Reactions of 5-Chloro-1,2,3-Thiadiazolium Salts with Activated Methylene Compounds

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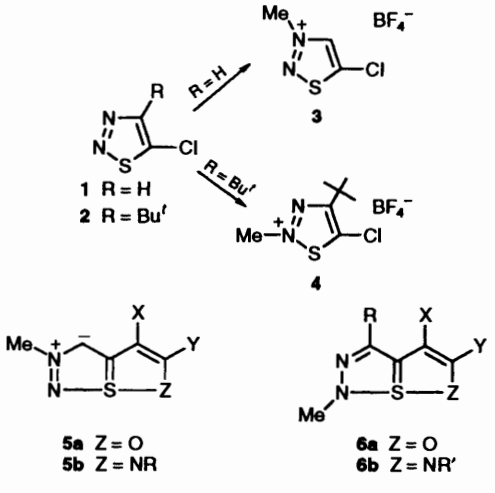
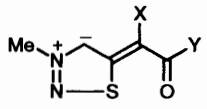
The N-3 and N-2 methylated 1,2,3-thiadiazolium tetrafluoroborates **3** and **4** react with aliphatic activated methylene ketones and esters in the presence of a base to give the substitution products **7–11** and **18–24**. Under similar conditions activated methylene azoles afford products formulated by NMR analysis as N–S • • • O rotamers (**25**, **26**), N–S • • • N rotamers (**12–15**, **27–29**), or a mixture of both (**16**, **17**, **30**). The X-ray crystal structure analysis of product **21**, derived from the thiadiazolium salt **4** and 2,2-dimethyl-1,3-dioxane-4,6-dione, reveals a nearly linear N–S • • • O sequence (169°) and a short S • • • O contact (2.37/2.34 Å) for the two independent molecules.

1,2,3-Thiadiazoles bearing a chloro substituent at the 5-position are readily prepared from chloroacetaldehyde or chloromethyl ketones by oxidative cyclization of the corresponding *N*-tosyl or *N*-acyl hydrazones with thionyl chloride (Hurd and Mori's method).[1,2] They can be methylated at N-2 and/or N-3 depending on the substituent at C-4.[3] Thus, the parent compound **1** is methylated exclusively at N-3 to give the salt **3**, whereas compound **2** with its bulky substituent at C-4 furnishes the salt **4** as a result of methylation at N-2. Both salts **3** and **4** are of interest for the construction of λ^4-thiapentalenes **5** and **6** which are characterized by a four-electron three-centre bonding N–S–Z.[4]

The first synthetic routes to 6-oxa-6aλ^4-thia-1,2-diazapentalenes and 6aλ^4-thia-1,2,6-triazapentalenes were reported by Reid and co-workers.[5] Later, Capuano *et al.*[6] obtained the two ring systems **5a** and **6a** by treating ester substituted thioketenes with diazomethane and showed by X-ray analysis that they exhibit short sulfur • • • oxygen contacts (2.5–2.6 Å). This paper describes a new method for the synthesis of compounds **5a**, **b** and **6a**, **b**.



The treatment of 3-methylthiadiazolium tetrafluoroborate **3** with 1 equiv. of pentane-2,4-dione, methyl acetoacetate, dimethyl malonate, 2,2-dimethyl-1,3-dioxane-4,6-dione (Meldrum's acid)[7] and ethyl cyanoacetate in the presence of potassium *tert*-butoxide yielded products **7–11**. They were characterized by IR, ^{1}H NMR, ^{13}C NMR and mass spectroscopy and microanalysis. In particular, compound **7** shows two singlets for the acetyl protons in the ^{1}H NMR spectrum (δ 2.47 and 2.54) as well as two acetyl carbon absorptions in the ^{13}C NMR spectrum (Me at δ 27.5/31.5 and CO at 187.5/190.2). The same phenomenon is observed for the carboxy groups of compounds **9** and **10** (see Tables 1 and 2). We attribute the magnetic non-equivalence of these groups in the NMR spectra to restricted rotation about C-5 due to the S • • • O interaction. Indeed, the X and Y proton signals of compounds **7** and **9** coalesced in [$^2H_6$]dimethyl sulfoxide upon raising the temperature to 40 °C.



	X	Y
7	COMe	Me
8	CO_2Me	Me
9	CO_2Me	OMe
10	—CO—O—CMe_2—O—	
11	CN	OEt

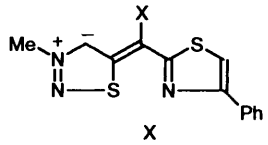
The salt **3** also reacted under basic conditions with (4-phenylthiazol-2-yl)acetonitrile, ethyl (4-phenylthiazol-2-yl)acetate, (benzothiazol-2-yl)acetonitrile and ethyl (benzothiazol-2-yl)-acetate to give the mesoionic compounds **12–15** having the N–S • • • N sequence. The structures **13** and **15** were preferred over the alternative N–S • • • O rotamers by a consideration of the carbonyl absorptions in the ^{13}C NMR spectra. These resonate at higher field (δ 163) than in **11** (δ 168) and at the same position as the free ester groups in **8** and **9** (Table 2). The influence of a heterocyclic ring (thiazole or oxazole) on the C=O chemical shift is less than 2 ppm.

When ethyl (5-phenyloxazol-2-yl)acetate and ethyl (benzoxazol-2-yl)acetate were combined with the salt **3**, the corresponding products **16** and **17** were shown by ^{1}H NMR spectroscopy to be composed of two rotamers in ratios of 80:20 and 73:27 respectively. The major rotamers, **16a** and **17a**, have the N–S • • • O sequence as shown by the carbonyl absorption at δ ~167, while **17b** absorbs at δ 163. The poor solubility of compound **16** in dimethyl sulfoxide prevented the ^{13}C NMR characterization of the minor rotamer; its presence, however, was inferred from the ^{1}H NMR spectrum where two signals are observed for the NMe, oxazole 4-H and thiadiazole 4-H protons (Table 1). The thiadiazole 4-H absorption of **16a** (δ 9.60) is deshielded by the oxazole ring and occurs at a lower field than that of **16b** (δ 9.54). The same holds for compound **17** where the 4-H of the two rotamers absorb at δ 9.81 and 9.62.

