Articles

Dealkylation Reactions of Trialkylamines with 1,3,5-Trichloro-1,2,4,6-cyclothiatriazine: A Novel Route to Regiospecific Dialkylamino Substitution on Cyclocarbathiazines†

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Reaction of trialkylamines and diamines with 1,3,5-trichloro-1,2,4,6-cyclothiatriazine, $(ClCN)_2(ClSN)$, is found to result in the facile cleavage of a C−N bond of the tertiary amine and regiospecific substitution of the dialkylamino group on the carbon atoms of the heterocycle. Reaction of $(ClCN)_2(ClSN)$ with tetramethylmethylenediamine in diethyl ether at room temperature gives the thiatriazine with dimethylamino groups substituted on the ring carbon atoms, $[(Me_2N)CN]_2(ClSN)$ (**1**). The reaction of triethylamine with $(ClCN)_2(ClSN)$ gives the diethylamino-substituted heterocycle $[(Et_2N)CN]_2[S(O)NH]$ (**2**) which is partially saturated as a result of the hydrolysis of the S−Cl bond. The crystal structure of this compound shows it to be a dimer with hydrogen bonding interactions between the N−H and S═O groups. Reaction of excess morpholine with $(ClCN)_2(ClSN)$ gives the trimorpholino-substituted compound $[(OC_4H_8N)CN]_2[(OC_4H_8N)SN]$ (**3**). The S−Cl bond of **1** has also been substituted with morpholine to give $[(Me_2N)CN]_2[(OC_4H_8N)SN]$ (**4**). It is also observed that by using diethyl ether as a solvent, dealkylations can be brought about even at room temperature with these heterocycles.

Introduction

Regiospecificity in substitution reactions of inorganic heterocycles having more than two hetero elements in the ring framework has been a matter of increasing attention in recent years in main group heterocyclic chemistry. Roesky and co-workers in their studies on chlorocarbaphosphazines have shown that C−Cl bonds of the PNC heterocycles react preferentially with silylated amines while metal alkoxides favor reaction at the P−Cl bonds.[1] Manners and co-workers have observed differences in the mode of substitution of metal alkoxides with halogenated PNS heterocycles having sulfur in the +4 and +6 oxidation states.[2] Recent studies by Shreeve and co-workers on the reactions of chlorocarbaphosphazines with polyfluorinated diols also indicate regiospecificity in substitution.[3]

Heterocycles based on a CNS framework have been the theme of diverse investigations.[4] A large variety of these compounds has been prepared with different substituents on the carbon and sulfur atoms of the heterocycles with ring size varying from six to sixteen.[5−10] Our interest in the chemistry of carbathiazines stems from the recent observation of dealkylation of tertiary amines by chlorinated carbaphosphazines[3] as well as similar reactions shown by some heteroaromatic halides.[11−13] In reactions of primary and secondary amines with trichlorothiatriazine known so far, replacement of the S−Cl bond by the amino group has been observed as the initial step followed by further reaction of the amine with one of the C−Cl bonds.[8−10] Attempts to make heterocycles with C-dialkylamino and S-chloro substituents by direct reactions involving NSCl and dialkylcyanamides or by

† Dedicated to Prof. Jean'ne M. Shreeve on the occasion of her 65th birthday.

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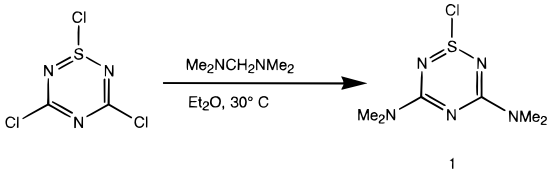
the reaction of $S_3N_2Cl_2$ and dimethylguanidine hydrochloride have resulted in the formation of $(R_2NCN)(NSCl)_2$ and larger ring systems.[14] Herein we report the first observation of dealkylation of tertiary amines in their reaction with chlorothiatriazines wherein regiospecific substitution at the ring carbon atoms by dialkylamino groups is observed.

