Dithiazoles and Related Compounds. Part 2.[1] Synthesis of 5-Aryl-1,4,2-dithiazolium Salts

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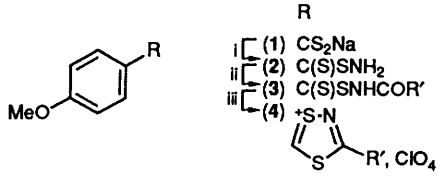
Reaction of 4-methoxythiobenzoylthiohydroxylamine (**2**) with acyl chlorides and pyridine, or with acetic formic anhydride, gives good yields of the *N*-acyl derivatives (**3**), which may be cyclised with perchloric acid and acetic anhydride to novel 1,4,2-dithiazolium salts (**4**), which include the first example unsubstituted at C-3. Evidence is presented for charge delocalisation and hence aromaticity in the cations. The salts are attacked at C-5 by nucleophilic reagents, yielding 5*H*-1,4,2-dithiazoles.

The 1,4,2-dithiazolium cation is a 6π-electron species and is potentially aromatic through delocalisation of the positive charge in the ring. The first reports describing the preparation of 1,4,2-dithiazolium salts, however, have been restricted to examples bearing a hetero-linked substituent at C-5;[1-4] in these the positive charge may be located to a significant extent outside the heterocyclic ring. Thus, for the 5-amino salts, NMR and X-ray crystallographic studies have shown that the charge resides mostly on the exocyclic nitrogen atom.[1]

We recently reported the first preparation of a 3,5-diaryl-1,4,2-dithiazolium salt in which the charge should be 'forced' into the heterocyclic ring;[5] however, the method gives poor yields, and has proved not be general for salts of this type. We now describe a simple synthesis for 5-aryl-1,4,2-dithiazolium salts having aryl or methyl substituents or hydrogen at C-3; the method is a development of Shibuya's approach to the 5-amino analogues.[4] Some simple reactions are also reported, and evidence is presented for charge delocalisation.

Results and Discussion

The synthetic route adopted for the target salts (**4**) is shown in Scheme 1. A 4-methoxyphenyl substituent was chosen for C-5,



a R' = Ph
b R' = 4-$MeOC_6H_4$
c R' = 4-ClC_6H_4
d R' = 4-$NO_2C_6H_4$
e R' = Me
f R' = H

Scheme 1. *Reagents:* i, H_2NOSO_3Na, H_2O; ii, RCOCl, pyridine or HCO_2COMe, $CHCl_3$; iii, 70% $HClO_4$, Ac_2O.

first because we have observed that charge density effects show up very clearly in the NMR spectra of this group, and second because of the ready availability of the dithiocarboxylate salt (**1**).[6] The *S*-thiobenzoylthiohydroxylamine (**2**) was prepared (84%) by treating the dithiobenzoate (**1**) with an excess of the preformed sodium salt of hydroxylamine-*O*-sulphonic acid in water.[4,7] The product is less stable than the dithiocarbamate analogues,[4] but may be stored below 0 °C for up to 1 week.

Benzoylation of *S*-aminodithiocarbamates has been carried out using benzoic anhydride in chloroform or, with less satisfactory results, with benzoyl chloride and sodium hydroxide in a two-phase system[4]. The thiohydroxylamine (**2**), however, was readily *N*-acylated to form the derivatives (**3a–d**) (57–71%) by stirring with the appropriate benzoyl chloride and pyridine in dichloromethane below room temperature. Under more carefully controlled conditions, the acetyl derivative (**3e**) was prepared with acetyl chloride, and the use of acetic formic anhydride in dichloromethane led to the formyl analogue (**3f**). Preparative conditions, physical, analytical, IR, and mass spectroscopic data for the *N*-acyl compounds (**3**) are in Table 1, while ^1H and ^{13}C NMR spectroscopic data are in Table 2.

