# Regioselection in the Reaction of 3-Amino-5-benzylthio-1,2,4-triazole with Unsymmetrical 1,3-Diketones



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The results of a study of the regioselection in the reaction of 3-amino-5-benzylthio-1,2,4-triazole with several unsymmetrical 1,3-diketones are reported. The 1,3-diketones studied are 1,1,1-trifluoro-2,4-pentanedione, benzoylacetone and 2-acetylcyclopentanone. Chemical, spectroscopic and X-ray crystallographic data are presented to support structural assignments of the major reaction products.

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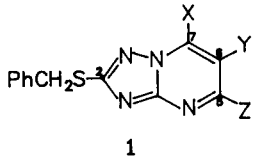
For several years we have been engaged in a search for new herbicides which act by inhibiting the enzyme acetolactate synthase (EC 4.1.3.18). We have recently described our successes in this effort in the development of a series of new herbicides containing the 1,2,4-triazolo[1,5-*a*]pyrimidine ring system [2]. We have needed a number of 2-benzylthio-1,2,4-triazolo[1,5-*a*]pyrimidines (*e.g.* **1**) substituted in the 5-, 6- and 7-positions with a variety of substituents as intermediates for our synthetic efforts. This report describes some of our work towards compounds with different substituents at the 5- and 7-positions.

The reaction of some aminoazoles with 1,3-dicarbonyl compounds to form azolo[*a*]pyrimidines is described in the literature [3]. The regioselection in the reaction of aminoazoles with some unsymmetrical 1,3-dicarbonyl compounds (*e.g.* β-ketoesters and β-ketoaldehyde derivatives) is well established [4,5]. In contrast the regiochemical outcome of the reactions of aminoazoles with unsymmetrical 1,3-diketones is unknown.

We have examined several examples of the reaction of a number of unsymmetrical 1,3-diketones with 3-amino-5-benzylthio-1,2,4-triazole (**2**) and have determined the structures of the reaction products. The reaction of **2** with 1,1,1-trifluoro-2,4-pentanedione, benzoylacetone and 2-acetylcyclopentanone in glacial acetic acid at reflux produced mixtures of **1a** and **1b** (97:3), **1c** and **1d** (82:18) and **1e** and **1f** (90:10) respectively. The ratios of products formed were determined by integration of appropriate resonances in the $^1$H nmr spectra of the crude products. Major products **1a** and **1e** were obtained in 84% and 61% yields respectively after recrystallization. Compound **1c** was obtained in 69% yield after chromatography on silica gel.



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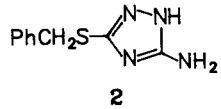


2

**a**: X = $CF_3$; Y = H; Z = Me
**b**: X = Me; Y = H; Z = $CF_3$
**c**: X = Ph; Y = H; Z = Me
**d**: X = Me; Y = H; Z = Ph
**e**: X,Y = $CH_2CH_2CH_2$; Z = Me
**f**: X = Me; Y,Z = $CH_2CH_2CH_2$
**g**: X = OH; Y,Z = $CH_2CH_2CH_2$
**h**: X = Cl; Y,Z = $CH_2CH_2CH_2$

Table 1.
Crystal and Refinement Parameters for **1a** and **1c**

A. Crystal Parameters

| | **1a** | **1c** |
|---|---|---|
| Formula | $C_{14}H_{11}F_3N_4S$ (324.3) | $C_{19}H_{16}N_4S$ (332.4) |
| Crystallization medium | acetone | acetone |
| Crystal size (mm) | 0.41 x 0.44 x 0.47 | 0.33 x 0.34 x 0.44 |
| Cell dimensions | | |
| a (Å) | 4.6605(6) | 7.0396(6) |
| b (Å) | 12.593(2) | 12.736(2) |
| c (Å) | 24.389(4) | 18.342(3) |
| α (°) | 90.0 | 90.0 |
| β (°) | 91.31(1) | 90.0 |
| γ (°) | 90.0 | 90.0 |
| V (Å$^3$) | 1431.0(4) | 1644.5(3) |
| Space group | $P2_1/C$ | $P2_12_12_1$ |
| Molecules/unit cell | 4 | 4 |
| Density observed (g/cm$^3$) | 1.48 | 1.32 |
| Density calculated (g/cm$^3$) | 1.505 | 1.342 |
| Linear absorption coefficient (cm$^{-1}$) | 23.2 | 17.5 |

