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Received December 29, 1978

The reaction of sulfur nitride (**1**) with acetylenes (**2a-m**) was carried out in refluxing toluene to give 1,2,5-thiadiazoles (**3a-m**) as a major product.

J. Heterocyclic Chem., **16**, 1009 (1979).

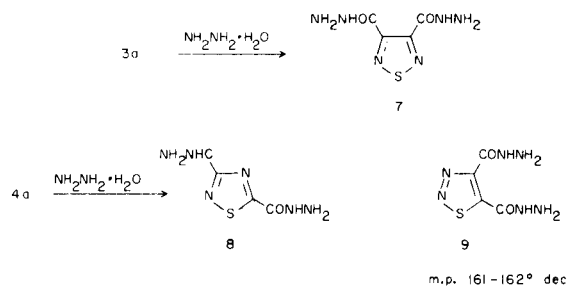
In 1968 Josey (3) reported the reaction of sulfur nitride with a few symmetrically substituted electron deficient acetylenes affording the corresponding 3,4-disubstituted 1,2,5-thiadiazoles. However, full details of this reaction have not yet been published up to the present time to our knowledge.

Our interest in sulfur nitride (**1**) as a synthetic reagent prompted us to reinvestigate and develop the reaction of **1** with some acetylenes (**2**) as a general preparative method of 1,2,5-thiadiazoles (**3**).

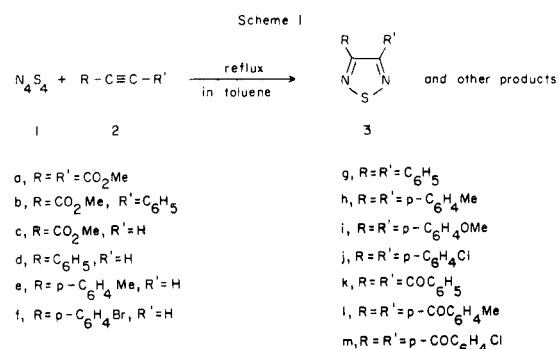
Results and Discussion.

The reaction of **1** with dimethyl acetylenedicarboxylate (**2a**), methylphenyl- (**2b**), methylpropiolate (**2c**), phenyl- (**2d**), *p*-tolyl- (**2e**), *p*-chlorophenyl- (**2f**), diphenyl- (**2g**), di-*p*-tolyl- (**2h**), di-*p*-anisyl- (**2i**), bis(*p*-bromophenyl)- (**2j**), dibenzoyl- (**2k**), bis(*p*-methylbenzoyl)- (**2l**), and bis(*p*-chlorobenzoyl)acetylene (**2m**) was carried out in refluxing toluene; the results are summarized in Table 1. The structural proofs of the products were based on spectral and elemental analysis, derivative-formation and authentic synthesis, as will be mentioned later.

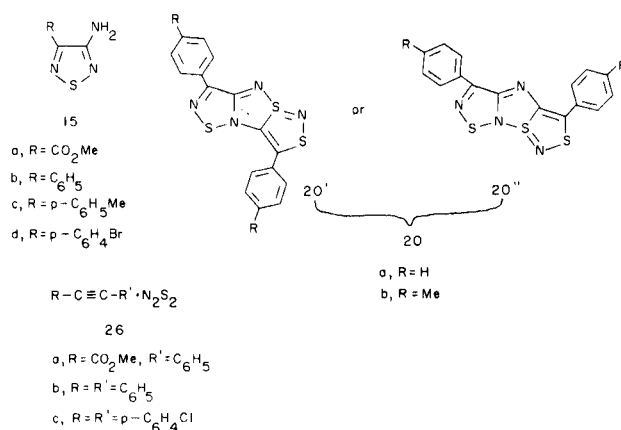
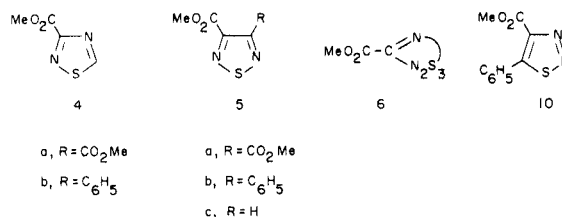
When a mixture of **1** and **2a** in toluene was refluxed for 6 hours, dimethyl 1,2,5-thiadiazole-3,4-dicarboxylate (**3a**) was obtained in 60% yield together with **4a**, **5a** and **6**. Although **3a** is described as a yellow oil (b.p. 84-85°/1 mm) in the literature (4), the product we obtained crystallized as colorless needles, m.p. 28°. The treatment of **3a** and **4a** with hydrazine hydrate in refluxing ethanol for a few minutes afforded the corresponding hydrazides, **7**, m.p. > 300° and **8**, m.p. 189-190° dec., in almost quantitative yields.



The melting point of the hydrazide (**9**) of dimethyl 1,2,3-thiadiazole-4,5-dicarboxylate was reported as 161-162° dec. (5).



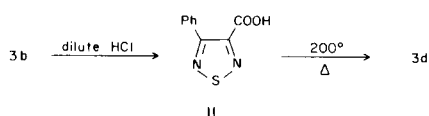
Other Products



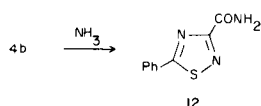
The structures of **5a** and **6** will be discussed later. The reaction with **2b** also gave the expected **3b**, but only in 22% yield, together with **4b**, **5b**, **6**, **10**, and **26**.

