

Preparation of some 1,2,3,5-Dithiadiazolium Chlorides from Trichlorocyclotrithiazene and Nitriles or Olefins, and from Amidinium Salts and Sulphur Dichloride

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1,2,3,5-Dithiadiazolium chlorides $[\text{RCN}_2\text{S}_2]\text{Cl}$ have been prepared by treating trichlorocyclotrithiazene [trithiazyl trichloride $(\text{NSCl})_3$] with (i) tetrachloroethylene to give $[\text{Cl}_3\text{C}\cdot\text{CN}_2\text{S}_2]\text{Cl}$ or (ii) nitriles RCN ($\text{R} = \text{Cl}_3\text{C}$ and Ph). 4-Phenyl-1,2,3,5-dithiadiazolium chloride has also been prepared from the amidinium salt $[\text{PhC}(\text{NH}_2)_2]\text{Cl}$ and sulphur dichloride. Structures and possible mechanisms of formation are discussed.

TRICHLOROCYCLOTRITHIAZENE [trithiazyl trichloride, $(\text{NSCl})_3$], which is a useful reagent for preparing inorganic and organic sulphur-nitrogen heterocycles,¹ has been shown² to react with *t*-butyronitrile to give the 1,2,3,5-dithiadiazolium chloride $[\text{Bu}^t\text{CN}_2\text{S}_2]\text{Cl}$. We now describe reactions with nitriles CCl_3CN and PhCN and the formation of the products $[\text{RCN}_2\text{S}_2]\text{Cl}$ ($\text{R} = \text{CCl}_3$ and Ph) by three other methods: (i) $(\text{NSCl})_3 + \text{C}_2\text{Cl}_4$ (to give a mixture of sulphur-nitrogen compounds which include 4-trichloromethyl-1,2,3,5-dithiadiazolium chloride); (ii) $\text{RCN} + \text{NH}_4^+$ salt + SCl_2 ; (iii) $\text{PhC}(\text{NH}_2)_2^+$ salt + SCl_2 .

As found for other dithiolium halides,³ the 'ionic' chlorine in $[\text{Cl}_3\text{C}\cdot\text{CN}_2\text{S}_2]^+\text{Cl}^-$ occupies a bridge position equidistant from the two sulphur atoms of the disulphide group.⁴ The reactions of these compounds are characteristic of ionic dithiadiazolium compounds rather than sulphenyl chlorides.

EXPERIMENTAL

I.r. spectra ($250\text{--}4000\text{ cm}^{-1}$), for Nujol mulls prepared under nitrogen, were recorded using KBr plates and a Perkin-Elmer 457 prism grating spectrophotometer. Mass spectra were obtained on an A.E.I. MS9 mass spectrometer at 70 eV with an accelerating potential of 8 keV.† Solvents and liquid reagents were purified as follows: benzene (stored over sodium wire for several days and distilled), antimony pentachloride (purified by distillation), and carbon tetrachloride and methylene dichloride (distillation and stored over P_2O_5). The nitriles (CCl_3CN and PhCN), tetrachloroethylene, nitrobenzene, and cyclohexene oxide were dried over magnesium sulphate, fractionally distilled, and stored over fresh magnesium sulphate. Sulphur dichloride was purified⁵ by fractional distillation; the middle fraction, b.p. $50\text{--}62^\circ$, was retained and refracted (collected at b.p. 60°). Thionyl chloride was fractionally distilled from triphenyl phosphite.⁶

Ammonium chloride and benzamidinium chloride were dried in an oven at 120°C . Trichlorocyclotrithiazene was obtained⁷ from $\text{S}_3\text{N}_2\text{Cl}_2$ and sulphuryl chloride. Products were manipulated under nitrogen. Carbon analyses were obtained using a Perkin-Elmer 240 Elemental Analyzer. Nitrogen was analysed by the standard micro-Kjeldahl method. In the analysis for (i) chlorine and (ii) sulphur, oxygen flask combustion was followed by (i) potentiometric titration of chloride ion with 0.01M-silver nitrate solution and, with a separate portion, (ii) titration against 0.01M-

