Generation of Thionitrosoarenes (ArN=S) from *N*-(Arylaminothio)phthalimides and *in situ* Trapping with Alkenes and Conjugated Dienes

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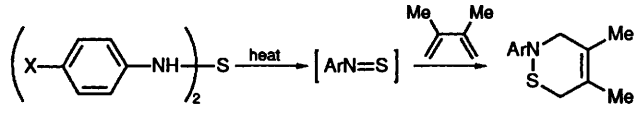
A series of *N*-(arylaminothio)phthalimide derivatives (**7a–h**) has been prepared by reaction of phthalimidesulphenyl chloride with the trimethylsilyl derivative of the appropriate arylamine. On treatment with triethylamine at room temperature, compounds (**7**) fragment to yield transient thionitroso species (**8**). Derivatives (**8a–h**) have been trapped in good yield as their Diels–Alder adducts [*e.g. N*-aryl-1,2-thiazine derivatives (**9**) and (**10**)] with the following conjugated dienes: butadiene, 2,3-dimethylbutadiene, 1,4-diphenylbutadiene, (*E,E*)- and (*E,Z*)-hexa-2,4-diene, 1,1′-bicyclopentenyl (**25**) and 1,1′-bicyclohexenyl (**26**). The stereochemistry of the diene is retained in the adducts (**19**)–(**24**). Thionitrosoarene derivatives (**8**) also afford sulphenamide derivatives, *e.g.* (**11**) and (**12**)–(**16**), by ene addition to dimethylbutadiene, isobutene, and α-methylstyrene. *N*-Aryliminosulphur dichlorides (**34**) react with 2,3-dimethylbutadiene to yield 1,2-thiazine and sulphenamide products, probably by way of thionitrosoarene intermediates.

The existence of thionitroso compounds was first reported from two laboratories in 1966. Middleton established that reaction of 1,1-dialkylhydrazines with sulphur, and reduction of sulphinylhydrazines (R_2N–N=S=O) with lithium aluminium hydride, yielded highly coloured *N*-thionitrosoamines (R_2N–N=S) which were stable at $< ca.\ -30\ °C$.[1] It was deduced from spectroscopic data that the high contribution of the dipolar resonance form $R_2\overset{+}{N}$=N–S^- was responsible for the stability of these thionitroso species. In the same year, Tavs reported that mild thermolysis (70–80 °C) of thiodiamines (**1**) in dimethylbutadiene as solvent led to the isolation of *N*-aryl-1,2-thiazine derivatives (**2**) (22–41% yield); this reaction provided good evidence for the intermediacy and Diels–Alder trapping of thionitrosoarenes, ArN=S (Scheme 1).[2] Subsequently, a few



(1)
X = H, Cl, Br

(2)

Scheme 1.

other routes to transient thionitroso species have been reported. The most notable are: (*a*), fragmentation of thi-iranium ylides (**3**) to provide the first alkylthionitroso intermediates,[3] (*b*), thermolysis or photolysis of 3-azido-2,1-benzisothiazoles to yield thionitrosobenzenes,[4] (*c*), spontaneous extrusion of acylthionitroso compounds from the cycloadducts formed by addition of alkenes to tetrachlorothiophene-*S,N*-ylides (**4**).[5] In all these examples, the evidence for the intermediacy of the thionitroso species, RN=S, was provided by Diels–Alder trapping with standard dienes (butadiene, cyclopentadiene, *etc.*). In the absence of trap, sulphur di-imides, RN=S=NR, and azo compounds are formed, sometimes in good yields;[3,4] these products formally arise by dimerisation of RN=S with loss of sulphur, although the mechanism of this reaction is not established. Davis and Skibo postulate a head-to-head dimerisation of the ArN=S species.[6] However, a head-to-tail dimerisation would seem to be a more likely mechanism for this reaction, by analogy with the dimerisation of thioketones and thioketenes.[7] The cyclic sulphur di-imide, naphtho[1,8-*c,d*]-[1,2,6]thiadiazine, prepared from reaction of 1,8-diaminonaphthalene and piperidine-1-sulphenyl chloride, is possibly formed by way of a thionitroso intermediate.[8] It is also known that thionitrosoamines function as electron-rich dienophiles in Diels–Alder reactions with electron-deficient tetrazines.[9]

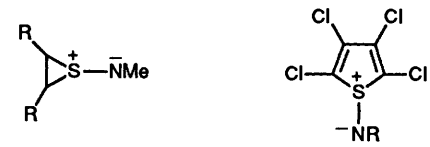
Direct spectroscopic observation of intermediate thionitrosoarenes at low temperature has been reported from the photolysis of 2,1,3-benzothiadiazole-2-oxide[10] and, more recently from the photolysis of sterically crowded 3-azido-2,1-benzisothiazole derivatives.[11] Transition-metal stabilised alkyl-, aryl-, dimethylamino- and diphenylamino-thionitroso derivatives are known, and some of these complexes have been characterised by X-ray crystallography.[12] The parent compound, HN=S, acts as a bridging ligand in the complex $Fe_2(CO)_6(HNS)$,[13] and HN=S has been tentatively postulated elesehwere as a fragment extruded from an intermediate R_2N–NHS^- compound.[14] *Ab initio* quantum chemical calculations concluded that HN=S is more stable than the isomeric structure HS≡N and that thermal isomerisation between the two species is unlikely.[15]

It is thus clear, both from experiment[1] and from theory,[15b] that electron-donating substituents attached to nitrogen stabilise the RN=S system, while electron-withdrawing substituents destabilise these compounds.

Results and Discussion

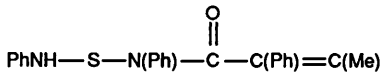
Preparation of N-(*Arylaminothio*)*phthalimides* (**7**).—We sought to establish an expedient route to thionitroso compounds that would enable the chemistry of this highly reactive functional group to be developed.[16] We chose to modify the original route of Tavs.[2] Thiodiamines (**1**) are thermally unstable[2] and (in our hands) they are difficult to purify. A few unsymmetrical analogues of (**1**) were known at the outset of our work: for example, compounds (**5**)[17] and (**6**),[6] both of which were reported to fragment to yield thionitrosoarenes which were trapped.

We now describe the related phthalimide derivatives (**7a–h**). Compounds (**7**) are the 'cleanest' precursors of thionitrosoarenes reported to date, and, notably, derivative (**7h**) yields the first example of a heterocyclic thionitroso intermediate, *viz.* (**8h**), that

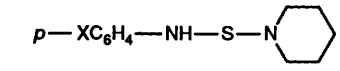


(3)
R = Me, Et, Pr^i

(4) R = CO_2Et, CO_2Ph, *p* - $SO_2C_6H_4Me$



(5)

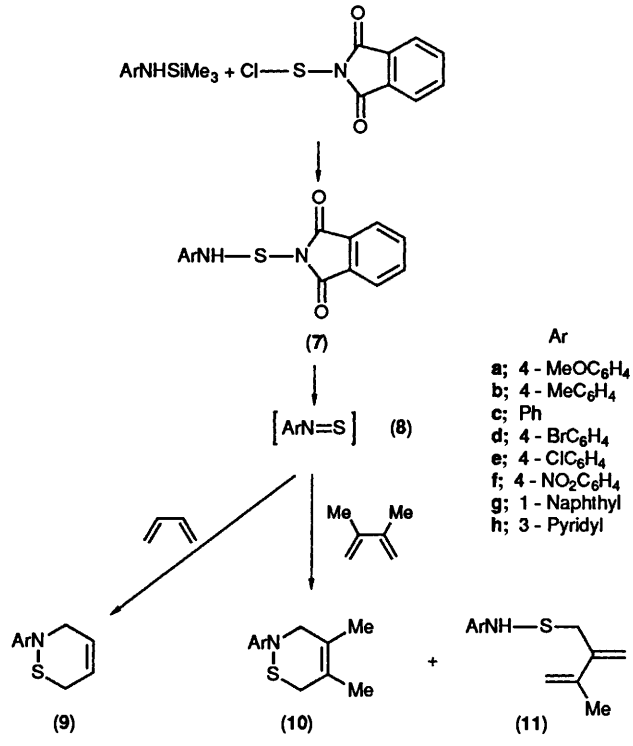


(6) X = H, OMe, Br, Cl, or *m* - NO_2

has been trapped. Compounds (**7a–h**) are air- and moisture-stable solids that have a shelf-life of more than 2 years at room temperature without any observable decomposition. Thionitrosoarene precursors (**7a–h**) are straightforward to prepare: the trimethylsilyl derivative of the appropriate arylamine was treated with 1 equivalent of *N*(-chlorothio)phthalimide in dry chloroform at 0–20 °C and compound (**7**) was precipitated in high yield (typically 85–95%) with no need for further purification (Scheme 2). Compounds (**7**) were easily identified by their characteristic IR spectra: a strong sulphenamide band is observed in the 3 310–3 370 cm^{-1} region for derivatives (**7a–g**), and in the 3 120–3 140 cm^{-1} region for heteroaryl derivative (**7h**), and there are two carbonyl absorptions, one at 1 775–1 785 cm^{-1} (strong) and the other at *ca.* 1 730 cm^{-1} (very strong and broad). The sulphenamide proton is observed in the ^1H NMR spectrum as a sharp singlet between δ_H 7.1 and 6.2.

