THE SYNTHESIS AND PROPERTIES OF SOME SULFANURIC TRIMERS

ROBERT L. MCKENNEY, JR. and NEIL R. FETTER Naval Weapons Center Corona Laboratories, Corona, California 91720

(Received 25 March 1968)

Abstract – α -sulfanuric chloride(I) reacts with diphenylmercury to form diphenylsulfanuric chloride, N₃S₃O₃Cl(C₆H₅)₂(II). Diphentylsulfanuric fluoride, N₃S₅O₃F(C₆H₅)₂(III), is readily produced by the reaction of (II) with potassium fluoride. Results of pyrolysis studies and of thermogravimetric and differential thermal analyses for compounds I, II and III are presented. Infrared and mass spectral data are also given.

IT HAS been established that α -sulfanuric chloride, α -N₃S₃O₃Cl₃[1], will undergo substitution reactions only in those cases where the nucleophile is of greatly reduced basicity[2] or the reaction conditions are carefully controlled[3]. This communication describes the reaction of α -sulfanuric chloride with diphenylmercury and the subsequent fluorination of the product. Infrared and mass spectral data and the results of thermal analyses are presented.

EXPERIMENTAL

Materials

All solvents and chemicals used were reagent grade and the solvents were dried and stored over calcium hydride. Most manipulations were performed in a dry box and all reactions were carried out in a dry inert atmosphere. Phosphorus(V) chloride was purchased from J. T. Baker Chemical Co. and sulfamic acid was purchased from Eastman Organic Chemicals. The former was pulverized with a mortar and pestle and the latter was pulverized in a ball mill and dried over phosphorus(V) oxide before use. Diphenylmercury was purchased from Eastman Organic Chemicals and used as received.

Analyses

Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y. Melting points were obtained on a Du Pont Model 900 Differential Thermal Analyzer and are listed as a single value which corresponds to the minimum point of the endothermic curve.

Infra-red spectra

Infra-red spectra were obtained on a Beckman Model IR-10 spectrophotometer. The spectra of the products were obtained using Nujol mulls and cesium bromide plates. The i.r. absorptions are listed in Table 1.

Mass spectra

Mass spectra were obtained with a Consolidated Electrodynamics Corporation Model 21-130 Mass Spectrometer operating with an ionization potential of 68 V and a Hitachi Perkin-Elmer RMU-6E Mass Spectrometer operating with an ionization potential of 80 eV. Mass spectral data are shown in Table 2. Molecular weight data for α -sulfanuric chloride and diphenylsulfanuric fluoride were obtained from the most intense molecular ion peak in the mass spectra.

- 1. A. Vandi, T. Moeller and T. L. Brown, Inorg. Chem. 2, 899 (1963).
- 2. T. Moeller and A. Ouchi, J. inorg. nucl. Chem., 28, 2147 (1966).
- 3. A. Failli, M. Krasge, C. Allen and T. Moeller, Inorg. nucl. Chem. Lett. 2, 165 (1966).

Table 1. Infra-red data* (cm⁻¹)

N₃S₃O₃Cl₃

1915 w; 1810 m; 1445 m; 1324 vs,b; 1155 sh; 1080 vs,b; 800 m; 695 vs; 650 vs; 630 sh; 530 vs; 420 m

$N_3S_3O_3Cl(C_6H_5)_2$

3070 vw; 3050 vw; 1970 vw; 1900 vw; 1830 w; 1765 vw; 1640 w; 1575 w; 1475 m; 1448 s; 1430 m; 1375 w; 1320 vs; 1270 vs; 1180 s; 1140 vs,b; 1090 sh; 1075 vs; 1020 sh; 1010 w; 995 m; 815 s; 750 sh; 740 vs; 720 sh; 710 s; 685 m; 675 s; 665 sh; 635 m; 565 vs; 535 vs; 470 w; 450 w

$N_3S_3O_3F(C_6H_5)_2$

1640 w; 1578 w; 1475 w; 1445 s; 1435 sh; 1430 sh; 1345 s; 1315 s; 1285 sh; 1270 vs; 1150 sh; 1125 vs; 1080 vs; 1018 w; 990 m; 918 vw; 830 sh; 823 s; 812 s; 775 m; 733 s; 708 vs; 670 m; 635 w; 622 m; 610 vw; 560 vs; 528 vs; 470 w

*s, strong; m, medium; w, weak; v, very; b, broad; sh, shoulder.

