# Addition-Rearrangement Reactions of 5-Amino-3-oxo-$\Delta^4$-1,2,4-thiadiazolines

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Bond-switching rearrangement *via* hypervalent sulfur occurs during the reactions of 5-anilino-2-benzyl-3-oxo-$\Delta^4$-1,2,4-thiadiazoline **5** with electrophilic nitriles, isothiocyanates, carbon disulfide and ketenes, yielding the products **6** and **7**. In contrast, *N,N'*-ditolylcarbodiimide reacts with **5** to give the normal addition product **8**, which rearranges only partially to **9** in several solvents (chloroform, acetonitrile and dimethyl sulfoxide). The equilibrium position depends on the temperature, favoring **9** at higher temperatures.

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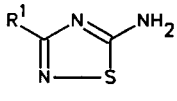
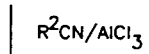
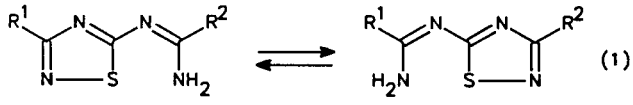
5-Amino-1,2,4-thiadiazoles **1** are converted by nitriles into amidine derivatives which are capable of rearranging to other thiadiazoles with a different substitution pattern (eq 1) [1]. These so-called bond-switching rearrangements are interpreted as proceeding through thiapentalene intermediates with a linear, three-center, four-electron N-S-N bond [2].



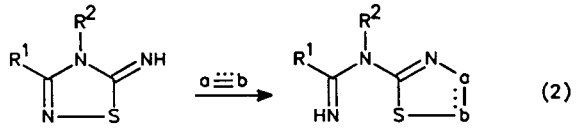
**1**





(1)

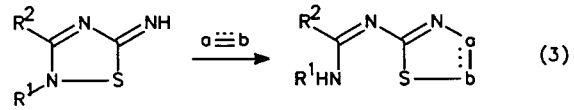
Similar transformations have been reported for the reactions of 5-imino-$\Delta^2$-1,2,4-thiadiazolines **2** and 5-imino-$\Delta^3$-1,2,4-thiadiazolines **3** with several unsaturated reagents a=b (eq 2 [3] and eq 3 [4]). We have recently found that 5-amino-3-oxo-$\Delta^4$-1,2,4-thiadiazolines **4** also undergo bond-switching rearrangements after addition of isocyanates (eq 4) [5]. In continuation of this research, we have now investigated the addition-rearrangement reactions of **4** with other heterocumulenes and with electrophilic nitriles; the results are described below.



(2)

**2**

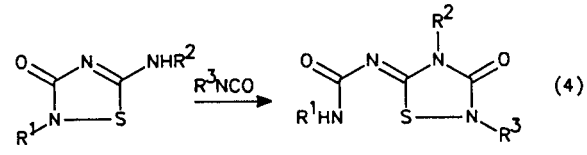
a=b = $R^3CN$, $CS_2$



(3)

**3**

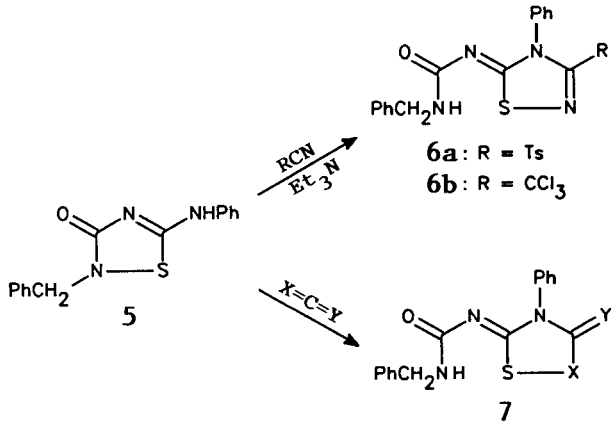
a=b = $Ph_2C{=}C{=}O$, MeOOC−C≡C−COOMe, $CH_2{=}SO_2$



(4)