Results and Discussion

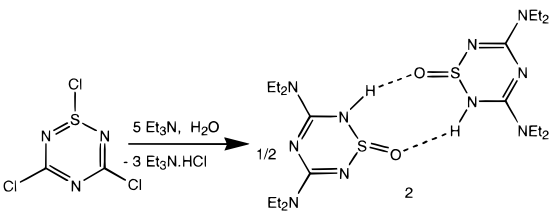
Reactions of $(ClCN)_2(ClSN)$ with aliphatic tertiary amines and diamines proceed readily resulting in the dealkylation of the tertiary amine and giving preferentially C-dialkylamino-substituted CNS heterocycles. Similar to the reactions of chlorocarbaphosphazines with tertiary amines where P−Cl bonds are found to remain inert in dealkylation reactions,[3] the S−Cl bonds of carbathiazines are found not to take part in these dealkylation reactions. Amine hydrochloride is isolated as the side product in these reactions. Reaction of tetramethylmethylenediamine with $(ClCN)_2(ClSN)$ proceeds readily at room temperature in diethyl ether yielding C-dimethylamino, S-chloro-substituted thiatriazine, $[(Me_2N)CN]_2(ClSN)$ (**1**). The compound crystallizes as air-sensitive bright yellow blocks. The proton NMR spectrum of **1** shows a highly deshielded N−CH_3 group (3.13 ppm) indicating the high electron withdrawing nature of the thiatriazine heterocycle. This observation which is comparable to the case of dialkylamino compounds of cyclocarbaphosphazines, indicates the similarity in the nature and reactivity of the C−Cl groups of these heterocycles.[3] The cleavage of the diamine at the bridging methylene group is akin to our observations on similar reactions with carbaphosphazines and cyanuric chloride.[12]



(1)

1

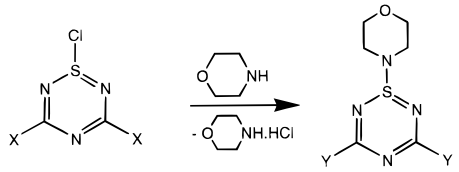
The initial product of the reaction of $(ClCN)_2(ClSN)$ with triethylamine, $[(Et_2N)CN]_2(ClSN)$ is found to be quite sensitive and undergoes hydrolysis of the S−Cl bond in the presence of traces of moisture to give a partially saturated thiatriazine heterocycle, $[(Et_2N)CN]_2[S(O)NH]$ (**2**). This observation is quite similar to the partial hydrolysis of C−diethylamino carbaphosphazine $[(Et_2N)CN]_2(Cl_2PN)$ where one of the P−Cl bonds is hydrolyzed with the formation of a P═O bond and protonation of one of the adjacent ring nitrogens.[3] The NH proton in the ^1H NMR spectrum of **2** appears as a broad peak at 6.50 ppm. Structural studies of **2** showed it to be a dimer with hydrogen-bonding interactions between the N−H and S═O bonds (eq 2).



(2)

2

To compare selectivity in substitution reactions with secondary amines, we also carried out reactions of $(ClCN)_2(ClSN)$ with excess morpholine to realize the compound $[(OC_4H_8N)CN]_2[(OC_4H_8N)SN]$ (**3**). Reactions of $(ClCN)_2(ClSN)$ with primary and secondary amines known so far have only resulted in partially substituted derivatives with one or more of the C−Cl bonds remaining unreactive.[8−10] On reacting **1** with 2 mol of morpholine we have isolated the derivative with the morpholino group substituted on the ring sulfur atom, $[(Me_2N)CN]_2[(OC_4H_8N)SN]$ (**4**) as well. This reaction further conforms the regiospecificity of the trialkylamine reactions with chlorothiatriazine. Compounds **3** and **4** are the first examples of fully amino-substituted cyclodicarbathiatriazines (eq 3).



(3)

X= Cl ; Y = OC_4H_8N (3) : X = Y = Me_2N (4)

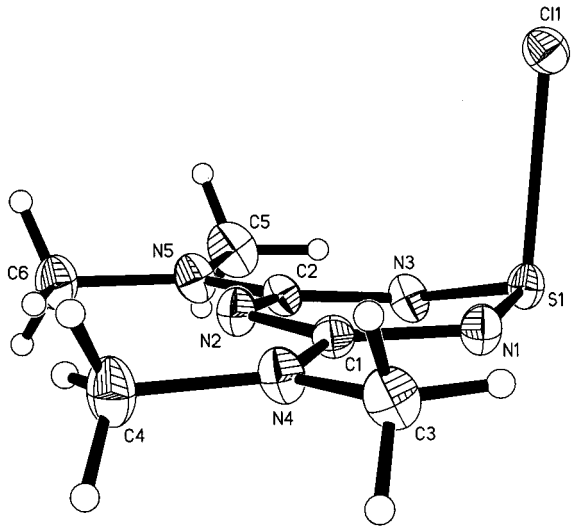


Figure 1. X-ray crystal structure of **1**.

