Some Reductions of Sulphur–Nitrogen–Chloride Compounds to give Tetrasulphur Tetranitride

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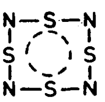
Tetrasulphur tetranitride is conveniently prepared by the reduction of cyclotetrathiatriazenium chloride or trichlorocyclotrithiatriazene with iron. Other new routes to tetrasulphur tetranitride, bis(tetrasulphur tetranitride)tin(IV) chloride, tetrathiotetraimide, and cyclopentathiapentazenium tetrachloroferrate(III) are also discussed.

WE have found that it is possible to produce tetrasulphur tetranitride (1) by the reduction of cyclotetrathiatriazenium chloride (S_4N_3Cl) (2), trichlorocyclotrithiatriazene $(NSCl)_3$ (3), chlorocyclotrithiadiazenium chloride ($S_3N_2Cl_2$) (4), or cyclotrithiadiazenium chloride (S_3N_2Cl) (5) using a variety of reducing agents. In comparison with the standard preparation of tetrasulphur tetranitride,[1] our syntheses, particularly the iron reductions of cyclotetrathiatriazenium chloride and of trichlorotrithiatriazene, offer quicker and more convenient routes. New routes to tetrasulphur tetranitride are of importance since it is one of the most valuable starting materials for preparing other inorganic (and some organic) sulphur–nitrogen compounds. In the course of these studies we have also found new syntheses of bis(tetrasulphur tetranitride)tin(IV) chloride $[SnCl_4(S_4N_4)_2]$,[2] tetrathiotetraimide $[S_4(NH)_4]$ (6),[3] and cyclopentathiapentazenium tetrachloroferrate(III) $\{[S_5N_5][FeCl_4]\}$ (7)[4] which avoid the isolation of potentially explosive tetrasulphur tetranitride.[5]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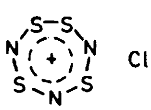
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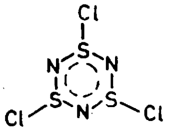
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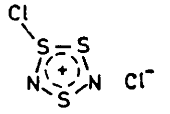
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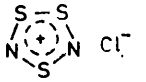
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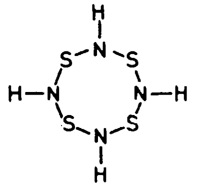
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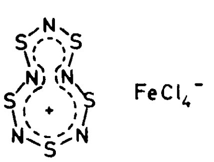
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More systematic names (based on 'Nomenclature of Organic Chemistry,' IUPAC, Pergamon Press, Oxford, 1979, section D): (1) cyclotetra-azathiene; (2) cyclo-3,5,7-triaza-1,2,4,6-tetrathienium chloride; (3) 1,3,5-trichlorocyclotriazathiene; (4) 1-chlorocyclo-3,5-diaza-1,2,4-trithienium chloride; (5) cyclo-3,5-diaza-1,2,4-trithienium chloride; (6) cyclotetra-azathiane; and (7) cyclopenta-azathienium tetrachloroferrate(III).

EXPERIMENTAL

Infrared spectra of Nujol mulls prepared under nitrogen were recorded on a Perkin-Elmer 457 (250—4 000 cm^{-1}) grating diffraction spectrometer. Benzene, dioxan, and diethyl ether were dried over sodium wire. Monoglyme (1,2-dimethoxyethane) was refluxed over potassium and purified by distillation. Methanol was refluxed over magnesium wire and purified by distillation. Carbon tetrachloride was dried over phosphorus pentaoxide and purified by distillation. Nitromethane was dried over phosphorus pentaoxide and purified twice by distillation. Thionyl chloride was purified by fractional distillation from triphenyl phosphite.[6] Chlorocyclotrithiadiazenium chloride, cyclotrithiadiazenium chloride, and cyclotetrathiatriazenium chloride were prepared by the methods of Jolly and Villena-Blanco,[1] and trichlorocyclotrithiatriazene was prepared by the action of sulphuryl chloride on chlorocyclotrithiadiazenium chloride.[7] Iron turnings were taken from a bar of mild steel. Tin(IV) chloride was purified by vacuum distillation. Sodium thiocyanate and sodium iodide were dried by heating *in vacuo*, and other reagents were commercial materials as supplied. Thin-layer chromatography separations were carried out using silica-coated glass plates (20 × 10 cm) eluted with carbon disulphide. Tetrasulphur tetranitride,[1] bis(tetrasulphur tetranitride)tin(IV) chloride,[2] tetrasulphur tetraimide,[8] and cyclopentathiapentazenium tetrachloroferrate(III)[4] were characterized by their i.r. spectra.