Cyclisation to the salts (**4**) was achieved by dissolving the appropriate *N*-acyl compound (**3**) in acetic anhydride and treating the solution with 70% perchloric acid at 25 °C; cooling was necessary, since the reaction was exothermic. Precipitation of the salts in high yield was completed by addition of anhydrous ether; all were found to be extremely sensitive to moisture. Compound (**4f**) is the first example of a 1,4,2-dithiazolium salt unsubstituted at one of the ring carbon atoms. Physical, analytical, IR, and mass spectroscopic data for the salts (**4**) are in Table 3 and ^1H and ^{13}C NMR spectroscopic data are in Table 4. A strong parent ion was observed in the mass spectra of all the salts, other prominent peaks arising from $MeOC_6H_4CS_2^{+\bullet}$ (*m/z* 183), $MeOC_6H_4CS^+$ (*m/z* 151) and their breakdown products. Peaks assignable to the fragment $RCN^{+\bullet}$ were of low intensity. The low field δ_H values for 3-Me in the salt (**4e**) and for 3-H in the salt (**4f**) provide strong evidence for significant positive charge and/or ring current effects at these sites, suggesting charge delocalisation and thus some degree of aromaticity. Further evidence for charge delocalisation in the salts (**4**) comes from comparing NMR spectroscopic data for the 4-chlorophenyl salt (**4c**) with that for the salt (**5**),[1] in which the positive charge lies predominantly on the exocyclic nitrogen atom. ^1H NMR signals for the 4-chlorophenyl ring are observed at higher field in the latter (δ 7.63 and 7.88), as are ^{13}C NMR signals for the heterocycle ring C-3, and for the aromatic ring C-*p* (δ 166.91 and 140.53, respectively), indicating less positive charge at these sites. The 4-methoxyphenyl ring in the salts (**4**) also carries appreciable positive charge, all ^1H and ^{13}C NMR signals, with the exception of that for C-*i*, being shifted substantially to lower field as compared with analogous signals for the open chain compounds (**3**). The highfield shift for C-*i* probably arises from polarisation of the (C-5)–aryl bond due to the high positive charge density at C-5.

5-Amino-1,4,2-dithiazolium salts are readily attacked by nucleophiles at C-5.[1,8] The salts (**4**) are even more electrophilic, reacting rapidly with water to give the acylsulphenamides (**3**)

Table 1. Physical, analytical, IR, and mass spectroscopic data for compounds (3).

Compound (formula)	Conditions		Yield	M.p.[a]	Found (%) (Required)				
	T/h	*t*/°C	(%)	(°C)	C	H	N	$M^{+\cdot}$	ν_{max} (Nujol)/cm^{-1}
(3a) $C_{15}H_{13}NO_2S_2$	28	0–25	57	132–133	59.8 (59.4)	4.3 (4.3)	4.45 (4.6)	303	3 245m, 1 655s, 1 590s, 1 425s, 1 305m, 1 245vs, 1 165s, 1 045s, 1 015m, and 830m
(3b) $C_{16}H_{15}NO_3S_2$	24	0–25	63	148–150	57.65 (57.65)	4.45 (4.5)	4.05 (4.2)	333	3 260m, 1 649s, 1 586s, 1 423s, 1 299m, 1 244vs, 1 165s, 1 043m, 1 017s, and 831m
(3c) $C_{15}H_{12}ClNO_2S_2$	28	0–25	71	166–168	53.25 (53.35)	3.55 (3.55)	3.75 (4.15)	338[b] 340[b]	3 240m, 1 659s, 1 589s, 1 434s, 1 303m, 1 245vs, 1 165s, 1 016s, and 835m
(3d) $C_{15}H_{12}N_2O_4S_2$	14	0–25	69	167.5–168.5	51.6 (51.7)	3.4 (3.45)	7.8 (8.05)	349[b]	3 224m, 1 662s, 1 590s, 1 515s, 1 438s, 1 339s, 1 309m, 1 247vs, 1 164s, 1 034m, 1 015m, and 835m
(3e) $C_{10}H_{11}NO_2S_2$	0.5	0–10	74	123.5–124.5	49.5 (49.8)	4.5 (4.55)	5.55 (5.8)	241	3 170m, 1 685s, 1 605s, 1 445s, 1 310m, 1 240vs, 1 175s, 1 040m, 1 020m, and 835m
(3f) $C_9H_9NO_2S_2$	2.5–3	0–10	72	106–108	47.6 (47.6)	3.95 (3.95)	6.05 (6.15)	227	3 200m, 1 680s, 1 595s, 1 440m, 1 310m, 1 255vs, 1 175s, 1 050m, 1 025w, and 835m

[a] From acetone. [b] $M + 1$ peak.