**4**

In 1980 Butler *et al.* [6] reported that Hector's Base (**2**, $R^1$ = PhNH, $R^2$ = Ph) reacts with methyl isocyanate and phenyl isocyanate to give the corresponding (unrearranged) addition products. With this knowledge at hand



**6a**: R = Ts
**6b**: R = $CCl_3$

**5**

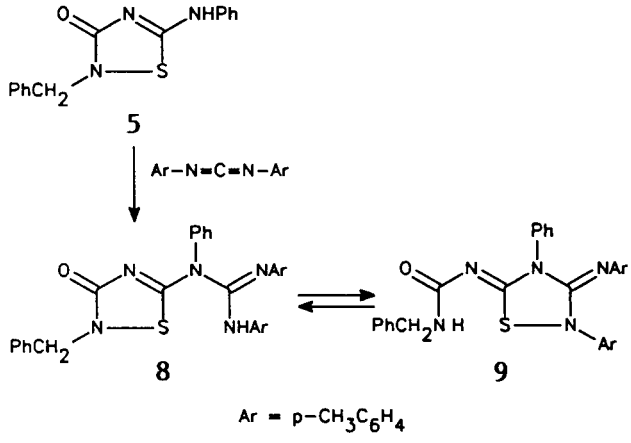
**7**

| 7 | X | Y |
|---|---|---|
| a | NEt | S |
| b | S | $NC_6H_4NO_2$(p) |
| c | S | $NCO_2Et$ |
| d | S | NCOPh |
| e | S | S |
| f | $Ph_2C$ | O |
| g | $(EtO_2C)_2C$ | O |

we expected that the thiadiazoline **5** would combine with electrophilic nitriles to furnish $\Delta^2$-thiadiazoline derivatives of structure **6** as a result of addition-rearrangement. This was indeed the case when **5** was reacted with tosyl cyanide and trichloroacetonitrile in refluxing tetrahydrofuran and in the presence of triethylamine as catalyst. The products **6a,b** were easily characterized by their methylene doublet at $\delta$ 4.4 in the $^1$H nmr spectra, and further supported by the $^{13}$C nmr spectra (see Experimental).

Compound **5** also reacted with isothiocyanates, carbon disulfide and ketenes to give rearranged addition products **7a-g**. They all exhibited a diagnostic methylene doublet at $\delta$ 4.35-4.4 in the $^1$H nmr spectra, and typical carbon resonances for the carbamoylimino side-chain in the $^{13}$C nmr spectra (CO at $\delta$ 162-164, C=N at $\delta$ 166-171) [5]. In addition, **7a** and **7e** showed a positive Feigl test for the C=S function [7], whereas **7b-d** did not. This criterion, as well as the $^{13}$C nmr data, allowed us to decide whether the isothiocyanate C=N or C=S function is involved in the heterocyclization process.

In contrast, the 1:1 adduct from **5** and *N,N'*-ditolylcarbodiimide corresponds to structure **8** since its $^1$H nmr spectrum in deuterated benzene or tetrachloroethane displayed a singlet methylene absorption at $\delta$ 4.7. In deuterated chloroform and in more polar solvents, such as acetonitrile and dimethyl sulfoxide, **8** equilibrates with **9** at room temperature (Table 1).




A detailed nmr analysis in tetrachloroethane at different temperatures revealed that the equilibrium position is shifted towards **9** at higher temperatures, while **8** also dissociates partially into the starting materials (see Table 1). We noticed that at 120° the two methyl singlets of **8** coalesced at $\delta$ 2.15. When this hot solution was cooled to room temperature, the amount of **8** increased at the expense of **5** and **9**.

A similar behavior was observed in deuterated dimethyl sulfoxide. Upon raising the temperature, **8** decomposed into **5** and carbodiimide while the ratio **8**:**9** decreased. At 70° the two methyl resonances of **8** coalesced, and at 110° a mixture was obtained composed mainly of **5** and the carbodiimide (Table 1). When this mixture was allowed to cool, recombination of **5** with carbodiimide occurred and the amount of **8** increased.