X-ray Structures of Compounds 1−3. The orientation of S−Cl bond of **1** (Figure 1) shows similarities to that of six-membered CNS(IV)-Cl[6,7,14] and PNS(IV)-Cl[15] heterocycles projecting almost perpendicular to the mean plane of the heterocycle. The N−S−Cl angles are 101.27 and 101.57° while for the parent trichorothiatriazine they are 102.0−102.3°.[7] However, the notable feature of this structure is the observation that exocyclic C−N bond distances are 1.342 and 1.344 Å while the endocyclic C−N bond distances fall in the range of 1.340 to 1.376 Å indicating a significant double bond character for the exocyclic C−N bonds. The C_2N- moiety of the exocyclic amino group is also oriented in a plane almost parallel to the mean plane of the ring itself and the sum of angle around both the exocyclic nitrogens [N(4) and N(5)] are 359.9°, further confirming unsaturation of the C−N bond. Similar short exocyclic C−N bonds are also reported for $(R_2NCN)(NSCl)_2$ (R = Me, Et).[14]

The partial saturation of the heterocycle **2** (Figure 2) has resulted in the lengthening of one of the endocyclic S−N bonds [S(1)−N(1) 1.713 Å]. The X-ray structure also indicates that the molecule is a dimer with significant intermolecular hydrogen-bonding interactions between the S═O and N−H groups. Due

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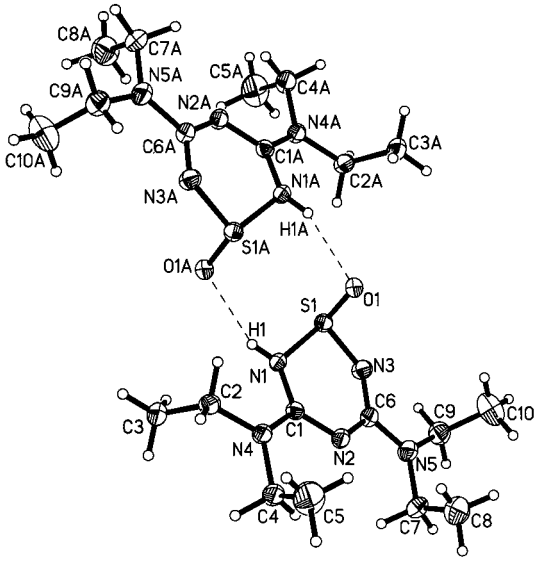

Figure 2. X-ray crystal structure of **2**.

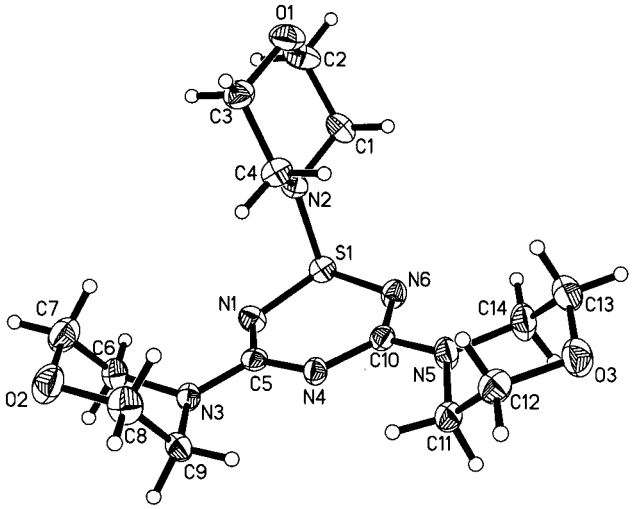

Figure 3. X-ray crystal structure of **3**.