Generation of Thionitrosoarenes (**8**).—Thionitroso compounds (**8**) were generated from precursors (**7**) by 1,2-elimination and trapped *in situ* with dienes in the following manner: compound (**7**) was suspended in acetone (or, occasionally, in chloroform) at room temperature and an excess of diene and triethylamine were added.* Dissolution of precursors (**7**) in these solvents occurred slowly at room temperature, and reaction was complete when all the precursor had dissolved to form a pale yellow solution (typically 3–72 h). This method has the attractive feature that the thionitroso intermediates (**8**) are formed in a very low steady-state concentration which should suppress dimerisation reactions and thus facilitate their trapping. Indeed, capture of intermediates (**8a–h**) was efficient.

Reaction with Buta-1,3-*diene*.—When butadiene was used as trap the 1:1 adducts (**9a–h**) were isolated in 50–75% yield, as yellow oils which often solidified on storage at <0 °C. The adduct structures followed simply and unambiguously from a combination of ^1H and ^{13}C NMR data (Table 2); the most



Scheme 2.

distinctive features were the thiazine ring methylene groups. The C-3 methylene unit, adjacent to nitrogen, is observed at δ_H 4.1 (±0.1) and δ_C 51 (±2), while the C-6 methylene unit, adjacent to sulphur, is observed at δ_H 3.1 (±0.1) and δ_C 26 (±1) ppm. The mass spectra of adducts (**9**) showed only two peaks of significant intensity, *viz.* that of the parent (**9**) and the fragment ArN=S (**8**), presumably formed by a retro Diels–Alder process as a result of electron impact. High-resolution mass spectral data confirmed the molecular formula of the ArN=S fragment (**8c**).

Reaction with 2,3-*Dimethylbutadiene*.—With 2,3-dimethylbutadiene as trap, each of the thionitroso compounds (**8a–h**) gave two products. These were identified as the Diels–Alder adducts (**10a–h**) and the corresponding ene adducts (**11a–h**); the latter compounds were formed regiospecifically with C–S bond formation, and were readily identified by a characteristic singlet at δ_H 3.4, assigned to the CH_2 protons adjacent to the sulphenamide sulphur, and by the presence of two vinylic CH_2 groups at δ_H 5.2–4.5 Integration of the ^1H NMR spectra of the crude product mixtures showed a very clear trend in the ratio of Diels–Alder:ene products with respect to the electronic properties of the aryl/heteroaryl substituent attached to the thionitroso group (Table 3). Electron-donating substituents on the benzene ring [notably methoxy derivative (**8a**)] favoured Diels–Alder reaction, while electron-withdrawing substituents favoured ene reaction. Indeed, the ene products (**11d–f**) and (**11h**) derived from *p*-bromo-, *p*-chloro-, and *p*-nitro-phenyl- and 3-pyridyl-thionitroso derivatives, predominate significantly over the Diels–Alder products, (**10d–f**), and (**10h**), respectively. It is possible that for 1-thionitrosonaphthalene (**8g**) both steric and electronic factors may influence the product isomer ratio, as, unlike the other members of the series (**8**), compound (**8g**) bears a substituent *ortho* to the thionitroso group. The trapping reactions of (**8a–h**) are clean, with side-products, which were tentatively identified (TLC evidence) as sulphur di-imides and/or azobenzene derivatives, being formed in only trace

* The related sulphenyl and selenenyl derivatives, XCH_2YZ (X = electron-withdrawing group, Y = S, Se, Z = leaving group) have recently been shown to yield thioaldehydes, XCH=S [18] and selenoaldehydes, XCH=Se [19] by analogous base-mediated 1,2-elimination. The point made by Kirby and Trethewey [19] concerning selenoaldehyde generation by this route also applies to the present thionitrosoarene generation: *viz.* we cannot exclude the possibility that triethylamine acts by initial displacement of the phthalimide group with subsequent elimination of triethylamine and a proton.

Table 1. Properties of *N*-(arylaminothio)phthalimides (7).

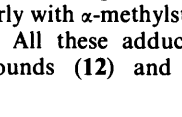
Compound formula	Yield (%) [m.p. (°C)]	ν_{max}/cm^{-1}	$\delta_H(CDCl_3; 250\ MHz)$
(7a)	85	3 300 (NH)	7.9–7.7 (4 H, m, P)[a]
$C_{15}H_{12}N_2O_3S$	[182–184]	1 780 (CO)	7.3–6.8 (4 H, m, Ar)[b]
		1 720 (CO)	6.20 (1 H, s, NH)
			3.75 (3 H, s, OMe)
(7b)	>95	3 310 (NH)	7.9–7.7 (4 H, m, P)
$C_{15}H_{12}N_2O_2S$	[194–196]	1 775 (CO)	7.25–7.05 (4 H, m, Ar)
		1 720 (CO)	6.26 (1 H, s, NH)
			2.25 (3 H, s, Me)
(7c)	85	3 340 (NH)	7.9–7.7 (4 H, m, P)
$C_{14}H_{10}N_2O_2S$	[189–192]	1 780 (CO)	7.4–6.9 (5 H, m, Ar)
		1 730 (CO)	6.38 (1 H, s, NH)
(7d)	>95	3 320 (NH)	7.9–7.7 (4 H, m, P)
$C_{14}H_9BrN_2O_2S$	[162–164 (decomp.)]	1 775 (CO)	7.4–7.2 (4 H, m, Ar)
		1 720 (CO)	6.32 (1 H, s, NH)
(7e)	65	3 320 (NH)	8.0–7.7 (4 H, m, P)
$C_{14}H_9ClN_2O_2S$	[165–166]	1 780 (CO)	7.3–7.1 (4 H, m, Ar)
		1 725 (CO)	6.28 (1 H, s, NH)
(7f)	85	3 320 (NH)	8.2–8.1 and 7.5–7.4 (4 H, AA'BB'Ar)
$C_{14}H_9N_3O_4S$	[166–168]	1 780 (CO)	8.0–7.7 (4 H, m, P)
		1 725 (CO)	6.73 (1 H, s, NH)
(7g)	70	3 370 (NH)	8.1–7.4 (11 H, m, Ar + P)
$C_{18}H_{12}N_2O_2S$[d]	[143–145]	1 785 (CO)	7.02 (1 H, s, NH)
		1 730 (CO)	
(7h)	60	3 140 (NH)	8.30 and 8.17 (both 1 H, m, Het)[c]
$C_{13}H_9N_3O_2S$	[130–132 (decomp.)]	1 790 (CO)	7.85 (4 H, m, P), 7.34 (1 H, m, Het)
		1 730 (CO)	6.80 (1 H, s, Het)

[a] P refers to hydrogen atoms on the phthalimide ring in formulae (**7a–h**). [b] Ar refers to hydrogen atoms on the substituent Ar in formulae (**7a–g**). [c] Het refers to hydrogen atoms on the heteroaryl substituent Ar in formula (**7h**). [d] Found: C, 67.5; H, 3.9; N, 8.4. $C_{18}H_{12}N_2O_2S$ requires C, 67.5; H, 3.8; N, 8.7%.

amounts. The isomeric products (**10**) and (**11**) could not be completely separated from one another even after repeated chromatography and distillation, except for compound (**10a**) which was isolated, spectroscopically pure, in 65% yield.

Other workers have pointed out that competitive ene and diene reactions of a methylbutadiene derivative, such as we have observed, are unusual.[5b,20] It is noteworthy that ene products have not been identified previously from reactions of thionitrosoarenes. However, the highly electron-deficient derivatives RN=S (R = CO_2Et, CO_2Ph, $SO_2C_6H_4Me$-*p*) studied by Meth-Cohn and van Vuuren are known to form ene products regiospecifically with dimethylbutadiene and other alkenes.[5a,b]

Reactions with Alkenes.—Ene adducts (**12**)–(**15**) were formed (45–65% isolated yield) from reaction of thionitrosoarenes (**8a**) and (**8g**) with isobutene and α-methylstyrene (Table 4). That reaction had occurred with C–S bond formation was quickly deduced from the presence of an NH absorption in the IR spectra of the products. 3-Thionitrosopyridine (**8h**) reacted similarly with α-methylstyrene to yield sulphenamide (**16**) (45% yield). All these adducts are thermally unstable, especially compounds (**12**) and (**13**), derived from methoxyphenyl