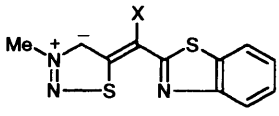
Table 1 ^{1}H NMR chemical shifts (δ values) of the heterocycles

No.	Solvent	NMe	4-H	Bu^t	Other absorptions
7	$(CD_3)_2SO$	4.43	9.81		2.47 (3 H, s), 2.54 (3 H, s)
8	$(CD_3)_2SO$	4.42	9.42		2.47 (3 H, s), 3.77 (3 H, s)
9	$(CD_3)_2SO$	4.38	9.41		3.67 (3 H, s), 3.72 (3 H, s)
10	$(CD_3)_2SO$	4.47	9.57		1.64 (6 H, s)
11	$(CD_3)_2SO$	4.33	9.00		1.3 (3 H, t), 4.2 (2 H, q)
12	$(CD_3)_2SO$	4.35	9.12		7.39, 7.52 and 8.08 (5 H, 2t + d, Ph), 7.79 (1 H, s, thiazole 5-H)
13	$(CD_3)_2SO$	4.42	9.42		1.40 (3 H, t), 4.35 (2 H, q), 7.37, 7.59 and 8.11 (5 H, 2t + d, Ph), 7.71 (1 H, s, thiazole 5-H)
14	$(CD_3)_2SO$	4.36	9.19		7.24, 7.42, 7.82 and 7.93 (4 H, 2t + 2d)
15	$(CD_3)_2SO$	4.44	9.49		1.41 (3 H, t), 4.36 (2 H, q), 7.21, 7.40, 7.89 and 7.91 (4 H, 2t + 2d)
16a	$(CD_3)_2SO$	4.39	9.60		1.39 (t), 4.30 (q), 7.27, 7.44 and 7.69 (2t + d, Ph), 7.62 (s, oxazole 4-H)
16b	$(CD_3)_2SO$	4.37	9.54		7.80 (s, oxazole 4-H)
17a	$(CD_3)_2SO$	4.44	9.81		1.34 (t), 4.33 (q), 7.20, 7.25, 7.56 and 7.58 (2t + 2d)
17b	$(CD_3)_2SO$	4.41	9.62		4.30 (q), 7.61 (d)
18	$CDCl_3$	3.95		1.43	2.49 (6 H, s)
19	$CDCl_3$	3.94		1.43	2.42 (3 H, s), 3.85 (3 H, s)
20	$CDCl_3$	3.83		1.38	3.82 (6 H, s)
21	$CDCl_3$	4.16		1.56	1.78 (6 H, s)
22	$CDCl_3$	3.95		1.56	1.38 (3 H, t), 4.35 (2 H, q)
23	$CDCl_3$	3.83		1.45	2.34 (3 H, s), 6.54 (1 H, s)
24	$CDCl_3$	3.80		1.39	3.65 (3 H, s), 5.76 (1 H, s)
25	$CDCl_3$	3.84		1.16	1.19 (3 H, t), 4.20 (2 H, q), 7.32, 7.41 and 7.66 (5 H, 2t + d, Ph), 7.45 (1 H, s, oxazole 4-H)
26	$CDCl_3$	3.85		1.11	1.17 (3 H, t), 4.20 (2 H, q), 7.3–7.8 (4 H, 3m)
27	$CDCl_3$	3.92		1.64	7.30 (1 H, s, thiazole 5-H), 7.39, 7.50 and 7.95 (5 H, 2t + d, Ph)
28	$CDCl_3$	3.94		1.64	7.26, 7.41, 7.76 and 7.87 (4 H, 2t + 2d)
29	$CDCl_3$	3.93		1.43	1.40 (3 H, t), 4.38 (2 H, q), 7.24, 7.39, 7.77 and 7.88 (4 H, 2t + 2d)
30a	$CDCl_3$[a]	3.85		1.15	1.2 (3 H, t), 4.20 (2 H, q), 7.71 (thiazole 5-H), 7.3–7.6 and 8.0 (m + d, Ph)
30b	$CDCl_3$[a]	4.0		1.50	1.4 (3 H, t), 4.41 (2 H, q), 7.28 (thiazole 5-H), 7.3–7.6 and 8.0 (m + d, Ph)

[a] Recorded at −35 °C.



12 X = CN
13 X = CO_2Et



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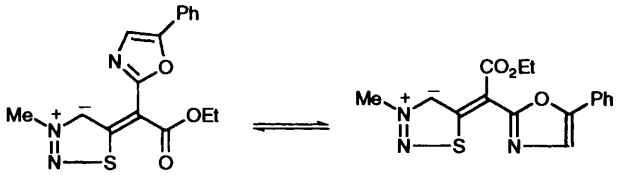
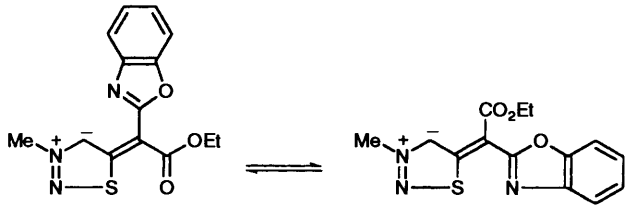
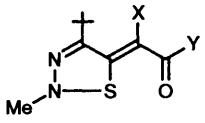


16a ⇌ **16b**



17a ⇌ **17b**



	X	Y
18	COMe	Me
19	CO_2Me	Me
20	CO_2Me	OMe
21	—CO—O—CMe_2—O—	
22	CN	OEt
23	H	Me
24	H	OMe

Irradiation of the signal at δ 9.81 caused the 4-H resonance at δ 9.62 to decrease in intensity by saturation transfer, showing that the two rotamers are in dynamic equilibrium.

In a second phase of this research we have investigated the reactions of 4-*tert*-butyl-2-methyl-1,2,3-thiadiazolium tetrafluoroborate **4** with the same activated methylene compounds as mentioned above. The aliphatic activated methylene compounds and Meldrum's acid[7] yielded the thiapentalenic derivatives **18**–**22**, and compounds **23** and **24** were obtained by acid catalysed methanolysis of **18** and **19** (or **20**), respectively. In contrast to the mesoionic compounds **7**, **9** and **10**, the ^{1}H NMR spectra of **18**, **20** and **21** do not differentiate between the two functional groups at room temperature (see Tables 1 and 2), indicating free rotation of the side-chain at the 5-position.

In order to gain more insight into the structural characteristics of such compounds, a single crystal of **21** was subjected to X-ray analysis and the results are shown in Fig. 1. The unit cell contains two pairs of independent molecules (denoted a and b) which differ in the conformation of the dioxane ring, with CMe_2 lying above or below the ring plane, while the bond lengths and angles are only slightly affected. Each conformation influences the positions of the other atoms. For instance, in conformation (a), where the CMe_2 group lies above the dioxane plane, the oxygen atoms O(8a) and O(10a) are tilted downwards. This, in turn, determines the orientation of the *tert*-butyl group and the position of the S(1a) atom. Indeed, the atom O(10a) lies in an extension of the C(15a)–C(16a) bond, allowing the other two methyls of the *tert*-butyl group to adopt the most favourable orientation for minimum interaction with O(10); and this is also rendered possible by distortion of the *tert*-butyl group away from the dioxane ring, C(5a)–C(4a)–C(15a) = 132°. The sulfur atom S(1a) follows the movement of O(8a) below the dioxane ring in order to optimize a close contact interaction. As a result, the mean deviation of