barium perchlorate solution using Sulphonazo III as indicator.⁸

4-Trichloromethyl-1,2,3,5-dithiadiazolium Chloride.—(i) From $(\text{NSCl})_3$ and C_2Cl_4 . Trichlorocyclotrithiazene (4.7 g) was added to tetrachloroethylene (19 ml) and heated ($60\text{--}80^\circ\text{C}$) under nitrogen with stirring. On warming, the solution first turned green, then dark brown, and finally deep orange-red with orange-red crystals of $\text{S}_3\text{N}_2\text{Cl}_2$ (characterised from their i.r. spectrum⁹) forming in the condenser; these were discarded. After complete reaction (*ca.* 48 h), the mixture was chilled to 0°C and filtered. The product (2.5 g) was recrystallised twice from thionyl chloride (25 ml g^{-1}) to give orange plates [1.0 g, 13% yield based on $(\text{NSCl})_3$] of 4-trichloromethyl-1,2,3,5-dithiadiazolium chloride (Found: C, 9.2; Cl, 54.5; N, 10.6; S, 24.5. $\text{C}_2\text{Cl}_4\text{N}_2\text{S}_2$ requires C, 9.4; Cl, 54.7; N, 10.9; S, 25.0%). The product hydrolysed in the atmosphere to a powder. I.r. absorptions were as for the $(\text{NSCl})_3\text{-CCl}_3\text{CN}$ product, but repeated crystallisations were sometimes necessary to eliminate contamination which gave additional characteristic peaks at 1116s, 1100s, 1000m, 878m, 781s, 708w, and 620wbr cm^{-1} . The main features of the mass spectrum at 150°C were closely similar to those recorded in (ii) below.

(ii) From $(\text{NSCl})_3$ and CCl_3CN . Trichlorocyclotrithiazene (2.4 g) was dissolved in trichloroacetonitrile (20 ml) and stirred (24 h) under reflux. The initial green solution turned claret after *ca.* 1 h and began to deposit crystals. The product (3.1 g) was filtered from a cold solution and recrystallised twice from thionyl chloride (25 ml g^{-1}) to give product [1.7 g, 42% yield based on $(\text{NSCl})_3$], m.p. $221\text{--}222^\circ$; ν_{max} 1280w, 1075w, 1055s, 1024w,sh, 911w, 861s, 827s,sh, 818vs, 796vs, 765m, 678vs, 673w,sh, 548s, 542w,sh, and 520w cm^{-1} ; λ_{max} [CH_3CN (dried spectroscopic grade)] 228 (ϵ 7550) and *ca.* 262sh nm (2315). Solutions decompose quite quickly. Mass spectrum peaks at 200°C (relative intensity) were: $\text{C}_2\text{Cl}_3\text{N}_2\text{S}_2$, 225(5), 223(14), 221(13); $\text{C}_2\text{Cl}_2\text{N}_2\text{S}_2$, 190(16), 188(73), 186(100); $\text{C}_2\text{Cl}_2\text{NS}$ 142(14), 140(21); CCl_3 , 121(4), 119(11), 117(11); $\text{C}_2\text{Cl}_2\text{N}$, 110(8), 108(13); CCl_2 , 84(13), 82(9); NS_2 , 78(39); CS_2 76(55); S_2 , 64(88); C_2N_2 , 52(44); SN , 46(50).

(iii) From NH_4Cl , SCl_2 , and CCl_3CN . To a round-bottomed flask with reflux condenser was added ammonium chloride (10.7 g, 0.20 mol), sulphur dichloride (25.4 ml, 0.40 mol), trichloroacetonitrile (20.2 ml, 0.20 mol), and nitrobenzene (50 ml). The mixture, under chlorine, was heated in an oil-bath at 120°C for 5 h. The hot solution was decanted and the crude $\text{C}_2\text{Cl}_4\text{N}_2\text{S}_2$ crystallised out on cooling to 0°C . It was recrystallised from benzene (15.5 g, 30% yield based on CCl_3CN). The atmosphere of chlorine is not

† 1 eV $\approx 1.60 \times 10^{-19}$ J.

essential for the preparation; it reduces the amount of $S_3N_2Cl_2$ formed in the condenser, and improves the yield.