Table 2. ^{1}H and ^{13}C NMR spectroscopic data ($CDCl_3$ and DMSO) for compounds (3).

Compound	δ_H		δ_C				
	4-$MeOC_6H_4$	R′	4-$MeOC_6H_4$		C=S	C=O	R′[a]
(3a)	3.86 (3 H) 6.89 (2 H), 8.00 (2 H)	7.40–7.55 (3 H) 7.92–8.03 (2 H)	55.48 (q)	134.36*i*, 128.77*o* 113.81*m*, 163.95*p*	224.94 (s)	168.04 (s)	133.38*i*, 128.18*o* 128.72*m*, 132.08*p*
(3b)	3.86 (3 H) 6.91 (2 H), 7.97 (2 H)	3.86 (3 H) 6.98 (2 H), 8.03 (2 H)	55.80 (q)	134.29*i*, 129.03*o* 114.13*m*, 162.84*p*	226.44 (s)	166.94 (s)	139.52*i*, 125.51*o* 114.72*m*, 164.34*p* 56.06 (q)
(3c)	3.89 (3 H) 6.93 (2 H), 8.02 (2 H)	7.48 (2 H), 7.92 (2 H)	55.48 (q)	134.26*i*, 128.72*o* 113.88*m*, 164.00*p*	224.78 (s)	166.98 (s)	131.82*i*, 128.42*o* 129.85*m*, 137.96*p*
(3d)	3.90 (3 H) 6.94 (2 H), 8.06 (2 H)	8.29 (4 H)	55.54 (q)	134.16*i*, 129.55*o* 113.94*m*, 164.08*p*	224.03 (s)	166.35 (s)	138.91*i*, 128.77*o* 123.30*m*, 149.57*p*
(3e)	3.87 (3 H) 6.92 (2 H), 7.97 (2 H)	2.30 (3 H)	55.27 (q)	133.89*i*, 128.56*o* 113.54*m*, 163.74*p*	223.05 (s)	171.03 (s)	23.68 (q)
(3f)	3.86 (3 H) 6.93 (2 H), 7.97 (2 H)	8.57 (1 H)	55.61 (q)	134.16*i*, 128.90*o* 114.07*m*, 164.27*p*	223.38 (s)	169.67 (d)	

[a] *i* = *ipso*, *m* = *meta*, *o* = *ortho*, *p* = *para* carbon signals.

Table 3. Physical, analytical, IR, and mass spectroscopic data for the dithiazolium salts (4).