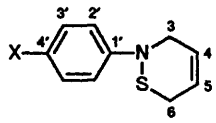
(**12**) Ar = 4 - $MeOC_6H_4$, X = Me
(**13**) Ar = 4 - $MeOC_6H_4$, X = Ph
(**14**) Ar = 1 - Naphthyl, X = Me
(**15**) Ar = 1 - Naphthyl, X = Ph
(**16**) Ar = 3 - Pyridyl, X = Ph

derivative (**8a**). The presence of the other possible regioisomer, arising from C–N bond formation, was not observed in these reactions (NMR evidence). The regiospecificity of the ene reaction of thionitrosoarenes (**8a–h**) is, therefore, the same as that found for thionitroso-formates and -sulphonates.[5a,b] Sulphinylamines react with the same regiospecificity,[21] while, thioaldehydes are known to yield both regioisomers in intermolecular ene reactions, with C–C bond formation competing with C–S bond formation.[22] Cyclohexene did not react with thionitrosoarenes (**8a**) or (**8f**), which contrast with the efficient reaction of cycloalkenes with the more reactive thionitroso-formates and -sulphonates, which may react by a radical mechanism.[5a,b]

Reactions with 1,4-Disubstituted and Tetrasubstituted Dienes.—We chose the commercially available 1,4-diphenylbutadiene, (*E,E*)- and (*E,Z*)-hexa-2,4-dienes, (**17**) and (**18**), respectively, for investigations into the stereochemical outcome of Diels–Alder addition to thionitrosoarenes. The analogous chemistry of *N*-sulphinylamines and sulphur di-imides is developing rapidly.[23–25] For example, cycloadditions of dienes (**17**) and (**18**) to these dienophiles show the usual Diels–Alder stereoselectivity (*i.e.* retention of stereochemistry with respect to the diene),[24] although the sterically overcrowded (*Z,Z*)-hexa-2,4-diene reacts by a non-concerted mechanism with $PhSO_2N$=S=O.[25a,e] The structures of the cycloadducts from RN=S=O and RN=S=NR derivatives (*viz.* dihydrothiazine *S*-oxides and *S*-imines) are complicated by chirality at sulphur: a feature which is, of course, absent in RN=S adducts. Recently, the addition of nitrosoarenes to hexa-2,4-diene has been reported but no information was given concerning the stereochemistry of the reaction.[26] A thionitrosoformate derivative gave a Diels–Alder adduct with 1,4-diphenylbutadiene,[5c] but analogous reactions of thionitrosoarenes have not been reported.

1-Methoxy-4-thionitrosobenzene (**8a**) and 3-thionitrosopyridine (**8h**) were both generated under our standard conditions in the presence of an excess of 1,4-diphenylbutadiene. Intermediate (**8a**) reacted cleanly with the diene to yield a single

Table 2. Properties of butadiene adducts (**9**).



Adduct mol. formula	M^+ Found (Required)	Yield[a] (%)	*m/z* M^+ (Ar–N=S fragment)	ν_{max}/cm^{-1}	$\delta_H(CDCl_3; 250\ MHz)$	$\delta_C(CDCl_3)$
(**9a**) $C_{11}H_{13}NOS$	207.0880 (207.0718)	65	207 (153)	1 645 (C=C)	7.25–6.75 (4 H, m, Ar) 6.1–5.8 (2 H, m, 2 × CH) 4.0 (2 H, m, CH_2N) 3.76 (3 H, s, MeO) 3.0 (2 H, m, CH_2S)	154.5 (C-4'), 145.3 (C-1') 126.6/125.0 (C-4 and C-5) 120.6 (C-2'), 113.9 (C-3') 55.6 (CH_3) 50.7 (C-3), 25.8 C-6)
(**9b**) $C_{11}H_{13}NS$	191.0438 (191.0769)	75	191 (137)	1 645 (C=C)	7.15–7.0 (4 H, m, Ar) 6.1–5.8 (2 H, m, 2 × CH) 4.1 (2 H, m, CH_2N) 3.1 (2 H, m, CH_2S) 2.28 (3 H, s, CH_3)	149.0 (C-1'), 129.3 (C-3' and C-4') 126.6/124.9 (C-4 and C-5) 118.8 (C-3) 50.2 (C-2), 26.3 (C-6) 20.5 (CH_3)
(**9c**) $C_{10}H_{11}NS$	177.0606 (177.0612)	65	177 (123)[b]	1 645 (C=C)	7.3–6.6 (5 H, m, Ar) 6.1–5.8 (2 H, m, 2 × CH) 4.0 (2 H, m, CH_2N) 3.0 (2 H, m, CH_2S)	151.5 (C-1'), 128.7 (C-3') 126.6/124.8 (C-4 and C-5) 120.8 (C-4'), 116.5 (C-2') 49.8 (C-3) 26.7 (C-6)
(**9d**) $C_{10}H_{10}BrNS$	254.9856 (254.9717)	75	255/7 (201/3)	1 645 (C=C)	7.75–7.05 (4 H, m, Ar) 6.1–5.8 (2 H, m, 2 × CH) 4.1 (2 H, m, CH_2N) 3.1 (2 H, m, CH_2S)	150.5 (C-1'), 131.5 (C-3') 126.2/124.8 (C-4 and C-5) 120.1 (C-2'), 113. 1 (C-4') 49.7 (C-3) 26.7 (C-6)
(**9e**) $C_{10}H_{10}ClNS$	211.0220 (211.0223)	75	211 (157)	1 645 (C=C)	7.8–7.1 (4 H, m, Ar) 6.1–5.8 (2 H, m, 2 × CH) 4.07 (2 H, m, CH_2N) 3.1 (2 H, m, CH_2S)	
(**9f**) $C_{10}H_{10}N_2O_2S$	222.0482 (222.0463)	50	222 (168)	1 490 (NO_2) 1 330 (NO_2)	8.1–8.0 7.2–7.1 } (4 H, m, Ar) 6.05–5.75 (2 H, m, 2 × CH) 4.1 (2 H, m, CH_2N) 3.2 (2 H, m, CH_2S)	156.1 (C-1'), 140.0 (C-4') 126.3 125.4 } (C-4, C-5 and C-3') 124.0 115.9 (C-2') 49.2 (C-3), 26.7 (C-6)
(**9g**) $C_{14}H_{13}NS$	227.0736 (227.0769)	55	227 (173)	1 650 (C=C)	8.3–7.2 (7 H, m, Ar) 6.3–6.0 (2 H, m, 2 × CH) 4.2 (2 H, br, s, CH_2N) 3.1 (2 H, br s, CH_2S)	150–115 (m) 53.2 (C-3) 25.6 (C-6)
(**9h**) $C_9H_{10}N_2S$	178.0735 (178.0565)	60	178 (124)	1 640 (C=C)	8.53 (1 H, m, py) 8.14 (1 H, m, py) 7.56 (1 H, m, py) 7.16 (1 H, m, py) 5.97 (2 H, m, 2 × CH) 4.13 (2 H, m, CH_2N) 3.13 (2 H, m, CH_2S)	147.2 141.6 140.6 126.0 125.3 124.8 123.1 49.3 (C-3) 26.8 (C-6)

[a] Yield is for spectroscopically pure material isolated after distillation under high vacuum. [b] High resolution mass of this fragment (Found *M*, 123.0143. C_6H_5NS requires *M*, 123.0137).

adduct in 60% yield, assigned the *cis* structure (**19**) (Scheme 3). Intermediate (**8h**) did not react cleanly; *cis* product (**20**) was obtained in low yield.

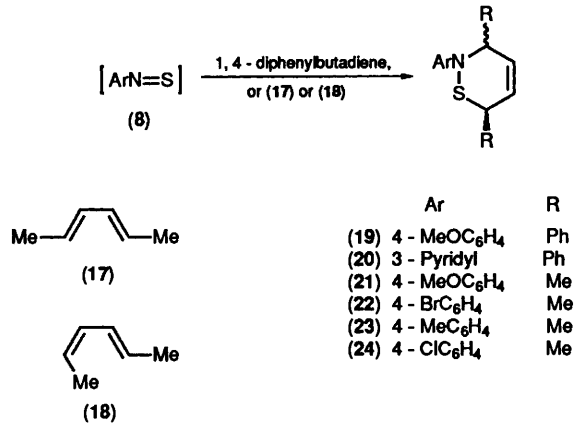
Thionitrosoarenes (**8a**) and (**8d**) both reacted with (*E,E*)-hexa-2,4-diene (**17**) to give the *cis* diastereoisomers (**21**) and (**22**) (70% yields, >98% diastereoisomeric excess) as judged by ^1H and ^{13}C NMR spectroscopic data. Thionitrosoarenes (**8a**), (**8d**), (**8b**), and (**8e**) each reacted with (*E,Z*)-diene (**18**) to give the expected diastereoisomers (**21**)–(**24**), respectively, which have the *trans* stereochemistry. The *trans* adduct was accompanied, in all cases, by a second product which was clearly the isomeric *cis* adduct (**21**)–(**24**). [^1H NMR spectra were identical with the *cis* adducts (**21**) and (**22**) prepared from (*E,E*)-diene (**17**)]. No ene products were detected in the reaction mixtures from either hexadiene (**17**) or (**18**).