1. *Reductions of Cyclotetrathiatriazenium Chloride*.—(*i*) A mixture of cyclotetrathiatriazenium chloride (5.0 g, 24 mmol) and iron turnings (1.5 g, 27 mmol) was stirred (1.5 h) in refluxing nitromethane (100 cm^3) to give a clear red solution. This was filtered while hot (G1 sinter); crude tetrasulphur tetranitride crystallized out on cooling. The filtered product was extracted (carbon tetrachloride, 50 cm^3) and recrystallized (benzene, 50 cm^3) to give 1.86 g tetrasulphur tetranitride. Yield 55% (Found: N, 29.6. Calc. for S_4N_4: N, 30.4%).

(*ii*) A mixture of cyclotetrathiatriazenium chloride (1.0 g, 4.9 mmol) and sodium thiocyanate (0.50 g, 6.2 mmol) was stirred (1 h) in refluxing monoglyme (30 cm^3). After cooling, the orange product was filtered and extracted (carbon tetrachloride, 30 cm^3) to give 0.22 g tetrasulphur tetranitride. Yield 33% (Found: N, 29.5%).

2. *Reduction of Trichlorocyclotrithiatriazene by Iron*.—A

mixture of trichlorocyclotrithiatriazene (7.0 g, 27 mmol) and iron turnings (2.5 g, 45 mmol) was stirred (1 h) in monoglyme (40 cm^3). An exothermic reaction occurred and thin-layer chromatography showed the cyclotetrathiatriazenium cation, tetrasulphur tetranitride, and tetrasulphur dinitride to be present. The mixture was refluxed (1 h), cooled, and the monoglyme evaporated under reduced pressure. Tetrasulphur tetranitride was extracted (carbon tetrachloride, 50 cm^3) from the crude product, and recrystallized (benzene, 65 cm^3) to give 2.65 g. Yield 67% (Found: N, 29.5%).

3. *Reduction of Chlorocyclotrithiadiazenium Chloride by Iron.*—A mixture of chlorocyclotrithiadiazenium chloride (7.0 g, 36 mmol) and iron turnings (2.5 g, 45 mmol) was stirred (6 h) in refluxing nitromethane (40 cm^3). The intermediate green and yellow colours indicated that the reaction probably proceeded *via* cyclotrithiadiazenium chloride and then cyclotetrathiatriazenium chloride and/or cyclotetrathiatriazenium tetrachloroferrate(III). (Similar colour changes were observed by Jolly *et al.*[9] in the reaction $S_3N_2Cl_2 \rightarrow S_4N_3Cl$.) After cooling and evaporation of the nitromethane under reduced pressure, the resultant solid was extracted (carbon tetrachloride, 50 cm^3) to give 0.60 g tetrasulphur tetranitride (yield 18%) and a residue of cyclotetrathiatriazenium tetrachloroferrate(III) which was the main product. It was characterized by its i.r. spectrum.[10]

4. *Reductions of Cyclotrithiadiazenium Chloride.*—(*i*) A mixture of cyclotrithiadiazenium chloride (6.0 g, 38 mmol) and anhydrous sodium iodide (8.45 g, 57 mmol) was stirred (1.5 h) in dry methanol (30 cm^3) at 0 °C. Anhydrous sodium thiosulphate (8.9 g, 57 mmol) in dry methanol (30 cm^3) was added to remove liberated iodine and the mixture was stirred (18 h). The filtered yellow-green product was extracted with 1,4-dioxan to give a mixture (1.8 g) which analysed as 66% tetrasulphur tetranitride and 34% sulphur by weight.

