Efficient Generation of Thionitrosoarenes (ArN=S) by Fragmentation of *N*-(Arylaminothio)phthalimides

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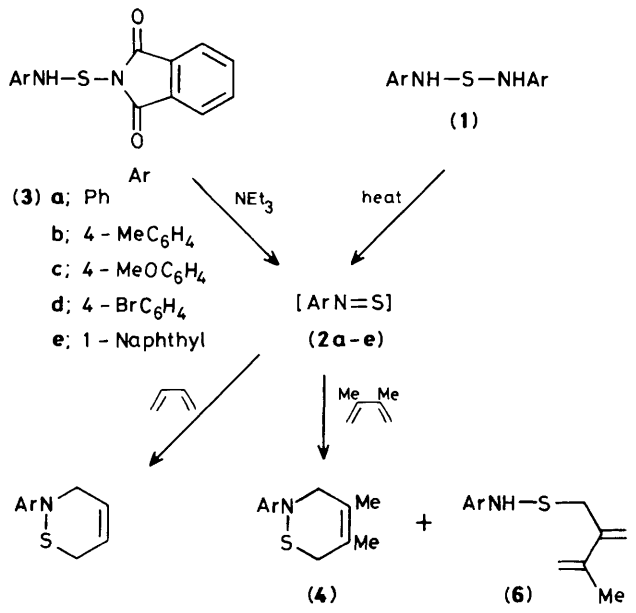
Base-induced fragmentation of a series of *N*-(arylaminothio)phthalimides (**3**) provides an efficient route to transient thionitrosoarenes (**2**); compounds (**2**) have been trapped as Diels–Alder cycloadducts with butadiene and 2,3-dimethylbutadiene, or as ene adducts with alkenes.

Organic thionitroso compounds (RN=S) are known to be highly reactive species; the only isolated derivatives are *N*-(thionitroso)amines, $R_2N–N=S$.[1] Although thionitrosoarenes (**2**) were first generated over 20 years ago from *N*,*N*′-thiobis(arylamine)s (**1**),[2] their chemistry remains virtually unexplored, because there is no general route available for their preparation. More recent routes to RN=S species include generation of thionitrosoalkanes from episulphide *S*,*N*-ylides,[3] production of thionitrosoarenes from 3-azido-2,1-benzisothiazoles,[4] and formation of acyl- and sulphonyl-thionitroso derivatives from tetrachlorothiophene *S*,*N*-ylides.[5] In all these reports,[2—5] the transient thionitroso intermediates were trapped by cycloaddition to butadiene or dimethylbutadiene to yield *N*-substituted 1,2-thiazines. In the absence of trap, the thionitroso compounds dimerise with loss of sulphur to yield sulphurdiimides, RN=S=NR, or diazo compounds.

We now report that thionitrosoarenes (**2**) can be generated efficiently under very mild conditions from *N*-(arylaminothio)phthalimides (**3**). Compounds (**3**) are by far the most convenient precursors of thionitroso compounds reported to date: they are air- and moisture-stable solids that have a shelf-life of several months at room temperature, without any observable decomposition. The markedly greater stability of compounds (**3**) than of compounds (**1**) (which are thermally unstable and difficult to purify) is due to N- - -H- - -O hydrogen bonding that occurs in the phthalimido series (**3**) (i.r. evidence). Compounds (**3**) are prepared from the reaction of the trimethylsilyl derivative of the appropriate arylamine with *N*-(chlorothio)phthalimide (1 equiv.; dry $CHCl_3$; 0 °C); the precipitate formed is analytically pure (**3**) (85—90% yield).

Fragmentation of compounds (**3**) occurs smoothly on stirring with triethylamine in acetone at room temperature. The thionitrosoarenes (**2**) thus formed have been trapped efficiently by 2,3-dimethylbutadiene and butadiene (10-fold excess of diene) in Diels–Alder reactions to yield 1,2-thiazine derivatives (**4**) and (**5**), respectively. When the trap is dimethylbutadiene, the ene reaction competes with the cycloaddition reaction, affording, in all cases, ene adducts (**6a**—**e**) alongside the 4,5-dimethyl-1,2-thiazines (**4a**—**e**). Similar ene addition has been observed with the highly electron-deficient acyl-thionitroso compounds,[5] but ene addition has not been observed previously for thionitrosoarenes. Indeed the ene product (**6d**) predominates significantly over the Diels-Alder product (**4d**) in the case of the most electron-deficient thionitrosobenzene derivative (**2d**) that we have studied. The most electron-rich derivative (**2c**) gave a high ratio of Diels-Alder to ene adduct [(**4c**) : (**6c**)] with dimethylbutadiene. The slight predominance of ene product (**6e**) over cycloadduct (**4e**) from 1-thionitrosonaphthalene (**2e**) may be due to the bulk of the naphthyl group. Ene reactions of 1-methoxy-4-thionitrosobenzene (**2c**) proceed cleanly with alkenes (**7a** and **b**) to yield the products (**8a** and **b**), respectively.

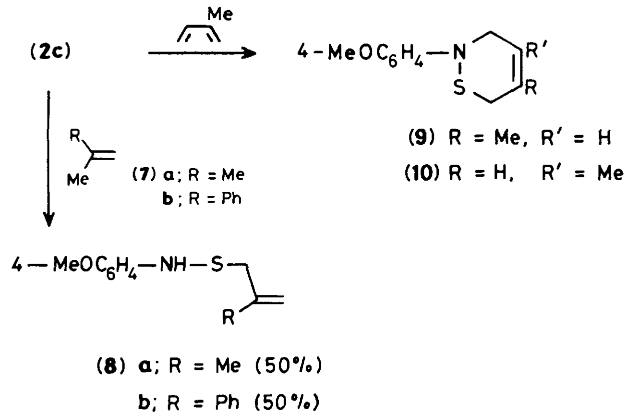
Acyl- and sulphonyl-thionitroso compounds show no regioselectivity when trapped with isoprene.[5] In contrast to this, 1-methoxy-2-thionitrosobenzene (**2c**) reacts with iso-



	Yield[a]
(5) a	65%
b	75%
c	65%
d	75%
e	55%

Ratio of products[b]	(4)	(6)
a	55	45
b	60	40
c	85[c]	15
d	25	75
e	45	55

Scheme 1. [a] Isolated yields: crude product was purified by chromatography on a silica column [eluant dichloromethane–cyclohexane (1 : 1)] then vacuum-distilled. [b] Based on ^{1}H n.m.r. spectra of crude reaction product [>80% conversion for all reactions (**3**) → (**4**) + (**6**)]. [c] Yield of isolated (**4c**) was 65% after separation by distillation from (**6c**).



Scheme 2

prene to give the thiazines (**9**) and (**10**) in 3 : 1 isomer ratio, as judged by ^{1}H n.m.r. spectroscopy of the crude reaction mixture. This observed ratio may be due solely to steric factors controlling the orientation of the diene during the addition reaction.

In conclusion, a highly efficient route to thiontrosoarenes, and hence to the 1,2-thiazine ring system, is now available from crystalline, shelf-stable precursors.

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