4-*t*-Butyl-1,2,3,5-dithiadiazolium chloride was prepared similarly and recrystallised from Bu^tCN .² It could not be recrystallised from thionyl chloride due to decomposition and failure to precipitate on cooling.

4-Phenyl-1,2,3,5-dithiadiazolium Chloride.—(i) From $(NSCl)_3$ and PhCN. Trichlorocyclotrithiazene (13.0 g, 0.053 mol) was added to carbon tetrachloride (20 ml) and benzonitrile (6.2 ml, 0.060 mol) and stirred at 60 °C for two days. The dark red mixture chilled to 0 °C gave crude 4-phenyl-1,2,3,5-dithiadiazolium chloride (8.2 g). The orange crystals were washed with benzene (2 × 20 ml) to remove excess of $(NSCl)_3$ and recrystallised twice from nitrobenzene (50 ml g⁻¹) (yield 6.5 g, 50% based on benzonitrile). A similar reaction occurred using excess of benzonitrile (*e.g.* 20 ml) instead of carbon tetrachloride as solvent (Found: C, 38.7; Cl, 15.9; N, 12.5; S, 30.3; H, 2.1. $C_7H_5ClN_2S_2$ requires C, 38.8; Cl, 16.4; N, 12.9; S, 29.6; H, 2.3%); ν_{max} 1 600w, 1 392m, 1 346w, 1 150m, 1 073m, 1 028m, 1 000w, 921m, 893s, 842s, 784s, 702s, 690m,sh, 549s, 515w, and 472w cm⁻¹; $\lambda_{max}(CH_2Cl_2)$ 396 nm (ϵ 685). The phenyl-dithiadiazolium chloride hydrolyses in the atmosphere to give a pale buff powder. The major mass-spectral peaks (200 °C) were found at *m/e* (relative intensity): PhCH₂S₂, 181(72); PhCNS, 135(47); PhCN, 103(90); PhC, 89(4); NS₂, 78(100); Ph, 77(57); CS₂, 76(53); NS, 46(22); HCl, 38(7), 36(19).

(ii) From NH_4Cl , SCl_2 , and PhCN. A suspension of ammonium chloride (16.0 g, 0.30 mol) in sulphur dichloride (40 ml, 0.63 mol), benzonitrile (31 ml, 0.30 ml), and nitrobenzene (45 ml) was stirred under nitrogen in a two-necked flask (250 ml) fitted with a water condenser. The reaction was essentially complete after 5 h in a 140 °C oil-bath. A little $S_3N_2Cl_2$ formed in the condenser. The mixture was cooled to 0 °C, filtered, and the crude product (25 g) washed with benzene and recrystallised from nitrobenzene as described earlier (16 g, 25%).

(iii) From $PhC(NH_2)_2Cl$ and SCl_2 . A stirred mixture of benzamidinium chloride (9.6 g, 0.061 mol), sulphur dichloride (18.6 g, 0.18 mol), and nitrobenzene (50 ml) was heated at 105 °C until no further hydrogen chloride was evolved (*ca.* 5 h), cooled to room temperature, and filtered. The crystals were washed with benzene (10.0 g crude material) and recrystallised from nitrobenzene as described earlier (2.5 g, 19% yield based on amidinium salt).

Attempted Reactions of $[RCN_2S_2]Cl$ (R = CCl_3 or Ph).—The trichloromethyl-dithiadiazolium chloride did not react with (i) diphenylacetylene (1 : 1 mole ratio; 5 days; 60°; carbon tetrachloride), or (ii) sulphur (1 : 4 mole ratio; 72 h; boiling toluene). $[PhCN_2S_2]Cl$ did not react with (i) cyclohexene oxide (1 : 1 mole ratio; 40 h; 20°; carbon tetrachloride), (ii) acetonitrile (0.7 g in 10 ml; refluxed for 22 h), or (iii) tetrachloroethylene (0.85 g in 40 ml, refluxed for 4 h).