Table 1
Product Distribution of **5**, **8** and **9** in Several Solvents

| Solvent | Temperature °C | **5** % | **8** % | **9** % |
|---|---|---|---|---|
| $C_6D_6$ | 20 | 0 | 100 | 0 |
| $CDCl_2CDCl_2$ | 20 | 0 | 100 | 0 |
| | 80 | 0 | 90 | 10 |
| | 120 | 26 | 35 | 39 |
| $CDCl_3$ | 20 | 0 | 80 | 20 |
| $CD_3CN$ | 20 | 0 | 70 | 30 |
| $(CD_3)_2SO$ | 20 | 0 | 69 | 31 |
| | 70 | 27 | 39 | 34 |
| | 110 | 58 | 21 | 21 |

## EXPERIMENTAL

The ir spectra (potassium bromide) were recorded on a Perkin Elmer 1720 FT spectrometer, the nmr spectra (deuteriochloroform) on a Bruker WM-250 spectrometer at 250 ($^1$H) and 62.9 MHz ($^{13}$C), and the mass spectra on a Kratos MS50 TC instrument operating at 70 eV. For the synthesis of compound **5**, see ref 5.

5-Benzylcarbamoylimino-4-phenyl-3-tosyl-$\Delta^2$-1,2,4-thiadiazoline (**6a**).

A suspension of **5** (500 mg, 1.77 mmoles), 1.05 equivalents of tosyl cyanide (336 mg) and five drops of triethylamine in tetrahydrofuran (15 ml) was refluxed for 90 minutes until a clear solution was obtained. The solvent was removed and the residue was triturated with diethyl ether to give **6a** in 90% yield (740 mg), mp 190° (ethanol); ir: 3431 (m, NH), 1631 (s, CO), 1484 (s), 1336 and 1163 cm$^{-1}$ (s, $SO_2$); $^1$H nmr: $\delta$ 2.45 (s, 3H, $CH_3$), 4.4 (d, 2H, $CH_2$), 5.65 (br t, 1H, NH), 7.15-7.65 (three m, 14 aromatic H); $^{13}$C nmr: $\delta$ 21.8 ($CH_3$), 44.8 ($CH_2$), 127.4-130.2, 133.6, 134.0, 138.0 and 146.5 (aromatic C-atoms), 151.8 (C-3), 163.2 (CONH), 176.1 (C-5); ms: m/z (%) 464 (13, $M^+$), 358 (14, $M^+$-$PhCH_2NH$), 309 (19, $M^+$-Ts), 266 (12), 145 (12, $PhN=C=NCO^+$), 132 (33), 118 (10), 106 (17, $PhCH_2NH^+$), 91 (100, $C_7H_7^+$).

*Anal.* Calcd. for $C_{23}H_{20}N_4O_3S_2$ (mol wt 464): C, 59.48; H, 4.31. Found: C, 59.38; H, 4.30.

5-Benzylcarbamoylimino-4-phenyl-3-trichloromethyl-$\Delta^2$-1,2,4-thiadiazoline (**6b**).

A suspension of **5** (500 mg, 1.77 mmoles), 1.05 equivalents of trichloroacetonitrile (268 mg) and five drops of triethylamine in tetrahydrofuran (15 ml) was refluxed until a clear solution was obtained (48 hours). The solvent was removed and the residue was triturated with ethanol to give **6b** in 64% yield (480 mg), mp 203° (acetonitrile); ir: 3388 (m, NH), 1621 (s, CO), 1495 cm$^{-1}$ (s); $^1$H nmr: $\delta$ 4.4 (d, 2H, $CH_2$), 5.65 (br t, 1H, NH), 7.1-7.6 (three m, 10H, 2 Ph); $^{13}$C nmr: $\delta$ 44.9 ($CH_2$), 88.3 ($CCl_3$), 127.4-130.4, 135.8 and

138.2 (Ph C-atoms), 149.0 (C-3), 163.3 (CONH), 178.4 (C-5); ms: m/z (%) 427 (25, $M^{+\cdot}$), 321 (30, $M^{+\cdot}$-3 Cl), 293 (20, $M^{+\cdot}$-$PhCH_2NHCO$), 285 (16), 259 (12), 250 (13), 144 (30), 118 (13), 106 (15, $PhCH_2NH^+$), 91 (100, $C_7H_7^+$).