The isomer ratios of *trans* and *cis* products (**21**)–(**24**) from thionitrosoarenes (**8**) and (*E,Z*)-hexadiene (**18**) were dependent upon the electronic nature of the substituent on the aryl ring: the electron-withdrawing halogeno-substituents favoured formation of the *trans* products (≥90% d.e.) while the electron-rich methoxy derivative gave a 1:1 mixture of *cis* and *trans* products. Diastereoisomeric ratios were determined primarily from the integrals of the methyl signals in the ^1H NMR spectra; these appeared, in all cases, as four distinct doublets between δ_H

Table 3. Properties of Diels–Alder products (**10**) and ene products (**11**) from dimethylbutadiene addition to thionitrosoarenes (**8**).

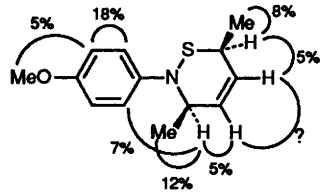
Phthalimide precursor (7)	Combined yield of adducts (10) + (11)[a]	Isomer ratio[b]	δ_H($CDCl_3$; 60 MHz) (excluding aromatics)[c]
(7a)	65%	(10a) (85%)	3.8 (2 H, m, CH_2N) 3.7 (3 H, s, CH_3O) 2.9 (2 H, m, CH_2S) 1.7 (6 H, s, 2 × CH_3)
		(11a) (15%)	5.2–4.5 (5 H, m, 2 × =CH_2 + NH) 3.7 (3 H, s, CH_3O) 3.4 (2 H, s, CH_2S) 1.9 (3 H, s, CH_3)
(7b)	55%	(10b) (60%)	3.8 (2 H, m, CH_2N) 2.9 (2 H, m, CH_2S) 2.2 (3 H, s, CH_3Ar) 1.7 (6 H, s, 2 × CH_3)
		(11b) (40%)	5.1–4.5 (5 H, m, 2 × =CH_2 + NH) 3.4 (2 H, s, CH_2S) 2.2 (3 H, s, CH_3Ar) 1.9 (3 H, s, CH_3)
(7c)	55%	(10c) (55%)	3.9 (2 H, m, CH_2N) 2.9 (2 H, m, CH_2S) 1.7 (6 H, s, 2 × CH_3)
		(11c) (45%)	5.2–4.6 (5 H, m, 2 × CH_2 + NH) 3.4 (2 H, s, CH_2S) 1.9 (3 H, s, CH_3)
(7d)	50%	(10d) (25%)	3.9 (2 H, m, CH_2N) 2.9 (2 H, m, CH_2S) 1.7 (6 H, s, 2 × CH_3)
		(11d) (75%)	5.5–4.6 (5 H, m, 2 × CH_2 + NH) 3.4 (2 H, s, CH_2S) 1.9 (3 H, s, CH_3)
(7e)	55%	(10e) (25%)	3.9 (2 H, m, CH_2N) 2.9 (2 H, m, CH_2S) 1.7 (6 H, s, 2 × CH_3)
		(11e) (75%)	5.5–4.5 (5 H, m, 2 × CH_2 + NH) 3.4 (2 H, s, CH_2S) 1.9 (3 H, s, CH_3)
(7f)	45%	(10f) (20%)	4.0 (2 H, m, CH_2N) 3.0 (2 H, m, CH_2S) 1.7 (6 H, s, 2 × CH_3)
		(11f) (80%)	5.3–4.7 (5 H, m, 2 × CH_2 + NH) 3.4 (2 H, s, CH_2S) 1.9 (3 H, s, CH_3)
(7g)	65%	(10g) (45%)	3.9 (2 H, m, CH_2N) 2.9 (2 H, m, CH_2S) 1.8 (6 H, s, 2 × CH_3)
		(11g) (55%)	5.6–4.6 (5 H, m, 2 × CH_2 + NH) 3.5 (2 H, s, CH_2S) 1.9 (3 H, s, CH_3)
(7h)[d]	55%	(10h) (25%)	4.00 (2 H, s, CH_2N) 3.00 (2 H, s, CH_2S) 1.75 (6 H, s, 2 × CH_3)
		(11h) (75%)	5.23 (1 H, s, NH) 5.16 (2 H, s, 2 × =CH) 5.11 (1 H, s, =CH) 4.87 (1 H, s, =CH) 3.49 (2 H, s, CH_2S) 1.9 (3 H, s, CH_3)

[a] The yield quoted is for the mixture of adducts, NMR spectroscopically pure, after column chromatography and/or bulb-to-bulb distillation. [b] Based on ^{1}H NMR analysis of the crude reaction mixture. [c] Aromatics were essentially identical with the parent anilines *i.e.* δ 8.6–7.1. [d] 250 MHz spectrum.

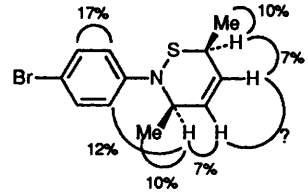


Scheme 3.

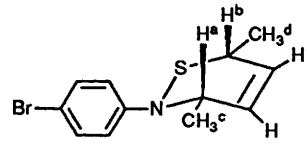
1.0 and 1.5. The two doublets with higher chemical shift values were assigned to the 3-methyl groups (due to the greater deshielding effect of ArN compared with S), and their coupling constants were very similar to each other [*e.g.* *J* 6.64 and 6.72 Hz] and distinctly different from those of the two higher field doublets [*J* 7.21 and 7.18 Hz]. Confirmation of the ^{1}H NMR assignments for the *cis* structures (**21**) and (**22**), formed by reaction of (*E,E*)-diene (**17**), was provided by NOE difference experiments [structures (21′) and (22′)]. (The resonances for protons on C-4 and C-5 were too close in chemical shift for an accurate value to be obtained.) Conclusive proof of the *cis* stereochemistry of adduct (**22**) was provided by a NOESY spectrum. This spectrum showed a nuclear Overhauser effect between H^a and H^b, but not between H^a and H^d, H^b and H^c, or



(21′)



(22′)



(22″)

between H^c and H^d. This is consistent with the *cis* structure (22″) with the methyl groups in equatorial positions.

The formation of the *cis* adducts (**21**)–(**24**), alongside their *trans* isomers, from reactions of the (*E,Z*)-hexadiene was a most unexpected result. We considered that this could be explained by isomerisation of (*a*) starting diene, (*b*) intermediates, or

Table 4. Properties of ene adducts of thionitrosoarenes (**8a**), (**8g**), and (**8h**) with isobutene and α-methylstyrene.

Compound formulae	M^+ Found (Required)	Yield (%)	*m/z* M^+ (ArNHS fragment)	ν_{max}/cm^{-1}	$\delta_H(CDCl_3; 250\ MHz)$	$\delta_C(CDCl_3)$
(**12**) $C_{11}H_{15}NOS$	209.0839 (209.0874)	65[a]	209 (153)		7.0–6.7 (4 H, m, Ar) 4.84 (1 H, s, CH) 4.66 (1 H, s, NH) 4.56 (1 H, s, CH) 3.74 (3 H, s, CH_3O) 3.12 (2 H, s, CH_2S) 1.86 (3 H, s, CH_3)	
(**13**) $C_{16}H_{17}NOS$	271.1020 (271.1031)	65[a]	271 (153)		7.4–6.7 (9 H, m, Ar) 5.40 (1 H, s, CH) 4.89 (1 H, s, NH) 4.65 (1 H, s, CH) 3.71 (3 H, s, CH_3O) 3.59 (2 H, s, CH_2S)	
(**14**) $C_{14}H_{15}NS$	229.1013 (229.0925)	45[b]	229 (173)	3 360 (NH)	7.9–7.25 (7 H, m, Ar) 5.16 (1 H, s, NH) 4.80 (1 H, m, CH) 4.43 (1 H, m, CH) 3.23 (2 H, s, CH_2S) 1.91 (3 H, s, CH_3)	44.4 (CH_2S) 21.1 (CH_3)
(**15**) $C_{19}H_{17}NS$	291.1068 (291.1082)	45[b]	291 (173)	3 380 (NH) 1 620 (C=C)	7.85–7.3 (12 H, m, Ar) 5.50 (1 H, s, NH) 5.38 (1 H, s, CH) 4.79 (1 H, m, CH) 3.75 (2 H, s, CH_2S)	41.8 (CH_2S)
(**16**) $C_{14}H_{14}N_2S$	242.0855 (242.0878)	45[b]	243 (M + 1) (124)	3 430 (NH) 1 620 (C=C)	8.24 (1 H, d, *J* 2.8 Hz, py) 8.09 (1 H, m, py) 7.5–7.3 (6 H, m, 5Ar + 1py) 7.13 (1 H, dd, *J* 4.6 Hz, py) 5.42 (1 H, s, CH) 5.08 (1 H, s. NH) 4.95 (1 H, s, CH) 3.68 (2 H, s, CH_2S)	42.3 (CH_2S)

[a] Crude isolated yield: the product could not be distilled or chromatographed. [b] Yield after column chromatography.

