

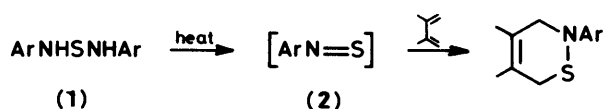
The Chemistry of Acyl- and Sulphonyl-thionitroso Compounds†¹

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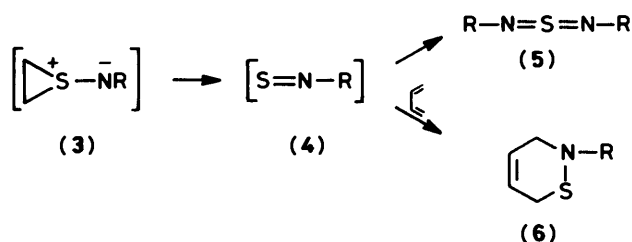
Thiophene *S,N*-ylides undergo cycloadditions with nucleophilic alkenes to give [4 + 2] adducts with concomitant extrusion of acylthionitroso compounds. These new and highly reactive species may be trapped by dienes (to give thiazines by [4 + 2] cycloaddition) or by enes (to give acylthiohydroxylamines by ene reaction). With suitable dienes such as isoprene and dimethylbutadiene, the ene reaction competes with the diene addition. In the absence of a trap, ethyl thionitrosoformate in aromatic solvents yields bis(ethoxycarbonyl amino) sulphide, while with cyclopentadiene a 2:1 adduct, a rare example of a 1,3,2,4-dithiadiazine, is formed. Thiophene is shown to yield a transient *S,N*-ylide on treatment with ethoxycarbonylnitrene.

The sulphur analogues of nitro compounds are unknown while those of nitroso compounds are uncommon and little studied. Fifteen thionitroso compounds have been reported to date. Thus in 1966 two independent reports of thionitroso compounds appeared. Tavs observed that the thiodiamines (1) which underwent slow decomposition at room temperature with development of a blue colour, on being heated with dimethylbutadiene gave a 1,2-thiazine derivative, evidently by way of a thionitrosobenzene (2) (Scheme 1).² Middleton noted



Scheme 1.

that *NN*-dimethylhydrazine and its piperidino and perhydroazepinyl analogues reacted with sulphur in ether to yield isolable purple products, the unstable thionitrosamines ($\text{R}_2\text{NN=S}$).³ He also showed that the compounds were considerably dipolar as with nitrosamines since the alkyl substituents were non-equivalent in n.m.r. studies at ambient temperature, indicating significant contribution of the mesomer $\text{R}_2\text{N}^+=\text{N-S}^-$. Since these seminal observations, Tavs' eliminative route has been extended⁴ and one more thionitrosamine has been made.⁵ The thionitrosamines have been shown to be efficient dienophiles with, for example, tetrazines,⁶ and to be sulphur ligands, giving stable chromium pentacarbonyl derivatives, the X-ray crystallography of which has been examined.⁵⁻⁷ Several thionitrosoalkanes (4) have been generated from episulphide ylides (3) (themselves produced *in situ* by the

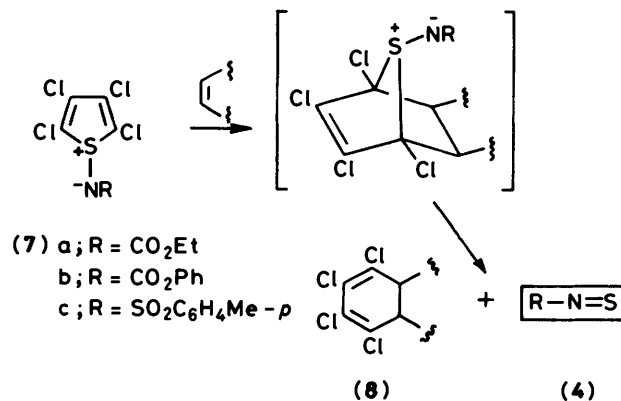


a; R = CO₂Et b; R = CO₂Ph c; R = SO₂C₆H₄Me-*p*

action of oxaziridines on episulphides) which in the absence of a trap gave sulphur di-imides (5), while with dienes, thiazines (6) were again produced.⁸ Thionitrosobenzenes have also been observed as intermediates in the photolysis of 2,1,3-benzothiadiazole 2-oxide⁹ and generated [and trapped as sulphur di-imides (5) or thiazines (6)] by thermolysis or photolysis of 3-azido-2,1-benzisothiazoles.¹⁰