Table 2 ^{13}C NMR chemical shifts (δ values) of the heterocycles

No.	Solvent	NMe[a]	C-4	C-5	C_5–*C*	CO···S	Free CO	Other absorptions
7	$(CD_3)_2SO$	45.6	133.3	160.4	110.1	190.2	187.5	27.5, 31.5
8	$(CD_3)_2SO$	45.6	132.9	160.5	96.5	188.0	165.1	26.3, 50.5
9	$(CD_3)_2SO$	45.7	132.3	164.8	82.0	169.2	164.3	50.3, 51.6
10	$(CD_3)_2SO$	46.1	133.8	160.8	77.5	165.1	160.1	26.0, 103.6
11	$(CD_3)_2SO$	45.7	130.6	163.9	60.1	168.1		14.5, 60.3, 117.8 (CN)
12	$(CD_3)_2SO$[b]	45.0	129.6	156.7	66.0			107.3, 152.8 and 164.2 (thiazole), 118.6 (CN), 125.5, 127.5, 128.3 and 133.5 (Ph)
13	$(CD_3)_2SO$	45.5	131.4	156.4	88.6		163.4	14.7, 59.4 (Et), 109.2, 150.8 and 164.4 (thiazole), 125.7, 127.5, 128.7 and 134.2 (Ph)
14	$(CD_3)_2SO$	45.6	131.0	158.1	65.8			119.2 (CN), 119.5, 122.1, 123.0, 126.3, 132.0 and 152.8 (benzene), 164.3 (thiazole C-2)
15	$(CD_3)_2SO$[c]	45.6	131.8	157.8	88.6		163.5	14.6 and 59.4 (Et), 118.8, 121.2, 122.3, 125.4, 132.9 and 150.5 (benzene), 164.4 (thiazole C-2)
16a	$(CD_3)_2SO$	45.4	130.9	160.2[d]	79.5	167.0		14.4 and 59.8 (Et), 122.5, 146.5 and 159.6[d] (oxazole), 122.9, 127.1, 128.4 and 128.8 (Ph)
17a	$(CD_3)_2SO$	45.9	132.1	161.5[d]	78.8	167.7		14.7 and 60.4 (Et), 109.6, 117.2, 122.5, 123.8, 142.0 and 149.0 (benzene), 162.1[d] (oxazole C-2)
17b	$(CD_3)_2SO$	45.6	132.5	160.5	79.8		163.3	14.7 and 59.0 (Et), 109.8, 116.6, 122.4, 123.9, 140.9 and 149.5 (benzene), 164.7 (oxazole C-2)
18	$CDCl_3$	39.5	153.9	154.1	114.8	189.1br	189.1br	27–29 (br Me), 30.3 and 36.3 (Bu^t)
19	$CDCl_3$	39.4	153.4	154.1	104.2	180.3	169.1	22.4, 30.1, 36.1, 52.0
20	$CDCl_3$	40.1	152.0	158.7	89.7	168.4	168.4	29.8 and 35.4 (Bu^t), 52.6 (OMe)
21	$CDCl_3$	41.9	159.0	159.0	82.0	164.1	164.1	25.8, 29.9, 37.3, 103.3
22	$CDCl_3$	40.4	152.8	160.0	67.5	170.9		14.5 and 62.5 (Et), 30.2 and 34.7 (Bu^t), 119.4 (CN)
23	$CDCl_3$	39.0	151.6	155.3	97.7	182.0		24.2, 28.9, 34.5
24	$CDCl_3$	40.3	151.9	158.2	85.8	170.3		28.6 and 34.2 (Bu^t), 51.9 (OMe)
25	$CDCl_3$	39.8	151.7	159.9	83.8	170.1		14.5 and 61.6 (Et), 29.6 and 34.8 (Bu^t), 122.6, 151.3 and 157.9 (oxazole)
26	$CDCl_3$	40.0	151.9	159.9[d]	83.3	169.6		14.5 and 61.7 (Et), 29.6 and 35.0 (Bu^t), 110.5, 119.9, 124.0, 125.0, 141.6 and 150.6 (benzene), 160.8[d] (oxazole C-2)
27	$CDCl_3$	40.0	151.7	151.8	73.6			30.4 and 34.8 (Bu^t), 109.9, 153.1 and 166.2 (thiazole), 121.2 (CN)
28	$CDCl_3$	39.9	151.9	152.8	72.9			30.4 and 34.8 (Bu^t), 119.5, 121.9, 123.8, 126.0, 133.5 and 150.8 (benzene), 121.1 (CN), 165.8 (thiazole C-2)
29	$CDCl_3$	40.3	154.1	155.0	95.1		167.1	14.6 and 60.8 (Et), 30.4 and 36.9 (Bu^t), 119.3, 121.4, 123.3, 125.6, 134.8 and 149.7 (benzene), 164.2 (thiazole C-2)
30a	$CDCl_3$[e]	39.5	151.3	159.0	87.5	168.9		14.4 and 61.5 (Et), 29.9 and 35.1 (Bu^t), 116.1, 153.1 and 164.4 (thiazole)
30b	$CDCl_3$[e]	40.5	153.8	152.2	95.3		166.5	14.4 and 60.3 (Et), 30.2 and 36.9 (Bu^t), 110.0, 150.5 and 163.8 (thiazole)

[a] $^1J_{CH}$ 144–146 Hz for **7**–**17** and $^1J_{CH}$ 140.5–143.5 Hz for **18**–**30**. [b] Recorded at 80 °C. [c] Recorded at 40 °C. [d] The reverse assignment is possible. [e] Recorded at −35 °C.

the eight atoms 1–8 from the best plane through the atoms is 0.093 Å.

The N(2)–S(1)···O(8) atoms are almost colinear (169°) and the S(1)···O(8) distance (2.37/2.34 Å) is considerably shorter than the sum of the corresponding van der Waals radii (3.2 Å), and also shorter than the Huggins constant energy distance of 2.58 Å,[8] showing a weak covalent bond of 2.6/3.0 kcal mol^{-1}.* The bond lengths C(4)–C(5), C(5)–C(6) and C(6)–C(7) are nearly equal (1.42–1.43 Å) and intermediate between a single and double bond. This is also the case for the N(3)–C(4) bond (1.33 Å), whereas N(2)–N(3) (1.31/1.30 Å) has pronounced double bond character.[9] From these results and the fact that C(7)–O(8) (1.23 Å) is longer than C(9)–O(10) (1.20 Å), we conclude that **21** is best represented by the canonical structures **21A** and **21B**, and that **21C** is only a minor contributor to the overall structure of the molecule.

