Study of the Diazoimine/Triazole Equilibria for Substituted Thiazoles and Thiadiazoles

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Several diazomethyl and diazoester substituted thiazoles and thiadiazoles were prepared and their ring/chain equilibria studied by nmr spectroscopy. The diazomethyl derivatives **17a,b,d** and **19a** exist predominantly or exclusively in the triazole form. Ring-opening is promoted by introducing an ester group at the diazo function (**17c,e, 19b, 21**) or by changing thiazoles for thiadiazoles in the following order: thiazole < 1,3,4-thiadiazole < 1,2,4-thiadiazole. The diazoimine/triazole equilibria are also shifted towards the diazo form by raising the temperature and by using less polar solvents in the order: dimethyl sulfoxide < acetonitrile < chloroform < benzene. The ir spectra (potassium bromide discs) of the compounds indicate that they all, except **21**, exist in the crystalline state in the triazole form.

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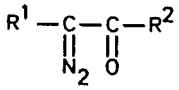
It is known that α-diazoketones exist exclusively in the open-chain structure **1** [1], whereas α-diazothioketones cyclize spontaneously during their preparation to give 1,2,3-thiadiazoles **2** [2].



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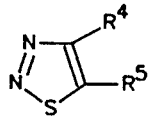
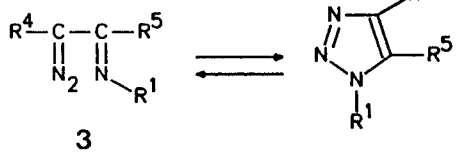
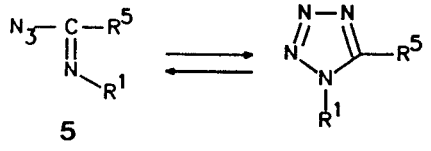


2

α-Iminodiazoalkanes, in contrast, may equilibrate with 1,2,3-triazoles, and the equilibrium position is governed by substituent effects, solent polarity and temperature [3]. Thus, electron-withdrawing substituents at the N-1 and C-4 positions, non-polar solvents and higher temperatures favor ring opening of the triazole **4** to the diazoimine **3**. A similar situation is found for the azidoimine/tetrazole equilibrium **5** ⇌ **6** [4].

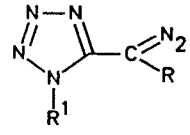


3 **4**

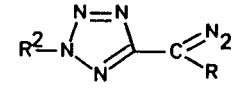


5 **6**

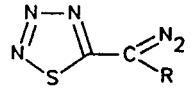
Much less information is available about the equilibrium position of **3** when R^1 and R^5 are part of an azole ring. The tetrazoles **7a-d** and **8a,b** [5], and the thiatriazoles **9a,b** [6] have been prepared and showed no tendency to cyclize. On the contrary, **10** is reported to exist in the bicyclic structure [7].



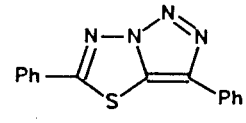
7 **a**: R = H
b: R = COOMe
c: R = CHO
d: R = $PO(OEt)_2$



8 **a**: R = H
b: R = COOMe



9 **a**: R = COOEt
b: R = COPh



10

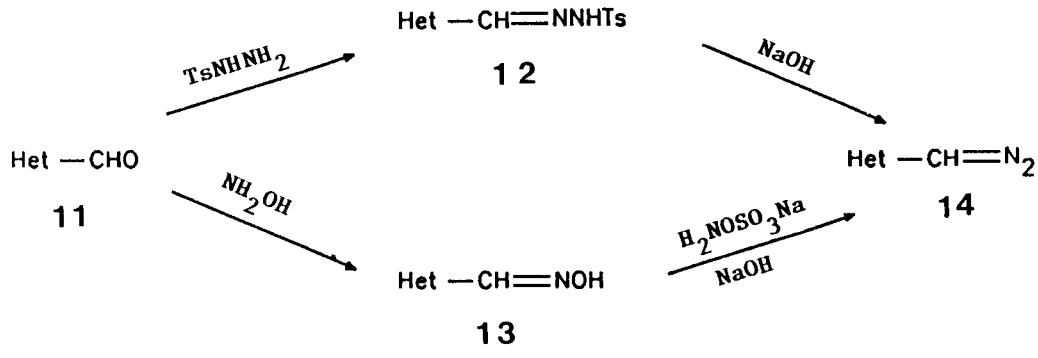
We have now prepared a series of diazomethyl and diazoester substituted thiazoles and thiadiazoles and determined their ring/chain equilibrium positions by nmr spectroscopy [8].