Thermogravimetric and differential thermal analyses

Differential thermal analyses were obtained from a DuPont Model 900 Differential Thermal Analyzer and a Perkin-Elmer Model DSC-1B Differential Scanning Calorimeter coupled with a gas evolution detector. The scan rate was 15°C/min for the former and 10°C/min for the latter. The samples were diluted with ground glass in some cases; however, this did not have any appreciable effect on the endothermic or exothermic events. Thermogravimetric analyses were obtained from a DuPont Model 950 Thermogravimetric Analyzer operating at a scan rate of 5°C/min. Dry nitrogen was passed directly over the sample when pan-loaded, and around the sample when capillary tubes were used.

Synthesis of α -sulfanuric chloride

 α -Sulfanuric chloride was prepared by a modification[2] of the Kirsanov[4] method. The compound was recrystallized twice from anhydrous *n*-heptane and vacuum sublimed three times: m.p. 143°C. The overall yield was 11·3 per cent of theory based on phosphorus(V) chloride. Anal. Calc. for N₃S₃O₃Cl₃: M.W., 291. Found: M.W., 291.

Preparation of $N_3S_3O_3Cl(C_6H_5)_2$

Diphenylmercury, 34.2 mmoles, and α -sulfanuric chloride, 17.1 mmoles, were dissolved in 30 ml of anhydrous benzene and sitred for 67 hr at $30-33^{\circ}$ C. The solvent was filtered free of insoluble phenylmercury chloride and evaporated to dryness under vacuum. The crude residual product was treated with small portions of boiling *n*-heptane until the insoluble residue turned green. All aliquots of extracts yielded white crystals upon cooling. Preparative layer chromatography, using neutral silica as a substrate and benzene as the solvent, was used for further purification. A total of 3.76 g of product was obtained with a melting point of 120° C; yield 58.5 per cent of theory.

Anal. Calc. for $N_3S_3O_3Cl(C_6H_5)_2$: C, 38·34; H, 2·68; N, 11·18; S, 25·59; Cl, 9·43. Found: C, 38·18; H, 2·78; N, 11·17; S, 25·30; Cl, 9·15.

The compound is soluble in benzene, toluene and acetonitrile, and in hot *n*-heptane, cyclohexane, and anhydrous ethanol. Diphenylsulfanuric chloride is not moisture sensitive.

A total of 10.3 g of crude phenylmercury chloride was obtained as a by-product of the above reaction. This represents 96.5 per cent of theory for disubstitution of the trimeric ring.

An attempt to trisubstitute the sulfanuric ring with phenyl groups by reacting α -N₃S₃O₃Cl₃ and (C₆H₅)₂Hg in a 1:3 mole ratio was not successful. The reaction was carried out in a manner similar to that described for the preparation of N₃S₃O₃Cl(C₆H₅)₂ with the exception that after stirring at 30-33°C the reaction was then heated to 83°C (external bath temperature) for an additional 1.5 hr. The reaction