On the basis of quantum chemical calculations, simple thionitroso compounds are predicted to be planar, polar, easily polarised, and coloured compounds.¹¹ They are expected to be unstable due to their large electron affinity, low-energy $n \rightarrow \pi^*$ excited states, and the small energy-gap between their singlet and triplet states. Indeed this triplet state could be the ground state. Electron-donating groups bonded to the N=S function should stabilise the system by increasing the singlet-singlet $n \rightarrow \pi^*$ transition energy and decreasing the electron affinity. By contrast, attached electron-withdrawing groups would be expected to destabilise the compounds.

We herein report the first synthesis of such electron-poor thionitroso compounds, the acyl- and sulphonyl-thionitroso systems (4; R = CO₂Et, CO₂Ph, and SO₂C₆H₄Me-*p*), and aspects of their chemistry. Their generation involves the novel, chelotropic elimination concomitant upon cycloaddition to the readily available thiophene *S,N*-ylides (7) (Scheme 2), a reaction

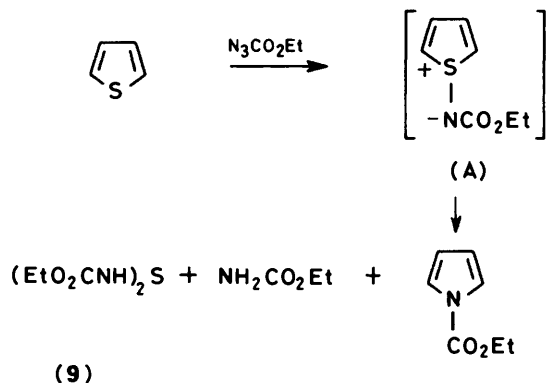


Scheme 2.

discussed fully in the accompanying paper.¹² The most effective alkene for this cycloaddition was found to be acenaphthylene, which reacted rapidly (10 min, 25 °C), almost quantitatively, and as a self-indicator [the yellow alkene colour disappeared with precipitation of the adduct (8)].

† This work constitutes part of the thesis of G. van Vuuren for the M.Sc. degree of the University of South Africa.

In the absence of a suitable trap the thionitrosoformates (**4a** and **b**) and their sulphonyl analogue (**4c**) in methylene dichloride solution gave a complex mixture of unidentified products, unlike the alkyl and aryl thionitroso compounds which yield sulphur di-imides. However, in benzene, toluene, or cumene solution the generated thionitroso compound (**4a**) decomposed to yield the bisurethano sulphide (**9**) in moderate yield (18%) without involvement of the solvent. This product is significant in that it is also produced when ethyl azidoformate is decomposed in refluxing thiophene,¹³ suggesting the involvement of a transient ylide (A) (Scheme 3). That this ylide does

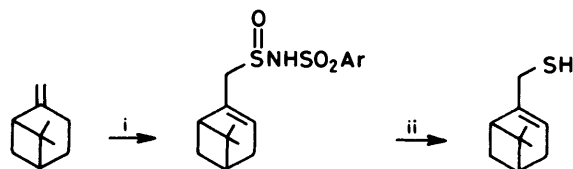


Scheme 3.

indeed mediate in the reaction of thiophene with ethyl azidoformate is demonstrated by the formation of fluoranthene, albeit in low yield (3%), when ethyl azidoformate and thiophene are heated at 135 °C in the presence of acenaphthylene. (Acenaphthylene is unchanged on heating in thiophene alone.) The dehydrogenation of the expected dihydrofluoranthene presumably arises by the action of the nitrene or merely the high temperature. Indeed, it would appear that thiophenes in general react initially at sulphur. The subsequent thermal 1,2-shift of the ylidic substituent has precedence in the chemistry of thiophene *S,C*-ylides.¹⁴ This feature is under active study. The formation of the bisurethano sulphide (**9**) in both Hafner's work and ours could derive from the interaction of the thionitroso compound and urethane. Indeed Hafner isolated urethane in his studies.¹³ The urethane is probably a triplet-derived by-product of the ethoxycarbonylnitrene or thionitroso compound. It is also possible that the fact that the sulphide (**9**) is formed from the thionitrosoformates in aromatic solvents but not in methylene dichloride is related to the well established role of the latter solvent in stabilising singlet nitrenes and other electron-deficient singlet sextet species.¹⁵