When activated methylene azoles were treated with salt **4**, two types of thiapentalenes were obtained; namely the oxazole derivatives **25** and **26** with an N–S···O sequence and the thiazole derivatives **27**–**29** with an N–S···N sequence. The oxazole derivatives show C=O carbon absorptions at δ ~170 in the ^{13}C NMR spectra, exactly at the position where our reference compounds **22** and **24** absorb (Table 2). The C=O resonance of the benzothiazole derivative **29**, on the contrary, is found at δ 167. Another useful criterion to distinguish between the N–S···O and N–S···N rotamers is the position of the *tert*-butyl protons in the ^1H NMR spectra. For **25** and **26** they lie in the shielding region of the aromatic oxazole, which is assumed to stand perpendicular to the thiapentalene ring. As a consequence, they absorb at higher field (δ 1.1) than in compounds **24** and **29** (δ 1.4).

It is worth pointing out that the barrier to rotation around the exocyclic double bond of compounds **25**–**29** is low and that free rotation of the side chain occurs at room temperature; hence, the indicated structures represent the most abundant rotamers present in solution. To demonstrate this contention we have cooled a chloroform solution of compound **29** and observed a broadening of the absorptions in the ^1H NMR spectrum, including that of the *tert*-butyl protons at δ 1.43. At −60 °C a small broad signal appears at δ 1.14 where the N–S···O rotamer is expected to absorb.

* 1 cal = 4.184 J.

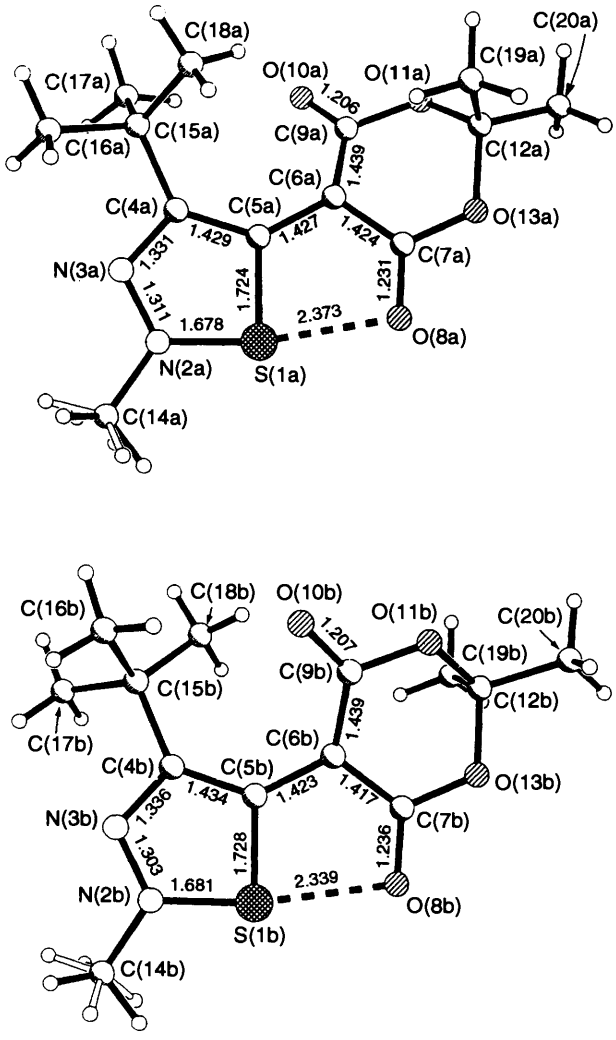
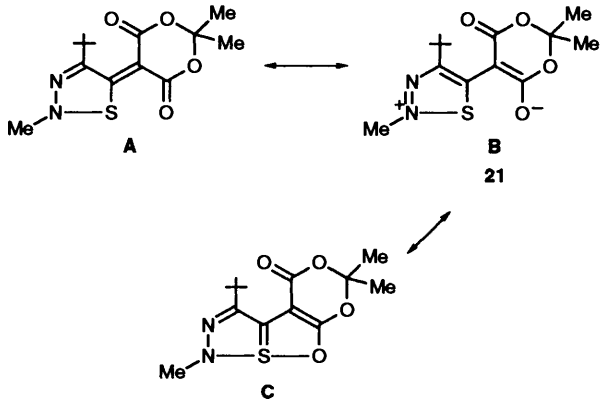
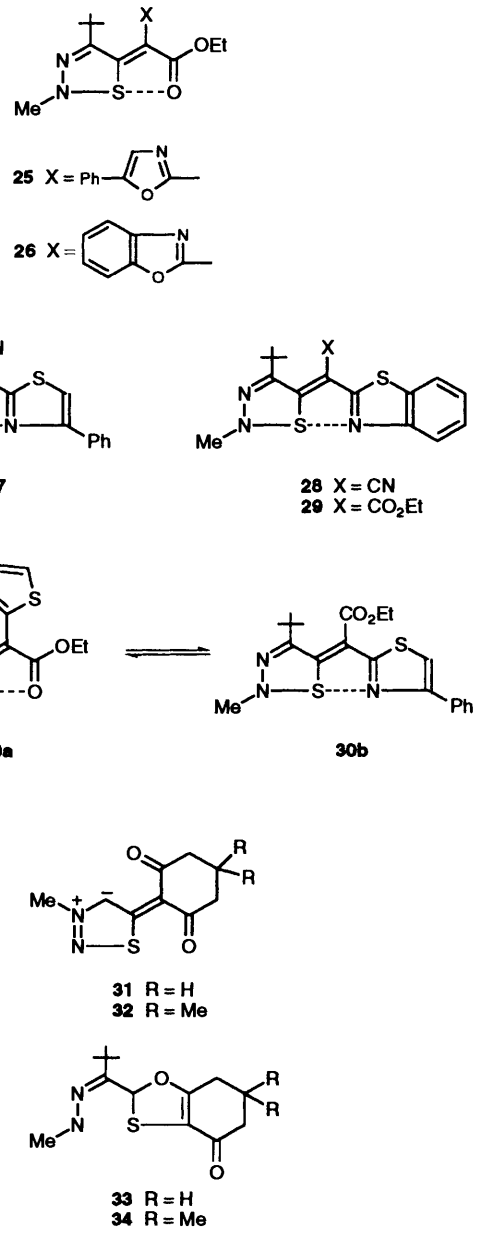


Fig. 1 Structures of the two crystallographically independent molecules of **21**



Compound **30**, prepared from salt **4** and ethyl (4-phenylthiazol-2-yl)acetate, is the only case where the two rotamers were observed in comparable concentrations by NMR in [^{2}H]chloroform. At room temperature, the product exhibits broad signals in the ^{1}H NMR spectrum, but at −35 °C the rotamers **30a** and **30b** are clearly distinguished and characterized by the two criteria discussed above (see Tables 1 and 2). The coalescence temperature is situated between 0 and −15 °C. It occurs at −30 °C in [$^2H_3$]acetonitrile, indicating that rotation is faster in a polar solvent. Also, the distribution



30a : **30b** is solvent dependent; the ratios are 45 : 55 in chloroform at −35 °C, 27 : 73 in acetonitrile at −45 °C and 37 : 63 in toluene at −35 °C.