(*c*) the thiazine products. The last possibility was easily eliminated by heating product mixtures overnight in refluxing chloroform whereupon no changes in the ^1H NMR spectra were observed. For isomerisation of intermediates to occur, a stepwise addition pathway was clearly necessary. The most probable outcome would be that the same diastereoisomer ratio would result from each example, (**8a**), (**8b**), (**8d**), and (**8e**); this has been observed with sulphur monoxide addition.[27] The presence of (*E,E*)-diene (**17**) as impurity in the commercial sample of (*E,Z*)-diene (**18**) seemed, therefore, to be the most likely explanation. Only a few percent of (*E,E*)-diene (**17**) impurity would be sufficient to explain our results, due to the higher reactivity of the less sterically hindered (*E,E*)-diene (**17**) and the large excess (35 equiv.) of diene used in the reactions. (Unfortunately, cycloaddition did not proceed satisfactorily with a smaller excess of diene.) To test this explanation, we generated thionitrosoarenes (**8a**) and (**8d**) in the presence of a 1:1 mixture of (*E,E*)- and (*E,Z*)-dienes (**17**) and (**18**). Methoxy derivative (**8a**) gave a remarkable result in that only the *cis* product (**21**) was observed (>96% d.e.); bromo derivative (**8d**) yielded a mixture of *cis* and *trans* products (**22**) but again the *cis* adduct was favoured, being formed in 80% d.e.

These results are very informative, and the marked preference for reaction with the (*E,E*)-diene isomer is strongly suggestive of a concerted mechanism. A similar competition experiment with sulphur monoxide showed only a 1.6:1 increase in reactivity of (*E,E*)- over (*E,Z*)-hexadiene;[27] our results represent a >97:1 increase with methoxy compound (**8a**), and a 9:1 increase with bromo compound (**8d**). These results also demonstrate that a very small amount of (*E,E*)-diene (**17**) contaminating the (*E,Z*)-diene (**18**) would give the observed results presented in Table 5.* The striking relationship between electronegativity of the aryl substituent and product diastereoisomer distribution can be rationalised on a reactivity–selectivity basis. The less-reactive thionitrosoarenes (**8a**) and (**8b**) are more selective, preferring to react with the small amount of (*E,E*)-diene present to give significant amounts of *cis* adduct, whereas, the more-reactive, more electron-deficient, thionitrosoarenes (**8d**) and (**8e**) are relatively indiscriminate, giving predominantly *trans* adducts, from reaction with (*E,Z*)-diene, as would be expected statistically. We have thus established that stereochemistry of the diene, (*E,E*)- (**17**) or (*E,Z*)- (**18**) is retained in the adducts.

The bicyclic dienes, 1,1′-bicyclopentenyl (**25**) and 1,1′-bicyclohexenyl (**26**) are predicted to be highly-reactive dienes as they are, effectively, tetra-alkyl substituted.[29] To our knowledge, the only heterodienophiles which have been reported to undergo cycloaddition with dienes (**25**) or (**26**) are *N*-sulphinylaniline and *N*-sulphinylethylcarbamate which gave the expected *cis* products (X-ray evidence).[29] Both dienes (**25**) and (**26**) reacted cleanly with 4-methoxythionitrosobenzene (**8a**) to yield single stereoisomeric products (75% yield) assigned the *cis* adduct structures (**27**) and (**28**), respectively (Scheme 4). The formation of these adducts demonstrates that thionitrosoarenes will react efficiently with highly substituted dienes.

Attempted Synthesis of Acylthionitroso Compounds.—In the

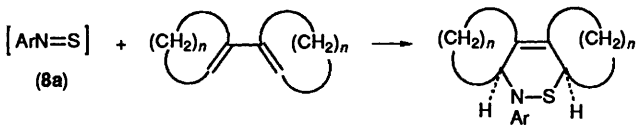
* A recent study of the relative rates of reaction of (*E,E*)-, (*E,Z*)- and (*Z,Z*)-hexadienes with tetracyanoethylene supports this conclusion.[28]

Table 5. Properties of Diels–Alder products (**21**)–(**24**) from (*E,E*)- and (*E,Z*)-hexadiene addition to thionitrosoarenes (**8**).

Adduct (yield)	δ_H($CDCl_3$; 250 MHz)	δ_C($CDCl_3$)
cis-(**21**) (70%)	7.2–6.7 (4 H, m, Ar), 5.9–5.7 (2 H, m, 2 × =CH), 3.9 (1 H, m, CHN), 3.76 (3 H, s, OCH_3), 3.5 (1 H, m, CHS), 1.44 [3 H, d, CH_3–C(3), *J* 6.64 Hz], 1.08 [3 H, d, CH_3–C(6), *J* 7.18 Hz]	154.5, 146.7, 131.4, 131.0, 121.0, 113.8, 55.5 (OCH_3), 52.9 (CH_2N), 30.6 (CH_2S), 21.0 and 16.0 (both CH_3)
cis-(**22**) (70%)	7.4–7.0 (4 H, m, Ar), 5.9–5.6 (2 H, m, 2 × =CH), 4.05 (1 H, m, CHN), 3.55 (1 H, m, CHS), 1.45 [3 H, d, CH_3–C(3), *J* 6.64 Hz], 1.09 [3 H, d, CH_3–C(6), *J* 7.16 Hz]	151.0, 131.5, 130.8, 120.0, 112.7, 52.2 (CH_2N), 32.2 (CH_2S), 20.3 and 16.1 (both CH_3)
trans-(**21**) (70%)[a]	7.3–6.7 (4 H, m, Ar), 6.0–5.75 (2 H, m, 2 × =CH), 4.14 (1 H, m, CHN), 3.75 (3 H, s, OCH_3), 2.94 (1 H, m, CHS), 1.38 [3 H, s, CH_3–C(3), *J* 6.62 Hz], 1.24 [3 H, d, CH_3–C(6), *J* 7.09 Hz]	
trans-(**22**) (65%)[a]	7.35–7.05 (4 H, m, Ar), 6.05–5.65 (2 H, m, 2 × =CH), 4.20 (1 H, m, CHN), 2.97 (1 H, m, CHS), 1.40 [3 H, d, CH_3–C(3), *J* 6.79 Hz], 1.31 ([3 H, d, CH_3–C(6), *J* 7.14 Hz]	
trans-(**23**) (75%)[a]	7.3–6.8 (4 H, m, Ar), 6.1–5.7 (2 H, m, 2 × =CH), 4.20 (1 H, m, CHN), 2.92 (1 H, m, CHS), 2.26 (3 H, s, Me), 1.40 [3 H, d, CH_3–C(3), *J* 6.62 Hz], 1.30 [3 H, d, CH_3–C(6), *J* 7.10 Hz]	
trans-(**24**) (65%)[a]	7.25–7.05 (4 H, m, Ar), 6.0–5.7 (2 H, m, 2 × =CH), 4.20 (1 H, m, CHN), 2.97 (1 H, m, CHS), 1.41 [3 H, d, CH_3–C(3), *J* 6.62 Hz], 1.32 [3 H, d, CH_3–C(6), *J* 7.04 Hz]	

[a] Yield includes inseparable isomeric *cis* adduct. Ratios of *trans*–*cis* adducts are as follows: compound (**21**) (1:1); compound (**22**) (9:1); compound (**23**) (7:3); compound (**24**), (9:1).

light of Meth-Cohn's work on thionitroso-formates and -sulphonates,[5] we attempted to extend our methodology (Scheme 2) to a new class of highly electron-deficient thionitroso compounds, *viz.* acylthionitroso compounds.[30] The ready availability of bis(trimethylsilyl)acetamide (BTMSA)



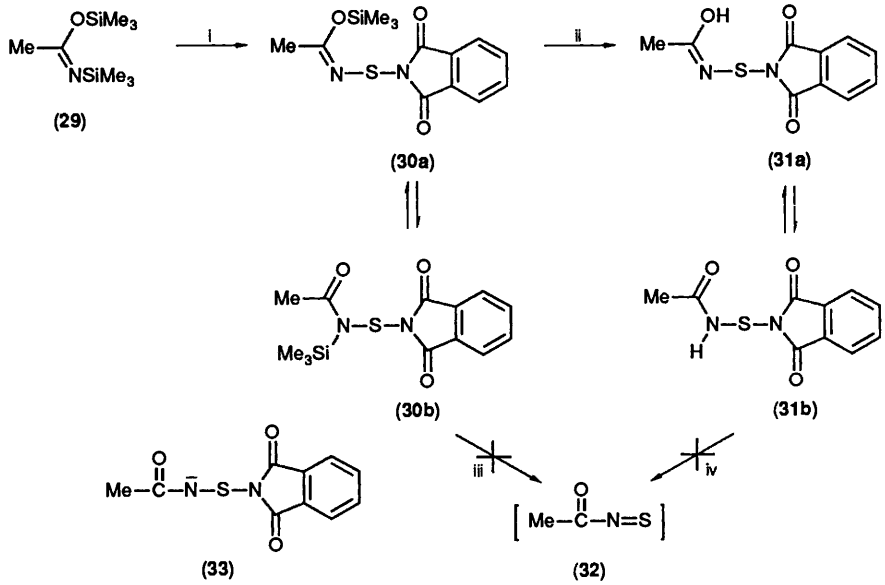
(**25**) *n* = 3
(**26**) *n* = 4
(**27**) *n* = 3
(**28**) *n* = 4

Scheme 4.