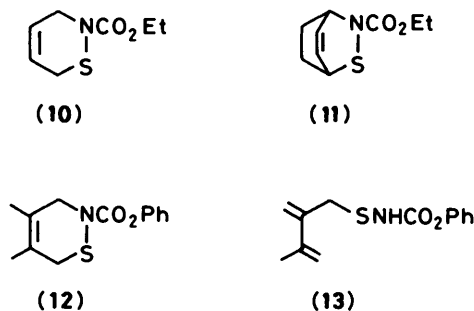
The acylthionitroso compounds were readily trapped by suitable alkenes and dienes. The isoelectronic nitrosoformates¹⁶ (e.g., $\text{EtO}_2\text{C}-\text{N}=\text{O}$) and thiocarbonylformates¹⁷ (e.g., $\text{EtO}_2\text{C}-\text{CH}=\text{S}$) are well documented reactive intermediates which have been readily trapped by electron-rich dienes such as thebaine and 9,10-dimethylantracene, as well as by butadiene, cyclopentadiene, and related compounds. The first two of these diene traps have been used for the thermal regeneration of the reactive dienophile and thus dienophile transfer.^{16,17} Analogues of the sulphonylthionitroso system (**4c**), the sulphonylsulphinyl amine ($\text{ArSO}_2\text{N}=\text{S}=\text{O}$), also undergo ready [4 + 2] cycloadditions with butadienes and cyclopentadiene (reversible) and also reveal considerable ene reactivity, particularly with terminal alkenes such as β -pinene.¹⁸ Indeed, a variety of terpenes have been functionalised with a thiol group by ene

addition of the sulphinylamine and subsequent reduction of the adduct (Scheme 4).¹⁹

Scheme 4. Reagents: i, ArSO_2NSO ; ii, LiAlH_4 .

Surprisingly, the present series of thionitroso compounds (**4a–c**) gave no defined adduct with thebaine, 9,10-dimethylantracene, or β -pinene! When an equimolar amount of phenyl thionitrosoformate (**4b**) was generated in the presence of thebaine, for example, phenyl carbamate (63%) was produced and half of the thebaine was recovered. The carbamate could possibly have arisen from the unstable adduct or by a triplet-mediated hydrogen abstraction. Despite these discouraging observations the electron-poor thionitroso compounds proved to be powerful dienophiles and especially enophiles. Because of their high reactivity and short lifetime, the reactions proceeded efficiently or else the characteristic plethora of decomposition products ensued.

When butadiene, acenaphthylene, and the ylide (**7a**) were stirred together in methylene dichloride solution the expected adduct (**8**) was formed quantitatively, and the trapped thionitroso adduct (**10**) was isolated in 82% yield. Using cyclohexa-1,3-diene, the analogous bicyclic thiazine (**11**) was



obtained in 40% yield. 2,3-Dimethylbutadiene gave an unexpected result in that both the Diels–Alder adduct (**12**) (43%) and the ene adduct (**13**) (43%) were isolated. The ene reaction is not observed to compete with the Diels–Alder cycloaddition with any of the isosteres ($\text{EtO}_2\text{CCH}=\text{S}$, $\text{EtO}_2\text{CN}=\text{O}$, or $\text{ArSO}_2\text{N}=\text{S}=\text{O}$) of the thionitroso compounds. Furthermore, unlike the case of thioaldehydes, which yield both regioisomers in ene reactions,²⁰ but like that of the sulphinylamines,¹⁸ the ene reaction of thionitroso compounds is totally regioselective. To our knowledge the only other examples in which a methylbutadiene undergoes competitive ene and diene reactions is with benzyne,²¹ with the reactive intermediate, $\text{Ph}^+\text{S}=\text{O}$,²² and with certain reactions of diethyl azodicarboxylate ($\text{EtO}_2\text{CN}=\text{NCO}_2\text{Et}$).²³

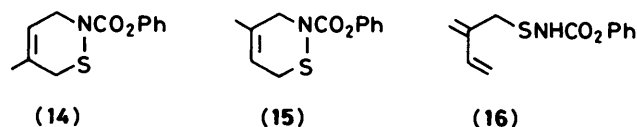

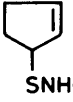






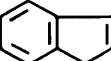
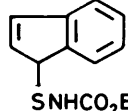