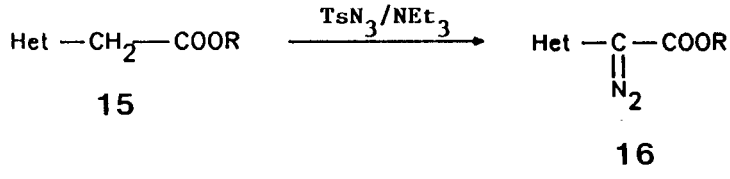
Results and Discussion.

The most obvious and useful precursors of diazomethyl substituted azoles **14** are the aldehydes **11**, which themselves are available by known procedures. They can be converted into **14** either *via* the tosylhydrazones **12** by the Bamford-Stevens reaction [9], or *via* the oximes **13** by the Forster reaction [10] (Scheme 1). For the synthesis of the required diazoester-substituted azoles **16**, we have carried out a diazo-transfer reaction on the corresponding activated methylene compounds **15** [11]. The diazo products thus obtained are discussed below.

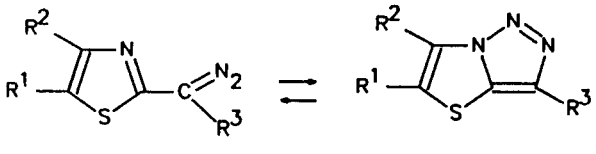
The parent 2-diazomethylthiazole **17a**, prepared by the Bamford-Stevens reaction under phase transfer conditions, exists in the solid state in the bicyclic structure **18a** since it shows no diazo absorption near 2100 cm^{-1} in the ir spectrum (potassium bromide disc). In solution, this compound equilibrates with a small amount of **17a**, whose con-

Scheme 1





centration is solvent and temperature dependent. For instance, in deuteriochloroform the diazo **17a** is present for 8% at 25° and for 15% at 60°, based on the averaged intensities of all hydrogen absorptions in the 250 MHz nmr spectra. In deuterated benzene, the estimated concentration of the diazo form is 15% at 25° and 24% at 60°. No diazo form is found in deuterated dimethyl sulfoxide at room temperature, while at 60° it accounts for *ca* 5% of the ^{1}H nmr spectrum. From these data, we conclude that the equilibrium position is shifted towards the diazo form **17a** in less polar solvents and by raising the temperature.



	R^1	R^2	R^3
a	H	H	H
b	H	Me	H
c	H	Me	COOEt
d	-CH=CH-CH=CH-		H
e	-CH=CH-CH=CH-		COOEt

The introduction of a methyl substituent at the 4-position of the thiazole ring increases the electron density at the ring nitrogen atom and disfavors the diazo form **17b**. This compound exists exclusively in the bicyclic structure **18b** in the solid state (ir evidence) as well as in solution (^{1}H nmr evidence).

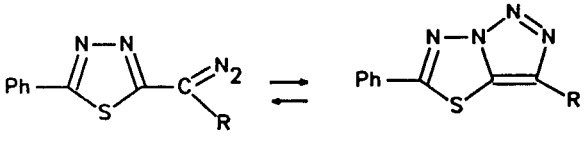
The corresponding ester substituted thiazolo[3,2-*c*][1,2,3]triazole **18c**, in contrast, equilibrates with the open-chain diazo form **17c** in non-polar solvents. The estimated diazo concentrations, based on the intensities of the methyl absorptions (R^2) in the 250 MHz nmr spectra, are 15% in deuteriochloroform and 29% in deuterated benzene at 25°. They decrease when the temperature is lowered: 5-10% at 0° in deuteriochloroform and 25% at 10° in deuterated benzene. The nmr spectra in deuterated acetonitrile and dimethyl sulfoxide exhibit only absorptions due to the bicycle **18c**; and this is also the only form present in the solid state.