(*ii*) A mixture of cyclotrithiadiazenium chloride (4.4 g, 28 mmol) and sodium metabisulphite (8.1 g, 43 mmol) was stirred (2 h) in refluxing nitromethane (40 cm^3). The mixture was cooled and the filtered product was extracted (carbon tetrachloride, 50 cm^3) and recrystallized (benzene, 25 cm^3) to give 1.05 g tetrasulphur tetranitride. Yield 41% (Found: N, 29.4%).

(*iii*) A mixture of cyclotrithiadiazenium chloride (1.67 g, 11 mmol) and iron turnings (0.6 g, 11 mmol) was stirred (2 h) in refluxing nitromethane (30 cm^3). The mixture was cooled, filtered, and the resultant brown solid extracted (carbon tetrachloride, 30 cm^3) to give 0.25 g tetrasulphur tetranitride. Yield 26%.

5. *Preparation of Cyclopentathiapentazenium Tetrachloroferrate*(III).—A mixture of trichlorocyclotrithiatriazene (6.0 g, 25 mmol) and iron turnings (2.5 g, 45 mmol) was stirred (18 h) in nitromethane (25 cm^3). The nitromethane was evaporated to low bulk, and the yellow product filtered and extracted (thionyl chloride, 50 cm^3). Recrystallization from thionyl chloride gave 2.62 g cyclopentathiapentazenium tetrachloroferrate(III). Yield 42%. It was characterised by its i.r. spectrum and melting point.[4]

6. *Preparation of Bis*(*tetrasulphur tetranitride*)*tin*(IV) *Chloride.*—A mixture of cyclotetrathiatriazenium chloride (2.2 g, 11 mmol) and iron turnings (0.7 g, 12.5 mmol) was stirred (1.5 h) in refluxing nitromethane (50 cm^3) to give a clear red solution. This was filtered hot (G1 sinter) and after cooling tin(IV) chloride (0.9 cm^3, 2.0 g, 7.7 mmol) was added. The mixture was stirred (18 h) and filtered to give a purple powder which was washed with 1,4-dioxan (50 cm^3) and diethyl ether (50 cm^3) [Found: Cl, 21.8; N, 17.25; S, 41.25. Calc. for $SnCl_4(S_4N_4)_2$: Cl, 22.55; N, 17.8; S, 10.75%]. Yield 1.6 g, 63% based on equations (1) and (2).

$$4S_4N_3Cl + 2Fe \longrightarrow \tfrac{1}{2}S_8 + 3S_4N_4 + 2FeCl_2 \qquad (1)$$

$$2S_4N_4 + SnCl_4 \longrightarrow SnCl_4(S_4N_4)_2 \qquad (2)$$

7. *Preparation of Tetrasulphur Tetraimide from Bis*(*tetrasulphur tetranitride*)*tin*(IV) *Chloride.*—Tin(II) chloride, $SnCl_2{\cdot}2H_2O$ (6.0 g, 26.5 mmol), in methanol–water (8 : 1 v/v) was added rapidly with vigorous stirring to $SnCl_4(S_4N_4)_2$ (2.6 g, 4.1 mmol) in refluxing dry benzene (40 cm^3). After 30 min the mixture was filtered at 0 °C to give a pinkish white sample of crude $S_4(NH)_4$. Yield 0.5 g. The crude solid was purified by recrystallization from nitromethane.

Tetrathiotetraimide can also be prepared from cyclotetrathiazenium chloride in a two stage synthesis [equations (3) and (4)]. This combines a reduction (experiment 1 above)

$$S_4N_3Cl \xrightarrow{Fe} S_4N_4 \qquad (3)$$

$$S_4N_4 \xrightarrow{SnCl_2{\cdot}2H_2O} S_4(NH)_4 \qquad (4)$$

with the usual method[3] of converting tetrasulphur tetranitride to tetrathiotetraimide.