The structure of **3b** was established by hydrolysis with dilute hydrochloric acid, followed by decarboxylation of

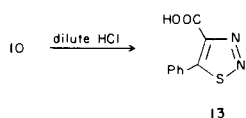
the carboxylic acid (**11**) to give the known 3-phenyl-1,2,5-thiadiazole (**3d**) (**6**), which is a product of the reaction of **1** with **2d**.



The structure **4b** was confirmed as methyl 5-phenyl-1,2,4-thiadiazole-3-carboxylate by the treatment of **4b** with concentrated ammonia to give the corresponding carboxamide (**12**) (**7**). Compound **10** was determined to be methyl

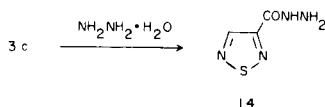


5-phenyl-1,2,3-thiadiazole-4-carboxylate, based on agreement of the melting point and ir spectra with those reported (**8**), and from saponification to the corresponding carboxylic acid (**13**) (**8**).

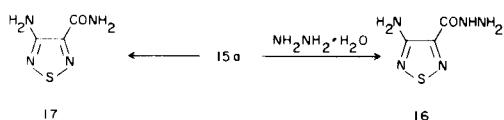


The reaction of **1** with **2c** also afforded the expected methyl 1,2,5-thiadiazole-3-carboxylate (**3c**), albeit in very poor yield, together with the formation of **15a**, **5c** and **6**.

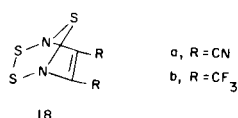
The structure of **3c** was determined by the elemental and spectral analysis and by conversion into the known hydrazide (**14**) (**9**).



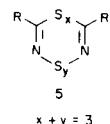
Compound **15a** was also confirmed as methyl 3-amino-1,2,5-thiadiazole-4-carboxylate by conversion into the hydrazide (**16**) (**10**) and amide (**17**) (**10**), both of which are known.



The molecular formula of **5** was found to correspond to the 1:1-adduct of N_2S_3 with the corresponding **2a**, **2b** or **2c**, which seems to correspond to the compound **18** reported by Josey (**3**).

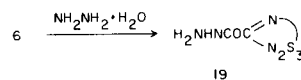


However, the nmr spectrum of **5a** exhibits a sharp singlet at δ 4.01 and that of **5c** shows two singlet at δ 3.98 and 8.90 ppm, with the intensity ratio of 3:1, the latter being ascribable not to an olefinic but to an azomethine proton. Therefore, the bicyclic structure proposed for **18** by Josey is not suitable for **5** and we propose the trithiadiazepine structure ($x + y = 3$) for **5**.



In the nmr spectrum of **5b**, a sharp singlet assigned to the methyl group was observed at δ 3.51 ppm, which is about 0.4-0.5 ppm higher than those of **5a**, **3a**, **3b**, and **3c**. This shift in **5b** might suggest that the methyl and phenyl groups are situated more closely to each other in **5b** than in **3b**. From the inspection of the model, this is most successfully done when $x = 0$ and $y = 3$ in **5b**. Based on the above considerations, **5** seems to be 1,2,3,4,7-trithiadiazepines.

Compound **6** was always obtained in the reaction of **1** with **2a**, **2b** and **2c**, though the yields were poor and inconsistent. Interestingly, the molecular formula of **6** corresponds to the 1:1 adduct of N_3S_3 , with the fragment arising from the cleavage of the $C\equiv C$ bond of **2a-2c**. On the treatment of **6** with hydrazine hydrate, the hydrazide (**19**) was obtained.



It is well known that some heterocyclic compounds undergo the transposition reaction photochemically and/or thermally. Therefore, the interconversion reaction between **3a** or **3b** and **4a** or **4b** was investigated. However, this reaction was not observed in refluxing conditions in toluene in the absence or presence of **1**.



The reaction of **1** with **2d** also gave the expected 3-phenyl-1,2,5-thiadiazole (**3d**) but only in 16% yield, together with such by-products as **15b** and **20a**. Compound **3d** is identical with an authentic specimen prepared in poor yield by the reaction of **1** with ethylbenzene (**21**) (**6**) and with the decarboxylation of **11** as mentioned above.

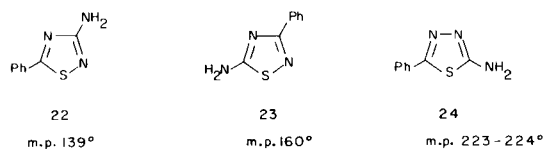
Compound **15b**, m.p. 100-102°, was deduced to have an amino thiadiazole structure based on elemental and spectral analysis. Of the six possible structures, 3-amino-5-phenyl- (**22**) (**11**), 5-amino-3-phenyl-1,2,4- (**23**) (**12**) and 2-amino-5-phenyl-1,3,4-thiadiazole (**24**) (**13**) were excluded. Further, two 1,2,3-thiadiazoles were also rejected based