Finally, we have found that cyclohexane-1,3-diones react differently with the salts **3** and **4**, giving the mesoionic 1,2,3-thiadiazoles **31**/**32** and the oxathioles **33**/**34**, respectively. For a detailed discussion of the spectroscopic and crystal structure data see ref. 10.

Experimental

M.p.s were determined using a Reichert Thermovar apparatus. IR spectra were recorded on a Perkin-Elmer 1720 FT spectrometer, NMR spectra on a Bruker WM-250 or AMX-400 spectrometer, and mass spectra (EI) on a Hewlett Packard 5989A or Kratos MS50 TC (for high resolution) instrument, both operating at 70 eV. The NMR data are summarized in Tables 1 and 2 (*J* values are given in Hz).

The activated methylene azoles were prepared according to the literature methods.[11] The thiadiazoles **1** and **2** were synthesized by the method of Hurd and Mori,[1a,2] and the salt **3** by methylation of thiadiazole **1** with Meerwein's reagent as

previously reported.[3] The salt **4** was similarly prepared from thiadiazole **2** in 69% yield, m.p. 132–137 °C (from EtOH); $\delta_H[(CD_3)_2SO]$ 1.5 (9 H, s, Bu^t) and 4.6 (3 H, s, NMe); $\delta_C[(CD_3)_2SO]$ 28.0 and 35.1 (Bu^t), 47.5 (NMe, $^1J_{CH}$ 147), 152.0 (C-5) and 164.6 (C-4) (Found: C, 30.2; H, 4.2. $C_7H_{12}BClF_4N_2S$ requires C, 30.19; H, 4.34%).

Typical Reaction.—Thiadiazolium salt **3** or **4** (2 mmol) was added to a suspension of the activated methylene compound (2–2.2 mmol) and potassium *tert*-butoxide (4.4 mmol) in dry acetonitrile (20 cm^3), and the mixture was stirred at room temperature for 15 min. After removal of the solvent under reduced pressure, the residue was chromatographed on silica gel with the appropriate eluent (*vide infra*). The products obtained are listed below.

5-(*Diacetylmethylene*)-3-*methyl*-4,5-*dihydro*-1,2,3-*thiadiazol*-3-*ium*-4-*ide* **7**.—Prepared from pentane-2,4-dione and salt **3** in 52% yield, eluent ethyl acetate–methanol (30:1), m.p. 184 °C (orange crystals from EtOH); ν_{max}(KBr)/cm^{-1} 3147m, 1600s and 1520s; *m/z* 198 (M$^{\bullet+}$, 28%), 183 (M$^{\bullet+}$ − Me, 34), 141 (M$^{\bullet+}$ − CH_2O − Me, 66) 43 (MeN_2^+ or $MeCO^+$, 100) and 42 ($CH_2N_2^{\bullet+}$, 17) (Found: C, 48.3; H, 5.1. $C_8H_{10}N_2O_2S$ requires C, 48.47; H, 5.08%).

5-[*Acetyl*(*methoxycarbonyl*)*methylene*]-3-*methyl*-4,5-*dihydro*-1,2,3-*thiadiazol*-3-*ium*-4-*ide* **8**.—Prepared from methyl acetoacetate and salt **3** in 69% yield, eluent ethyl acetate–methanol (5:1), m.p. 150 °C (orange crystals from EtOH); ν_{max}(KBr)/cm^{-1} 3145m, 1655s and 1550s; *m/z* 214 (M$^{\bullet+}$, 51%), 199 (M$^{\bullet+}$ − Me, 62), 183 (M$^{\bullet+}$ − OMe, 13), 169 (38), 141 (M$^{\bullet+}$ − CH_2CO − MeO, 50), 66 (11), 43 (MeN_2^+ or $MeCO^+$, 100) and 42 ($CH_2N_2^{\bullet+}$, 30) (Found: C, 44.95; H, 4.7. $C_8H_{10}N_2O_3S$ requires C, 44.85; H, 4.71%).

5-[*Bis*(*methoxycarbonyl*)*methylene*]-3-*methyl*-4,5-*dihydro*-1,2,3-*thiadiazol*-3-*ium*-4-*ide* **9**.—Prepared from dimethyl malonate and salt **3** in 75% yield, eluent diethyl ether–methanol (10:1), m.p. 182 °C (orange crystals from EtOH); ν_{max}(KBr)/cm^{-1} 3137m, 1655s and 1585s; *m/z* 230 (M$^{\bullet+}$, 98%), 199 (M$^{\bullet+}$ − CO, 92), 172 (89), 169 (M$^{\bullet+}$ − MeO − CH_2O, 100), 141 (M$^{\bullet+}$ − CO_2Me − CH_2O, 67), 140 (26), 114 (83), 69 (27), 66 (24), 43 (MeN_2^+, 85) and 42 ($CH_2N_2^{\bullet+}$, 85) (Found: C, 41.6; H, 4.3. $C_8H_{10}N_2O_4S$ requires C, 47.71; H, 4.38%).

5-(2,2-*Dimethyl*-4,6-*dioxo*-1,3-*dioxan*-5-*ylidene*)-3-*methyl*-4,5-*dihydro*-1,2,3-*thiadiazol*-3-*ium*-4-*ide* **10**.—Prepared from 2,2-dimethyl-1,3-dioxane-4,6-dione and salt **3** in 76% yield, eluent chloroform–methanol (15:1), m.p. 206 °C (orange crystals from EtOH); ν_{max}(KBr)/cm^{-1} 3120s, 1695s and 1625s; *m/z* 242 (M$^{\bullet+}$, 13%), 185 (M$^{\bullet+}$ − Me − CMe_2, 12), 140 (M$^{\bullet+}$ − Me_2CO − CO_2, 79), 94 (19), 69 (12), 53 (45), 43 (MeN_2^+, 100) and 42 ($CH_2N_2^{\bullet+}$, 63) (Found: C, 44.8; H, 4.2. $C_9H_{10}N_2O_4S$ requires C, 44.62; H, 4.16%).

5-[*Cyano*(*ethoxycarbonyl*)*methylene*]-3-*methyl*-4,5-*dihydro*-1,2,3-*thiadiazol*-3-*ium*-4-*ide* **11**.—Prepared from ethyl cyanoacetate and salt **3** in 81% yield, eluent chloroform–methanol (10:1), m.p. 145 °C (lit.,[6] 143 °C); ν_{max}(KBr)/cm^{-1} 3082m, 2188s and 1631s; *m/z* 211 (M$^{\bullet+}$, 47%), 183 (M$^{\bullet+}$ − C_2H_4, 48), 166 (M$^{\bullet+}$ − OEt, 47), 139 (M$^{\bullet+}$ − C_2H_4 − CO_2, 69), 114 (16), 93 (12), 91 (14), 64 (11), 52 (12), 46 (EtOH$^{\bullet+}$, 100), 43 (MeN_2^+, 78) and 42 ($CH_2N_2^{\bullet+}$, 40).