Formation of Dithiadiazolium Hexachloroantimonates(v).—Antimony pentachloride (2.8 g, 8.7 mmol) was added to a stirred suspension of 4-phenyl-1,2,3,5-dithiadiazolium chloride (1.8 g, 8.3 mmol) in refluxing thionyl chloride (25 cm³) to give a bright red precipitate. After 10 min at reflux temperature, the mixture was cooled and filtered. The solid 4-phenyl-1,2,3,5-dithiadiazolium hexachloroantimonate(v) was recrystallised from dry nitromethane and dried *in vacuo* (Found: C, 16.2; Cl, 42.8; N, 4.8; S, 12.3. $C_7H_5Cl_6N_2S_2Sb$ requires C, 16.3; Cl, 41.2; N, 5.4; S, 12.4%); ν_{max} (KCl disc) 1 600m, 1 505m, 1 459m, 1 400s, 1 268w,

1 190m, 1 168m, 1 035w, 939w, 928s, 845s, 784m, 698s, 675s, 629m, 566s, 355s,sh, and 348s cm⁻¹.

A similar reaction occurs between antimony pentachloride and 4-trichloromethyl-1,2,3,5-dithiadiazolium chloride in thionyl chloride solution to give 4-trichloromethyl-1,2,3,5-dithiadiazolium hexachloroantimonate(v).

DISCUSSION

Cyanogen chloride, NCCl, is an important reagent for heterocyclic synthesis¹⁰ and therefore, by analogy, the possibility of using thiazyl chloride, NSCl, for the synthesis of new heterocycles was investigated. It is known¹¹ that trichlorocyclotrithiazene $(NSCl)_3$ dissociates into the monomer on warming and so hot solutions of the trimer were reacted with the unsaturated molecules C_2HCl_3 , C_2Cl_4 , and CCl_3CN . In each case the main product analysed as $C_2Cl_4N_2S_2$.

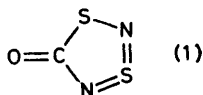
The synthesis of dithiadiazolium chlorides from nitriles and cyclotrithiazene was found to be unsatisfactory for nitriles with α -CH bonds. Thiazyl chloride probably reacts, like NOCl,¹² with the activated hydrogen. Reactions of trichlorocyclotrithiazene (2 g) with excess (15 ml) of acetonitrile, propionitrile, and isobutyronitrile gave black sticky solids and with benzyl cyanide gave a red semi-solid. These mixtures were not investigated further.

As found¹³ for the related Herz compounds (1,2,3-benzodithiazolium chloride and derivatives), the dithiadiazolium chlorides were not easily purified. I.r. spectra indicated that crude materials probably contained other related ring systems. Even recrystallised compounds with good analyses showed spectral and m.p. variations depending upon the synthetic route and the conditions. For instance the i.r. of the recrystallised product from $(NSCl)_3-C_2Cl_4$ shows peaks in addition to those characteristic of the $[CCl_3CN_2S_2]Cl$ obtained from $(NSCl)_3-CCl_3CN$.

The three compounds $[RCN_2S_2]Cl$ (R = CCl_3 , Bu^t , or Ph) are hydrolysed slowly in the atmosphere and rapidly in water. In dioxan at room temperature the CCl_3 derivative reacted rapidly to give the amidine hydrate. Recrystallisation from water converted the latter to CCl_3CONH_2 . Ethanol and ethanethiol were also found to react with the dithiadiazolium chlorides but gave complex mixtures. The compounds $[RCN_2S_2]Cl$ did not appear to be sulphenyl chlorides,¹⁴ since they were unaffected by diphenylacetylene, *etc.* (see Experimental section). The reaction of $[PhCN_2S_2]Cl$ (orange) with diphenylmercury gave a small quantity of a black photosensitive phenyl derivative analysing close to $Ph_2CN_2S_2$, probably 1,4-diphenyl-1,2,3,5-dithiadiazole. On standing in the sunlight at room temperature the black crystals decomposed to give diphenyl disulphide (identified by i.r.) and a black tar.