Table 1

The reaction of Sulfur Nitride (**1**) with Acetylenes (**2a-2m**) in Toluene under Refluxing Conditions (a)

Acetylene	Time (hours)	Product (mole %) (b)
2a	6	3a (60), 42 (8), 5a (5), 6 (6)
2b	8	3b (22), 4b (3), 5b (2), 6 (5), 10 (9), 26a (+)
2c	6	3c (7), 5c (2), 6 (5), 15a (9)
2d	6	3d (16), 15b (5), 20a (8)
2e	6	3e (12), 15c (3), 20b (+)
2f	6	3f (6), 15d (4)
2g	48	3g (87), 26b (+)
2h	48	3h (56)
2i	48	3i (56)
2j	48	3j (46), 26c (+)
2k	12	3k (39)
2l	12	3l (45)
2m	12	3m (49)

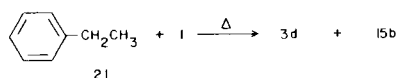
(a) The molar ratio of 1/2 = 1 mole/2 mole. (b) The isolated yields are shown and calculated based on **2**. (c) The plus (+) sign means less than 1%.



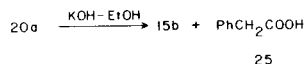
on inspection of the fragmentation in the mass spectrum of **15b**. Thus, **15b** was determined to be 3-amino-4-phenyl-1,2,5-thiadiazole.

Although Bertini and Pino (6) did not mention the formation of **15b** in the reaction of **1** with **21**, **3d** and **15b** were obtained in 4 and 0.7% yields, respectively, in our reinvestigation of this reaction.

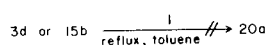
The molecular formula of **20a** corresponds to the 2:1-adduct of **2d** and **1** with a loss of hydrogen sulfide.



Its structure was deduced from elemental and spectral analysis and from the result of hydrolysis with ethanolic potassium hydroxide, affording **15b** in 64% yield with a trace amount of phenylacetic acid (**25**). Unfortunately it was not determined which structure, **20a'** or **20a''**, is correct based on the available data.



Although the pathway of the formation of **20a** is still unknown, **3d** and **15b** are probably not intermediates, since no amount of **20a** was formed when **3d** and **15b** were heated with **1** in toluene at reflux conditions.

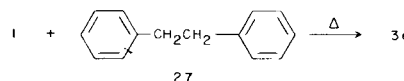


Similarly, the reaction with **2e** or **2f** afforded **3e** or **3f** together with **15c** and **20b** or **15d** in poor yields, respec-

tively. Compounds **15c** and **15d** were determined to be 3-amino-4-*p*-tolyl- and 3-amino-4-*p*-bromophenyl-1,2,5-thiadiazole, respectively, by elemental and spectral analysis. Also, **20b** seems to be an analog of **20a** based on elemental and spectral analysis. However, the yield of **20b** was too poor to do further investigations for its structural proof.

In contrast to the reaction of **1** with monosubstituted acetylenes such as **2c-2f**, the reaction with **2e-2k** afforded the expected 3,4-disubstituted 1,2,5-thiadiazoles (**3e-3k**) in good yields, respectively, together with a small amount of by-products such as **26a-26c**.

The structure of **3e** was determined by comparison with an authentic specimen which was prepared by the reaction of **1** with bibenzyl (**27**), in poor yield (6).



The structures of **3f-3k** were determined by their elemental and spectral analysis. Compounds **26a-26c** correspond to the 1:1-adduct of N_2S_2 with **2b**, **2g** and **2j**, respectively. However, the structures are still not clear; further investigation concerning the structural proof of **26** could not be carried out because of the small amount of **26** which was obtained.

Based on the above results it might be concluded that the reaction of **1** with **2** is useful for the preparation of symmetrically disubstituted, especially diaryl- and diroyl, 1,2,5-thiadiazoles such as **3g-3m**, but not for the preparation of monosubstituted derivatives such as **3c-3f**, because yields are very poor and many by-products are formed.

EXPERIMENTAL

All melting and boiling points are uncorrected. IR spectra were measured on a Nippon Bunko IR-A spectrophotometer as potassium bromide

pellets or as liquid films on sodium chloride plates. $^1\text{H-Nmr}$ and $^{13}\text{C-Nmr}$ were determined at 60 MHz on a Hitachi R-20 nmr spectrometer and on a Nippon Denshi JEOL FT-100 spectrometer using TMS as an internal standard, respectively. Mass spectra were obtained on a Hitachi R-4 mass spectrometer at 70 eV using a direct inlet system. Uv spectra were measured on a Hitachi 124 spectrophotometer.

General Procedure for the Reaction of Sulfur Nitride (1) with Acetylenes (2).

After a mixture of sulfur nitride (**1**, 10.9 mmoles) and acetylene (**2a-2k**, 21.8 mmoles) in 50 ml. of toluene was heated at reflux for a specified reaction time, it was allowed to cool to room temperature. An insoluble material containing tars and unidentified inorganic compounds was filtered off and the filtrate was condensed to about 10 ml. This mixture was subject to column chromatography on silica gel (Wako gel C-300) using at first hexane (A) and then a mixture of hexane and benzene (B), benzene (C), and finally chloroform (D) as eluents. Sulfur was obtained

from the fraction A. All of **3** was isolated from the fraction C. Physical and spectral data of the products are as follows. The yields of the products are shown in Table 1.