to protonation, the ring becomes unsymmetrical (mean plane deviation 0.221 Å) and the intermolecular H1···O1 interactions are at 2.13(4) Å with N1−H1···O1 = 157(3)°. Structures of **2** and **3** (Figure 3) make interesting comparison with the structures of partially amino-substituted thiatriazine derivatives $[(i\text{-}Pr_2N)SN][(X)(Y)CN]_2$ (X = Cl, S−C_6H_5, Y = Cl, S−C_6H_5, NH−C_6H_{11}).[16] The exocyclic C−N bond distances of **2** are 1.341 and 1.358 Å while for **3** they are 1.354 and 1.357 Å, respectively. For the compound $[(i\text{-}Pr_2N)SN][Cl(NH{-}C_6H_{11})CN]_2$ the exocyclic C−N distance is observed at 1.333 Å.[16] A comparison of these data with the exocyclic C−N bond distances of mono- and dialkylamino-substituted triazines[12,17] and dialkylamino-substituted carbaphosphazines[3] indicates a similar shortening of the bond distances. The observed unsaturation of these bonds is further confirmed by the fact that the sum of the angles around the exocyclic nitrogens N(4), N(5) in **2**, and N(3), N(5) in **3** are close to 360° (359.8°, 360° for **2** and 357°, 359.3° for **3**). However, quite interestingly, the exocyclic S−N bond distance of **3** (1.694 Å) is comparatively longer than the ring S−N bond distances (1.619, 1.620 Å) and is quite close to S(1)−N(1)H of **2** which is more toward an S−N single bond. In addition, the sum of the angles around the nitrogen of the sulfur-substituted morpholine is 341.8°.

It is to be concluded from these data that, unlike the ring carbon and nitrogen of morpholine of **3**, there is comparatively little π interaction between the sulfur of the heterocycle and nitrogen of the morpholine. The structure also shows the S−substituted morpholino group as oriented at an angle above the plane of the ring. The general observation that in all the known structures of C−dialkylamino-substituted cyclocarbathiazines and cyclocarbaphosphazines[3] the exocyclic C−N bond has appreciable double bond character, which in some cases is even shorter than the endocyclic C−N distances provides a possible evidence for the dealkylation reactions shown by tertiary amines with these heterocycles. During the dealkylation, a C−N single bond of the tertiary amine is cleaved and another C−N bond having partial double-bond character is formed with the heterocycle. As this also reduces considerably the available electron density on the amino nitrogen, further dealkylation of the amino substituent is not found to occur.

Experimental Section

Materials. Trichlorothiatriazine is prepared from sodium dicyanoamide and thionyl chloride (Fluka) as per literature methods[10] and purified by kugelrohr distillation. Tetramethylmethylenediamine,[18] triethylamine, and morpholine (E. Merck) are dried and distilled prior to use. Hexane, toluene, and petroleum ether (E. Merck) are dried and distilled by standard procedures.

General Procedures. A conventional vacuum line equipped with dry nitrogen facility and Schlenk glassware is used for all reactions. Reactions are carried out and worked up under an atmosphere of dry nitrogen. Infrared spectra are recorded on a Perkin−Elmer 1320 spectrometer as Nujol mulls. The ^1H and ^{13}C NMR spectra are recorded using a Bruker WM-400 or a JEOL JNM−PMX60SI spectrometers using $CDCl_3$ as a solvent. Mass spectra are obtained on a JEOL D-300 (EI/CI) spectrometer in the EI mode. Elemental analyses are carried out on a Carlo Erba CHNS-O 1108 elemental analyzer.

X-ray Diffraction Studies. The X-ray diffraction data on compounds **1**, **2**, and **3** are collected on a Siemens SMART diffractometer. Data collection parameters are listed in Table 1. The frame data are acquired with the SMART[19] software using a Siemens 3-circle platform using Mo Kα radiation (λ = 0.710 73 Å) from a fine focus tube. The P−axis on this platform is fixed at 54.74° and the diffractometer is equipped with a CCD detector maintained near −54 °C. Cell constants are determined from 60 10-s frames. The structures are solved by direct methods using SHELXS−90 program[20] and refined by least-squares method on F^2, SHELX-93[21] incorporated in SHELXTL-PC v 5.03. All non-hydrogen atoms are refined anisotropically. The hydrogen atoms are located from the difference electron density maps and are included in the refinement process in an isotropic manner. Table 1 lists the X-ray crystallographic parameters and Table 2 selected bond distances and angles for compounds 1−3.