5-[*Cyano*(4-*phenylthiazol*-2-*yl*)*methylene*]-3-*methyl*-4,5-*dihydro*-1,2,3-*thiadiazol*-3-*ium*-4-*ide* **12**.—Prepared from (4-phenylthiazol-2-yl)acetonitrile and salt **3** in 72% yield, eluent chloroform–methanol (10:1), m.p. 243–246 °C (orange crystals from EtOH); ν_{max}(KBr)/cm^{-1} 3096m and 2177s; *m/z* 298 (M$^{\bullet+}$, 45%), 134 (PhC–CHS$^{\bullet+}$, 31), 89 (23), 77 (Ph$^+$, 11), 69 (12), 63 (18), 51 (17), 50 (11), 45 (60), 43 (MeN_2^+, 100) and 42 ($CH_2N_2^{\bullet+}$, 35) (Found: C, 56.6; H, 3.7. $C_{14}H_{10}N_4S_2$ requires C, 56.36; H, 3.38%).

5-[(*Ethoxycarbonyl*)(4-*phenylthiazol*-2-*yl*)*methylene*]-3-*methyl*-4,5-*dihydro*-1,2,3-*thiadiazol*-3-*ium*-4-*ide* **13**.—Prepared from ethyl (4-phenylthiazol-2-yl)acetate and salt **3** in 52% yield, eluent chloroform–methanol (10:1), m.p. 176 °C (orange crystals from EtOH); ν_{max}(KBr)/cm^{-1} 3126m and 1630s; *m/z* 345 (M$^{\bullet+}$, 100%), 273 (M$^{\bullet+}$ − C_2H_4 − CO_2, 21), 227 (28), 186 (30), 170 (17), 166 (10), 134 (PhC–CHS$^{\bullet+}$, 31), 102 (PhC≡CH$^{\bullet+}$, 16), 89 (30), 77 (Ph$^+$, 20), 69 (20), 63 (14), 51 (17), 46 (47), 45 (39), 43 (MeN_2^+, 68) and 42 ($CH_2N_2^{\bullet+}$, 34) (Found: C, 55.35; H, 4.4. $C_{16}H_{15}N_3O_2S_2$ requires C, 55.63; H, 4.38%).

5-[(*Benzothiazol*-2-*yl*)*cyanomethylene*]-3-*methyl*-4,5-*dihydro*-1,2,3-*thiadiazol*-3-*ium*-4-*ide* **14**.—Prepared from (benzothiazol-2-yl)acetonitrile and salt **3** in 64% yield, eluent ethyl acetate, m.p. 304 °C (orange needles from HOAc); ν_{max}(KBr)/cm^{-1} 3078m and 2181s; *m/z* 272 (M$^{\bullet+}$, 36%), 229 (M$^{\bullet+}$ − MeN_2, 13), 202 (11), 198 (22), 94 (11), 69 (21), 63 (10), 45 (18), 43 (MeN_2^+, 100) and 42 ($CH_2N_2^{\bullet+}$, 17) (Found: C, 52.8; H, 3.0. $C_{12}H_8N_4S_2$ requires C, 52.92; H, 2.96%).

5-[(*Benzothiazol*-2-*yl*)(*ethoxycarbonyl*)*methylene*]-3-*methyl*-4,5-*dihydro*-1,2,3-*thiadiazol*-3-*ium*-4-*ide* **15**.—Prepared from ethyl (benzothiazol-2-yl)acetate and salt **3** in 69% yield, eluent ethyl acetate, m.p. 216 °C (orange crystals from HOAc); ν_{max}(KBr)/cm^{-1} 3148m and 1644s; *m/z* 319 (M$^{\bullet+}$, 93%), 247 (M$^{\bullet+}$ − Et − MeN_2, 20), 232 (22), 204 (35), 201 (40), 173 (37), 160 (60), 109 (27), 108 (24), 69 (60), 46 (30), 43 (MeN_2^+, 100) and 42 ($CH_2N_2^{\bullet+}$, 29) (Found: C, 52.5; H, 4.1. $C_{14}H_{13}N_3O_2S_2$ requires C, 52.65; H, 4.10%).

5-[(*Ethoxycarbonyl*)(5-*phenyloxazol*-2-*yl*)*methylene*]-3-*methyl*-4,5-*dihydro*-1,2,3-*thiadiazol*-3-*ium*-4-*ide* **16**.—Prepared from ethyl (5-phenyloxazol-2-yl)acetate and salt **3** in 33% yield, eluent chloroform–methanol (15:1), m.p. 180 °C (brown crystals from EtOH); ν_{max}(KBr)/cm^{-1} 3129m and 1618s; *m/z* 329 (M$^{\bullet+}$, 100%), 257 (M$^{\bullet+}$ − CO_2Et, 41), 158 (15), 125 (14), 105 ($PhCO^+$, 23), 77 (Ph$^+$, 36), 43 (MeN_2^+, 41) and 42 ($CH_2N_2^{\bullet+}$, 16) (Found: C, 58.3; H, 4.7. $C_{16}H_{15}N_3O_3S$ requires C, 58.35; H, 4.59%).

5-[(*Benzoxazol*-2-*yl*)(*ethoxycarbonyl*)*methylene*]-3-*methyl*-4,5-*dihydro*-1,2,3-*thiadiazol*-3-*ium*-4-*ide* **17**.—Prepared from ethyl (benzoxazol-2-yl)acetate and salt **3** in 68% yield, eluent diethyl ether, m.p. 125–130 °C (orange crystals from $CHCl_3$–Et_2O); ν_{max}(KBr)/cm^{-1} 3156m and 1640s; ν_{max}($CHCl_3$)/cm^{-1} 1595s; *m/z* 303 (M$^{\bullet+}$, 100%), 231 (M$^{\bullet+}$ − Et − MeN_2, 47), 188 (16), 185 (25), 158 (18), 144 (22), 101 (11), 64 (15), 43 (MeN_2^+, 40) and 42 ($CH_2N_2^{\bullet+}$, 13) (Found: C, 55.3; H, 4.4. $C_{14}H_{13}N_3O_3S$ requires C, 55.43; H, 4.32%).

4-tert-*Butyl*-5-(*diacetylmethylene*)-2-*methyl*-2,5-*dihydro*-1,2,3-*thiadiazole* **18**.—Prepared from pentane-2,4-dione and salt **4** in 34% yield, eluent diethyl ether–hexane (2:1), m.p. 87 °C (yellow crystals from Et_2O–hexane); ν_{max}(KBr)/cm^{-1} 1655s; *m/z* 254 (M$^{\bullet+}$, 12%), 239 (M$^{\bullet+}$ − Me, 11), 211 (M$^{\bullet+}$ − MeCO or MeN_2, 21), 197 (M$^{\bullet+}$ − Bu^t, 31) and 43 (MeN_2^+ or $MeCO^+$, 100) (Found: C, 56.5; H, 7.0. $C_{12}H_{18}N_2O_2S$ requires C, 56.67; H, 7.13%).