Compound (formula)	Yield (%)	M.p.[a] (°C)	Found (%) (Required)			M^+	ν_{max}(Nujol)/cm^{-1}
			C	H	N		
(4a) $C_{15}H_{12}ClNO_5S_2$	92	163–165	46.3 (46.7)	3.1 (3.1)	3.25 (3.6)	286	1 589s, 1 299s, 1 260s, 1 167s, 1 086bs, 1 007m, 831m, 770m, 622m, and 599m
(4b) $C_{16}H_{14}ClNO_6S_2$	93	226–228	46.0 (46.2)	3.15 (3.35)	3.25 (3.35)	316	1 583s, 1 298s, 1 260s, 1 168s, 1 080vs, 992m, 837m, and 599m
(4c) $C_{15}H_{11}Cl_2NO_5S_2$	94	243.5–245.5	42.9 (42.85)	2.6 (2.6)	2.9 (3.3)	320 322	1 593s, 1 301s, 1 276s, 1 179s, 1 094vs, 1 075vs, 1 001m, 829m, 626m, and 597m
(4d) $C_{15}H_{11}ClN_2O_7S_2$	81	219–220	41.75 (41.8)	2.45 (2.55)	6.35 (6.5)	331	1 597s, 1 526s, 1 347m, 1 308s, 1 286s, 1 184s, 1 083vs, 1 011m, 853m, 625m, and 593m
(4e) $C_{10}H_{10}ClNO_5S_2$	95	178.5–180.5	37.2 (37.1)	2.9 (3.1)	4.15 (4.35)	224	1 590s, 1 303s, 1 278s, 1 180s, 1 087vs, 996m, 845m, 794m, 627m, and 594m
(4f) $C_9H_8ClNO_5S_2$	88	199–200.5	35.0 (34.9)	2.45 (2.6)	4.4 (4.5)	210	1 589s, 1 308s, 1 279s, 1 172s, 1 071vs, 994m, 837m, 803m, 619m, and 589m

[a] From CF_3CO_2H–Et_2O.

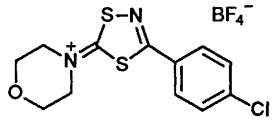
and with solvents more nucleophilic than trifluoroacetic acid to give addition and fragmentation products.* Reaction of the salts (**4d**) and (**4e**) with a solution of sodium ethoxide in ethanol gave the 5-ethoxy-5*H*-1,4,2-dithiazoles (**6a**) and (**6b**), a class of compound which may be solvolysed back to the salts (**4**) by treatment with strong acid.[5] Under the same conditions, the 3-unsubstituted salt (**4f**) fragmented to the thiobenzoate (**7**),[9] for which IR and NMR spectroscopic data do not appear to have been reported. Addition of the salts (**4d–f**) to a stirred, ice-

* 3,5-Diphenyl-1,4,2-dithiazolium perchlorate, prepared apparently by the same approach as for the salts (**4**), reacts with malononitrile in the presence of base by addition followed by rearrangement.[8c]

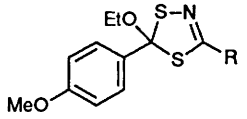
Table 4. ^1H and ^{13}C NMR spectroscopic data (CF_3CO_2D) for the dithiazolium salts (**4**).

	δ_H		δ_C				
Compound	4-$MeOC_6H_4$	R′	4-$MeOC_6H_4$		C-5	C-3	R′[a]
(**4a**)	4.10 (3 H) 7.27 (2 H), 8.14 (2 H)	7.6–7.8 (3 H) 8.0–8.2 (2 H)	57.94 (q)	121.02*i*, 135.39*o* 118.94*m*, 172.98*p*	211.41 (s)	182.10 (s)	131.29*i*, 130.77*o* 132.00*m*, 137.15*p*
(**4b**)	4.10 (3 H) 7.28 (2 H), 8.12 (2 H)	4.04 (3 H) 7.22 (2 H), 8.13 (2 H)	57.75 (q)	120.82*i*, 135.26*o* 118.68*m*, 172.33*p*	210.63 (s)	183.37 (s)	124.40*i*, 132.98*o* 117.38*m*, 169.92*p* 57.03 (q)
(**4c**)	4.11 (3 H) 7.27 (2 H), 8.14 (2 H)	7.67 (2 H), 8.08 (2 H)	57.91 (q)	120.99*i*, 135.58*o* 118.91*m*, 172.98*p*	211.25 (s)	180.68 (s)	129.70*i*, 131.85*o* 132.27*m*, 144.20*p*
(**4d**)	4.13 (3 H) 7.29 (2 H), 8.20 (2 H)	8.43 (2 H), 8.54 (2 H)	58.07 (q)	121.02*i*, 136.04*o* 119.07*m*, 173.63*p*	211.47 (s)	178.76 (s)	136.69*i*, 132.07*o* 126.99*m*, 152.75*p*
(**4e**)	4.10 (3 H) 7.25 (2 H), 8.09 (2 H)	3.13 (3 H)	57.93 (q)	120.95*i*, 135.52*o* 118.80*m*, 172.52*p*	213.03 (s)	182.00 (s)	22.04 (q)
(**4f**)	4.10 (3 H) 7.26 (2 H), 8.16 (2 H)	9.98 (1 H)	57.88 (q)	120.69*i*, 135.91*o* 118.87*m*, 172.98*p*	211.34 (s)	168.16 (d)	