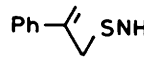

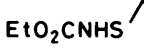
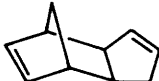



Table 1. Ene adducts of the thionitroso compounds (4)

General method		Conditions		Ene adduct	Yield (%)	M.p. (°C)
Ylide (7)	Alkene ^a	t/h	T/°C			
(7a)	ACN + 	0.25	20	 (17)	98	oil
(7a)	ACN + 	0.25	20	 (18)	98	oil
(7b)		3	reflux	 (19)	72	71–72 ^d
(7c)		3	reflux	 (20)	64 ^b	107–108 ^e
(7a)		0.25	20	 (21)	18	oil
(7a)	ACN + 	0.25	20	 (22)	79	46–47 ^d
(7a)	ACN + 	0.25	20	 (23)	92	oil
(7a)	ACN + 	0.25	20	 (24)	95 ^c	oil
(7a)	ACN + 	0.25	20	 (25)	59	oil

^a ACN = acenaphthylene. ^b Toluene-*p*-sulphonamide also produced (25%). ^c Mixture of *cis* and *trans* isomers was formed. ^d Recrystallised from light petroleum. ^e Recrystallised from light petroleum–ethyl acetate.

Isoprene showed a similar competitive reactivity and with phenyl thionitrosoformate (4b) gave the two Diels–Alder regioisomers (14) and (15) in 25% yield each and the ene adduct (16) in 50% yield, as indicated by ¹H n.m.r. spectroscopy.

A wide variety of alkenes gave ene adducts with the thionitroso compounds (4a–c). The alkene could be utilised both as dienophile for reaction with the thiophene ylide (7) and as an ene trap for the liberated thionitroso compound. However, yields of adducts were generally better utilising acenaphthylene and the alkene. Thus, cyclohexene reacted to yield the adducts (18), (98%), (19), (72%), and (20), (64%) from ylides (7a), (7b), and (7c) respectively. Various ene adducts were isolated and are recorded in Table 1.

When the ylide (7a) was allowed to interact with cyclopentadiene at –78 °C and the solution allowed to warm up to room temperature, two main products were isolated.

The first, (26), has been dealt with in our accompanying publication.¹² The second, a 2:1 adduct of ethyl thionitrosoformate and cyclopentadiene, proved to be the dithiadiazine (27), apparently the first true case of a 1,3,2,4-dithiadiazine apart from a benzo-fused trioxide derivative.^{24,*} This [2 + 2 + 2] pale yellow adduct reveals the appropriate empirical formula and mass spectral fragmentations showing losses of CO₂Et and EtO₂CNS from the molecular ion followed by consecutive loss of S and CO₂Et to give a base peak for C₅H₆N. The ¹³C n.m.r. spectrum showed two non-equivalent carbonyl

* A supposed 1,3,2,4-dithiadiazine (M. Tashiro and S. Mataka, *Heterocycles*, 1976, 4, 1243; S. Mataka, K. Takahashi, Y. Yamada, and M. Tashiro, *J. Heterocycl. Chem.*, 1979, 16, 1009) has been shown to be a 1,4,2,6-dithiadiazine (S. T. A. K. Daley, C. W. Rees, and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1984, 57).

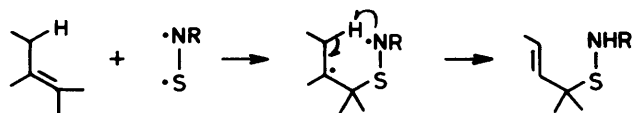


(von Baeyer-type numbering scheme)

absorptions, alkenic CHs, aliphatic CHs, and OCH_2s as well as the ring CH_2 and equivalent CH_3 absorptions. However, the ^1H n.m.r. spectrum proved most conclusive. Thus 6-H appeared as a low-field double doublet (δ 6.75), deshielded by the anisotropy of the nearby carbonyl group, while the 1-H signal, also a double doublet, appeared at δ 4.95. The former showed coupling to one of the olefinic protons (7-H, δ 5.77, dd) and to 1-H, while the latter coupled to one of the non-equivalent (and thus geminally split) C-9 protons and to 6-H. These geminally split C-9 protons were distinctive in that one showed no significant extra coupling while the other coupled with the adjacent olefinic (8-H) and aliphatic (1-H) CH groups. This indicated, as borne out by Dreiding models, that one of the 9- H_2 protons (the *endo*) was roughly at right angles to both 8-H and 1-H.