4. A. V. Kirsanov, J. Gen. Chem. U.S.S.R., 22, 101 (1952).

				the second second second second								
	N ₃ S ₃ O ₃ Cl ₃ (MW, 291)						72·4	151	15.6	278	17.2	
							70·3	152	47·9	280	19·8	
		(%)			(%)	77	96.9	153	57.3	313	14-1	
m/e	ion	80 V	m/e	ion	80 V	78	76·0	154	89 .6	315	17.2	
28	$-N_{2}^{+}$	11.1	256	$N_3S_3O_3Cl_2^+$	100.0							
36	HCl ⁺	15.7	258	$N_3S_3O_3Cl_2^+$	81·0		$N_3S_3O_3F(C_6H_5)_2$					
46	SN+	50 ·0	260	$N_3S_3O_3Cl_2^+$	23.2		(MW , 359)					
48	SO+	49 ·0	291	N ₃ S ₃ O ₃ Cl ₃ ⁺	1.31†		(%)		(%)		(%)	
63	HOSN+	62·1	293	N ₃ S ₃ O ₃ Cl ₃ +	1.31†	m/e	80 V	m/e	80 V	m/e	80 V	
64	SO ₂ +	63·7	295	N ₃ S ₃ O ₃ Cl ₃ +	0.65†	28	21·0	97	50 ·0	184	14.3	
						29	14.3	105	27.6	185	33-3	
N ₃ S ₃ O ₃ Cl(C ₆ H ₅) ₂						39	11.4	108	11.4	186	30.5	
(MW , 375)						41	17.1	109	71.4	199	10.5	
	(%)		(%)		(%)	50	33.3	110	75.2	200	14.3	
m/e	80 V	m/e	80 V	m/e	80 V	51	61.0	111	21.0	202	17.6	
27	22.4	84	10.4	155	20.8	52	10.5	123	71.4	216	35.2	
37	26.0	99	13.5	184	38 ∙0	57	13.3	124	12.4	218	84 ·3	
38	26.0	99·5	20.8	185	83.3	64	25.7	125	77.6	219	16·7	
39	38-5	100	27.1	186	90 ·1	65	38-1	126	18.1	220	19·0	
49	35-4	100-5	17.7	187	22.4	69	10.5	127	13.3	266	24.8	
50	77.1	101	33.9	198	60·4	74	19.0	137	1 9 ·0	277	13.3	
51	83.3	102	14.1	199	89 ∙6	75	17.1	139	13.3	279	17.1	
52	34.9	108	10·4	200	96·4	76	23.8	140	13.3	312	11·9	
61	13.5	109	65·1	201	79·2	77	81.9	141	25.7	314	16.2	
62	17.7	110	43·8	202	100.0	78	42·9	149	31.9	359	100.0	
63	1 7 ·7	111	24·0	218	96·4	81	10.5	153	16.2	360	22·9	
65	22.9	112	87·0	219	20.3	84	14.3	154	27.6	361	19·0	
66	15.6	113	20.8	220	14.6	91	61.9	166	11.4	403	11.4	
69	12.0	114	59·9	235	12.5	92	24.8	167	35.2	404	15.2	
73	40.6	115	17·2	237	16·7	93	24.8	168	89.5	405	10.0	
74	79·2	1 49	16.7	277	13.5	96	13.3	169	37.1	406	20.0	

Table 2. Mass spectral data

*Intensity of mass spectral peaks listed is 10 per cent or greater.

[†]Molecular ion peak for N₃S₃O₃Cl₃ with intensity less than 10 per cent.

 \pm Molecular ion peak for N₃S₃O₃F(C₆H₅)₂.

product was identified as $N_3S_3O_3Cl(C_6H_5)_2$; m.p. 115-118°C. The yield of C_6H_5HgCl was 93.4 per cent of theory for disubstitution of the ring.

Preparation of $N_3S_3O_3F(C_6H_5)_2$

Diphenylsulfanuric chloride, 1.6 mmoles, was reacted with anhydrous potassium fluoride, 3.2 mmoles, in 10 ml of dry acetonitrile. Approximately 0.01 ml of water was added to the mixture. The reactants were rapidly stirred and refluxed for 21 hr, after which the solvent was filtered free of solid and evaporated to dryness by vacuum. The tan, residual solid was extracted with several 10 ml portions of dry *n*-heptane. Upon cooling, the heptane yielded 0.41 g of a white solid with a melting point of 107° C; yield 71.4 per cent of theory.

Anal. Calc. for $N_3S_3O_3F(C_8H_3)_2$: N, 11-71; F, 5-29; M.W., 359. Found: N, 11-41; F, 5-55; M.W., 359.

The compound is soluble in benzene, toluene and acetonitrile, and in hot *n*-hexane, *n*-heptane, and cyclohexane. The material readily sublimes in vacuum and is not moisture sensitive at room temperature.

Reaction of $N_3S_3O_3Cl(C_6H_5)_2$ with C_6H_5Li

Diphenylsulfanuric chloride, 1.6 mmole, was dissolved in 60 ml of a 50:50 mixture of benzene and

ether and cooled to -40 to -45°C. To this rapidly stirred solution was added, dropwise, 1.6 mmoles of phenyl lithium dissolved in 20 ml of anhydrous ether. After the addition was complete, the system was allowed to slowly warm to room temperature and then allowed to stand for an additional 1.5 hr. The solvent was filtered free of solid and evaporated to dryness by vacuum. The residue was recrystallized from absolute ethanol and identified as diphenylsulfanuric chloride; m.p. 117°C. The residue obtained upon evaporation of the ethanol yielded an additional portion of the diphenyl derivative when separated into various components by preparative layer chromatography. A total of approximately 30-35 per cent of $N_3S_3O_3Cl(C_6H_5)_2$ was recovered. No other compounds were identified.