Dimethyl 1,2,5-Thiadiazole-3,4-dicarboxylate (3a).

This compound was obtained as colorless needles from ether, m.p. 27-28°, b.p. 111°/3 mm (lit. (4) b.p. 84-85°/0.1 mm); ir (film): ν CO 1730 cm^{-1} ; $^1\text{H-nmr}$ (deuteriochloroform): δ 4.01 ppm (s); ms: m/e (relative intensity) 202 (21), 171 (100), 144 (9), 141 (16), 86 (8.5), 78 (6), 59 (10).

Anal. Calcd. for $\text{C}_6\text{H}_8\text{N}_2\text{O}_4\text{S}$: C, 35.64; H, 2.99; N, 13.86. Found: C, 35.67; H, 2.97; N, 14.06.

Methyl 4-phenyl-1,2,5-thiadiazole-3-carboxylate (3b).

This compound was obtained as colorless needles (petroleum ether), m.p. 45-46°; $^1\text{H-nmr}$ (deuteriochloroform) δ 3.97 (s, 3H), 7.40-7.85 ppm (m, 5H); ms: m/e (relative intensity) 220 (100), 205 (32), 189 (48), 162 (5), 135 (49), 103 (25), 86 (32), 78 (15), 77 (13), 59 (8), 51 (12).

Anal. Calcd. for $\text{C}_{10}\text{H}_8\text{N}_2\text{O}_2\text{S}$: C, 54.53; H, 3.66; N, 12.72. Found: C,

Table 2

The $^{13}\text{C-Nmr}$ Spectra of 1,2,5-Thiadiazoles **3** and **15**

Substrate	> C=N-	Aromatics	> C=O	CH ₃
3a	153.0	—	160.7	53.5
3b	150.0 161.5 (or 162.0)	—	162.0 (or 161.5)	52.9
3c	152.1 153.2	—	159.8	53.0
3d	161.7 147.2	131.6, 129.8 128.9, 127.2	—	—
3e	161.7 147.2	140.0, 129.7 129.0, 127.1	—	21.3
3f	160.6 147.1	132.3, 130.6 128.7, 124.4	—	—
3g	159.6	133.1, 129.1 128.9, 128.3	—	—
3h	159.7	139.2, 130.5 129.1, 128.8	—	21.3
3i	159.2	160.3, 130.3 125.9, 113.8	—	55.2
3j	158.4	135.7, 131.3 130.2, 128.4	—	—
3k	160.9	135.0, 134.2 130.3, 128.6	181.4	—
3l	161.1	145.5, 132.6 130.5, 129.4	186.1	21.8
3m	160.5	141.1, 133.2 131.7, 129.1	185.0	—
15a	161.4 (or 161.5) 135.7	—	161.5 (or 161.4)	52.8
15b	157.1 148.8	132.4, 129.3 129.0, 127.4	—	—
15c	156.9 147.6	132.3, 131.3 129.0, 123.8	—	—
15d	157.0 148.9	139.5, 129.7 123.3	—	21.3

54.49; H, 3.61; N, 12.70.

Methyl 1,2,5-Thiadiazole-3-carboxylate (**3c**).

This compound was obtained as colorless prisms (hexane), m.p. 42°; ir (potassium bromide): ν CO 1730 cm^{-1} ; $^1\text{H-nmr}$ (deuteriochloroform): δ 4.05 (s, 3H), 9.11 ppm (s, 1H); ms: m/e (relative intensity) 144 (41), 114 (81), 113 (100), 86 (78), 78 (57), 59 (56), 58 (43).

Anal. Calcd. for $\text{C}_4\text{H}_4\text{N}_2\text{O}_2\text{S}$: C, 33.33; H, 2.80; N, 19.43. Found: C, 33.13; H, 2.76; N, 19.45.

3-Phenyl-1,2,5-thiadiazole (**3d**).

This compound was obtained as colorless prisms (ether), m.p. 43-44°; $^1\text{H-nmr}$ (deuteriochloroform): δ 7.28-7.51 (m, 3H), 7.79-7.98 (m, 2H), 8.78 ppm (s, 1H); ms: m/e (relative intensity) 162 (100), 135 (74), 103 (24), 77 (21), 59 (13), 51 (16).

Anal. Calcd. for $\text{C}_8\text{H}_6\text{N}_2\text{S}$: C, 59.24; H, 3.73; N, 17.26. Found: C, 59.28; H, 3.94; N, 17.01.

3-*p*-Tolyl-1,2,5-thiadiazole (**3e**).

This compound was obtained as colorless needles (petroleum ether), m.p. 56-57°; $^1\text{H-nmr}$ (deuteriochloroform): δ 2.33 (s, 3H), 7.10-7.84 (m, 4H), 8.75 ppm (s, 1H); ms: m/e (relative intensity) 176 (100), 149 (51), 117 (26), 116 (25), 91 (14), 90 (12), 89 (15).

Anal. Calcd. for $\text{C}_9\text{H}_8\text{N}_2\text{S}$: C, 61.34; H, 4.58; N, 15.89. Found: C, 61.23; H, 4.59; N, 15.80.