Complex unidentified mixtures of products were produced on attempted trapping of compound (4a) with limonene, but-2-yne, and 2,3-dihydropyran (known to react with sulphinylamines in a [2 + 2] manner¹⁸).

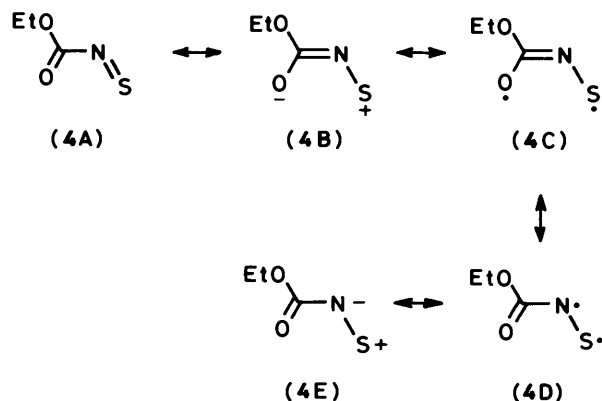
The mechanism of the above ene reaction is open to question. It is not unreasonable to view the surprising *peri* selectivity of the thionitroso compounds (4a-c) as a manifestation of their triplet-state reactivity, especially since in electron-poor thionitroso compounds the NS bond order should be considerably reduced. (Scheme 5). These thionitroso compounds



Scheme 5.

would thus be isoelectronic with oxygen and sulphur monoxide, both known to have triplet ground states.

In summary, the electron-poor thionitroso compounds, which can be described in terms of the canonical forms indicated in Scheme 6, are both highly reactive yet selective and have



Scheme 6.

a surprising preference for ene over diene reactivity, a characteristic which may support the involvement of the triplet species (4C) and (4D).

Experimental

The general conditions and the preparation of the ylides (7) are described in our accompanying paper.¹²

Generation and Trapping of the Thionitroso Compounds (4a-c).—*General methods.* (a) The ylide (7) (1.6 mmol), acenaphthylene (1.6 mmol), and the trapping agent (1.6 mmol) were dissolved in methylene dichloride (2 ml) and the mixture was stirred under the conditions shown in Table 1. The solvent was removed and the residue was chromatographed on silica gel. Elution with light petroleum gave the corresponding acenaphthylene adduct (8) (91–98%) and further elution with light petroleum–chloroform (30:70) yielded the thionitroso adducts recorded in the text and Table 1. The properties of the adducts are collated in Table 2. The oily adducts were not stable to distillation and were thus purified solely by chromatography, and were analysed by accurate mass measurement.

(b) The ylide (7) (1.6 mmol) was dissolved in the alkene (3 ml) and the solution was treated as recorded in Table 1. Work-up of the mixture was as in method (a), the appropriate adduct (8) being eluted with light petroleum.

Generation of Ethyl Thionitrosoformate (4a) in Aromatic Solvents.—The ylide (7a), (0.50 g, 1.6 mmol) and acenaphthylene (0.25 g, 1.6 mmol) were dissolved in benzene, toluene, or cumene (2 ml) and the solution was stirred at ambient temperature for 24 h. Removal of the solvent and chromatography of the residue on silica gel gave, on elution with chloroform bis(ethoxycarbonylamino) sulphide (9) (0.06 g, 18%) as crystals from ethyl acetate–light petroleum, m.p. 140–141 °C (Hafner and Kaiser¹³ reported m.p. 139 °C); ν_{max} . 3 280 (NH) and 1 710 cm^{-1} (CO); m/z 208 (M^+), 162 ($M^+ - \text{EtOH}$), and 120 ($M^+ - \text{NHCO}_2\text{Et}$); δ_{H} 7.20 (2 H, brs, 2 × NH), 4.25 (4 H, q, 2 × CH_2), and 1.25 (6 H, t, 2 × Me).