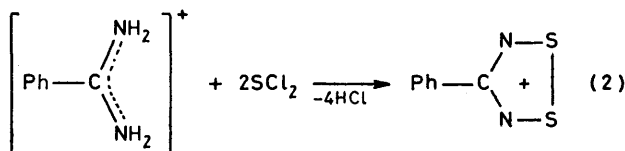
In contrast, the compounds $[RCN_2S_2]Cl$ showed several properties which are characteristic of an ionic structure. They were found to be insoluble in most organic, low polarity solvents and could not be sublimed at 80 °C and 10⁻³ mmHg. They also gave strong peaks in the mass

spectra corresponding to RCN_2S_2^+ . The trichloromethyl and phenyl compounds reacted with antimony pentachloride to give products whose i.r. spectra were very similar to those of the starting materials. These indications of an ionic structure were confirmed⁴ by X-ray analysis; the $\text{CCl}_3\text{CN}-(\text{NSCl})_3$ product is a 1,2,3,5-dithiadiazolium salt. The crude $\text{C}_2\text{Cl}_4-(\text{NSCl})_3$ product probably contains several isomeric and other closely related compounds. A related dithiadiazole (1) has been prepared by Roesky and Wehner.¹⁵

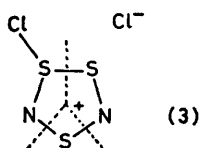


The X-ray study⁴ of $[\text{Cl}_3\text{C}(\text{CN}_2\text{S}_2)]\text{Cl}$ shows that there is a triangular arrangement involving the halide ion. Similar interactions, involving the disulphide link of a 1,2-dithiolium ion and the anion, have been found not only in organic dithiolium and 1,2,4-dithiazolium salts,³ but also in salts of SN cations such as $\text{S}_3\text{N}_2\text{Cl}^+\text{Cl}^-$ ¹⁶ and $\text{S}_4\text{N}_3^+\text{Cl}^-$.¹⁷

The structure of 4-trichloromethyl-1,2,3,5-dithiadiazolium chloride indicated that the ring system should be preparable from amidinium salts. This was confirmed using benzamidinium chloride.

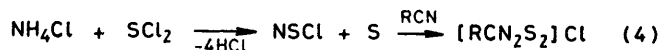


Since 1-chloro-1,2,4,3,5-cyclotrithiadiazonium chloride (thiodithiazyl dichloride, $\text{S}_3\text{N}_2\text{Cl}_2$) is structurally composed of NSCl and S it seemed likely that this could be



used as an alternative source of NSCl. This was found to be the case but $\text{S}_4\text{N}_3\text{Cl}$ proved to be an additional side product. However, $\text{S}_3\text{N}_2\text{Cl}_2$ is usually prepared^{11,18} by heating ammonium chloride and disulphur dichloride, and so the possibility of *in situ* formation of NSCl was investigated. It was found, for both CCl_3CN and PhCN ,

that the reaction of 1:2:1 $\text{NH}_4\text{Cl}-\text{SCL}_2-\text{RCN}$ with nitrobenzene provided a simple single-stage synthesis of dithiadiazolium chlorides [reaction (4)].



It is possible that the ammonium halide also reacted with the nitrile to form the corresponding amidine and amidinium salt,¹⁹ which then condensed with SCL_2 to form the dithiadiazolium chloride. Several other mechanisms are also possible, for instance the nitrile may first form an addition product such as $\text{RCCI}=\text{NH}$ or $\text{RCCI}=\text{NSCl}$. The formation of $\text{PhCCI}=\text{NH}$ from benzonitrile and hydrogen chloride²⁰ and the Bu_4NCl -catalysed addition of SCL_2 to PhSO_2CN to give $\text{PhSO}_2\text{CCI}=\text{NSCl}$ ²¹ have been described.

We thank the S.C.S. College, Omerga (India), the S.R.C., and Ferodo Ltd. for Research Studentships to G. G. A., B. B., and P. W. M. respectively. We also gratefully acknowledge the technical assistance of Mr. T. M. Caygill and Mr. J. Lincoln, and analyses by Mr. R. Coult.

[7/450 Received, 14th March, 1978]

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