*Anal.* Calcd. for $C_{17}H_{13}Cl_3N_4OS$ (mol wt 427.5): C, 47.72; H, 3.04. Found: C, 47.63; H, 3.13.

5-Benzylcarbamoylimino-2-ethyl-4-phenyl-1,2,4-thiadiazolidine-3-thione (**7a**).

A suspension of **5** (500 mg, 1.77 mmoles), 1.1 equivalents of ethyl isothiocyanate (169 mg) and five drops of triethylamine in tetrahydrofuran (20 ml) was refluxed overnight to furnish a clear solution. The reaction mixture was flash chromatographed on silica gel with dichloromethane as the eluent to give **7a** in 61% yield (400 mg), mp 150° (methanol); ir: 3430 (m, NH), 1619 (s, CO), 1490 $cm^{-1}$ (s); $^1H$ nmr: $\delta$ 1.4 (t, 3H, $CH_3$), 4.1 (q, 2H, $CH_2Me$), 4.4 (d, 2H, $CH_2NH$), 5.8 (br t, 1H, NH), 7.1-7.6 (two m, 10 H, 2 Ph); $^{13}C$ nmr: $\delta$ 13.1 and 43.9 ($CH_3CH_2$), 45.0 ($CH_2NH$), 127.6-129.5, 137.5 and 137.7 (Ph C-atoms), 164.3 (CONH), 167.9 (C-5), 173.4 (C-3); ms: m/z (%) 370 (72, $M^{+\cdot}$), 283 (6, $M^{+\cdot}$-EtNCS), 265 (11), 236 (9, $M^{+\cdot}$-$PhCH_2NHCO$), 177 (15), 145 (66, $PhN=C=NCO^+$), 135 (42), 119 (18), 106 (24, $PhCH_2NH^+$), 91 (100, $C_7H_7^+$).

*Anal.* Calcd. for $C_{18}H_{18}N_4OS_2$ (mol wt 370): C, 58.38; H, 4.86. Found: C, 58.41; H, 4.93.

3-Benzylcarbamoylimino-5-(*p*-nitrophenylimino)-4-phenyl-1,2,4-dithiazolidine (**7b**).

A suspension of **5** (500 mg, 1.77 mmoles), 1.1 equivalents of *p*-nitrophenyl isothiocyanate (350 mg) and five drops of triethylamine in tetrahydrofuran (20 ml) was stirred overnight at room temperature to furnish a clear solution. The solvent was removed and the residue was triturated with diethyl ether to give **7b** in 84% yield (690 mg). This compound formed a 1:1 complex with acetonitrile upon crystallization from this solvent, mp 148°; ir: 3300 (w, NH), 1625 (s, CO), 1582 (s), 1495 and 1339 $cm^{-1}$ ($NO_2$); $^1H$ nmr: $\delta$ 1.95 (s, 3H, $CH_3CN$), 4.35 (d, 2H, $CH_2$), 5.7 (br t, 1H, NH), 7.0 and 8.2 (two d, 4H, *p*-$NO_2C_6H_4$), 7.15-7.6 (two m, 10H, 2 Ph); $^{13}C$ nmr: $\delta$ 44.9 ($CH_2$), 121.6, 125.4, 144.6 and 155.2 (*p*-$NO_2C_6H_4$), 127.7-129.6, 137.7 and 138.7 (Ph C-atoms), 156.4 (C-5), 163.1 (CONH), 168.9 (C-3); ms: m/z (%) no $M^{+\cdot}$, 283 (31, $M^{+\cdot}$-*p*-$NO_2C_6H_4NCS$), 180 (8, *p*-$NO_2C_6H_4NCS^{+\cdot}$), 145 (25, $PhN=C=NCO^+$), 118 (14), 91 (100, $C_7H_7^+$).

*Anal.* Calcd. for $C_{22}H_{17}N_5O_3S_2 \cdot CH_3CN$ (mol wt 504): C, 57.14; H, 3.97. Found: C, 56.88; H, 3.87.