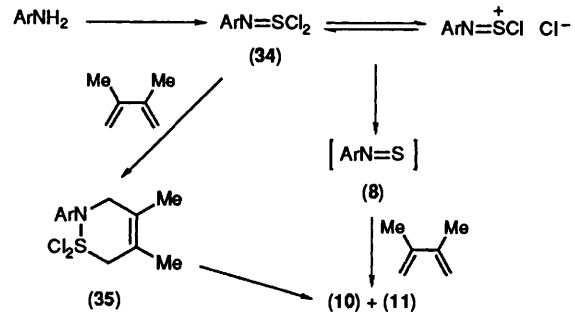
(**29**) made thionitrosocarbonylmethane (**32**) an attractive target. Reaction of BTMSA (**29**) with 1 equivalent of phthalimidesulphenyl chloride resulted in a *ca.* 1:1 mixture of the two tautomeric mono-silylated compounds (**30a**) and (**30b**) (Scheme 5). The ^1H NMR spectrum of the product mixture displayed two methyl singlets at δ_H 1.9 and 2.6, which were assigned to the *O*-silylated and *N*-silylated tautomers, (**30a**) and (**30b**), respectively, by comparison with the spectra of BTMSA (**29**) and acetamide. This mixture of (**30a**) and (**30b**) was easily converted into the desired sulphenamide (**31**) by hydrolysis in wet chloroform. Interconversion of tautomers (**31a**) and (**31b**) was observed in deuteriochloroform solution at room temperature: the NMR spectrum showed two very broad singlets at δ_H 7.4 (NH/OH) and 2.5 (CH_3).

Unfortunately, all attempts to generate acylthionitroso compound (**32**) by 1,2-elimination from precursor (**31**) using triethylamine failed. Unchanged starting material (**31**) was recovered in all cases. It is possible that the anion (**33**) that forms initially is too stable to fragment into the highly reactive thionitroso compound (**32**). Also, attempted fluoride-ion induced elimination of the silyl and phthalimide groups from compound (**30**) was unsuccessful.

Generation of Thionitrosoarenes from N-*Aryliminosulphur Dichlorides* (**34**).—*N*-Aryliminosulphur dichlorides (**34**) are known to be very unstable compounds;[31] nonetheless, we decided to explore their potential as a novel source of ArN=S species *via* a 1,1-elimination process. The iminosulphur dichloride derivatives (**34a**) and (**34e**) were prepared by chlorination of a chloroform solution of the appropriate aniline derivative and sulphur dichloride, and isolated as hygroscopic oils which were used immediately in subsequent reactions. Addition of an excess of dimethylbutadiene to compounds (**34**),



Scheme 5. *Reagents:* i, phthalimidesulphenyl chloride; ii, water; iii, fluoride ion; iv, triethylamine.



Scheme 6.

dissolved in acetone, resulted in slow fading of the deep orange colour to give a pale yellow solution containing a mixture of products (TLC and NMR analysis) (Scheme 6). These products were quickly identified as the expected thiazine and sulphenamide products arising from Diels–Alder and ene addition, respectively, to thionitroso species (**8a**) and (**8e**). Reaction was clean and efficient (*ca.* 70% yield) with dimethylbutadiene acting as both the dechlorinating agent and the diene. Small amounts of azobenzene derivatives were isolated; the by-products of dechlorination, presumably chloroalkanes and chloroalkenes, were not investigated. The product mixture from compound (**34a**) contained the expected small amount (*ca.* 15%) of ene adduct (**11a**). This product distribution provides very good evidence for the intermediacy of thionitroso species (**8a**) in the reaction of (**34a**) and dimethylbutadiene. However, the Diels–Alder:ene product ratio from reaction of derivative (**34e**) and dimethylbutadiene showed significantly less ene adduct (**11e**) than was the case when (**8e**) was generated from phthalimido precursor (**7e**). This result could be explained by initial cycloaddition of dimethylbutadiene to the iminosulphur dichloride (**34e**), to form the intermediate adduct (**35e**), occurring in competition with initial dechlorination of (**34e**) and generation of thionitroso intermediate (**8e**) which is then trapped. We have not investigated these reactions further as the instability of precursors (**34**) clearly limits their synthetic utility. However, we have established that *N*-aryliminosulphur dichlorides (**34**) are a new source of thionitrosoarenes.

Detailed mechanistic studies of cycloadditions of ArN=S species (**8**), aided by MNDO calculations, will be reported separately.

Conclusions

We have developed an efficient synthetic route to a series of *N*-(arylaminothio)phthalimides (**7**) and established that thionitrosoarenes (**8**) can be efficiently generated therefrom by base-induced 1,2-elimination. Trapping reactions of (**8**) with a range of dienes and alkenes has yielded 1,2-thiazine and sulphenamide derivatives by Diels–Alder and ene reactions, respectively. (*E,E*)- and (*E,Z*)-Hexa-2,4-dienes react with thionistrosoarenes in a Diels–Alder fashion with retention of diene stereochemistry. *N*-Aryliminosulphur dichlorides (**34**) also appear to yield thionitrosoarenes, by a 1,1-elimination process.

Experimental

General Information.—Proton and carbon NMR spectra were recorded on a Bruker AC 250 spectrometer with the exception of data in Table 3 which were obtained on a Hitachi Perkin-Elmer R248 spectrometer at 60 MHz. Chemical shifts are quoted in ppm relative to tetramethylsilane as the internal standard. Mass spectra were recorded in either electron impact (EI) or chemical ionisation (CI) mode. In the CI mode, ammonia was employed as the impingent gas; high resolution masses were measured in the EI mode. Elemental analysis was obtained using a Carlo Erba 1106 analyser. IR spectra were recorded as thin films or KBr discs on a Perkin-Elmer 577 spectrophotometer. M.p.s were obtained on a Kofler hot-stage microscope apparatus and are uncorrected. Column chromatography on silica refers to gravity chromatography on Merck silica gel (70–230 mesh). Kugelrohr distillations were carried out on a Büchi GKR-51 apparatus. Solvents were distilled from the following drying agents: diethyl ether (sodium–benzophenone), tetrahydrofuran (potassium), chloroform and dichloromethane (phosphorus pentoxide), acetone (anhydrous potassium carbonate), and triethylamine (3 Å molecular sieves). Ether refers to diethyl ether.

N,N′-*Dithiobis(phthalimide)*. This was prepared in 60% yield following the procedure of Cava *et al.*[32] (An alternative literature procedure[33] was far less satisfactory in our hands.)

Phthalimide sulphenyl chloride. This was prepared in quantitative yield by chlorinolysis of *N,N′*-dithiobis(phthalimide) and stored in a dry box under nitrogen.[33]

N-(*Trimethylsilyl*)*arylamines and* N-(*trimethylsilyl*)-3-*aminopyridine.* These were prepared as follows. A stirred solution of arylamine (20 mmol) and triethylamine (3 ml, 22 mmol) dissolved in ether (100 ml) was cooled to 0 °C under nitrogen. Chlorotrimethylsilane (2.8 ml, 22 mmol) was added dropwise over 5 min and stirring was continued for a further 1 h at 20 °C (72 h for 4-nitroaniline). Triethylamine hydrochloride was filtered off and the filtrate evaporated to afford the product in >95% yield and pure enough for further reaction.

Preparation of Phthalimido Precursors.—N-(*Arylaminothio*)*phthalimides* (**7a–h**). The preparation of *N*-(1-naphthylaminothio)phthalimide (**7g**) is representative. To a stirred solution of *N*-(trimethylsilyl)naphthylamine (2.4 g, 11.1 mmol) in chloroform (25 ml) under dry nitrogen, was added phthalimide sulphenyl chloride (2.4 g, 11.1 mmol) dissolved in chloroform (25 ml) dropwise over 5 min at room temperature. A precipitate quickly formed and stirring was continued for 12 h. The precipitate was filtered off and dried to afford *product* (**7g**) as a pale yellow solid (2.5 g, 70%). Analogues prepared using this procedure are collated in Table 1. These are *N*-(4-methoxyphenylaminothio)phthalimide (**7a**), *N*-(4-methylphenylaminothio)phthalimide (**7b**), *N*-(phenylaminothio)phthalimide (**7c**), *N*-(4-bromophenylaminothio)phthalimide (**7d**), *N*-(4-chlorophenylaminothio)phthalimide (**7e**), *N*-(4-nitrophenylaminothio)phthalimide (**7f**), and *N*-(3-pyridylaminothio)phthalimide (**7h**). Compounds (**7**) could be recrystallised from chloroform–methanol, but only compound (**7g**) gave satisfactory elemental analysis. High resolution mass spectra could not be obtained as compounds (**7a**)–(**7f**) and (**7h**) did not give a parent ion. ^{13}C NMR spectra of compounds (**7**) could not be obtained due to their insolubility in standard NMR solvents.