B. Refinement Parameters

| | **1a** | **1c** |
|---|---|---|
| Number of reflections | 1487 | 1010 |
| Nonzero reflections (1>1.0σ) | 1409 | 965 |
| R-index = Σ\|\|Fo\|-\|Fc\|\|/Σ\|Fo\| | 0.043 | 0.045 |
| GOF = $[\Sigma w(Fo^2-Fc^2)^2/(m-s)]^{1/2}$ | 2.86 | 2.05 |
| Scale factor | 0.860(4) | 0.809(3) |
| Secondary extinction coefficient | 6.6(7) x 10$^{-6}$ | 18.4(8) x 10$^{-6}$ |

Table 2
Atomic Coordinates (x $10^4$) for **1a** and **1c**. Standard deviations are Given in Parenetheses
(See figure 1 for Atom Numbering)

**1a**

| Atom | x/a | y/b | z/c | Atom [a] | x/a | y/b | z/c |
|---|---|---|---|---|---|---|---|
| S1 | 7781( 2) | 8775(1) | 1314(0) | H( C8) | -331 | 4649 | 2438 |
| N1 | 3500( 6) | 6516(2) | 1905(1) | H(C10) | 9731 | 7246 | 912 |
| N2 | 5352( 6) | 6880(2) | 1515(1) | H(C10) | 10917 | 8312 | 610 |
| C3 | 5655( 7) | 7887(3) | 1666(1) | H(C12) | 7295 | 9343 | -11 |
| N4 | 4226( 6) | 8208(2) | 2115(1) | H(C13) | 3890 | 9073 | -757 |
| C5 | 2860( 7) | 7331(3) | 2261(1) | H(C14) | 1815 | 7366 | -905 |
| N6 | 1073( 6) | 7185(2) | 2680(1) | H(C15) | 2908 | 5935 | -299 |
| C7 | -60( 7) | 6226(3) | 2735(1) | H(C16) | 6245 | 6202 | 463 |
| C8 | 540( 7) | 5379(3) | 2374(1) | H(C21) | -795 | 5952 | 3548 |
| C9 | 2324( 7) | 5538(3) | 1951(1) | H(C21) | -3027 | 6848 | 3276 |
| C10 | 9098( 8) | 7960(3) | 757(2) | H(C21) | -3334 | 5491 | 3103 |
| C11 | 7019( 7) | 7789(3) | 289(2) | | | | |
| C12 | 6310( 9) | 8612(3) | -63(2) | | | | |
| C13 | 4403(11) | 8450(4) | -497(2) | | | | |
| C14 | 3182(10) | 7481(5) | -584(2) | | | | |
| C15 | 3866(10) | 6660(4) | -239(2) | | | | |
| C16 | 5784( 9) | 6814(3) | 198(2) | | | | |
| C17 | 3018( 8) | 4737(3) | 1522(2) | | | | |
| F18 | 1803( 5) | 3812(2) | 1625(1) | | | | |
| F19 | 2030( 5) | 5044(2) | 1030(1) | | | | |
| F20 | 5813( 5) | 4574(2) | 1482(1) | | | | |
| C21 | -2066( 8) | 6073(3) | 3199(2) | | | | |