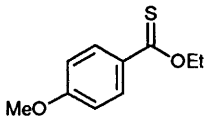
[a] *i* = *ipso*, *m* = *meta*, *o* = *ortho*, *p* = *para* carbon signals.



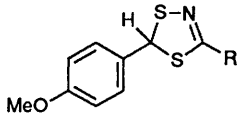
(**5**)



(**6a**) R = 4 - $NO_2C_6H_4$
(**6b**) R = Me



(**7**)



(**8a**) R = 4 - $NO_2C_6H_4$
(**8b**) R = Me
(**8c**) R = H

cold mixture of aqueous sodium borohydride and ether led to the 5*H*-1,4,2-dithiazoles (**8a–c**) (41–83%), the latter being the first monosubstituted example of this ring system. The mass spectra of compounds (**8**) show prominent $M + 1$ ions, these being the base peaks for examples (**8b**) and (**8c**), in addition to parent and $M - 1$ ions. The ^1H NMR spectrum for the monosubstituted compound (**8c**) shows no evidence of coupling between 3-H and 5-H at 90 MHz. NMR signals for C-3 (δ_C 157.54) and 3-Me (δ_H 2.27; δ_C 19.77) in compound (**8b**), and for C-3 (δ_C 146.38) and 3-H (δ_H 7.75) in compound (**8c**) all lie substantially to higher field relative to those in the precursors (**4e**) and (**4f**), providing additional evidence for high positive charge density at C-3 in the salts. We believe this to demonstrate a significant degree of π-electron delocalisation, and hence of aromaticity, in the 1,4,2-dithiazolium cation.

Experimental

IR spectra were recorded in KBr pellets on a Nicolet 5DX FT IR spectrometer, ^1H and ^{13}C NMR spectra were recorded on a JEOL FX-90Q spectrometer with Me_4Si as internal reference, and mass spectra on a VG ZAB-HS instrument. ^{13}C NMR signals refer to single carbon atoms, unless otherwise stated.

Sodium 4-methoxydithiobenzoate (**1**)[6] and hydroxylamine-*O*-sulphonic acid[10] were prepared according to literature procedures.

S-(4-*Methoxythiobenzoyl*)*thiohydroxylamine* (**2**).—The method used is a modification of those described in refs. 4 and 7 for analogous compounds. A solution of hydroxylamine-*O*-sulphonic acid (1.3 g, 11.5 mmol) in water (15 ml) at 5 °C was adjusted to pH 7–8 with 1M NaOH, and then added slowly, with stirring, to a cooled (5 °C) solution of sodium 4-methoxydithiobenzoate (10.2 mmol) in water (35 ml). Some effervescence was observed, and the colour turned from red, through pink, to yellow. The mixture was extracted with ether (2 × 20 ml), and the organic phase was dried ($MgSO_4$), filtered, and evaporated under reduced pressure, to yield S-(4-*methoxythiobenzoyl*)-*thiohydroxylamine* (**2**) (84%), m.p. 78–79 °C (hexane) (Found: C, 48.4; H, 4.55; N, 7.2. $C_8H_9NOS_2$ requires C, 48.2; H, 4.55; N, 7.05%); ν_{max} 3 220, 1 598, 1 241, 1 173, 820, and 703 cm^{-1}; $\delta_H(CDCl_3)$ 3.27 (2 H, br s), 3.87 (3 H, s), 6.92 (2 H, m), and 8.00 (2 H, m).