Very recently, Jones *et al.* [12] reported the synthesis of the methyl and phenyl derivatives of **18** ($R^1 = R^2 = H$, R^3 = Me or Ph) and concluded from their nmr spectra in deuteriochloroform that no diazo form is present.

2-Diazomethylbenzothiazole **17d** was also prepared by the Bamford-Stevens reaction and compared with 2-diazomethylthiazole **17a**. No diazo form is found in the ir (potassium bromide) and only traces (2-5%) in the nmr spectra (perdeuteriobenzene, deuteriochloroform, deuterioacetonitrile, DMSO-d_6) at room temperature, indicating that the fusion of an electron-rich benzene ring onto the thiazole favors the triazole form **18**.

The ester derivative **17e** is also stabilized in the triazole form **18e** in the solid state (no diazo peak in the ir spectrum), but shows the presence of 22% of **17e** by ^{1}H nmr in deuterated dichloromethane at −90°.

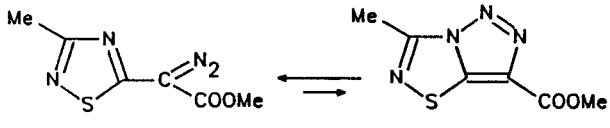
In order to evaluate the influence of additional ring-nitrogen atoms on the diazoimine/triazole equilibrium, we have prepared the 1,3,4-thiadiazoles **19a** and **19b**. Compound **19a** exists essentially in the triazole form **20a** since it gives no diazo absorption in the solid state ir spectra and less than 4% ^{1}H nmr resonances corresponding to **19a** in different solvents at 25°; the concentration of **19a** rises to 12% in deuterated benzene at 75°. On the contrary, the diazoester **19b** is the major component present in deuterated benzene (70% at 5-10°) and in deuteriochloroform (60-65% at −5° and 75-80% at 25°). Even in the more polar solvents acetonitrile and dimethyl sulfoxide it is present in substantial amounts: 50 and 40% respectively at 25°. In contrast, the solid state ir spectrum still lacks a diazo absorption near 2100 cm^{-1}.



19 **20**

a: R = H, **b**: R = COOEt

Finally, the diazoester substituted 1,2,4-thiadiazole **21** was synthesized as yellow crystals which showed no tendency to cyclize. Thus, the solid state ir spectrum manifests a strong diazo stretching absorption at 2130 cm^{-1}, and the ^{1}H and ^{13}C nmr spectra in deuterated benzene, chloroform, acetonitrile and dimethyl sulfoxide show the presence of only the open-chain form. Compared with **17c**, it is evident that the introduction of a nitrogen atom in β-position to the thiazole N-3 atom strongly favors the diazo form, as expected from the reduced electron density at the N-3 atom.



21 **22**

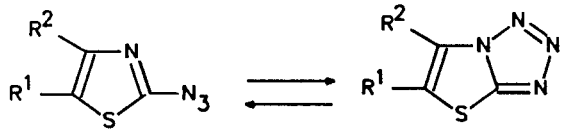
In summary, the following major conclusions can be drawn from this investigation:

(i) The propensity of the diazo substituted azoles to exist in the triazole form decreases in the order: thiazole > 1,3,4-thiadiazole > 1,2,4-thiadiazole, and also: diazomethyl > diazoester.

(ii) Electron-donating substituents (*e.g.* Me) and benzofusion favor the triazole form.

(iii) The amount of the diazo component increases by raising the temperature and by using less polar solvents.

Thus, the diazoimine/triazole equilibria in the series of thiazoles and thiadiazoles are governed by the same factors which determine the azido/tetrazole equilibria [13]. In the latter cases, however, the azide concentrations are much more pronounced as can be seen by comparing the data for **17** and **23** in Table 1.