**1c**

| Atom | x/a | y/b | z/c | Atom [a] | x/a | y/b | z/c |
|---|---|---|---|---|---|---|---|
| S1 | 8713( 3) | 5366(1) | 7322(1) | H( C8) | 6859 | 9916 | 5257 |
| N1 | 7701( 6) | 7759(2) | 6160(2) | H(C10) | 9982 | 3908 | 6673 |
| N2 | 8168( 7) | 6704(4) | 6194(2) | H(C10) | 10122 | 4967 | 6174 |
| C3 | 8179( 8) | 6562(5) | 6920(3) | H(C12) | 5701 | 3900 | 6970 |
| N4 | 7792( 7) | 7398(4) | 7342(2) | H(C13) | 3175 | 3253 | 6251 |
| C5 | 7486( 9) | 8159(5) | 6861(3) | H(C14) | 3488 | 3081 | 4927 |
| N6 | 7047( 7) | 9164(4) | 6994(2) | H(C15) | 6132 | 3786 | 4360 |
| C7 | 6835( 8) | 9771(5) | 6409(3) | H(C16) | 8810 | 4463 | 5058 |
| C8 | 7060( 8) | 9397(5) | 5699(3) | H(C18) | 6887 | 6377 | 5032 |
| C9 | 7484( 8) | 8365(4) | 5553(3) | H(C19) | 7091 | 5822 | 3741 |
| C10 | 9210( 9) | 4555(5) | 6548(4) | H(C20) | 7858 | 7100 | 2834 |
| C11 | 7540(10) | 4219(4) | 6089(4) | H(C21) | 8692 | 8833 | 3133 |
| C12 | 5857(12) | 3858(6) | 6393(4) | H(C22) | 8700 | 9396 | 4398 |
| C13 | 4401(11) | 3464(6) | 5978(5) | H(C23) | 6522 | 11323 | 6036 |
| C14 | 4568(12) | 3438(6) | 5239(5) | H(C23) | 7323 | 11246 | 6854 |
| C15 | 6156(15) | 3804(6) | 4907(4) | H(C23) | 4919 | 10906 | 6785 |
| C16 | 7622(11) | 4196(5) | 5338(4) | | | | |
| C17 | 7687( 8) | 7946(4) | 4806(3) | | | | |
| C18 | 7262( 8) | 6916(4) | 4621(3) | | | | |
| C19 | 7340( 9) | 6612(5) | 3896(3) | | | | |
| C20 | 7820( 9) | 7307(5) | 3357(3) | | | | |
| C21 | 8281( 9) | 8325(6) | 3538(3) | | | | |
| C22 | 8220( 8) | 8642(4) | 4257(3) | | | | |
| C23 | 6334(11) | 10903(5) | 6534(3) | | | | |

[a] Hydrogen parameters were not refined.

The structures of **1a** and **1c** were determined by single crystal X-ray analysis [1b]. Table 1 contains crystallographic and refinement data, Table 2 contains atomic coordinates and Table 3 contains bond lengths and bond angles for **1a** and **1c**. Figure 1 shows stereoscopic views of **1a** and **1c**.

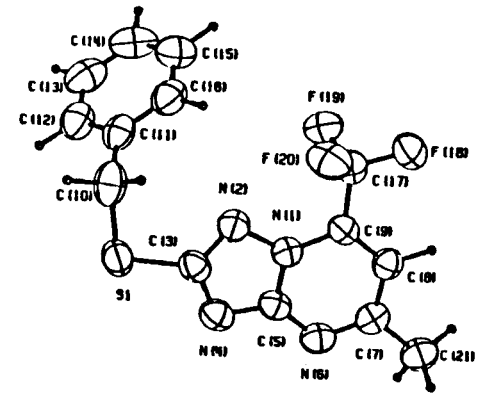
The structure of **1e** was determined by comparison with an authentic sample of isomeric **1f**. Minor isomer **1f** was prepared by a three step sequence beginning with the regiospecific reaction of **2** with 2-carbethoxycyclopentanone to form **1g**. The assignment of the structure of the reaction product as **1g** is based on the well established

Table 3
Bond Lenths (Å) and Bond Angles (°) for **1a** and **1c**
(See Figure 1 for Atomic Numbers)