Preparation of the N-*Acyl Derivatives* (**3a–d**).—A general procedure is described. To a solution of the *S*-thioacylthiohydroxylamine (**2**) (1.0 g, 5.0 mmol) in dry CH_2Cl_2 (20 ml) was added dry pyridine (1 ml). The solution was cooled to 0 °C, and the appropriate acid chloride was added all at once with stirring. The mixture was stirred for various periods of time (Table 1) at 25 °C [10 °C for the acetyl derivative (**3e**)], and washed with water (3 × 20 ml). Any insoluble material (product) was filtered off, and the filtrate was dried ($MgSO_4$), concentrated, and further product induced to crystallise by addition of light petroleum (b.p. 60–80 °C). The combined product was recrystallised from acetone; relevant data are in Tables 1 and 2.

Preparation of the N-*formyl derivative* (**3e**). To a solution of the *S*-thioacylthiohydroxylamine (**2**) (1.1 g, 5.5 mmol) in dry CH_2Cl_2 (20 ml) was added dry formic acid (1 ml), and the solution was cooled to 0 °C. Freshly prepared acetic formic anhydride (1.5 g, 17.0 mmol) was added all at once, the mixture was stirred at < 10 °C for 20 min, and at 25 °C for 3 h. The product was isolated as for compounds (**3a–e**).

Cyclisation to the 1,4,2-*Dithiazolium Salts* (**4**).—The appropriate *N*-acyl compound (**3**) (1.0 mmol) was dissolved in redistilled acetic anhydride (4 ml), with warming if necessary. The solution was cooled to 25 °C, perchloric acid (0.6 ml; 70%) was added with stirring, and cooling if necessary, and stirring was continued for 20 min. The mixture was cooled in ice for 30 min, dry ether (20 ml) was added with stirring, and the product was filtered off and washed with acetic anhydride (2 × 2 ml) and dry ether (10 ml). Salts so isolated were essentially pure, but could be recrystallised by dissolving in trifluoroacetic acid and reprecipitating with dry ether, taking care to exclude all traces of moisture. Physical, analytical, and spectroscopic data are in Tables 3 and 4.

Reactions with Sodium Ethoxide in Ethanol.—Sodium (0.33 g, 14.3 mmol) was dissolved in absolute ethanol (30 ml), and the salt (**4d**) (0.5 g, 11.6 mmol) was added. The mixture was stirred on a hot water bath for 20 min, during which time the solid dissolved and the solution became red. The solvent was removed under reduced pressure, and the product was purified by column chromatography [SiO_2; eluant dichloromethane–light petroleum (1:5)] to yield the 5-ethoxy-5*H*-1,4,2-dithiazole (**6a**) (80%), m.p. 115–117 °C; ν_{max} 2 810, 1 590, 1 520, 1 500, 1 340, 1 250, 1 160, and 1 050 cm^{-1}; $\delta_H(CDCl_3)$ 1.36 (3 H, t), 3.56 (2 H, q), 3.83 (3 H, s), 6.89 (2 H, m), 7.80 (2 H, m), 7.95 (2 H, m), and 8.27 (2 H, m); δ_C 14.57 (q), 55.27 (q), 60.67 (t), 113.29 (2 C, d), 115.82 (s), 123.88 (2 C, d), 128.56 (2 C, d), 129.21 (2 C, d), 129.41 (s), 138.32 (s), 148.34 (s), 156.13 (s), and 159.84 (s). The 3-methyl analogue (**6b**) was prepared similarly, but without heating, from the salt (**4e**) as an oil (64%); ν_{max} 2 810, 1 600, 1 500, 1 250, 1 160, and 1 050 cm^{-1}; $\delta_H(CDCl_3)$ 1.34 (3 H, t), 2.35 (3 H, s), 3.53 (2 H, q), 3.80 (3 H, s), 6.85 (2 H, m), and 7.75 (2 H, m); δ_C 14.63 (q), 20.74 (q), 55.14 (q), 60.02 (t), 113.02 (2 C, d), 115.62 (s), 128.95 (2 C, d), 130.25 (s), 157.37 (s), and 159.45 (s); and *O*-ethyl 4-methoxythiobenzoate (**7**) from the salt (**4f**) (73%) (Found: C, 61.05; H, 6.25. Calc. for $C_{10}H_{12}O_2S$: C, 61.2; H, 6.1%); ν_{max} 1 590, 1 250, 1 160, 1 015, and 825 cm^{-1}; $\delta_H(CDCl_3)$ 1.49 (3 H, t), 3.82 (3 H, s), 4.69 (2 H, q), 6.83 (2 H, m), and 8.17 (2 H, m); δ_C 13.85 (q), 55.34 (q), 68.02 (t), 113.15 (2 C, d), 130.84 (2 C, d), 131.49 (s), 163.48 (s), and 210.11 (s).