3-Benzylcarbamoylimino-5-ethoxycarbonylimino-4-phenyl-1,2,4-dithiazolidine (**7c**).

A suspension of **5** (500 mg, 1.77 mmoles), 1.1 equivalents of ethoxycarbonyl isothiocyanate (255 mg) and five drops of triethylamine in tetrahydrofuran (20 ml) was stirred at room temperature for 2 hours to furnish a clear solution. The solvent was removed and the residue was triturated with hexane/diethyl ether (2:1) to give **7c** as a pale yellow powder in 87% yield (640 mg), mp 192° (toluene); ir: 3342 (m, NH), 1630 (s, CO), 1489 $cm^{-1}$ (s); $^1H$ nmr: $\delta$ 1.25 (t, 3H, $CH_3$), 4.2 (q, 2H, $CH_2Me$), 4.35 (d, 2H, $CH_2$), 7.15-7.5 (two m, 10H, 2 Ph); $^{13}C$ nmr: $\delta$ 14.2 and 62.9 ($CH_3CH_2$), 44.7 ($CH_2NH$), 127.4-129.6, 137.7 and 138.9 (Ph C-atoms), 162.2 (CONH), 163.3 (COO), 168.3 (C-3), 173.0 (C-5); ms: m/z (%) 414 (7, $M^{+\cdot}$), 283 (6, $M^{+\cdot}$-EtOCONCS), 145 (12, $PhN=C=NCO^+$), 119 (21), 91 (100, $C_7H_7^+$).

*Anal.* Calcd. for $C_{19}H_{18}N_4O_3S_2$ (mol wt 414): C, 55.07; H, 4.35. Found: C, 55.00; H, 4.34.

3-Benzoylimino-5-benzylcarbamoylimino-4-phenyl-1,2,4-dithiazolidine (**7d**).

A suspension of **5** (500 mg, 1.77 mmoles) and 1.1 equivalents of benzoyl isothiocyanate (317 mg) in dry tetrahydrofuran (20 ml) was refluxed until a clear solution was obtained (21 hours). The reaction mixture was subjected to column chromatography on silica gel with dichloromethane and dichloromethane/methanol (100:1) as the eluents to give **7d** in 57% yield (450 mg), mp 187°; ir: 3421 (m, NH), 1636 (s, CO), 1610 (m), 1449 $cm^{-1}$ (s); $^1H$ nmr: $\delta$ 4.4 (d, 2H, $CH_2$), 5.7 (br t, 1H, NH), 7.2-7.9 (two m + one d, 15H, 3 Ph); $^{13}C$ nmr: $\delta$ 44.8 ($CH_2$), 127.6-129.9, 133.0, 134.4, 137.8 and 139.4 (Ph C-atoms), 162.2 (CONH), 167.8 (C-5), 171.8 (C-3), 176.2 (COPh); ms: m/z (%) 446 (3, $M^{+\cdot}$), 283 (12, $M^{+\cdot}$-PhCONCS), 145 (14, $PhN=C=NCO^+$), 105 (100, $PhCH_2N^{+\cdot}$), 91 (62, $C_7H_7^+$).

*Anal.* Calcd. for $C_{23}H_{18}N_4O_2S_2$ (mol wt 446): C, 61.89; H, 4.04. Found: C, 61.75; H, 4.13.

5-Benzylcarbamoylimino-4-phenyl-1,2,4-dithiazolidine-3-thione (**7e**).

A suspension of **5** (500 mg, 1.77 mmoles) in carbon disulfide (50 ml) containing ten drops of triethylamine was refluxed until a clear solution was obtained (24 hours). The solvent was removed and the residue was triturated with diethylether to give **7e** in 63% yield (400 mg), mp 143° (carbon tetrachloride); ir: 3400 (m, NH), 1631 (s, CO), 1495 $cm^{-1}$ (s); $^1H$ nmr: $\delta$ 4.35 (d, 2H, $CH_2$), 5.7 (br t, 1H, NH), 7.1-7.6 (two m, 10H, 2 Ph); $^{13}C$ nmr: $\delta$ 44.8 ($CH_2$), 127.4-1.29.7, 137.4 and 139.5 (Ph C-atoms), 162.4 (CONH), 171.2 (C=N), 196.0 (C=S); ms: m/z (%) 359 (11, $M^{+\cdot}$), 283 (11, $M^{+\cdot}$-$CS_2$), 226 (14, $M^{+\cdot}$-$PhCH_2NCO$), 224 (14), 167 (23), 135 (52, $PhNCS^{+\cdot}$), 133 (22, $PhCH_2NCO^{+\cdot}$), 105 (11, $PhCH_2N^{+\cdot}$), 91 (100, $C_7H_7^+$).