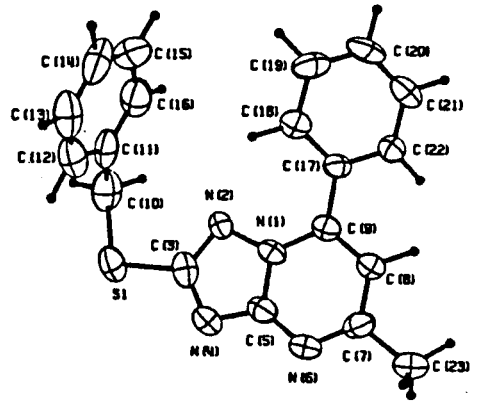
| Bond | 1a | 1c | Angles | 1a | 1c |
|---|---|---|---|---|---|
| S1- 3 | 1.734(4) | 1.733( 6) | 10-S1- 3 | 102.2(2) | 102.2(3) |
| S1-10 | 1.820(4) | 1.790( 7) | 5- 1- 2 | 109.6(3) | 109.9(4) |
| 1 - 2 | 1.378(4) | 1.385( 6) | 9- 1- 2 | 128.4(3) | 127.7(4) |
| 1 - 5 | 1.381(4) | 1.390( 6) | 9- 1- 5 | 122.0(3) | 122.4(5) |
| 1 - 9 | 1.354(4) | 1.365( 6) | 3- 2- 1 | 101.0(3) | 100.2(4) |
| 2 - 3 | 1.327(5) | 1.343( 7) | 2- 3-S1 | 122.5(3) | 122.8(4) |
| 3 - 4 | 1.357(5) | 1.345( 7) | 4- 3-S1 | 120.2(3) | 119.6(4) |
| 4 - 5 | 1.328(4) | 1.329( 7) | 4- 3- 2 | 117.3(3) | 117.6(5) |
| 5 - 6 | 1.346(4) | 1.339( 8) | 5- 4- 3 | 102.5(3) | 103.1(4) |
| 6 - 7 | 1.326(5) | 1.330( 7) | 4- 5- 1 | 109.7(3) | 109.2(5) |
| 7 - 8 | 1.417(5) | 1.396( 7) | 6- 5- 1 | 121.5(3) | 122.9(5) |
| 7 -21 | 1.497(5) | | 6- 5- 4 | 128.8(3) | 127.9(5) |
| 7 -23 | | 1.502( 8) | 7- 6- 5 | 117.1(3) | 115.7(4) |
| 8 - 9 | 1.353(5) | 1.373( 7) | 8- 7- 6 | 122.6(3) | 122.8(5) |
| 9 -17 | 1.494(5) | 1.477( 7) | 21- 7- 6 | 116.8(3) | |
| 10-11 | 1.496(5) | 1.509(10) | 21- 7- 8 | 120.6(3) | |
| 11-12 | 1.382(6) | 1.388(11) | 23- 7- 6 | | 117.5(5) |
| 11-16 | 1.372(6) | 1.378(10) | 23- 7- 8 | | 119.8(5) |
| 12-13 | 1.380(6) | 1.370(11) | 9- 8- 7 | 119.7(3) | 122.2(5) |
| 13-14 | 1.360(8) | 1.362(13) | 8- 9- 1 | 117.1(3) | 114.0(4) |
| 14-15 | 1.367(7) | 1.356(13) | 17- 9- 1 | 117.5(3) | 122.8(5) |
| 15-16 | 1.389(6) | 1.393(12) | 17- 9- 8 | 125.4(3) | 123.2(4) |
| 17-18 | 1.322(4) | 1.387( 7) | 11-10-S1 | 115.3(3) | 117.0(5) |
| 17-19 | 1.333(4) | | 12-11-10 | 120.5(3) | 122.3(6) |
| 17-20 | 1.325(4) | | 16-11-10 | 121.0(3) | 122.1(6) |
| 17-22 | | 1.393( 7) | 16-11-12 | 118.5(3) | 115.5(7) |
| 18-19 | | 1.385( 7) | 13-12-11 | 120.4(4) | 122.5(7) |
| 19-20 | | 1.370( 8) | 14-13-12 | 120.8(4) | 119.8(7) |
| 20-21 | | 1.377(10) | 15-14-13 | 119.4(4) | 120.6(8) |
| 21-22 | | 1.379( 7) | 16-15-14 | 120.3(4) | 118.7(7) |
| | | | 15-16-11 | 120.6(4) | 122.9(7) |
| | | | 18-17- 9 | 111.2(3) | 123.2(5) |
| | | | 19-17- 9 | 111.0(3) | |
| | | | 20-17- 9 | 112.6(3) | |
| | | | 19-17-18 | 106.6(3) | |
| | | | 20-17-18 | 107.7(3) | |
| | | | 20-17-19 | 107.4(3) | |
| | | | 22-17- 9 | | |
| | | | 22-17-18 | | 117.8(5) |
| | | | 19-18-17 | | 118.9(4) |
| | | | 20-19-18 | | 119.4(5) |
| | | | 21-20-19 | | 121.4(5) |
| | | | 22-21-20 | | 119.6(5) |
| | | | 21-22-17 | | 119.9(5) |
| | | | | | 120.9(5) |