5-[*Acetyl*(*methoxycarbonyl*)*methylene*]-4-tert-*butyl*-2-*methyl*-2,5-*dihydro*-1,2,3-*thiadiazole* **19**.—Prepared from methyl acetoacetate and salt **4** in 41% yield, eluent diethyl ether–hexane

(2:1), m.p. 91 °C (yellow crystals from Et_2O–hexane); ν_{max}(KBr)/cm^{-1} 1700s; *m/z* 270 ($M^{\bullet+}$, 17%), 255 ($M^{\bullet+}$ – Me, 24), 227 ($M^{\bullet+}$ – MeCO or MeN_2^+, 14), 213 ($M^{\bullet+}$ – Bu^t, 20), 153 (11) and 43 (MeN_2^+ or $MeCO^+$, 100) (Found: C, 53.4; H, 6.6. $C_{12}H_{18}N_2O_3S$ requires C, 53.31; H, 6.71%).

4-tert-*Butyl*-5-[*bis*(*methoxycarbonyl*)*methylene*]-2-*methyl*-2,5-*dihydro*-1,2,3-*thiadiazole* **20**.—Prepared from dimethyl malonate and salt **4** in 88% yield, eluent diethyl ether–hexane (4:1), m.p. 118 °C (yellow crystals from Et_2O–hexane); ν_{max}(KBr)/cm^{-1} 1715s and 1595s; *m/z* 286 ($M^{\bullet+}$, 23%), 271 ($M^{\bullet+}$ – Me, 100), 255 ($M^{\bullet+}$ – OMe, 20), 211 (11), 183 (16), 155 (33), 111 (15), 59 ($MeOCO^+$, 32), 57 (Bu^{t+}, 12), 45 (11), and 43 (MeN_2^+, 40) (Found: C, 50.2; H, 6.3. $C_{12}H_{18}N_2O_4S$ requires C, 50.34; H, 6.34%).

4-tert-*Butyl*-5-(2,2-*dimethyl*-4,6-*dioxo*-1,3-*dioxan*-5-*ylidene*)-2-*methyl*-2,5-*dihydro*-1,2,3-*thiadiazole* **21**.—Prepared from 2,2-dimethyl-1,3-dioxane-4,6-dione and salt **4** in 52% yield, eluent diethyl ether, m.p. 196 °C decomp. (yellow crystals from EtOAc); ν_{max}(KBr)/cm^{-1} 1715s and 1620s; *m/z* 298 ($M^{\bullet+}$, 3%), 196 ($M^{\bullet+}$ – Me_2CO – CO_2, 11), 181 (*m/z* 196 – Me, 22), 153 (*m/z* 181 – CO or N_2, 38) and 43 (MeN_2^+, 100) (Found: C, 52.05; H, 6.0. $C_{13}H_{18}N_2O_4S$ requires C, 52.33; H, 6.08%).

4-tert-*Butyl*-5-[*cyano*(*ethoxycarbonyl*)*methylene*]-2-*methyl*-2,5-*dihydro*-1,2,3-*thiadiazole* **22**.—Prepared from ethyl cyanoacetate and salt **4** in 77% yield, eluent diethyl ether–hexane (1:1), m.p. 210 °C (yellow crystals from $CHCl_3$–Et_2O); ν_{max}(KBr)/cm^{-1} 2193s and 1607s; *m/z* 267 ($M^{\bullet+}$, 39%), 252 ($M^{\bullet+}$ – Me, 21), 227 ($M^{\bullet+}$ – CH_2 – CN, 100), 199 (35), 57 (Bu^{t+}, 14) and 43 (MeN_2^+, 63) (Found: C, 53.8; H, 6.4. $C_{12}H_{17}N_3O_2S$ requires C, 53.91; H, 6.41%).

5-*Acetylmethylene*-4-tert-*butyl*-2-*methyl*-2,5-*dihydro*-1,2,3-*thiadiazole* **23**.—Compound **23** was prepared in 37% yield by acid catalysed methanolysis of compound **18** at reflux for 15 min. The reaction was worked up by pouring the reaction mixture into water, extraction with diethyl ether and then chromatography on silica gel with diethyl ether–hexane (1:1) as the eluent to give the title compound, m.p. 36–40 °C (brown solid); ν_{max}(KBr)/cm^{-1} 1521s; *m/z* 212 ($M^{\bullet+}$, 24%), 197 ($M^{\bullet+}$ – Me, 45), 155 (12), 57 (Bu^{t+}, 18) and 43 (MeN_2^+, 100) (Found: $M^{\bullet+}$, 212.098 47. $C_{10}H_{16}N_2OS$ requires *M*, 212.0983).

4-tert-*Butyl*-5-(*methoxycarbonyl*)*methylene*-2-*methyl*-2,5-*dihydro*-1,2,3-*thiadiazole* **24**.—This compound was similarly prepared by methanolysis of heterocycle **19** or **20** in 60 and 39% yield, respectively, m.p. 110–112 °C (from Et_2O–hexane); ν_{max}(KBr)/cm^{-1} 1615s; *m/z* 228 ($M^{\bullet+}$, 37%), 213 ($M^{\bullet+}$ – Me, 100), 155 (16), 125 (17) and 43 (MeN_2^+, 33) (Found: C, 52.5; H, 6.9. $C_{10}H_{16}N_2O_2S$ requires C, 52.61; H, 7.06%).

4-tert-*Butyl*-5-[(*ethoxycarbonyl*)(5-*phenyloxazol*-2-*yl*)*methylene*]-2-*methyl*-2,5-*dihydro*-1,2,3-*thiadiazole* **25**.—Prepared from ethyl (5-phenyloxazol-2-yl)acetate and salt **4** in 29% yield, eluent diethyl ether–hexane (1:1), m.p. 146 °C (yellow crystals from Et_2O–hexane); ν_{max}(KBr)/cm^{-1} 1598s; *m/z* 385 ($M^{\bullet+}$, 34%), 370 ($M^{\bullet+}$ – Me, 89), 342 (15), 227 (45), 199 (26), 105 ($PhCO^+$, 82), 91 (17), 77 (Ph^+, 100) and 43 (MeN_2^+, 81) (Found: C, 62.45; H, 6.0. $C_{20}H_{23}N_3O_3S$ requires C, 62.32; H, 6.01%).