N-*Acetyl*-N-(*trimethylsilylaminothio*)*phthalimide* (**30**). A stirred solution of phthalimidesulphenyl chloride (0.5 g, 2.3 mmol) in chloroform (10 ml) was cooled to 0 °C under nitrogen. Bis(trimethylsilyl)acetamide (**29**) (0.6 ml, 2.4 mmol) was added dropwise causing the yellow solution to become completely clear. Evaporation afforded a white solid consisting of product (**30**) (0.85 g, 97%) as the two tautomeric forms (**30a**) and (**30b**) (*ca.* 1:1 ratio); $\delta_H(CDCl_3)$ 7.75 (4 H, m, Ar), 2.60 and 1.92 (both 1.5 H, s), and 0.3 and 0.25 (both 4.5 H, s, Me_3Si).

N-(*Acetylaminothio*)*phthalimide* (**31**). To a stirred solution of compound (**30**) (0.85 g, 2.3 mmol) in chloroform (25 ml) at

20 °C was added water (0.5 ml). Vigorous stirring was continued for 1 h, the solution was evaporated, and the white residue dried *in vacuo* to afford *compound* (**31**) (0.62 g, 96%), m.p. 160–165 °C (Found: C, 50.3; H, 3.5; N, 11.6. $C_{10}H_8N_2O_3S$ requires C, 50.8; H, 3.4; N, 11.9%); *m/z* (CI) 235 ($M^+ - 1$); ν_{max}(KBr) 3 300 (NH), 1 795, 1 745 and 1 695 (C=O) cm^{-1}; $\delta_H(CDCl_3)$ 7.89 (4 H, m, Ar), 7.4 (1 H, br s, NH/OH) and 2.5 (3 H, br s, Me).

Generation of Thionitrosoarenes (**8a**)–(**h**) *and Trapping with Butadiene: Synthesis of* 2-*Aryl*-3,6-*dihydro*-2H-1,2-*thiazines* (**9a**–**h**).—*General procedure.* A suspension of *N*-(arylaminothio)-phthalimide derivative (**7**) (0.7 mmol) in freshly distilled acetone (20–40 ml) [chloroform was used as solvent for compound (**7f**)] was cooled to liquid nitrogen temperature. Butadiene (1.0 g, 18 mmol) and triethylamine (2 ml, 14 mmol) were condensed onto the frozen suspension under high vacuum. This mixture, in a sealed vessel was allowed to warm to 20 °C with stirring. Stirring was continued at 20 °C until the suspension had become a clear yellow solution (3–72 h). Solvent was evaporated and the residue was chromatographed on a silica column (20 × 4 cm) eluting with cyclohexane–dichloromethane (1:1 v/v) to yield the product as a yellow oil which was distilled (Kugelrohr at 150–180 °C, 0.01 mbar*) to afford the 1,2-thiazines (**9a**–**h**) as yellow oils. Spectroscopic data and yields are collated in Table 2. By this method the following compounds were obtained: 2-(4-*methoxyphenyl*)-3,6-*dihydro*-2H-1,2-*thiazine* (**9a**), 2-(4-*methylphenyl*)-3,6-*dihydro*-2H-1,2-*thiazine* (**9b**), 2-*phenyl*-3,6-*dihydro*-2H-1,2-*thiazine*(**9c**),2-(4-*bromophenyl*)-3,6-*dihydro*-2H-1,2-*thiazine* (**9d**), 2-(4-*chlorophenyl*)-3,6-*dihydro*-2H-1,2-*thiazine* (**9e**), 2-(4-*nitrophenyl*)-3,6-*dihydro*-2H-1,2-*thiazine* (**9f**), 2-(1-*naphthyl*)-3,6-*dihydro*-2H-1,2-*thiazine* (**9g**), and 2-(3-*pyridyl*)-3,6-*dihydro*-2H-1,2-*thiazine* (**9h**).

Trapping of Thionitrosoarenes (**8a**–**h**) *with Dimethylbutadiene.—General procedure.* To a stirred suspension of *N*-(arylaminothio)phthalimide derivative (**7**) (0.5 mmol) in freshly distilled acetone (50 ml) [acetone (10 ml) was used for derivative (**7a**) and chloroform (50 ml) was used for derivative (**7f**)] at 20 °C under dry nitrogen, was added, sequentially, dimethylbutadiene (1.0 ml, 9 mmol) and triethylamine (2.0 ml, 14 mmol). Stirring was continued at 20 °C until the suspension became a clear solution (3–72 h) whereupon solvent was removed under reduced pressure and the residue was stirred vigorously with cyclohexane (50 ml) for 0.5 h. Triethylammonium phthalimide which precipitated was filtered off and the filtrate was evaporated to yield an oily product mixture. ^1H NMR analysis of the mixture was carried out at this stage to assess isomer ratios. Separation of the mixtures of adducts (**10**) and (**11**) from minor byproducts (*e.g.* azobenzene derivatives) was achieved by chromatography (silica column, 20 × 4 cm) eluting with cyclohexane–dichloromethane (1:1 v/v) which yielded an inseparable mixture of *adducts* (**10**) *and* (**11**) as yellow oils. Yields and NMR data for the chromatographed isomer mixtures are presented in Table 3. The only single isomer which could be separated was compound (**10a**): Kugelrohr distillation of the mixture of adducts (**10a**) and (**11a**) afforded spectroscopically pure *isomer* (**10a**) as a yellow oil (60 mg, 50%) (Found: C, 65.0; H, 7.2; N, 5.5%; *M*, 235.1041. $C_{13}H_{17}NOS$ requires C, 66.3; H, 7.3; N, 6.0%: *M*, 235.1031); $\delta_H(CDCl_3)$ 7.1–6.75 (4 H, m, Ar), 3.87 (2 H, m, CH_2N), 3.79 (3 H, s, OMe), 2.90 (2 H, m, CH_2S), and 1.71 (6 H, S, 2 × Me); $\delta_C(CDCl_3)$ 154.4, 145.4, 124.8, 124.2, 120.5, 113.9, 55.8 and 55.5 (CH_2N, OMe), 30.2 (CH_2S), 19.8 and 16.9 (both Me).

By this method mixtures of the following compounds were prepared: 2-(4-*methoxyphenyl*)-4,5-*dimethyl*-3,6-*dihydro*-2H-1,2-*thiazine* (**10a**) and N-(4-*methoxyphenyl*)-3-*methyl*-2-*methylenebut*-3-*ene*-1-*sulphenamide* (**11a**), 2-(p-*tolyl*)-4,5-*dimethyl*-3,6-*dihydro*-2H-1,2-*thiazine* (**10b**) and N-(p-*tolyl*)-3-*methyl*-2-*methylenebut*-3-*ene*-1-*sulphenamide* (**11b**), 2-*phenyl*-4,5-*dimethyl*-3,6-*dihydro*-2H-1,2-*thiazine* (**10c**) and N-*phenyl*-3-*methyl*-2-*methylenebut*-3-*ene*-1-*sulphenamide* (**11c**), 2-(4-*bromophenyl*)-4,5-*dimethyl*-3,6-*dihydro*-2H-1,2-*thiazine* (**10d**) and N-(4-*bromophenyl*)-3-*methyl*-2-*methylenebut*-3-*ene*-1-*sulphenamide* (**11d**), 2-(4-*chlorophenyl*)-4,5-*dimethyl*-3,6-*dihydro*-2H-1,2-*thiazine* (**10e**) and N-(4-*chlorophenyl*)-3-*methyl*-2-*methylenebut*-3-*ene*-1-*sulphenamide* (**11e**), 2-(4-*nitrophenyl*)-4,5-*dimethyl*-3,6-*dihydro*-2H-1,2-*thiazine* (**10f**) and N(4-*nitrophenyl*)-3-*methyl*-2-*methylenebut*-3-*ene*-1-*sulphenamide* (**11f**), 2-(1-*naphthyl*)-4,5-*dimethyl*-3,6-*dihydro*-2H-1,2-*thiazine* (**10g**) and N(1-*naphthyl*)-3-*methyl*-2-*methylenebut*-3-*ene*-1-*sulphenamide* (**11g**), and 2-(3-*pyridyl*)-4,5-*dimethyl*-3,6-*dihydro*-1,2-*thiazine* (**10h**) and N-(3-*pyridyl*)-3-*methyl*-2-*methylenebut*-3-*ene*-1-*sulphenamide* (**11h**).