regioselectivity in the reactions of aminoazoles with β-ketoesters [4]. Compound **1g** is converted to **1h** by reaction with phosphoryl chloride and **1h** is reacted with methylmagnesium bromide to yield **1f**. Compound **1f** clearly corresponded to the minor isomer in the reaction of **2** with 2-acetylcyclopentanone by comparison of the $^1$H nmr resonance for the methyl group with those present in the spectrum of the crude mixture of **1e** and **1f**.

We have demonstrated that a high degree of regioselection can be achieved in the reaction of 3-amino-5-benzylthio-1,2,4-triazole with unsymmetrical 1,3-diketones. Further study is necessary to determine if the regioselectivity observed in these reactions is operable in reactions involving other aminoazoles. Future reports will describe the use of these intermediates in the synthesis of biologically active compounds [6].




1a




1c

Figure 1. ORTEP drawings of **1a** and **1c**.

## EXPERIMENTAL

### General Methods.

All melting points are uncorrected. The $^1$H nmr spectra were recorded on a Varian EM-390 spectrometer equipped with a $^{19}$F probe. The $^1$H nmr chemical shifts are expressed as delta values (ppm) relative to a TMS internal standard. Significant $^1$H nmr data are tabulated in order: number of protons, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad), coupling constant(s) in hertz. The $^{19}$F nmr chemical shifts are expressed in ppm relative to hexafluorobenzene internal standard.

Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. Anhydrous tetrahydrofuran (THF) was obtained by distillation from sodium-benzophenone immediately prior to use. 3-Amino-5-benzylthio-1,2,4-triazole (**2**) [7] was prepared in 83% yield following a previously described general procedure [8].

### Reaction of **2** with 1,1,1-Trifluoro-2,4-pentanedione.

A solution of 20.6 (0.100 mole) of **2** and 12.2 ml (15.5 g, 0.101 mole) of 1,1,1-trifluoro-2,4-pentanedione in 150 ml of glacial acetic acid was heated at reflux for 17 hours. The reaction mix-

ture was cooled to room temperature and poured onto ice. The solid which separated was collected by filtration and dried to afford 33.3 g of a pale yellow solid which was a crude mixture of **1a** and **1b** (97:3) as determined by $^1H$ and $^{19}F$ nmr. The crude product was recrystallized from benzene-hexane to afford 27.3 g (84%) of 1a as a tan solid in two crops, mp 83.5-84.5°: ir (chloroform): 1626, 1367, 1339, 1293, 1253, 1187, 1172 $cm^{-1}$; $^1H$ nmr (deuteriochloroform): δ 7.0-7.7 (6 H, m), 4.49 (2 H, s), 2.72 (3 H, s); $^{19}F$ nmr (deuteriochloroform): 95.0 ppm upfield from $C_6F_6$ (s).

*Anal.* Calcd. for $C_{14}H_{11}F_3N_4S$: C, 51.85; H, 3.42; N, 17.27; S, 9.89. Found: C, 51.69; H, 3.43; N, 17.20; S, 10.08.

Reaction of **2** with Benzoylacetone.