DISCUSSION

Padma and Vasudeva Murthy[11] have shown that vigorous reduction of cyclotetrathiatriazenium chloride gives ammonia and hydrogen sulphide and so in our search for new routes to tetrasulphur tetranitride we investigated reductions under milder conditions.

Many reduction reactions of sulphur–nitrogen–halogen compounds in non-aqueous solvents were studied, including cyclotetrathiatriazenium chloride with titanium (1 : 2), sodium oxalate (2 : 1), oxalic acid (3 : 2), sodium thiosulphate (1 : 2), sodium (1 : 1), magnesium (1 : 1) and chlorocyclotrithiadiazenium chloride with zinc (1 : 1) and phenyl-lithium (1 : 1). All these reactions gave tetrasulphur tetranitride; but the syntheses described in the Experimental section gave highest yields and purity.

We have investigated a variety of solvents in an attempt to find a less toxic recrystallization solvent than benzene, but without great success. The difficulties of purifying tetrasulphur tetranitride are well known. Indeed, for some purposes it is necessary to recrystallize several times from benzene and then sublime the product.[12] An alternative is to purify by column chromatography. Unfortunately this method is laborious, but under ideal conditions[13] the recovery of S_4N_4 is good. However, our product is sufficiently pure for most purposes. In view of this, and of the explosive nature of pure tetrasulphur tetranitride,[5] our recommended procedures include only one recrystallization (and quoted analyses are consequently low in nitrogen due to the presence of S_8).

Comparing the numerous methods of preparation, the highest yields (based on nitrogen content) of recrystallized tetrasulphur tetranitride produced from chlorocyclotrithiadiazenium chloride were obtained as in methods (5) and (6). Procedure (6) provides the best

$$3S_3N_2Cl_2 + 3SO_2Cl_2 \longrightarrow 2(NSCl)_3 + 3SCl_2 + 3SO_2\ (90\%)$$

$$4(NSCl)_3 \xrightarrow{Fe} 3S_4N_4\ (67\%) \qquad (5)$$

$$3S_3N_2Cl_2 + S_2Cl_2 \longrightarrow 2S_4N_3Cl + 3SCl_2\ (55\%)$$

$$4S_4N_3Cl \xrightarrow{Fe} 3S_4N_4\ (55\%) \qquad (6)$$

route to $SnCl_4(S_4N_4)_2$ since the (clear red) S_4N_4 solution can be used directly after decantation from the residual iron. The overall yield of adduct from chlorocyclotrithiadiazenium chloride was 35% based on nitrogen.

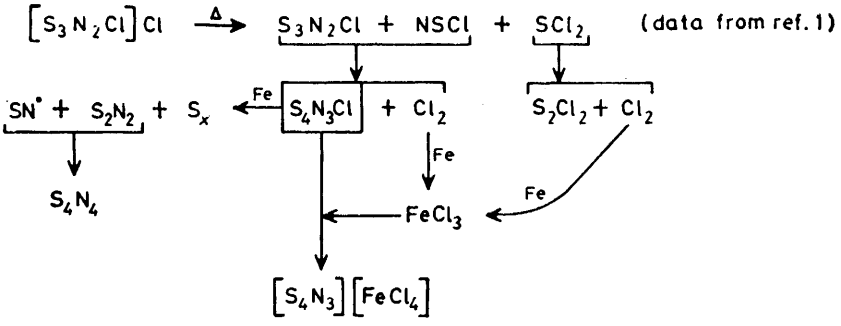
The difference between the reaction of trichlorocyclotrithiatriazene with iron in monoglyme and in nitromethane is striking. In the first case, tetrasulphur tetranitride is produced in high yield and is easily isolated, the other main product analyses as an impure 1 : 1 monoglyme complex with iron(III) chloride. In nitromethane, cyclopentathiapentazenium tetrachloroferrate(III) is the main product. It is most likely that this reaction proceeds as described earlier,[14,15] *i.e.* tetrasulphur tetranitride (produced by reduction) reacts with residual trichlorocyclotrithiatriazene [probably as a reactive adduct with the iron(III) chloride formed in the reduction], see equations (7) and (8). The latter adduct