Interaction of Cyclopentadiene with Ethyl Thionitrosoformate (4a).—The ylide (7a) (0.50 g, 1.6 mmol) and cyclopentadiene (~1 ml) in methylene dichloride (5 ml) were allowed to react as described in our accompanying paper.¹² Work-up as described in this same paper gave firstly the adduct (26) already discussed¹² (0.12 g, 20%). Further elution of the silica column with chloroform gave a band which, on purification by preparative t.l.c. with diethyl ether as developer gave the 1,3,2,4-dithiadiazine (27) (0.07 g, 14%) as pale yellow crystals from ethyl acetate–light petroleum, m.p. 75–76 °C (Found: M^+ , 304.0551. $\text{C}_{11}\text{H}_{16}\text{N}_2\text{O}_4\text{S}_2$ requires M , 304.0551); m/z 304 (M^+), 231 ($M^+ - \text{CO}_2\text{Et}$), 185 ($M^+ - \text{EtO}_2\text{CNS}$), 153 (185 - S), 80 ($\text{C}_5\text{H}_6\text{N}$, base peak), and 29 (C_2H_5); ν_{max} . 1 700 br cm^{-1} (CO); δ_{H} 6.75 (1 H, dd, J 6 and 2.5 Hz, 6-H), 5.77 (1 H, dd, J 5 and 3 Hz, 7-H), 5.62 (1 H, dd, J 6 and 3 Hz, 8-H), 4.95 (1 H, dd, J 7 and 2.5 Hz, 1-H), 4.5–4.1 (4 H, m, OCH_2), 2.76 (1 H, d, J 15 Hz, 9-H), 2.25 (1 H, m, 9-H), and 1.35 (6 H, t, Me_2); δ_{C} 156.7 and 156.0 (each s, CO), 140.5 and 132.0 (each d, olefinic CH), 65.7 and 65.3 (each d, CH), 63.3 and 63.0 (each t, OCH_2), 33.8 (t, CH_2), and 14.4 p.p.m. (q, CH_3).

Interaction of Thiophene, Acenaphthylene, and Ethyl Azidoformate.—A mixture of acenaphthylene (5.30 g, 35 mmol), ethyl azidoformate (4.00 g, 35 mmol), and thiophene (50 ml) was heated at 135 °C for 1 h in a Teflon-lined autoclave. Removal of the excess of thiophene gave a brown oil which crystallised after a time. This oil was eluted through a column of silica gel with

Table 2. Properties of the adducts of the thionitroso compounds (4)