Trapping of Thionitrosoarenes (**8a**), (**8g**), *and* (**8h**) *with Alkenes.—General procedure.* To a stirred suspension of *N*-(arylaminothio)phthalimide derivative (**7**) (0.7 mmol) in acetone (40 ml) was added either isobutene (1.0 g, 18 mmol) and triethylamine (2.0 ml, 14 mmol) (added by vacuum transfer) or α-methylstyrene (1.0 ml, 8 mmol) and triethylamine (2.0 ml, 14 mmol), dropwise at 20 °C. Following the procedure described above for reaction of thionitrosoarenes (**8**) with dimethylbutadiene, the sulphenamides (**12**)–(**16**) were isolated as unstable oils. (Excess of α-methylstyrene was removed under high vacuum). Compounds (**12**) and (**13**) decomposed on attempted distillation *in vacuo* and during column chromatography; compounds (**14**), (**15**), and (**16**) were, however, sufficiently stable to be chromatographed (silica column) but they could not be distilled. Yields and spectroscopic data for sulphenamides (**12**)–(**16**) are presented in Table 4.

By this method the following compounds were obtained: N-(4-*methoxyphenyl*)-2-*methylprop*-2-*ene*-1-*sulphenamide* (**12**), N-(4-*methoxyphenyl*)-2-*phenylprop*-2-*ene*-1-*sulphenamide* (**13**), N-(1-*naphthyl*)-2-*methylprop*-2-*ene*-1-*sulphenamide* (**14**), N-(1-*naphthyl*)-2-*phenylprop*-2-*ene*-1-*sulphenamide* (**15**), and N-(3-*pyridyl*)-2-*phenylprop*-2-*ene*-1-*sulphenamide* (**16**).

Trapping of Thionitrosoarene (**8a**) *with 1,4-Diphenylbutadiene.*—Reaction was carried out under the same conditions, and using the same molar ratios of reagents, as described for the reactions with dimethylbutadiene. Purification by chromatography (silica column) eluting first with cyclohexane to recover unchanged diene and then with cyclohexane–dichloromethane (1:1 v/v) afforded cis-(±)-2-(4-*methoxyphenyl*)-3,6-*diphenyl*-3,6-*dihydro*-2H-1,2-*thiazine* (**19**) (60%) as a white solid, m.p. 71–72 °C (Found: C, 76.2; H, 5.8; N, 3.7%; *M*, 359.1768. $C_{23}H_{21}NOS$ requires C, 76.8; H, 5.9; N, 3.9%, *M*, 359.1344); ν_{max}(KBr) 1 645 (C=C) cm^{-1}; $\delta_H(CDCl_3)$ 7.5–7.1 (14 H, m, Ar), 6.4–6.2 (2 H, m, 2 × =CH), 5.0 (1 H, m, CHN), 4.6 (1 H, m, CHS), and 3.74 (3 H, s, OCH_3); $\delta_C(CDCl_3)$ 155–114 (m), 60.1 (CHN), 55.6 (OCH_3), and 41.2 (CHS).

Trapping of Thionitrosoarenes (**8**) *with* (E,E)- *and* (E,Z)-2,4-*hexadienes* (**17**) *and* (**18**).—*General procedure.* The reaction was carried out, and the product mixtures were purified and analysed, in the same manner as described above for dimethylbutadiene. Obtained from (*E,E*)-hexa-2,4-diene (**17**) were: cis-(±)-2-(4-*methoxyphenyl*)-3,6-*dimethyl*-3,6-*dihydro*-2H-1,2-*thiazine* (**21**) as a white solid, m.p. 26–28 °C (Found: *M*, 235.0996. $C_{13}H_{17}NOS$ requires *M*, 235.1031) and cis-(±)-2-(4-*bromophenyl*)-3,6-*dimethyl*-3,6-*dihydro*-2H-1,2-*thiazine* (**22**) as a yellow oil (Found: *M*, 282.9968. $C_{12}H_{14}BrNS$ requires *M*, 283.0030). Yields and spectroscopic data are recorded in Table 5.

* 1 mbar = 100 Pa.

Obtained from (*E,Z*)-hexa-2,4-diene (**18**) were: trans-(±)-2-(4-*methoxyphenyl*)-3,6-*dimethyl*-3,6-*dihydro*-2H-1,2-*thiazine* (**21**),trans-(±)-2-(4-*bromophenyl*)-3,6-*dimethyl*-3,6-*dihydro*-2H-1,2-*thiazine* (**22**), trans-(±)-2-(p-*tolyl*)-3,6-*dimethyl*-3,6-*dihydro*-2H-1,2-*thiazine* (**23**), and trans-(±)-2-(4-*chlorophenyl*)-3,6-*dimethyl*-3,6-*dihydro*-2H-1,2-*thiazine* (**24**) as yellow oils, each formed together with the corresponding cis enantiomer which arose from reaction of a small amount of (*E,E*)-diene (**17**) present as contaminant in the (*E,Z*)-diene (**18**). Yields and spectroscopic data are recorded in Table 5.

Trapping of Thionitrosoarene (**8a**) *with* 1,1′-*Bicyclopentenyl* (**25**)[34] *and* 1,1′-*Bicyclohexenyl* (**26**).[34]—*General procedure.* The reaction was carried out as described above for dimethylbutadiene reaction. The crude product mixture was chromatographed (silica column, 20 × 4 cm) eluting first with cyclohexane to recover excess of diene, then with cyclohexane–dichloromethane (1:1, v/v) to afford the adduct which was then distilled (Kugelrohr; 180 °C; 0.01 mbar). By this procedure we obtained from bicyclopentenyl (**25**), the adduct cis-(±)-5-(4-*methoxyphenyl*)-1,2,3,3a,5a,6,7,8-*octahydro*-5H-4-*thia*-5-*aza*-as-*indacene* (**27**) (75% yield) as a yellow oil (Found: *M*, 287.1304. $C_{17}H_{21}NOS$ requires *M*, 287.1344); ν_{max}(neat) 1 245 and 1 035 cm^{-1}; $\delta_H(CDCl_3)$ 7.1–6.7 (4 H, m, Ar), 3.7 (4 H, m, CHN and OCH_3), 3.3 (1 H, m, CHS), 2.3 [4 H, m, C(3)–H_2 and C(6)–H_2], and 2.1–1.1 (8 H, 4 × CH_2); $\delta_C(CDCl_3)$ 154.1, 146.9, 137.5, 133.5, 120.1, 114.2, 63.8 (CHN), 55.6 (OCH_3), 40.2 (CHS), 31.1, 30.2, 28.6, 26.2, 23.6, and 19.8.

From bicyclohexenyl (**26**) the adduct cis-(±)-10-(4-*methoxyphenyl*)-1,2,3,4,5,6,7,8,8a,10a-*decahydro*-10H-9-*thia*-10-*aza*-*phenanthrene* (**28**) (75% yield) was obtained as a yellow oil (Found: *M*, 315.1657. $C_{19}H_{25}NOS$ requires *M*, 315.1657); ν_{max}(neat) 1 245 and 1 035 cm^{-1}; $\delta_H(CDCl_3)$ 7.1–6.7 (4 H, m, Ar), 3.76 (3 H, s, OCH_3), 3.6 (1 H, m, CHN), 3.4 (1 H, m, CHS), 2.9 [2 H, m, C(1)–H_2], and 2.2–1.1 (14 H, m, 7 × CH_2); $\delta_C(CDCl_3)$ 154.3, 147.0, 132.8, 129.1, 120.7, 113.7, 63.0 (CHN), 55.3 (OCH_3), 37.5 (CHS), 35.0, 30.7, 28.8, 28.7, 28.1, 26.8, 26.1, and 25.2 ppm.

Preparation of N-*Aryliminosulphur Dichloride Derivatives* (**34**).—*General procedure.* Chlorine gas was bubbled for 1 h through a solution of 4-methoxyaniline or 4-chloroaniline (1 mmol) and freshly distilled sulphur dichloride (0.125 g, 1.2 mmol) in chloroform (20 ml) at 20 °C under dry nitrogen. The resulting solution was evaporated under nitrogen to yield a viscous yellow oil which was very air and moisture sensitive. The products, which were assumed to be compounds (**34a**) and (**34e**), were used immediately.

Reaction of N-*aryliminosulphur dichlorides* (**34a**) *and* (**34e**) *with dimethylbutadiene.* To a stirred solution of freshly prepared compound (**34a**) or (**34e**) (obtained from 1 mmol of amine) in dry acetone (50 ml) under dry nitrogen, was added dimethylbutadiene (20 mmol). The solution was stirred at 20 °C for 48 h by which time the deep orange colour had faded to leave an almost colourless solution which was evaporated to give a residue which was stirred vigorously with cyclohexane (50 ml) and then filtered. The filtrate was evaporated to afford yellow oils (70% yield) identified as mixtures of compounds (**10**) and (**11**), by comparison of the ^1H NMR spectra with those of the mixtures prepared independently from phthalimido precursors (**7a**) and (**7e**). Isomer ratios were assessed at this stage. Thus, compound (**34a**) yielded products (**10a**) and (**11a**) in the ratio 85:15; compound (**34e**) yielded products (**10e**) and (**11e**) in the ratio 45:55.

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