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Preparation and Reactions of Aminosulphenyl Chlorides R₂NSCl

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Summary Aminosulphenyl chlorides have been prepared from diamino-sulphides by use of sulphur dichloride and benzenesulphenyl chloride; they are orange, pungent, unstable liquids which have been used to synthesise the three new classes of sulphur-nitrogen compound, $R_2NSN=S=O$ [dialkylcatenadi(azathian)-3-ene 4-oxide], Me₂-NSNRSNMe₂ (3-alkyl-1,1,5,5-tetramethyltriazathiane), and $R_2^1NSSR^2$ (S-dialkylamino S'-alkyl disulphide).

AMINOSULPHENYL CHLORIDES can be synthesised directly from a secondary amine and sulphur dichloride,¹ by cleaving the sulphur-sulphur bond of a diamino-disulphide with chlorine,² or from benzoyl chloride and a diamino-sulphide. All these routes have their particular drawbacks, along with the general one that the products readily decompose, and so have to be quickly extracted and used.

Dialkylaminosulphenyl chlorides result in ca. 90% yield as the only product from the exothermic reaction of diamino-sulphides and sulphur dichloride [reaction (1)].

$$(R_2N)_2S + SCl_2 \rightarrow 2 R_2NSCl R = Me, Et, Pr^n, or Pr^i$$
 (1)

They are pungent, orange liquids that can be readily distilled under vacuum, but which visibly decompose within 1 h even if sealed in ampoules and kept in the dark. Cooling, or the introduction of bulky substituents, appears to reduce decomposition; thus Me₂NSCl can be kept at -20 °C for several months without apparent decomposition, while Pri₂NSCl is stable at room temperature for similar periods in the absence of direct sunlight.

This exchange between amino-groups and chlorine can be used to synthesise sulphenamides. Benzenesulphenyl chloride and diamino-sulphides react exothermically to yield the aminosulphenyl chloride and the sulphenamide [reaction (2)]. Symmetrical diamino-sulphides readily $(R_2N)_2S + PhSCl \rightarrow R_2NSCl + PhSNR_2 \quad R = Me \text{ or Et } (2)$ form from aminosulphenyl chlorides and aminosilanes [reaction (3)], but attempts to prepare unsymmetrical diamino-sulphides by the same method result in the $R_2NSCl + R_2NSiMe_3 \rightarrow (R_2N)_2S + Me_3SiCl \quad R = Me \text{ or Et } (3)$

isolation of only the two symmetrical products, along with

the chlorosilane [reactions (4) and (5)].

2 Me₂NSCl +2
$$(N-SiMe_3)$$

2 Me₃SiCl + (Me₂N)₂ S + $(N-S-N)$ (4)

2
$$Et_2NSCl + 2 R_2NSiMe_3$$

2 $Me_3SiCl + (Et_2N)_2S + (R_2N)_2S$ (R = Me or Prⁿ) (5)

With N-trimethylsilylsulphinylamine, the di(azathian)-3-ene 4-oxide readily forms [reaction (6)]. These are yellow liquids which, in contrast to the aminosulphenyl chlorides and unsymmetrical diamino-sulphides, do not readily decompose on warming, nor in sunlight, and provide an example of a class of compound containing sulphur in two oxidation states.

$$Me_3SiNSO + R_2NSCl \rightarrow Me_3SiCl + R_2NSN = S = O$$
 (6)

Aminosulphenyl chlorides react with disilazanes and cleavage of both Si-N bonds yields triazadithianes containing the N-S-N-S-N skeleton [reaction (7)]. These are lemonyellow distillable liquids which appear to dissociate on heating into the diamino-sulphide.

$$\begin{array}{l} (\mathrm{Me_{3}Si})_{2}\mathrm{NR} + 2\mathrm{Me_{2}NSCl} \rightarrow \mathrm{Me_{2}NSNRSNMe_{2}} \\ + 2\mathrm{Me_{3}SiCl} \quad \mathrm{R} = \mathrm{Me} \ \mathrm{or} \ \mathrm{Et} \end{array} \tag{7}$$

S-Amino-S'-alkyl and S-amino-S'-aryl disulphides are conveniently synthesised from thiosilanes and the aminosulphenyl chloride (reaction (8)]. These readily distillable

$$\begin{aligned} \mathrm{R}^{1}{}_{2}\mathrm{NSCl} + \mathrm{M}\mathrm{e}_{3}\mathrm{SiSR}^{2} &\rightarrow \mathrm{M}\mathrm{e}_{3}\mathrm{SiCl} + \mathrm{R}^{1}{}_{2}\mathrm{NSSR}^{2} \\ \mathrm{R}^{1} &= \mathrm{alkyl}, \ \mathrm{R}^{2} &= \mathrm{alkyl} \ \mathrm{or} \ \mathrm{aryl} \end{aligned} \tag{8}$$

liquids appear more stable than perhaps would be expected for while amino-disulphides and organic polysulphides readily lose sulphur in the presence of base,3 and while sulphenamides can be readily transaminated,⁴ S-dimethylamino S'-phenyl disulphide can be recovered in high yield after heating under reflux with diethylamine for 36 h.

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¹G. Weiss and G. Schulze, Ger. Pat. 1,131,222/1962 from W. H. Mueller and P. E. Butler, *J. Org. Chem.*, 1968, **33**, 2111. ²Houben-Weyl, 'Methoden der Organischen Chemie, XI/2, Stickstoff Verbingdungen III', Georg Thieme Verlag, 1958, pp. 745 and 746.
³ E. E. Reid, 'Organic Chemistry of Bivalent Sulphur', Chemical Publishing Co., New York, 1960, vol. 3, 391.
⁴ D. A. Armitage, M. J. Clark, and A. M. White, J. Chem. Soc. (C), 1971, 3141.