5-[(*Benzoxazol*-2-*yl*)(*ethoxycarbonyl*)*methylene*]-4-tert-*butyl*-2-*methyl*-2,5-*dihydro*-1,2,3-*thiadiazole* **26**.—Prepared from ethyl (benzoxazol-2-yl)acetate and salt **4** in 53% yield, eluent diethyl ether–hexane (3:1), m.p. 134 °C (yellow crystals from Et_2O–hexane); ν_{max}(KBr)/cm^{-1} 1610s, 1597s and 1561s; *m/z* 359 ($M^{\bullet+}$, 36%), 344 ($M^{\bullet+}$ – Me, 100), 316 ($M^{\bullet+}$ – MeN_2, 20), 272 (10), 270 (12), 227 (69), 199 (30) and 43 (MeN_2^+, 34) (Found: C, 60.15; H, 6.0. $C_{18}H_{21}N_3O_3S$ requires C, 60.15; H, 5.89%).

4-tert-*Butyl*-5-[*cyano*(4-*phenylthiazol*-2-*yl*)*methylene*]-2-*methyl*-2,5-*dihydro*-1,2,3-*thiadiazole* **27**.—Prepared from (4-phenylthiazol-2-yl)acetonitrile and salt **4** in 68% yield, eluent diethyl ether–hexane (1:1), m.p. 223 °C (brown crystals from EtOH); ν_{max}(KBr)/cm^{-1} 2180s; *m/z* 354 ($M^{\bullet+}$, 100%), 339 ($M^{\bullet+}$ – Me, 16), 314 (29), 286 (11), 134 (PhC–CHS$^{\bullet+}$, 31), 102 (PhC≡CH$^{\bullet+}$, 13), 89 (22), 77 (Ph^+, 11), 57 (Bu^{t+}, 29), 45 (16) and 43 (MeN_2^+, 86) (Found: C, 61.1; H, 5.3. $C_{18}H_{18}N_4S_2$ requires C, 60.99; H, 5.12%).

5-[(*Benzothiazol*-2-*yl*)*cyanomethylene*]-4-tert-*butyl*-2-*methyl*-2,5-*dihydro*-1,2,3-*thiadiazole* **28**.—Prepared from (benzothiazol-2-yl)acetonitrile and salt **4** in 89% yield, eluent diethyl ether–hexane (10:1), m.p. 247 °C (orange crystals from EtOH); ν_{max}(KBr)/cm^{-1} 2184s; *m/z* 328 ($M^{\bullet+}$, 100%), 313 ($M^{\bullet+}$ – Me, 26), 288 ($M^{\bullet+}$ – CH_2 – CN, 52), 285 ($M^{\bullet+}$ – MeN_2, 13), 260 (13) and 43 (MeN_2^+, 24) (Found: C, 58.3; H, 4.9. $C_{16}H_{16}N_3S_2$ requires C, 58.51; H, 4.91%).

5-[(*Benzothiazol*-2-*yl*)(*ethoxycarbonyl*)*methylene*]-4-tert-*butyl*-2-*methyl*-2,5-*dihydro*-1,2,3-*thiadiazole* **29**.—Prepared from ethyl (benzothiazol-2-yl)acetate and salt **4** in 49% yield, eluent diethyl ether–hexane (1:1), m.p. 99 °C (orange–red crystals from EtOH); ν_{max}/cm^{-1} 1686s and 1652s; *m/z* 375 ($M^{\bullet+}$, 61%), 360 ($M^{\bullet+}$ – Me, 42), 332 ($M^{\bullet+}$ – MeN_2, 13), 318 ($M^{\bullet+}$ – Bu^t, 35), 302 (18), 286 (44), 258 (18), 243 (14), 227 ($M^{\bullet+}$ – benzothiazole – CH_2, 100), 199 (30), 109 (17) and 43 (MeN_2^+, 47) (Found: C, 57.3; H, 5.5. $C_{18}H_{21}N_3O_2S_2$ requires C, 57.58; H, 5.64%).

4-tert-*Butyl*-5-[(*ethoxycarbonyl*)(4-*phenylthiazol*-2-*yl*)*methylene*]-2-*methyl*-2,5-*dihydro*-1,2,3-*thiadiazole* **30**.—Prepared from ethyl (4-phenylthiazol-2-yl)acetate and salt **4** in 45% yield, eluent diethyl ether–hexane (1:1) and ethyl acetate–hexane (1:10), m.p. 78 °C (red crystals from pentane); ν_{max}(KBr)/cm^{-1} 1681s; *m/z* 401 ($M^{\bullet+}$, 100%), 386 ($M^{\bullet+}$ – Me, 42), 344 ($M^{\bullet+}$ – Bu^t, 13), 328 ($M^{\bullet+}$ – CO_2Et, 14), 312 (15), 284 (12), 227 (91), 199 (25), 155 (15), 134 (PhC–CHS$^{\bullet+}$, 40), 102 (PhC≡CH$^{\bullet+}$, 10), 91 (22), 57 (Bu^{t+}, 24) and 43 (MeN_2^+, 59) (Found: C, 60.0; H, 5.7. $C_{20}H_{23}N_3O_2S_2$ requires C, 59.82; H, 5.77%).

Crystal Structure of Compound **21**.—*Crystal data.* $C_{13}H_{18}N_2O_4S$, *M* = 298.35. Triclinic, *a* = 9.002(1), *b* = 11.914(1), *c* = 14.892(1) Å, α = 73.764(8), β = 80.071(7), γ = 72.764(9)°, *V* = 1457.6(2) Å^3 (by least-squares refinement on diffractometer angles for 20 automatically centred reflections, λ = 1.541 78 Å), space group $P\bar{1}$ (No. 2), *Z* = 4, D_x = 1.36 g cm^{-3}. Yellow blocks from dichloromethane–hexane, crystal dimensions 0.30 × 0.30 × 0.20 mm, μ(Cu-Kα) = 21.16 cm^{-1}.

Data Collection and Processing.—Siemens P4-PC diffractometer, ω–2θ mode with ω scan width 0.60°, ω scan speed 2–60 deg min^{-1}, graphite-monochromatized Cu-Kα radiation; 3899 reflections measured ($6.22 \leqslant 2\theta \leqslant 100.9°$, $-8 \leqslant h \leqslant +8$, $-11 \leqslant k \leqslant +11$, $0 \leqslant l \leqslant +14$), 3024 unique of which 2797 are observed [$I > 2\sigma(I)$, merging R = 0.0668 after absorption correction (max., min. transmission factors = 0.194 042 5)]. Three check reflections measured every 100 reflections showed no significant decrease in intensity.

Structure Analysis and Refinement.—The structure was refined using direct methods, full-matrix least-squares on F^2

with all non-hydrogen atoms anisotropic and hydrogen atoms with isotropic *U*. Final *R*1 and *wR*2 values are 0.0411 and 0.1242. Siemens SHELXTL PLUS (PC version)[12] and SHELXL-93[13] programs were used for calculations and drawings.

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