3-*p*-Bromophenyl-1,2,5-thiadiazole (**3f**).

This compound was obtained as colorless prisms (hexane), m.p. 120-121°; ms: m/e (relative intensity) 242 (100), 240 (98), 215 (47), 213 (47), 183 (20), 181 (20), 134 (18), 102 (40), 76 (15), 75 (22), 59 (17), 53 (13), 50 (20).

Anal. Calcd. for $\text{C}_8\text{H}_5\text{BrN}_2\text{S}$: C, 39.85; H, 2.09; N, 11.62. Found: C, 39.80; H, 2.11; N, 11.68.

3,4-Diphenyl-1,2,5-thiadiazole (**3g**).

This compound was obtained as pale yellow needles (hexane), m.p. 83-84° (lit (6) m.p. 85-86°); $^1\text{H-nmr}$ (deuteriochloroform): δ 7.43 ppm (m, 10H); uv (ethanol): λ max (log ϵ) 258 (3.96), 305 (4.05) nm; ms: m/e (relative intensity) 238 (100), 135 (84), 119 (6), 103 (17), 77 (13).

3,4-Di-*p*-tolyl-1,2,5-thiadiazole (**3h**).

This compound was obtained as colorless needles (hexane), m.p. 109-110°; $^1\text{H-nmr}$ (deuteriochloroform): δ 2.35 (s, 6H), 7.0-7.40 ppm (q, 8H).

Anal. Calcd. for $\text{C}_{10}\text{H}_{14}\text{N}_2\text{S}$: C, 72.15; H, 5.30; N, 10.52. Found: C, 72.17; H, 5.37; N, 10.39.

3,4-Di-*p*-anisyl-1,2,5-thiadiazole (**3i**).

This compound was obtained as colorless needles (hexane), m.p. 100-101°.

Anal. Calcd. for $\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_2\text{S}$: C, 64.41; H, 4.73; N, 9.39. Found: C, 64.40; H, 4.69; N, 9.45.

3,4-Di-*p*-chlorophenyl-1,2,5-thiadiazole (**3j**).

This compound was obtained as colorless prisms (hexane), m.p. 122-123°.

Anal. Calcd. for $\text{C}_{14}\text{H}_8\text{Cl}_2\text{N}_2\text{S}$: C, 54.47; H, 2.62; N, 9.12. Found: C, 54.83; H, 2.53; N, 9.13.

3,4-Dibenzoyl-1,2,5-thiadiazole (**3k**).

This compound was obtained as colorless needles (ethanol), m.p. 124° (lit. (14) m.p. 123-124°); ms: (relative intensity) 294 (29), 217 (4), 105 (100), 77 (34), 51 (10).

3,4-Di-*p*-methylbenzoyl-1,2,5-thiadiazole (**3l**).

This compound was obtained as pale yellow needles (ethanol), m.p. 108-109°; ir (potassium bromide): ν CO 1650 cm^{-1} .

Anal. Calcd. for $\text{C}_{18}\text{H}_{14}\text{N}_2\text{O}_2\text{S}$: C, 67.07; H, 4.38; N, 8.68. Found: C, 66.95; H, 4.38; N, 8.45.

3,4-Di-*p*-chlorobenzoyl-1,2,5-thiadiazole (**3m**).

This compound was obtained as pale yellow needles (ethanol), m.p. 154.5-155.4°; ir (potassium bromide): ν CO 1050 cm^{-1} .

Anal. Calcd. for $\text{C}_{16}\text{H}_{10}\text{Cl}_2\text{N}_2\text{O}_2\text{S}$: C, 52.91; H, 2.22; N, 7.71. Found: C, 53.03; H, 2.14; N, 7.56.

The $^{13}\text{C-nmr}$ spectra of **3** in deuteriochloroform are summarized in Table 2. Compounds **4a** and **4b** were obtained from fraction D.

Dimethyl 1,2,4-Thiadiazole-3,5-dicarboxylate (**4a**).

This compound was obtained as colorless needles (hexane), m.p. 89-90°; ir (potassium bromide): ν CO 1740, 1720 cm^{-1} ; $^1\text{H-nmr}$ (deuteriochloroform): δ 4.07 (s, 3H), 4.09 ppm (s, 3H); δ 180.2, 165.3, 158.6, 158.1, 54.0, 53.6 ppm.

Anal. Calcd. for $\text{C}_6\text{H}_6\text{N}_2\text{O}_4\text{S}$: C, 35.46; H, 2.99; N, 13.86. Found: C, 35.80; H, 2.92; N, 13.36.

Methyl 5-Phenyl-1,2,4-thiadiazole-3-carboxylate (**4b**).

This compound was obtained as colorless needles (hexane), m.p. 91-92°; ir (potassium bromide): ν CO 1745 cm^{-1} ; $^1\text{H-nmr}$ (deuteriochloroform): δ 4.07 (s, 3H), 7.45-7.65 ppm (m, 5H); $^{13}\text{C-nmr}$ (deuteriochloroform): δ 162.1, 160.8, 147.7, 130.0, 129.7, 128.6, 125.9, 52.7 ppm; ms: m/e (relative intensity) 220 (51), 189 (6), 162 (7), 135 (100), 121 (6), 118 (8), 109 (6), 103 (12), 91 (4), 89 (2), 86 (4), 77 (31), 59 (12).

