129.6, 130.5, 134.9, 136.3, 136.5 (two Ph), 150.8 (C-3), 155.9 (C-5).

Anal. Calcd. for C₂₁H₁₄N₆O₉S₂ (mol wt 558): C, 45.16; H, 2.51. Found: C, 45.01; H, 2.52.

4-Benzyl-5-picrylimino-1,2,4-thiadiazolidin-3-one (**7**).

Compound **5a** (0.2 g, 0.5 mmole) was allowed to react with chlorosulfonyl isocyanate (105 mg, 1.5 mmoles) in chloroform (3 ml) at room temperature for 1 hour. A precipitate was formed soon after mixing the components. The solvent was removed and the residue was refluxed in methanol for 1 hour. After cooling the solution to -15°, **7** was isolated in 84% yield (226 mg), mp 242° (ethanol/acetonitrile); ir (potassium bromide): 3095 (m), 1715 (m, C=O), 1630 (s, C=N), 1595 (s), 1535 and 1345 cm⁻¹ (s); ¹H nmr (dimethyl sulfoxide-d₆): δ 4.90 (s, 2H, CH₂), 7.3 (s, 5H, Ph), 9.05 (s, 2H, picryl); ¹³C nmr (dimethyl sulfoxide-d₆): δ 46.0 (CH₂), 124.6, 140.5, 141.5 and 142.6 (picryl), 127.7, 128.3 and 135.0 (Ph), 154.1 (C-4), 159.4 (C-5).

Anal. Calcd. for C₁₅H₁₀N₆O₇S (mol wt 418): C, 43.06; H, 2.39. Found: C, 43.07; H, 2.35.

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