23 **24**

	R^1	R^2
a	H	H
b	H	Me
c	-CH=CH-CH=CH-	

Table 1

Equilibrium Concentration of the Diazo or Azide [13] Form (%) in Diifferent Solvents at Room Temperature

Compound	C_6D_6	$CDCl_3$	$(CD_3)_2SO$
17a	15	8	<2
17b	0	0	0
17c	29	15	0
17d	5	<5	<2
23a	94	85	17
23b	63	46	3
23c	50		7.5

Table 2

^{1}H NMR Data (δ-values) of the Heterocycles **17a-c/18a-c**

17/18	Solvent	**17**			**18**		
		R^1	R^2	R^3	R^1	R^2	R^3
a	C_6H_6	6.35	7.4	4.45	5.7	6.9	7.3
	$CDCl_3$	7.1	7.6	5.5	7.3	8.1	7.8
	$(CD_3)_2SO$			6.4	7.75	8.6	7.95
b	$CDCl_3$				6.82	2.65	7.8
c	C_6D_6	6.3	2.2	0.9	5.4	1.8	1.1
				3.9			4.2
	$CDCl_3$	6.9	2.4	1.4	6.95	2.7	1.45
				4.4			4.5
	CD_3CN				7.1	2.6	1.4
							4.4
	$(CD_3)_2SO$				7.5	2.6	1.3
							4.3

EXPERIMENTAL

The ir spectra were recorded on a Perkin-Elmer FTIR 1720 spectrophotometer, ^{1}H and ^{13}C nmr spectra on a Bruker WM-250 spectrometer operating at 250 (^{1}H) and 62.9 MHz (^{13}C), and mass spectra on a Kratos MS50 TC instrument.

The ^{1}H nmr spectra of the products **17a,d** ⇌ **18a,d** and **19a** ⇌ **20a** exhibit separate signals for the diazo and triazole forms,

indicating slow exchange on the nmr time scale. For the ester substituted products **17c,e** ⇌ **18c,e** and **19b** ⇌ **20b** exchange broadening occurs at room temperature and a more precise interpretation of the isomeric composition was obtained at lower temperature.

Thiazolo[3,2-*c*][1,2,3]triazole (**18a**).

A solution of thiazole-2-carbaldehyde [14] (3.9 g, 34.5 mmoles) and tosylhydrazide (6.4 g, 34.5 mmoles) in methanol-water (1:1), containing a trace of acetic acid, was stirred overnight at room temperature. The precipitated hydrazone **12** (Het = thiazol-2-yl) was filtered off and crystallized from ethanol in 63% yield (6.1 g), mp 142-144°.

This compound (2.5 g, 8.9 mmoles) was dissolved in dichloromethane (25 ml), and an aqueous solution (20 ml) of sodium hydroxide (2.87 g, 71.2 mmoles) and tetrabutylammonium bromide (0.31 g, 8.9 mmoles) was added. After stirring at room temperature for 3 days, the mixture was filtered and the filtrate was extracted with chloroform. The extracts were washed twice with water, dried and concentrated to give **18a** in 49% yield (0.54 g), mp 118-120°; ir (potassium bromide): 3080, 3110, 3160 cm^{-1} (m), no diazo absorption at *ca* 2100 cm^{-1}; ^1H nmr: see Table 2; ^{13}C nmr (dimethyl sulfoxide-d_6): δ 119.8 (C-6, $^1J_{CH}$ = 199 Hz, $^2J_{CH}$ = 8.5 Hz), 121.8 (C-5, $^1J_{CH}$ = 195 Hz, $^2J_{CH}$ = 10.5 Hz), 123.8 (C-3, $^1J_{CH}$ = 202 Hz), 137.4 (C-3a); ms: (%) m/z 125 (100, $M^{+\cdot}$), 97 (74, $M^{+\cdot}$-N_2), 70 (46, m/z 97 - HCN), 52 (64, m/z 97 - HCS), 45 (52, HCS^+).

Anal. Calcd. for $C_4H_3N_3S$ (mol wt 125): C, 38.39; H, 2.42. Found: C, 38.30; H, 2.34.