Anal. Calcd. for $\text{C}_{10}\text{H}_8\text{N}_2\text{O}_2\text{S}$: C, 54.53; H, 3.66; N, 12.72. Found: C, 54.59; H, 3.68; N, 12.67.

Compounds, **5a** and **5b** were isolated from fraction B but **5c** was obtained from fraction C.

Dimethyl 1,2,3,4,7-Trithiadiazepine-5,6-dicarboxylate (**5a**).

This compound was obtained as colorless needles (hexane), m.p. 73.5-74°; ir (potassium bromide): ν CO 1725, 1705 cm^{-1} ; $^1\text{H-nmr}$ (deuteriochloroform): δ 3.92 ppm (s, 3H); $^{13}\text{C-nmr}$ (deuteriochloroform): δ 162.6, 140.7, 54.09 ppm.

Anal. Calcd. for $\text{C}_6\text{H}_6\text{N}_2\text{O}_4\text{S}_3$: C, 27.06; H, 2.27; N, 10.52. Found: C, 26.97; H, 2.16; N, 10.58.

The 1:1-Complex of **5b** with **2b**.

This compound was obtained as pale yellow needles (hexane), m.p. 50-51°; ir (potassium bromide): ν CO (2205, 1730, 1710 cm^{-1}); $^1\text{H-nmr}$ (deuteriochloroform): δ 3.53 (s, 3H), 3.81 (s, 3H), 7.2-7.7 ppm (m, 10H).

Anal. Calcd. for $\text{C}_{20}\text{H}_{16}\text{N}_4\text{O}_4\text{S}_3$: C, 54.04; H, 3.30; N, 6.30. Found: C, 53.77; H, 3.59; N, 6.32.

Compound **5b** was first isolated as the 1:1-complex of **5b** with **2b** from the reaction mixture. On being heated at 90° in 1 mm for 12 hours **5b** was made free from **2b**.

Methyl 6-Phenyl-1,2,3,4,7-trithiadiazepine-5-carboxylate (**5b**).

This compound was obtained as pale yellow prisms (hexane), m.p. 84-85°; ir (potassium bromide): ν CO 1725 cm^{-1} ; $^1\text{H-nmr}$ (deuteriochloroform): δ 3.53 (s, 3H), 7.43 ppm (s, 5H); ms: m/e (relative intensity) 284 (43), 253 (3), 248 (28), 133 (18), 129 (26), 124 (100), 121 (50), 89 (60), 78 (46), 46 (27).

Anal. Calcd. for $\text{C}_{10}\text{H}_8\text{N}_2\text{O}_2\text{S}_3$: C, 42.24; H, 2.84; N, 9.85. Found: C, 42.55; H, 2.88; N, 9.71.

Methyl 1,2,3,4,7-Trithiadiazepine-5-carboxylate (**5c**).

This compound was obtained as colorless needles (hexane), m.p. 109-111°; ir (potassium bromide): ν CO 1697 cm^{-1} ; $^1\text{H-nmr}$ (deuteriochloroform): δ 3.98 (s, 3H), 8.90 ppm (s, 1H); ms: m/e (relative intensity) 208 (87), 177 (6), 102 (60), 130 (12), 124 (9), 103 (27), 88 (9), 78 (100), 59 (62), 46 (40).

Anal. Calcd. for $\text{C}_8\text{H}_6\text{N}_2\text{O}_2\text{S}_3$: C, 23.07; H, 1.94; N, 13.44. Found: C, 23.17; H, 1.95; N, 13.56.

Compound **6**.

This compound was obtained as colorless needles from fraction C (hexane), m.p. 82-83°; ir (potassium bromide): ν CO 1700 cm^{-1} ; $^1\text{H-nmr}$ (deuteriochloroform): δ 4.00 ppm (s, 3H); uv (ethanol): λ max (log ϵ) 276 (4.54), 335 (3.91); $^{13}\text{C-nmr}$ (deuteriochloroform): δ 161.8, 151.0, 53.7 ppm; ms: m/e (relative intensity) 209 (54), 163 (4.8), 138 (5), 124 (8), 103 (4), 92 (4), 80 (4), 78 (100), 76 (10), 59 (10), 57 (6), 55 (9), 46 (50).

Anal. Calcd. for $\text{C}_7\text{H}_5\text{N}_3\text{O}_2\text{S}_3$: C, 17.22; H, 1.44; N, 20.08. Found: C,

17.25; H, 1.38; N, 20.03.

Methyl 5-Phenyl-1,2,3-thiadiazole-3-carboxylate (**10**).

This compound was obtained as colorless needles from fraction D (hexane); m.p. 61-62°; ¹H-nmr (deuteriochloroform): δ 3.98 (s, 3H), 7.54 ppm (s, 5H); ¹³C-nmr (deuteriochloroform): δ 162.1, 160.8, 147.9, 130.6, 129.7, 128.6, 125.9, 52.7; ms: m/e (relative intensity) 220 (34), 192 (74), 189 (9), 177 (4), 164 (13), 161 (13), 150 (15), 147 (19), 133 (88), 121 (92), 115 (10), 105 (18), 103 (12), 93 (14), 90 (14), 89 (100), 77 (32), 63 (36), 59 (35).