Pyrolysis of α -sulfanuric chloride

A small sample of α -sulfanuric chloride, sealed in a Pyrex glass tube under high vacuum, was placed in a furnace and the temperature was rapidly raised to a maximum of 290°C. The compound decomposed explosively with a bright orange flash at approximately 285°C. The gaseous products of the decomposition were analyzed by mass spectrometry. The major components of the mixture were identified as sulfur(IV) oxide and molecular nitrogen. Other gaseous ions observed in the mass spectrum after the majority of the nitrogen and sulfur(IV) oxide was removed were tentatively identified as SCl⁺, SOCl₂⁺, SOCl₂⁺, SOCl₂⁺, SOCl₂⁺, and HCl⁺.

Another sample of α -sulfanuric chloride sealed in an evacuated Pyrex glass tube was heated to 160–180°C for a period of several hours. The gaseous decomposition products, which occurred only in minor amounts in this temperature range, were analyzed periodically by mass spectrometry and identified as nitrogen and sulfur(IV) oxide. Trace amounts of other gaseous ions were observed but, because of the complexity of overlapping peaks in the mass spectra, they could not be positively identified. They appear to be mixtures of sulfur nitrides, sulfur oxynitrides, and nitrogen oxides. The gaseous hydrogen chloride molecular ion and chloronium ion were also observed in trace amounts.

Pyrolysis of diphenylsulfanuric halides

Small samples of diphenylsulfanuric chloride and diphenylsulfanuric fluoride were placed in individual sealed glass tubes, evacuated to a pressure less than 1 μ , and rapidly heated to a maximum of 310°C. After cooling the tubes were immersed in a cold bath maintained at -78°C, and the volatile products removed. These gases were identified by mass spectrometry as sulfur(IV) oxide and nitrogen in both cases and were the major products. The residues in the tubes were reheated to 310°C. The mass spectrum of the volatile material from each tube after reheating showed the presence of chlorobenzene and benzene. Since diphenylsulfanuric fluoride is prepared from the chloro derivative, contamination by traces of diphenylsulfanuric chloride is possible, thereby accounting for the presence of chlorobenzene.

Solid products were obtained in both cases; however, identification was not attempted.

DISCUSSION

The reaction of α -sulfanuric chloride with diphenylmercury in a 1:2 mole ratio afforded diphenylsulfanuric chloride in moderate yield. Attempts to synthesize the triphenyl derivative, N₃S₃O₃(C₆H₅)₃ by two different procedures were not successful. The first reaction involved the use of the above named reactants in a 1:3 mole ratio in refluxing benzene for a short period. The product of the reaction was identified as the diphenyl derivative. Another reaction, involving phenyl lithium and diphenylsulfanuric chloride under carefully controlled conditions, resulted in the decomposition of a considerable portion of the starting trimer. There was no evidence for the formation of the desired product, N₃S₃O₃(C₆H₅)₃, from either of the above-mentioned reactions. The physical properties of the triphenyl derivative have been previously described [2].

Diphenylsulfanuric chloride was easily fluorinated by use of potassium fluoride in acetonitrile. This procedure is identical to that used by Moeller and Ouchi[2] for the complete fluorination of α -sulfanuric chloride. The above authors prepared

2930

diphenylsulfanuric fluoride by another method; however, the two fluorides differ in both melting point and infra-red spectrum and it is possible they are isomers.

Both $N_3S_3O_3Cl(C_6H_5)_2$ and $N_3S_3O_3F(C_6H_5)_2$ appear to have been prepared in essentially one isomeric form. Analysis of a sample of each recrystallized derivative by thin layer chromatography revealed the presence of one major component and at least three trace components. Separation of the desired compound from the mixture was afforded by preparative layer chromatography. The melting points of the two derivatives were raised a few degrees by this procedure.