6-Methylthiazolo[3,2-*c*][1,2,3]triazole (**18b**).

This compound was similarly prepared from 4-methylthiazole-2-carbaldehyde [15] in 42% overall yield, mp 73-74° (*n*-hexane); ^1H nmr: see Table 2; ^{13}C nmr (deuteriochloroform): δ 12.1 (CH_3), 113.4 (C-5, $^1J_{CH}$ = 190 Hz, $^3J_{CH}$ = 5 Hz), 124.2 (C-3, $^1J_{CH}$ = 200 Hz), 129.3 (C-6), 136.6 (C-3a, $^2J_{CH}$ = 15 Hz, $^3J_{CH}$ = 4.5 Hz); ms: (%) m/z 139 (100, $M^{+\cdot}$), 111 (53, $M^{+\cdot}$-N_2), 84 (53, m/z 111 - HCN), 72 (11, $MeCH{=}C{=}S^{+\cdot}$), 71 (24), 66 (85, m/z 111 - HCS).

Anal. Calcd. for $C_5H_5N_3S$ (mol wt 139): C, 43.15; H, 3.62. Found: C, 43.31; H, 3.55.

3-Ethoxycarbonyl-6-methylthiazolo[3,2-*c*][1,2,3]triazole (**18c**).

A solution of 2-ethoxycarbonylmethyl-4-methylthiazole [16] (3.0 g, 16.2 mmoles), tosyl azide (4.9 g, 24.3 mmoles) and triethylamine (1.6 g, 16.2 mmoles) in acetonitrile (50 ml) was stirred at room temperature for 4 days. After removal of the solvent, the crude product was flash chromatographed on silica gel, first with *n*-hexane-ethyl acetate (80:20) and then with ethanol as the eluents. The ethanol fractions were again chromatographed with *n*-hexane-ethyl acetate (50:50) and then crystallized from ethyl acetate to give **18c** in 27% yield (930 mg), mp 131.5-133°; ir (potassium bromide): no diazo absorption, 1750 cm^{-1} (s, CO); ^1H nmr: see Table 2; ^{13}C nmr (deuteriochloroform): δ 12.0 (ring CH_3), 14.3 and 61.3 (C_2H_5), 114.9 (C-5, $^1J_{CH}$ = 192 Hz, $^3J_{CH}$ = 6 Hz), 130.2 (C-3), 130.3 (C-6), 141.3 (C-3a, $^3J_{CH}$ = 5 Hz), 160.4 (CO); ms: (%) m/z 211 (72, $M^{+\cdot}$), 139 (100, molecular ion of **18b**), 126 (42), 111 (85, m/z 139 - N_2), 99 (14), 84 (36).

Anal. Calcd. for $C_8H_9N_3O_2S$ (mol wt 211): C, 45.49; H, 4.29. Found: C, 45.65; H, 4.27.

[1,2,3]Triazolo[4,3-*b*]benzothiazole (**18d**).

This compound was prepared in the same way as **18a** from benzothiazole-2-carbaldehyde [17] in 27% overall yield, mp 115-117° (ethanol); ^1H nmr (deuteriochloroform): δ 7.50 (td, C_6-H), 7.58 (td, C_7-H), 7.76 (dd, C_5-H), 7.87 (s, C_3-H), 8.25 (dd, C_8-H); ^{13}C nmr (deuteriochloroform): δ 114.8 (C-8), 124.5 (C-3, $^1J_{CH}$ = 201 Hz), 124.6 (C-5), 127.0 and 127.3 (C-6 and C-7), 131.1 and 133.3 (C-4a and C-8a), 135.6 (C-3a, $^2J_{CH}$ = 14.5 Hz); ms: (%), m/z 175 (63, $M^{+\cdot}$), 147 (100, $M^{+\cdot}$ - N_2), 120 (52, $M^{+\cdot}$ - CHN_3), 103 (46), 94 (14), 76 (19).

Anal. Calcd. for $C_8H_5N_3S$ (mol wt 175): C, 54.84; H, 2.88. Found: C, 54.67; H, 3.02.