Anal. Calcd. for C₁₀H₉N₂O₂S: C, 54.53; H, 3.66; N, 12.72. Found: C, 54.53; H, 3.63; N, 12.76.

Compounds **15a-15d** were obtained from fraction C.

Methyl 3-Amino-1,2,5-thiadiazole-4-carboxylate (**15a**).

This compound was obtained as colorless needles (hexane), m.p. 142-143°; ¹H-nmr (deuteriochloroform): δ 4.01 (s, 3H), 6.00 ppm (broad s, 2H, deuterium oxide exchangeable); ¹³C-nmr (deuteriochloroform): δ 161.4, 135.7, 52.8; ir (potassium bromide): ν NH 3430, 3270, 3200, ν CO 1710 cm⁻¹.

Anal. Calcd. for C₆H₇N₃O₂S: C, 30.18; H, 3.17; N, 26.40. Found: C, 30.25; H, 3.19; N, 25.92.

3-Amino-4-phenyl-1,2,5-thiadiazole (**15b**).

This compound was obtained as straw-colored plates (hexane), m.p. 100-102°; ir (potassium bromide): ν NH 3290, 3200 cm⁻¹; ¹H-nmr (deuteriochloroform): δ 4.92 (s, 2H, deuterium oxide exchangeable), 7.43-7.51 (m, 3H), 7.61-7.80 ppm (m, 2H); ¹³C-nmr (deuteriochloroform): δ 157.0, 148.4, 132.4, 129.3, 129.0, 127.4; ms: m/e (relative intensity) 177 (100), 135 (36), 103 (8), 74 (94); uv (ethanol): λ max (log ε) 322 nm (3.18).

Anal. Calcd. for C₈H₇N₃S: C, 54.21; H, 3.98; N, 23.71. Found: C, 54.53; H, 3.84; N, 23.48.

3-Amino-4-tolyl-1,2,5-thiadiazole (**15c**).

This compound was obtained as straw-colored plates (hexane), m.p. 100-101°; ir (potassium bromide): ν NH 3420, 3290, 3200 cm⁻¹; ¹H-nmr (deuteriochloroform): δ 2.41 (s, 3H), 4.90 (broad s, 2H deuterium oxide exchangeable), 7.21-7.71 ppm (m, 4H); ¹³C-nmr (deuteriochloroform): δ 157.0, 148.9, 139.5, 129.7, 127.3, 21.3.

Anal. Calcd. for C₉H₉N₃S: C, 56.52; H, 4.74; N, 21.97. Found: C, 56.37; H, 4.70; N, 21.75.

3-Amino-4-*p*-bromophenyl-1,2,5-thiadiazole (**15d**).

This compound was obtained as pale yellow needles (hexane), m.p. 134-135°; ir (potassium bromide) ν NH 3420, 3290, 3200 cm⁻¹; ¹³C-nmr (deuteriochloroform): δ 156.8, 147.6, 132.3, 129.0, 128.3, 123.8; ms: m/e (relative intensity) 257 (18), 255 (18), 170 (73), 169 (41), 168 (100), 155 (31), 149 (65), 141 (76), 139 (33), 105 (31), 94 (90), 71 (59), 69 (59).

Anal. Calcd. for C₈H₆BrN₃S: C, 37.52; H, 2.36; N, 16.41. Found: C, 37.44; H, 2.30; N, 16.25.

Compounds **20a** and **20b** were obtained from fraction B.

Compound **20a**.

This compound was obtained as deep violet needles (hexane); m.p. 178-179°; uv (ethanol): λ max (log ε) 520 (3.49), 364 (4.04), 322 (3.98), 255 (4.12), 237 (4.21) nm; ¹H-nmr (deuteriochloroform): δ 7.35-7.64 (m, 6H), 7.90-8.21 (m, 2H), 8.41-8.62 (m, 2H); ¹³C-nmr (deuteriochloroform): δ 129.9, 129.3, 129.0, 128.6, 128.4, 128.1 ppm; ms: m/e (relative intensity) 354 (36), 308 (2), 275 (3), 250 (2), 205 (2), 177 (5), 146 (2), 135 (2), 121 (100), 163 (2), 89 (1), 77 (10).

Anal. Calcd. for C₁₆H₁₀N₆S₃: C, 54.25; H, 2.85; N, 15.81. Found: C, 54.00; H, 2.86; N, 15.47.

Compound **20b**.

This compound was obtained as deep violet needles (hexane), m.p. 182-183°; ms: m/e 382.

Anal. Calcd. for C₁₈H₁₄N₆S₃: C, 56.52; H, 3.69; N, 14.56. Found: C, 56.52; H, 3.63; N, 14.39.

Compound **26a**.

This compound was obtained as red needles (hexane), m.p. 49-50°; ¹H-nmr (deuteriochloroform): δ 3.93 (s, 3H), 7.38-7.62 (m, 3H), 7.78-7.98

ppm (m, 2H); ¹³C-nmr (deuteriochloroform): δ 159.5, 153.1, 134.8, 132.5, 128.6, 116.5, 53.9 ppm; ms: m/e (relative intensity) 252 (100), 193 (8), 149 (72), 121 (94), 118 (34), 103 (55), 90 (53), 77 (51), 59 (67).