A solution of 20.6 g (0.100 mole) of **2** and 16.2 g (0.100 mole) of benzoylacetone in 150 ml of glacial AcOH was heated at reflux for 14 hours. The reaction mixture was cooled to room temperature and evaporated at reduced pressure. The residual oil contained (tlc, silica gel, ethyl acetate-hexane, 3:7, v/v) **1c** ($R_f$ 0.13) and **1d** ($R_f$ 0.32) in a ratio of 82:18 as determined by $^1H$ nmr. Hplc of the residue eluting with ethyl acetate-hexane (3:7, v/v) produced fractions containing pure **1c** and **1d**. Fractions containing **1c** were concentrated to afford 22.8 g (69%) of **1c** as a pale yellow solid, mp 110-111°: ir (chloroform): 1610, 1542, 1343 $cm^{-1}$; $^1H$ nmr (deuteriochloroform): δ 7.9-8.3 (2 H, m), 7.1-7.9 (8 H, m), 7.01 (1 H, s), 4.51 (2 H, s), 2.64 (3 H, s).

*Anal.* Calcd. for $C_{19}H_{16}N_4S$: C, 68.65; H, 4.85; N, 16.85; S, 9.65. Found: C, 68.52; H, 4.75; N, 16.93; S, 9.61.

Fractions containing **1d** were concentrated to afford 4.81 g (14%) of **1d** as a pale yellow solid, mp 149.5-151.5°. An analytical sample of **1d** was obtained by recrystallization from ethyl acetate-hexane to afford **1d** as colorless plates, mp 154-155°; ir (chloroform): 1617, 1552, 1348 $cm^{-1}$; $^1H$ nmr (deuteriochloroform): δ 7.9-8.3 (2 H, m), 7.0-7.8 (9 H, m), 4.54 (2 H, s), 2.76 (3 H, s).

*Anal.* Calcd. for $C_{19}H_{16}N_4S$: C, 68.65; H, 4.85; N, 16.85; S, 9.65. Found: C, 68.76; H, 4.82; N, 16.98; S, 9.93.

Reaction of **2** with 2-Acetylcyclopentanone.

A solution of 51.6 g (0.250 mole) of **2** and 31.5 g (0.250 mole) of 2-acetylcyclopentanone in 600 ml of glacial acetic acid was heated at reflux for 9.5 hours. The reaction mixture was cooled to room temperature and evaporated at reduced pressure to afford a solid residue containing **1e** and **1f** (90:10) as determined by $^1H$ nmr. The crude solid was recrystallized twice from ethanol to afford 45.4 g (61%) of **1e** as a light brown solid, mp 157-158.5°; ir (chloroform): 1621, 1343, 1290 $cm^{-1}$; $^1H$ nmr (deuteriochloroform): δ 7.0-7.6 (5 H, m), 4.51 (2 H, s), 3.29 (2 H, br t), 2.97 (2 H, br t), 2.0-2.7 (5 H, m including s at 2.52).

*Anal.* Calcd. for $C_{16}H_{16}N_4S$: C, 64.84; H, 5.44; N, 18.90; S, 10.82. Found: C, 64.88; H, 5.47; N, 18.98; S, 10.72.

Preparation of **1g**.

A solution of 51.6 g (0.250 mole) of **2** and 39.0 g (0.250 mole) of 2-carbethoxycyclopentanone in 275 ml of glacial acetic acid was heated at reflux for 23 hours and cooled to room temperature. The solid which separated was collected by filtration, washed with acetic acid and dried under vacuum to afford 53.8 g (72%) of **1g** as a colorless crystalline solid, mp 244-245°; ir (potassium bromide): 3400, 1673, 1631, 1578, 1273, 1240 $cm^{-1}$; $^1H$ nmr (DMSO-$d_6$): δ 7.0-7.6 (5 H, m), 4.40 (2 H, s), 2.4-3.1 (4 H, m), 1.7-2.3 (2 H, m).

*Anal. Calcd. for* $C_{15}H_{14}N_4OS$: C, 60.38; H, 4.73; N, 18.78; S, 10.75. Found: C, 60.10; H, 4.66; N, 18.91; S, 10.72.