Adduct (Formula)	Found (%) [M^+] (required)			$\nu_{\max.}/\text{cm}^{-1}$	m/z	$^1\text{H N.m.r.} (\delta; J/\text{Hz})$	$^{13}\text{C N.m.r.}$ ($\delta/\text{p.p.m.}$)
	C	H	N				
(10) ($\text{C}_7\text{H}_{11}\text{NO}_2\text{S}$)	[173.0510] (173.0511)			1 685 (CO)	128 ($M^+ - \text{OEt}$), 100 ($M^+ - \text{CO}_2\text{Et}$)	6.05 and 5.75 (2 H, m, =CH), 4.15 (2 H, q, OCH_2), 3.30 (4 H, m, 2 CH_2), 1.25 (3 H, t, Me)	
(11)* ($\text{C}_9\text{H}_{13}\text{NO}_2\text{S}$)	[154.0322] (154.0327)			1 680 (CO)	112 ($M^+ - \text{NCO}_2\text{Et}$), 80 ($M^+ - \text{SNCO}_2\text{Et}$)	6.55 (2 H, m, =CH), 5.00 and 3.73 (2 H, m, 2 \times CH), 4.18 (2 H, q, OCH_2), 2.32–1.52 (4 H, m, 2 \times CH_2), 1.30 (3 H, t, Me)	
(12) ($\text{C}_{13}\text{H}_{19}\text{NO}_2\text{S}$)	[249.0820] (249.0824)			1 710 (CO)	249 (M^+) 156 ($M^+ - \text{OPh}$), 128 ($M^+ - \text{CO}_2\text{Ph}$), 94 (PhOH)	7.50–7.10 (5 H, m, Ph), 4.12 (2 H, s, CH_2), 3.25 (2 H, s, CH_2), 1.75 and 1.65 (6 H, s, 2 \times Me)	
(13) ($\text{C}_{13}\text{H}_{15}\text{NO}_2\text{S}$)	[249.0820] (249.0824)			3 260 (NH) 1 710 (CO)	249 (M^+) 156 ($M^+ - \text{OPh}$), 128 ($M^+ - \text{CO}_2\text{Ph}$), 111 ($M^+ - \text{NHCO}_2\text{Ph}$), 94 (PhOH), 81 ($M^+ - \text{SNHCO}_2\text{Ph}$)	7.52–7.10 (5 H, m, Ph), 5.90 (1 H, b, NH), 5.15, (4 H, m, = CH_2), 3.65 (2 H, s, CH_2), 1.90 (3 H, s, Me)	
(14) + (15) ($\text{C}_{12}\text{H}_{13}\text{NO}_2\text{S}$)	[235.0660] (235.0667)			1 690 (CO)	236 ($M^+ + 1$), 142 ($M^+ + 1 - \text{OPh}$), 114 ($M^+ + 1 - \text{CO}_2\text{Ph}$), 94 (PhOH)	8.0–7.1 (10 H, m, Ph), 5.88 and 5.55 (2 H, br s, =CH) 4.30 and 4.20 (4 H, br s, CH_2N), 3.40 and 3.30 (4 H, br s, CH_2S), 1.81 and 1.75 (6 H, br s, Me)	
(16) ($\text{C}_{12}\text{H}_{13}\text{NO}_2\text{S}$)	[235.0670] (235.0667)			3 300 (NH) 1 690 (CO)	235 (M^+), 141 ($M^+ - \text{PhOH}$), 113 ($M^+ - \text{CO}_2\text{Ph}$), 94 (PhOH)	7.55–7.10 (5 H, m, Ph), 5.88 (1 H, br, NH), 5.25 (4 H, m, = CH_2), 3.75 (2 H, s, CH_2), 1.98 (3 H, s, Me)	
(17) ($\text{C}_8\text{H}_{13}\text{NO}_2\text{S}$)	[187.0660] (187.0667)			3 310 (NH) 1 675 (CO)	187 (M^+), 142 ($M^+ - \text{OEt}$), 114 ($M^+ - \text{CO}_2\text{Et}$), 99 ($M^+ - \text{NHCO}_2\text{Et}$), 67 ($M^+ - \text{SNHCO}_2\text{Et}$)	6.12 (1 H, br, NH), 5.93 and 5.75 (2 H, m, =CH), 4.20 (2 H, q, OCH_2), 3.93 (1 H, m, CH), 2.50–1.55 (4 H, m, CH_2CH_2), 1.28 (3 H, t, Me)	
(18) ($\text{C}_9\text{H}_{15}\text{NO}_2\text{S}$)	[201.0820] (201.0824)			3 260 (NH) 1 680 (CO)	201 (M^+), 81 ($M^+ - \text{SNHCO}_2\text{Et}$)	6.02 (2 H, br, NH), 5.95 and 5.66 (2 H, m, =CH), 4.20 (2 H, q, OCH_2), 3.67 (1 H, m, CH), 2.25–1.50 (6 H, m, 3 CH_2), 1.25 (3 H, t, Me)	
(19) ($\text{C}_{13}\text{H}_{15}\text{NO}_2\text{S}$)	[249.0817] (249.0824)			3 260 (NH) 1 690 (CO)	249 (M^+), 155 ($M^+ - \text{PhOH}$), 94 (PhOH), 81 ($M^+ - \text{SNHCO}_2\text{Ph}$)	7.55–7.05 (5 H, m, Ph), 6.45 (1 H, br, NH), 5.90 and 5.65 (2 H, m, =CH), 3.75 (1 H, m, CH), 2.20–1.70 (6 H, m, CH_2)	
(20) ($\text{C}_{13}\text{H}_{17}\text{NO}_2\text{S}_2$)	54.8 6.1 4.9 (55.09 6.05 4.94)			3 230 (NH)	283 (M^+), 128 ($M^+ - \text{SO}_2\text{-C}_6\text{H}_4\text{Me}$), 155 ($\text{SO}_2\text{C}_6\text{H}_4\text{-Me}$), 81 ($M^+ - \text{SNHSO}_2\text{C}_6\text{-H}_4\text{Me}$)	7.85 and 7.32 (4 H, d, J 8, C_6H_4), 6.20 (1 H, br, NH), 5.90 and 5.60 (2 H, m, =CH), 3.80 (1 H, m, CH), 2.43 (3 H, s, Me), 2.15–1.65 (6 H, m, CH_2)	143.3 (s, C–Me), 136.3 (s, SO_2C), 133.5 and 122.6 (d, =CH), 129.5, 127.5 (d, arom. CH), 47.9 (d, C–S), 26.1, 25.0, 21.5, (t, CH_2), 18.1 (q, Me)
(21) ($\text{C}_9\text{H}_{13}\text{NO}_2\text{S}$)	[235.0674] (235.0667)			3 240 (NH) 1 680 (CO)	235 (M^+), 206 ($M^+ - \text{Et}$), 162 ($M^+ - \text{CO}_2\text{Et}$), 115 ($M^+ - \text{SNHCO}_2\text{Et}$)	7.9–7.0 (4 H, m, ArH), 6.87 (1 H, br, J 6, 3-H), 6.53 (1 H, dd, J 6 and 2, 2-H), 5.57, (1 H, s, NH) 5.64 (1 H, br s, 1-H), 4.15 (2 H, q, CH_2), 1.21 (3 H, t, Me)	
(22) ($\text{C}_9\text{H}_{17}\text{NO}_2\text{S}$)	[203.0970] (203.0980)			3 300 (NH)	203 (M^+), 130 ($M^+ - \text{CO}_2\text{Et}$), 115 ($M^+ - \text{NHCO}_2\text{Et}$), 83 ($M^+ - \text{SNHCO}_2\text{Et}$)	5.73 (1 H, br, NH), 5.52 (2 H, m, =CH), 4.22 (2 H, q, OCH_2), 3.35 (2 H, m, CH_2S), 2.05 and 1.45 (4 H, m, CH_2CH_2), 1.25 (3 H, t, OCH_2Me), 0.90 (3 H, m, Me)	
(23) ($\text{C}_{12}\text{H}_{15}\text{NO}_2\text{S}$)	[237.0823] (237.0824)			3 360 (NH) 1 700 (CO)	192 ($M^+ - \text{OEt}$), 149 ($M^+ - \text{NHCO}_2\text{Et}$), 117 ($M^+ - \text{SNHCO}_2\text{Et}$), 77 (Ph)	7.60–7.12 (5 H, m, Ph), 5.92 (1 H, s, NH), 5.45 and 5.12 (2 H, br s, =C), 4.10 (2 H, q, OCH_2), 3.75 (2 H, s, CH_2S), 1.20 (3 H, t, Me)	
(24) ($\text{C}_6\text{H}_{10}\text{BrNO}_2\text{S}$)	[238.9620] (238.9616)			3 320 (NH) 1 700 (CO)	241/239 (M^+), 160 ($M^+ - \text{Br}$), 72 (160 – NHCO_2Et), 39 (160 – SNHCO_2Et)	5.76 (1 H, br, NH), 6.28 (2 H, m, =CH), 4.20 (2 H, q, OCH_2), 3.56 and 3.32 (4 H, dd, CH_2), 1.20 (3 H, t, Me)	