3-Ethoxycarbonyl[1,2,3]triazolo[4,3-*b*]benzothiazole (**18e**).

A solution of 2-ethoxycarbonylmethylbenzothiazole [18] (2.0 g, 9.0 mmoles), tosyl azide (1.8 g, 9.0 mmoles) and triethylamine (0.9 g, 9.0 mmoles) in acetonitrile (25 ml) was stirred overnight at room temperature. The precipitate was discarded, the filtrate evaporated and chromatographed on silica gel with ether-*n*-hexane (1:1) as the eluent to give **18e** in 43% yield (964 mg), mp 135.7-136.7° (diethyl ether); ir (potassium bromide): no diazo absorption, 1700 cm^{-1} (s, CO); ^1H nmr (dichloromethane, −90°): δ 1.38 (t, CH_3), 4.48 (q, CH_2), 7.46 (td, C_6-H), 7.54 (td, C_7-H), 7.75 (dd, C_5-H), 8.14 (dd, C_8-H) [Note: the diazo **17e** resonates at 7.18 and 7.31 (C_5-H and C_6-H), 7.70 and 7.75 (C_4-H and C_7-H)]; ^{13}C nmr (dichloromethane, −80°): δ 14.5 and 61.7 (C_2H_5), 114.9 (C-8), 125.2 (C-5), 127.7 (C-7), 128.0 (C-6), 130.7 (C-3), 131.3 and 133.7 (C-4a and C-8a), 140.9 (C-3a), 160.4 (CO) [Note: the diazo **17e** resonates at 14.5 and 62.3 (C_2H_5), 121.4 and 121.5 (C-4 and C-7), 123.8 and 126.4 (C-5 and C-6), 160.4 (CO)]; ms: (%) m/z 247 (62, $M^{+\cdot}$), 175 (98, molecular ion of **18d**), 162 (38), 147 (100, m/z 175 - N_2), 134 (52), 103 (22), 90 (14).

Anal. Calcd. for $C_{11}H_9N_3O_2S$ (mol wt 247): C, 53.43; H, 3.67. Found: C, 53.37; H, 3.74.

5-Phenyl[1,2,3]triazolo[5,1-*b*][1,3,4]thiadiazole (**20a**).

To a solution of 5-phenyl-1,3,4-thiadiazole-2-carbaldehyde [8,19] (1.3 g, 7 mmoles) in methanol (20 ml) was added at 15° hydroxylamine hydrochloride (0.5 g, 7 mmoles) and aqueous sodium acetate (0.3 g, 3.5 mmoles in 20 ml). The mixture was stirred at 15° for 2 hours, the precipitated oxime **13** (Het = 5-phenyl-1,3,4-thiadiazol-2-yl) was filtered off in 93% yield (1.3 g) and crystallized from methanol. It consisted of a *Z*/*E* mixture in a ratio of 70:30.

This compound (1.3 g, 6.3 mmoles) was suspended in aqueous sodium hydroxide (35 ml, 1*N*) and stirred with hydroxylamine-*O*-sulfonic acid (1 g, 8.8 mmoles) at 0° for 20 hours. Then, the precipitate was filtered off and purified by column chromatography on silica gel with dichloromethane as the eluent to give **20a** in 35% yield (0.45 g), mp 133° (carbon tetrachloride); ^1H nmr (deuteriochloroform): δ 7.86 (s, 1H, C_3-H), 7.50-7.68 and 7.95-8.03 (two m, 5H, Ph); ^{13}C nmr (deuteriochloroform): δ 123.1 (C-3, $^1J_{CH}$ = 203 Hz), 127.3, 128.9, 129.5 and 132.9 (Ph C-atoms), 131.5 (C-3a, $^2J_{CH}$ = 15 Hz), 167.3 (C-5, $^3J_{CH}$ = 6 Hz); ms: (%) m/z 202 (36, $M^{+\cdot}$), 174 (8, $M^{+\cdot}$ - N_2), 146 (91, $M^{+\cdot}$ - 2 N_2), 145 (85), 121 (98, $PhCS^+$), 102 (100, $PhCN^{+\cdot}$ - H), 77 (48).