*Anal.* Calcd. for $C_{16}H_{13}N_3OS_3$ (mol wt 359): C, 53.48; H, 3.62. Found: C, 53.61; H, 3.49.

2-Benzylcarbamoylimino-3,5,5-triphenylthiazolidin-4-one (**7f**).

A suspension of **5** (500 mg, 1.77 mmoles) and 1.2 equivalents of diphenylketene (411 mg) in dry tetrahydrofuran (20 ml) was stirred at room temperature until a clear solution was obtained (5 hours). The reaction mixture was subjected to column chromatography on silica gel with dichloromethane as the eluent to give **7f** in 30% yield (240 mg), mp 80°; ir: 3413 (m, NH), 1733 (s, CO), 1658 (s, CO), 1577 (s), 1494 $cm^{-1}$ (s); $^1H$ nmr: $\delta$ 4.4 (d, 2H, $CH_2$), 5.75 (br t, 1H, NH), 7.15-7.5 (m, 20H, 4 Ph); $^{13}C$ nmr: $\delta$ 44.7 ($CH_2$), 65.5 (C-5), 127.6-129.3, 135.2, 138.1 and 140.4 (Ph C-atoms), 161.8 (CONH), 166.1 (C-2), 174.9 (C-4); ms: m/z (%) 477 (36, $M^{+\cdot}$), 371 (11, $M^{+\cdot}$-$PhCH_2NH$), 283 (48, $M^{+\cdot}$-$Ph_2C=C=O$), 208 (13), 198 (16, $Ph_2CS^{+\cdot}$), 194 (100, $Ph_2C=C=O^{+\cdot}$), 165 (62, $Ph_2C^+$-H), 145 (43, $PhN=C=NCO^+$), 121 (23), 106 (21, $PhCH_2NH^+$), 91 (35, $C_7H_7^+$).

*Anal.* Calcd. for $C_{29}H_{23}N_3O_2S$ (mol wt 477): C, 72.96; H, 4.82. Found: C, 72.79; H, 4.88.

2-Benzylcarbamoylimino-5,5-bis(ethoxycarbonyl)-3-phenylthiazolidin-4-one (**7g**).

A suspension of **5** (500 mg, 1.77 mmoles) and 0.9 equivalent of bis(ethoxycarbonyl)ketene (296 mg) in dry tetrahydrofuran (15 ml) was stirred at room temperature for 5 hours. The excess of **5** was filtered off and the filtrate was evaporated. The residue was crystallized from diethyl ether/hexane (20 ml, 3:1) to give **7g** in 50% yield (375 mg), mp 111° (dichloromethane/hexane, 2:1); ir: 3441 (m, NH), 1768, 1749, 1728 and 1660 (s, CO), 1581 (m), 1505

$cm^{-1}$ (s); $^1H$ nmr: δ 1.35 (t, 6H, 2 $CH_3$), 4.3-4.4 (d + q, 6H, 3 $CH_2$), 5.8 (br t, 1H, NH), 7.15-7.5 (two m, 10H, 2 Ph); $^{13}C$ nmr: δ 13.8 and 63.8 ($CH_3CH_2$), 44.7 ($CH_2N$), 64.4 (C-5), 127.6-129.2, 134.6 and 137.6 (Ph C-atoms), 161.5 (CONH), 163.6 (COO), 165.7 (C-4), 166.0 (C-2); ms: m/z (%) 469 (37, $M^{+\cdot}$), 363 (19, $M^{+\cdot}$-$PhCH_2NH$), 337 (55), 245 (45), 219 (32), 145 (33, $PhN=C=NCO^+$), 118 (22), 106 (24, $PhCH_2NH^+$), 91 (100, $C_7H_7^+$).