Anal. Calcd. for C₁₀H₈N₂O₂S₂: C, 47.60; H, 3.20; N, 11.10. Found: C, 47.34; H, 3.27; N, 10.93.

Compound **26b**.

This compound was obtained as orange needles (hexane), m.p. 79-80.5°; uv (ethanol): λ max (log ε) 280 (4.30), 457 (3.42) nm; ¹H-nmr (deuteriochloroform): δ 7.3-7.57 (m, 3H), 7.87-8.07 ppm (m, 2H); ¹³C-nmr (deuteriochloroform): δ 151.6, 132.6, 129.2, 128.5, 126.7 ppm; ms: m/e (relative intensity) 270 (32), 167 (5), 135 (3), 121 (100), 103 (75), 77 (14).

Anal. Calcd. for C₁₄H₁₀N₂S₂: C, 62.22; H, 3.73; N, 10.37. Found: C, 61.96; H, 3.77; N, 10.21.

Compound **26c**.

This compound was obtained as red needles (ethanol), m.p. 205-207°.

Anal. Calcd. for C₁₄H₈N₂S₂Cl₂: C, 49.56; H, 2.38; N, 8.26. Found: C, 49.38; H, 2.34; N, 8.28.

Compounds **26a**, **26b** and **26c** were isolated from fraction B. Conversion into Hydrazides **7**, **8**, **14**, **16** and **19**, and amides **12** and **17**.

The conversions of the products into the corresponding hydrazides or amides are easily performed by the reaction with excess of hydrazino hydrate in refluxing ethanol or with concentrated aqueous ammonia on a steam bath for several minutes. Their physical and spectral data are given below.

Compound **7**.

This compound was obtained as pale yellow needles (ethanol), m.p. > 300°; ir (potassium bromide): ν NH 3350, 3300, ν CO 1670, 1640 cm⁻¹.

Anal. Calcd. for C₄H₆N₆O₂S: C, 23.76; H, 2.99; N, 41.56. Found: C, 23.53; H, 2.94; N, 41.25.

Compound **8**.

This compound was obtained as a yellow crystalline powder (water), m.p. 189-191° (d); ir (potassium bromide): ν NH 3300, 3150, ν CO 1700, 1600 cm⁻¹.

Anal. Calcd. for C₄H₆O₂N₆S: C, 23.76; H, 2.99; N, 41.56. Found: C, 23.29; H, 3.04; N, 41.07.

Compound **14**.

This compound was obtained as colorless needles (ethanol), m.p. 155-157° (lit. (9) m.p. 155-156°).

Compound **16**.

This compound was obtained as colorless needles (ethanol), m.p. 208-209° (lit. (10) m.p. 204-206°).

Compound **19**.

This compound was obtained as colorless needles (chloroform), m.p. 214-216°.

Anal. Calcd. for C₂H₃N₅OS₃: C, 11.48; H, 1.44; N, 33.47. Found: C, 11.44; H, 1.42; N, 33.64.

Compound **12**.

This compound was obtained as colorless needles (ethanol), m.p. 163-164°; ir (potassium bromide): ν NH 3350, 3160, ν CO 1685 cm⁻¹.

Compound **17**.

This compound was obtained as colorless needles (ethanol), m.p. 172-173° (lit. (10) m.p. 171-172°).

Hydrolysis of **3b**.

Compound **3b** (2.0 g.) in dilute hydrochloric acid was heated at reflux for 30 minutes. Unreacted **3b** (1.0 g.) was filtered and the filtrate was neutralized with aqueous sodium hydroxide, then extracted with ether (100 ml. × 3). The ether solution was dried over sodium sulfate and evaporated *in vacuo* to give 4-phenyl-1,2,5-thiadiazole-3-carboxylic acid (**11**) in 70% yield.

Compound **11**.

This compound was obtained as colorless prisms (hexane), m.p. 129-131°; ir (potassium bromide): ν NH 3300-2500, ν CO 1720 cm^{-1} .

Anal. Calcd. for $\text{C}_9\text{H}_6\text{N}_2\text{O}_2\text{S}$: C, 52.42; H, 2.93; N, 13.58. Found: C, 52.34; H, 2.88; N, 13.48.

Decarboxylation of **11**.

Compound **11** (300 mg.) was heated in a test tube at 260-280° in a silicon oil bath for 1 hour. Sublimation of the reaction mixture afforded 3-phenyl-1,2,5-thiadiazole (**3d**) in 49% yield.

Hydrolysis of **10**.

Compound **10** was treated with dilute hydrochloric acid and worked up as described above to give 3-phenyl-1,2,5-thiadiazole-4-carboxylic acid (**13**) as colorless prisms (hexane), m.p. 154-155° (lit. (8) m.p. 157° dec).

Hydrolysis of Compound **20a**.

After a mixture of **20a** (0.3 mmole) and potassium hydroxide (1.4 g.) in 30 ml. of ethanol was refluxed for 8 hours, it was cooled to room temperature. The precipitate was filtered and washed with water to give **15b** in 64% yield. The filtrate was poured into water, acidified with 10% hydrochloric acid and extracted with ether. The ether solution was dried over sodium sulfate and evaporated to afford a small amount of phenylacetic acid (**25**).

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