Preparation of **1h**.

A solution of 53.5 g (0.179 mole) of **1g** in 1 ℓ of phosphoryl chloride was heated at reflux for 1.5 hours. The excess phosphoryl chloride was removed by distillation at reduced pressure. The residue was poured onto ice. The aqueous mixture was extracted twice with dichloromethane. The combined organic phases were dried (sodium sulfate) and evaporated at reduced pressure to give a red oil. Flash chromatography on silica gel eluting with ethyl acetate-hexane (2:3, v/v) afforded 49.3 g (87%) of **1h** as colorless plates, mp 119-120°: ir (chloroform): 1626, 1494, 1338, 1290 $cm^{-1}$; $^1H$ nmr (deuteriochloroform): δ 7.0-7.6 (5 H, m), 4.47 (2 H, s), 2.8-3.3 (4 H, m), 1.9-2.5 (2 H, m).

*Anal.* Calcd. for $C_{15}H_{13}ClN_4S$: C, 56.87; H, 4.14; N, 17.68; Cl, 11.19; S, 10.12. Found: C, 57.10; H, 4.15; N, 17.56; Cl, 11.18; S, 10.03.

Preparation of **1f**.

A solution of 2.47 g (7.80 mmoles) of **1h** in 40 ml of dry THF was cooled to 5° and 5.9 ml (17 mmoles) of 2.9*M* methylmagnesium bromide in ether was added over 5 minutes. The solution was warmed to room temperature and stirred overnight (17 hours). The reaction mixture was quenched by addition of 10 ml of saturated ammonium chloride. The organic phase was separated, dried (sodium sulfate) and evaporated at reduced pressure to afford a red oil containing (tlc, silica gel, ethyl acetate-hexane, 3:2, v/v) **1f** ($R_f$ 0.25) and minor impurities ($R_f$ 0.08, 0.32, 0.39, 0.54). Hplc on silica gel eluting with ethyl acetate-hexane (1:1, v/v) gave 1.12 g (48%) of **1f** as a pale red solid, mp 109-111°: ir (chloroform): 1631, 1545, 1518, 1342, 1292 $cm^{-1}$; $^1H$ nmr (deuteriochloroform): δ 7.1-7.8 (5 H, m), 4.57 (2 H, s), 2.0-3.3 (9 H, m including s at 2.67).

*Anal.* Calcd. for $C_{16}H_{16}N_4S$: C, 64.84; H, 5.44; N, 18.90; S, 10.82. Found: C, 64.42; H, 5.52; N, 18.50; S, 10.42.

Single Crystal X-ray Analyses of **1a** and **1c**.

A representative crystal was surveyed and a 1-Å data set (maximum $\sin\theta/\lambda = 0.5$) was collected on a Syntex P1 diffractometer. The diffractometer wa equipped with a graphite monochrometer and copper radiation ($\lambda = 1.5418$ Å). Atomic scattering factors were taken from the "International Tables for X-ray Crystallography" [9], except hydrogen which was taken from Stewart, Davidson and Simpson [10]. All crystallographic calculations were facilitated by the CRYM system [11]. All diffractometer data were collected at room temperature.

A trial structure was obtained by direct methods using the MULTAN program [12]. This trial structure refined routinely. The methyl hydrogen were located by difference Fourier techniques. The hydrogen parameters were added to the structure factor calculations but were not refined. The final cycles of full matrix least-squares refinement contained the scale factor, secondary extinction coefficient, coordinates and anisotropic temperature factors in a single matrix. The shifts calculated in the final cycle were all less than 0.0 of their corresponding standard deviation. The final R-index was 0.043 for **1a** and 0.045 for **1c**. A final difference Fourier revealed no missing or displaced electron density. The refined structures were plotted using the ORTEP computer program of Johnson [13].

Supplementary Material Available.

Complete details and data for the single crystal X-ray analyses of **1a** and **1c** are available from one of the authors (JB).

## REFERENCES AND NOTES

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