Table 2. (continued)

Adduct (Formula)	Found (%) [M^+] (required)			$\nu_{\max.}/\text{cm}^{-1}$	m/z	^1H N.m.r. (δ ; J/Hz)	^{13}C N.m.r. (δ /p.p.m.)
	C	H	N				
(25) $(\text{C}_{13}\text{H}_{17}\text{NO}_2\text{S})$	[251.0980] (251.0980)			3 240 (NH) 1 720 (CO)	251 (M^+), 131 ($M^+ -$ SNHCO ₂ Et), 66 (C_5H_6)	6.05—5.35 (4 H, m, =CH), 4.15 (2 H, q, OCH ₂), 3.00 (1 (2 H, m, CH ₂), 3.00 (1 H, m, OCH ₂), 2.80 and 1.85—1.45 (4 H, m, CH), 1.25 (3 H, t, Me)	157.8 (s, CO), 136.3, 136.1, 131.8, 130.6 (d, =CH), 62.3 (t, OCH ₂), 59.25, 54.45, 48.9, 45.6, 44.9 (d, CH), 50.3 (CH ₂), 14.4 (q, Me)

pentane to give firstly acenaphthylene (4.55 g, 86% recovered) followed by fluoranthene, which recrystallised from methanol as needles (0.22 g, 3%), m.p. 108—110 °C (lit.,²⁵ 110 °C).

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