J. CHEM. SOC., CHEM. COMMUN., 1988

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## 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),<sup>2</sup> 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,<sup>3</sup> production of thionitrosoarenes from 3-azido-2,1-benzisothiazoles,4 and formation of acyl- and sulphonylthionitroso derivatives from tetrachlorothiophene S,Nylides.<sup>5</sup> In all these reports,<sup>2-5</sup> 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 - - Ohydrogen 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.<sup>5</sup> In contrast to this, 1-methoxy-2-thionitrosobenzene (2c) reacts with iso-

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



prene to give the thiazines (9) and (10) in 3:1 isomer ratio, as judged by <sup>1</sup>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.

We thank S.E.R.C. for financial support (to P. C. T).

Received, 10th March 1988; Com. 8/00985F

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