Reductions with Sodium Borohydride.—The appropriate salt (**4**) (2.3 mmol) was added portionwise to an ice-cold, vigorously stirred mixture of aqueous sodium borohydride (0.7 g, 18.5 mmol; 20 ml) and diethyl ether (20 ml), and stirring was continued between 0 and 10 °C for 2.5–4.5 h. The ether layer was separated, washed with water (3 × 20 ml), dried ($MgSO_4$), and evaporated under reduced pressure. The residue was purified by column chromatography (SiO_2; eluant dichloromethane–light petroleum) and recrystallised from light petroleum (b.p. 40–60 °C). Prepared by this method were the 3-(4-*nitrophenyl*) *compound* (**8a**) (41%), m.p. 127–129 °C (Found: C, 53.85; H, 3.55; N, 8.25. $C_{15}H_{12}N_2O_3S_2$ requires C, 54.2; H, 3.65; N, 8.43%); *m/z* 333 ($M^+ + 1$, 16%), 332 (M^+, 12), and 331 ($M^+ - 1$, 4); ν_{max} 1 595, 1 505, 1 335, 1 250, 1 105, and 1 015 cm^{-1}; $\delta_H(CDCl_3)$ 3.80 (3 H, s), 6.37 (1 H, s), 6.87 (2 H, m), 7.30 (2 H, m), 7.92 (2 H, m), and 8.25 (2 H, m); δ_C 55.36 (q), 60.62 (d), 114.36 (2 C, d), 123.89 (2 C d), 128.61 (2 C, d), 128.99 (2 C, d), 133.48 (s), 137.82 (s), 148.38 (s), 156.56 (s), and 160.08 (s); the 3-methyl compound (**8b**) (79%), m.p. >120 °C (decomp.); *m/z* 226 ($M^+ + 1$, 100%), 225 (M^+, 35), and 224 ($M^+ - 1$, 82); ν_{max} 2 820, 1 600, 1 580, 1 300, 1 250, 1 160, and 1 020 cm^{-1}; $\delta_H(CDCl_3)$ 2.27 (3 H, s), 3.79 (3 H, s), 6.21 (1 H, s), 6.85 (2 H, m), and 7.27 (2 H, m); δ_C 19.77 (q), 55.09 (q), 60.08 (d), 113.98 (2 C, d), 128.34 (2 C, d), 134.02 (s), 157.54 (s), and 159.54 (s); and the 3-*unsubstituted compound* (**8c**) (83%), m.p. 68–70 °C (Found: C, 51.4; H, 4.4; N, 6.25. $C_9H_9NOS_2$ requires C, 51.15; H, 4.3; N, 6.6%); *m/z* 212 ($M^+ + 1$, 100%), 211 (M^+, 48), and 210 ($M^+ - 1$, 36); ν_{max} 1 600, 1 580, 1 230, 1 165, 1 100, and 1 015 cm^{-1}; $\delta_H(CDCl_3)$ 3.80 (3 H, s), 6.19 (1 H, s), 6.85 (2 H, m), 7.24 (2 H, m), and 7.75 (1 H, s); δ_C 55.31 (q), 57.48 (d), 114.20 (2 C, d), 128.50 (2 C, d), 134.13 (s), 146.38 (d), and 159.81 (s).

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