Anal. Calcd. for $C_9H_6N_4S$ (mol wt 202): C, 53.45; H, 2.99. Found: C, 53.21; H, 2.98.

3-Ethoxycarbonyl-5-phenyl[1,2,3]triazolo[5,1-*b*][1,3,4]thiadiazole (**20b**).

A solution of 2-ethoxycarbonylmethyl-5-phenyl-1,3,4-thiadiazole [20] (2.0 g, 8.1 mmoles), tosyl azide (1.6 g, 8.1 mmoles) and triethylamine (0.8 g, 8.1 mmoles) in acetonitrile (30 ml) was stirred at room temperature for 24 hours. After removal of the solvent, the residue was flash chromatographed on silica gel with *n*-hexane-ethyl acetate (80:20) as the eluent to give **20b** in 31% yield (690 mg), mp 105.5-107°; ir (potassium bromide): no diazo absorption, 1700 and 1750 cm^{-1} (CO); ^1H nmr (deuteriochloroform): δ 1.33-1.53 and 4.36-4.54 (two t and two q, C_2H_5 of **19b** and **20b**), 7.37-7.53 (m, *meta* and *para* Ph of **19b**), 7.53-7.72 (m, *meta* and *para* Ph of **20b**), 7.85-8.08 (m, *ortho* Ph of **19b** and **20b**); ^1H nmr (deuterated benzene): δ 0.79 (t, CH_3 of **19b**), 1.11 (t, CH_3 of **20b**), 3.84 (q, CH_2 of **19b**), 4.16 (q, CH_2 of **20b**), 6.81-7.08 (m, *meta* and *para* Ph of **19b** and **20b**), 7.39 (d, *ortho* Ph of **20b**), 7.86 (br, *ortho* Ph of **19b**); ^{13}C nmr (deuteriochloroform at −5°) **19b**: δ 14.4 and 62.4 (C_2H_5), 127.5, 129.2, 130.0 and 130.9 (Ph C-atoms), 155.9 (C-2), 163.5 (CO), 168.1 (C-5); **20b**: δ 14.4 and 61.9 (C_2H_5), 127.5, 128.3, 129.7 and 133.5 (Ph C-atoms), 136.1 (C-3a), 159.9 (CO), 168.9 (C-5); ms: (%) m/z 274 (48, $M^{+\cdot}$), 202 (100, molecular ion of **20a**), 174 (30, m/z 202 - N_2), 146 (54, m/z 202 - 2 N_2), 145 (64), 121 (93, $PhCS^+$), 103 (21, $PhCN^{+\cdot}$), 77 (32).

Anal. Calcd. for $C_{12}H_{10}N_4O_2S$ (mol wt 274): C, 52.54; H, 3.67. Found: C, 52.66; H, 3.79.

5-(α-Methoxycarbonyl)diazomethyl-3-methyl-1,2,4-thiadiazole (**21**).

This compound was similarly prepared as **20b** from 5-methoxycarbonylmethyl-3-methyl-1,2,4-thiadiazole [21] in 47% yield, mp 79-80° (MeOH); ir (potassium bromide) 2130 (s, CN_2), 1700 cm^{-1} (s, CO); ^1H nmr (deuteriochloroform): δ 2.60 (s, 3H, ring CH_3), 3.96 (s, 3H, CH_3O); ^{13}C nmr (deuteriochloroform): δ 18.6 (ring CH_3), 53.0 (CH_3O), 66.3 (C=N_2), 163.6 (CO), 171.3 (C-3), 174.1 (C-5); ms: (%) m/z 198 (34, $M^{+\cdot}$), 163 (11), 129 (19), 91 (10), 85 (36), 73 (31, $MeCNS^+$), 70 (98), 59 (97, $HNCS^{+\cdot}$), 56 (100).

Anal. Calcd. for $C_6H_6N_4O_2S$ (mol wt 198): C, 36.36; H, 3.05. Found: C, 36.26; H, 3.08.

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