The mass spectral analyses of α -sulfanuric chloride and the diphenylchloro and diphenylfluoro derivatives are shown in Table 2. The most intense peak in the spectrum of diphenylsulfanuric fluoride results from the molecular ion, while the other peaks in the spectrum result from ring substituents and from ring fragments. These data are consistent with the evidence obtained from chemical reactions that the remaining fluorine atom of the diphenyl derivative is difficult to remove without ring degradation. The mass spectrum of α -sulfanuric chloride contains low intensity molecular ion peaks; however, the most intense peak results from the molecular ion minus one chlorine atom. The only other significant peaks seen in the mass spectrum of the trichloride are those fragments which would result from ring degradation. A molecular ion peak, or peaks associated with systematic removal of ring substituents, are not observed in the mass spectrum of diphenylsulfanuric chloride.

The thermal behavior of α -sulfanuric chloride and the two diphenyl derivatives was studied by thermogravimetric and differential thermal methods. When applicable, the gaseous effluent from decomposition was studied by mass spectrometry. All three compounds exhibit only one well defined endothermic peak between room temperature and the point where evaporation and/or decomposition begins. This event is associated with a phase change from solid to liquid and is somewhat broad in all cases.

The differential thermal analysis curves also show that exothermic decomposition begins for all three compounds between 200 and 300°C. A temperature range is reported because the exact temperature at which decomposition begins for each compound is dependent upon purity and scan rate. The exothermic peaks are broad and complex for the two diphenyl derivatives; however, the peak for α -sulfanuric chloride is very sharp. In some cases the decomposition of the trichloride is explosive and the heating of large quantities, especially in a confined vessel, should be undertaken with caution. The heating of solid mixtures of this compound with powdered metals, such as zinc, titanium and zirconium, and with hydrides, such as decaborane and lithium aluminum hydride, causes violent explosions. The sensitivity of these mixtures to shock or friction has not been established; however, it has been shown that pure α -sulfanuric chloride is not very shock sensitive.

Both α -sulfanuric chloride and diphenylsulfanuric fluoride readily sublime in vacuum. Also, the trichloride sublimes slowly at atmospheric pressure at temperatures under 100°C. This phenomenon is not encountered with the diphenylfluoro derivative. α -Sulfanuric chloride vaporizes with some decomposition at temperatures just above its melting point, but data from pyrolysis experiments indicate the decomposition process only occurs to a small extent. Results obtained from a

differential scanning calorimeter coupled with a gas evolution detector also indicate the only important process occurring at temperatures just above the melting point of the trichloride is vaporization.

The major gaseous products from the thermal decomposition of the sulfanuric derivatives are molecular nitrogen and sulfur(IV) oxide. The formation of these two compounds clearly illustrates the oxidative-reductive property of the S-N system. The nature of the small amount of other products from the pyrolysis of α -sulfanuric chloride, by far the most studied, appears to be dependent upon whether or not the sample is slowly decomposed or decomposed explosively by rapid heating. The products of explosive decomposition are identified as thionyl chloride, sulfur(II) chloride, sulfur(VI) oxide and hydrogen chloride. Other gaseous ions observed were tentatively identified as S₂OCl₂⁺ and S₂O₃⁺. Hydrogen chloride was produced by reaction of compounds containing S-Cl bonds with water retained in the glass walls of the reaction vessel, or in the mass spectrometer itself, or both.

Slow thermal decomposition with intermittent analysis of the gaseous products yielded minor amounts of materials which are probably mixtures of sulfur nitrides, sulfur oxynitrides, and nitrogen oxides. Tentative identification of some of the mass spectral peaks include such gaseous ions as SN^+ , HSN^+ , $HSON^+$, NO^+ , and N_2O^+ . It should be pointed out again that the major gaseous products were sulfur(IV) oxide and molecular nitrogen.

Other minor gaseous products from the thermal decomposition of diphenylsulfanuric chloride and diphenylsulfanuric fluoride were chlorobenzene and benzene. The presence of chlorobenzene in the mass spectrum of the fluoro derivative probably results from contamination of the compound by traces of diphenylsulfanuric chloride. Solid residues, representing approximately one quarter of the original weight of the sample, were obtained from the decomposition of both of the above compounds, but were not identified.

Acknowledgements – We are pleased to acknowledge support of this work by the foundational research fund provided to this Laboratory by the Director of Naval Laboratories. Also, thanks are extended to Dr. Lohr A. Burkardt and Mr. William Ayres for supplying thermal and sensitivity data and to Dr. Wayne Carpenter for supplying the Hitachi mass spectral data.