*Anal.* Calcd. for $C_{23}H_{23}N_3O_6S$ (mol wt 469): C, 58.85; H, 4.90. Found: C, 58.66; H, 4.87.

2-Benzyl-5-(2,3-di-*p*-tolyl-1-phenylguanidino)-3-oxo-$\Delta^4$-1,2,4-thiadiazoline (**8**).

A suspension of **5** (500 mg, 1.77 mmoles), 1.1 equivalents of *N,N'*-ditolylcarbodiimide (431 mg) and five drops of triethylamine in tetrahydrofuran (20 ml) was refluxed overnight until a clear solution was obtained. The reaction mixture was subjected to column chromatography on silica gel with dichloromethane/methanol (100:1) as the eluent to give **8** in 87% yield (780 mg), mp 175° (chloroform/hexane, 1:2); ir: 3210 (w, NH), 1641 (s, CO), 1596 (s), 1505 $cm^{-1}$ (s); $^1H$ nmr: δ 2.1 (s, 3H, $CH_3$), 2.2 (s, 3H, $CH_3$), 4.7 (s, 2H, $CH_2$), 6.25 (s, 1H, NH), 6.5 and 6.9 (two d, 8H, 2 tolyl), 6.65-6.75 and 7.2-7.5 (two m, 10H, 2 Ph) (Note: the nmr spectrum in deuteriochloroform also shows the presence of 20% **9** with a $CH_2$ doublet at δ 4.4); $^{13}C$ nmr: δ 20.6 and 20.8 ($CH_3$), 44.9 ($CH_2$), 122.0, 122.1, 127.2-130.0, 133.3-137.8 (aromatic C-atoms), 143.0 (N-C=N), 163.3 (C-3), 167.5 (C-5); ms: m/z (%) 505 (0.4, $M^{+\cdot}$), 283 (17, $M^{+\cdot}$-Tol-N=C=N-Tol), 222 (80, Tol-N=C=N-$Tol^{+\cdot}$), 145 (19, $PhN=C=N-CO^+$), 91 (100, $C_7H_7^+$).

*Anal.* Calcd. for $C_{30}H_{27}N_5OS$ (mol wt 505): C, 71.29; H, 5.35. Found: C, 71.06; H, 5.48.

Acknowledgment.

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## REFERENCES AND NOTES

[1] K.-y. Akiba, T. Kobayashi and S. Arai, *J. Am. Chem. Soc.*, **101**, 5857 (1979); Y. Yamamoto and K.-y. Akiba, *Bull. Chem. Soc. Japan*, **62**, 479 (1989).

[2] C. Th. Pedersen, *Sulfur Rep.*, **1**, 1 (1980); J. C. Martin, *Science*, **221**, 509 (1983).

[3] K.-y. Akiba, T. Tsuchiya, N. Inamoto, K. Onuma, N. Nagashima and A. Nakamura, *Chem. Letters*, 723 (1976); K.-y. Akiba, S. Arai, T. Tsuchiya, Y. Yamamoto and F. Iwasaki, *Angew. Chem., Int. Ed. Engl.*, **18**, 166 (1979); A. R. Butler, C. Glidewell and D. C. Liles, *J. Chem. Soc., Chem. Commun.*, 652 (1978); A. R. Butler, C, Glidewell and D. C. Liles, *Acta Cryst.*, **B34**, 2570 (1978).

[4] G. L'abbé, G. Vermeulen, S. Toppet, G. S. D. King, J. Aerts and L. Sengier, *J. Heterocyclic Chem.*, **18**, 1309 (1981).

[5] G. L'abbé, E. Albrecht and S. Toppet, *J. Heterocyclic Chem.*, **28**, 1619 (1991).

[6] A. R. Butler, C. Glidewell, I. Hussain and P. R. Maw, *J. Chem. Res. (S)*, 114 (1980).

[7] F. Feigl in Spot Tests in Organic Analysis, Elsevier, Amsterdam, 5th English Ed, 1956, pp 228-232.