$$4(NSCl)_3 + 4Fe \longrightarrow 3S_4N_4 + 4FeCl_3 \qquad (7)$$

$$(NSCl)_3 + 3FeCl_3 \longrightarrow (NSCl)_3{\cdot}2FeCl_3 + FeCl_3 \qquad (8)$$

and iron(III) chloride mixture reacts as if it were $[NS][FeCl_4]$ according to equation (9).[16]

$$[NS][FeCl_4] + S_4N_4 \longrightarrow [S_5N_5][FeCl_4] \qquad (9)$$



SCHEME 1

The reduction of chlorocyclotrithiadiazenium chloride in nitromethane with iron or zinc (to give largely cyclotetrathiatriazenium salt and some tetrasulphur tetranitride) may be understood by reference to Scheme 1. This reaction scheme is probably much oversimplified (*e.g.* there are likely to be numerous other species involved); other plausible mechanisms no doubt exist.

The S_4N_3Cl–Fe system was studied in different solvents and conditions and products examined using t.l.c. and i.r. spectroscopy. These studies indicated that the S_4N_3Cl reduction systems were complex, producing S_4N_4, S_4N_2, S_8, and, with moisture present, smaller quantities of S_7NH and other imides.

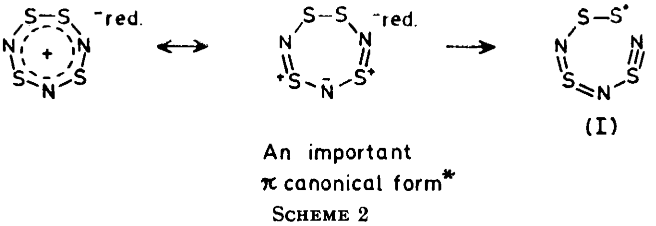
In view of the stability of sulphur–nitrogen free radicals (*e.g.* $S_2N_2^{+}$)[17] the reductions of S_4N_3Cl may well proceed *via* such species, which recombine to form the compounds observed.

For reactions of S_4N_3Cl with reducing anions *e.g.* NCS^- metathesis is probably the first reaction step (to maximize lattice energies) [equation (10)]. The solubility of

$$[S_4N_3]Cl + Na^+\ red.^- \longrightarrow Na^+Cl^- + [S_4N_3][red.] \qquad (10)$$

S_4N_3Cl, hence the rate of exchange, is favoured by use of a high polarity solvent such as nitromethane. The intermediate $[S_4N_3][red.]$ is then likely to rearrange (electron transfer) to form radical species, *e.g.* $S_4N_3^{\bullet}$.

Svenningsen and Hazell[18] have shown that the lowest unoccupied molecular orbital (l.u.m.o.) in $S_4N_3^+$ is antibonding with respect to the bonds from disulphide S to N, and bonding with respect to S–S. Thus, a likely bond scission on reduction of $S_4N_3^+$ is that in Scheme 2.



(I)

SCHEME 2

The breakdown into smaller sulphur and sulphur–nitrogen radicals, and subsequent recombination, would rationalise formation of a wide variety of products. The formation of S_7NH (in undried solvents) can also be explained by protonation of the terminal nitrogen of the radical species (I).

In the case of the S_4N_3Cl–Fe reaction, metallic iron is

*An all-valence-electron SCF molecular orbital treatment (D. B. Adams, A. J. Banister, D. T. Clark, and D. Kilcast, *Internat. J. Sulphur Chem. A*, 1971, **1**, 143) and CNDO/2 calculations (J. A. Durrant, Ph.D. Thesis, University of Durham, 1977) show that the lower sulphur atoms bear a high positive charge.

probably oxidised to iron(II) chloride during the reaction. A free-radical mechanism again explains the formation of other products S_4N_2 and S_8, and why the yield of S_4N_4 is not quantitative (50—60%).

Thus, these studies have given two new convenient routes to tetrasulphur tetranitride, of value for both small and large scale preparations, and a simpler route to cyclopentathiapentazenium salts.

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