Reaction of $(ClCN)_2(ClSN)$ with Tetramethylmethylenediamine in 1:2 Molar Ratio. $(ClCN)_2(ClSN)$ (0.50 g, 2.45 mmol) and tetramethylmethylenediamine (0.50 g, 4.89 mmol) are reacted in dry diethyl ether (25 mL) at 30 °C. Formation of a white solid is observed on addition of the diamine. After 5 h the solution is filtered using a

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Table 1. X-ray Crystallographic Parameters for **1**, **2**, and **3**

	1	**2**	**3**
empirical formula	$C_6H_{12}ClN_5S$	$C_{10}H_{21}N_5OS$	$C_{14}H_{24}N_6O_3S$
fw	221.72	259.38	356.45
cryst syst; space group	triclinic, $P\bar{1}$	tetragonal, $I4(1)/a$	orthorhombic, $Pna2(1)$
unit cell dimensions			
a (Å)	7.5271(7)	23.0672(2)	18.1577(6)
b (Å)	8.5196(8)	23.0672(2)	5.7507(2)
c (Å)	9.4443(8)	10.4973(1)	16.6389(7)
α (deg)	93.5410 (10)	90	90
β (deg)	110.533(2)	90	90
γ (deg)	111. 944(2)	90	90
V (Å^3)	512.95(8)	5585.57(9)	1737.43(11)
Z	2	16	4
D_{calc} (g cm $^{-3}$)	1.436	1.234	1.363
μ (cm^{-1})	5.40	2.26	2.13
T (°C)	−60 (2)	−60 (2)	27 (2)
λ (Å)	0.710 73	0.710 73	0.710 73
final indices (2σ data), R (wR2)[a]	0.0465 (0.1163)	0.0593 (0.1165)	0.0383 (0.0811)
all data, R (wR2)[a]	0.0534 (0.1206)	0.1152 (0.1864)	0.0732 (0.1143)

[a] $R = \sum|F_o| - |F_c|/\sum|F_o|$; $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compounds **1**, **2**, and **3**

	Compound **1**		
	Bond Lengths		
Cl(1)−S(1)	2.3232(9)	S(1)−N(3)	1.572(2)
S(1)−N(1)	1.575(2)	N(1)−C(1)	1.370(3)
N(2)−C(2)	1.340(3)	N(2)−C(1)	1.349(3)
N(3)−C(2)	1.376(3)	N(4)−C(1)	1.344(3)
N(5)−C(2)	1.342(3)		
	Bond Angles		
N(3)−S(1)−N(1)	111.97(11)	N(3)−S(1)−Cl(1)	101.27(9)
N(1)−S(1)−Cl(1)	101.57(9)	C(1)−N(1)−S(1)	116.3(2)
C(2)−N(2)−C(1)	118.7(2)	C(2)−N(3)−S(1)	116.1(2)
N(2)−C(1)−N(1)	126.9(2)	N(2)−C(2)−N(3)	126.3(2)
	Compound **2**		
	Bond Lengths		
S(1)−O(1)	1.482 (2)	S(1)−N(3)	1.603(3)
S(1)−N(1)	1.713(3)	N(1)−C(1)	1.362(4)
N(2)−C(1)	1.323(4)	N(2)−C(6)	1.360(4)
N(3)−C(6)	1.333(4)	N(4)−C(1)	1.341(4)
N(5)−C(6)	1.358(4)		
	Bond Angles		
O(1)−S(1)−N(3)	110.6(2)	O(1)−S(1)−N(1)	105.35(14)
N(3)−S(1)−N(1)	100.0(2)	C(1)−N(1)−S(1)	120.8(2)
C(1)−N(2)−C(6)	118.7(3)	C(6)−N(3)−S(1)	120.7(2)
N(2)−C(1)−N(1)	122.7(3)	N(3)−C(6)−N(2)	128.2(3)
	Compound **3**		
	Bond lengths		
S(1)−N(1)	1.619(3)	S(1)−N(6)	1.620(3)
S(1)−N(2)	1.694(2)	N(1)−C(5)	1.348(4)
N(2)−C(4)	1.468(4)	N(2)−C(1)	1.472(4)
N(3)−C(5)	1.357(4)	N(4)−C(10)	1.342(4)
N(4)−C(5)	1.347(4)	N(5)−C(10)	1.354(4)
N(6)−C(10)	1.350(4)		
	Bond Angles		
N(1)−S(1)−N(6)	109.88(12)	N(1)−S(1)−N(2)	101.40(13)
N(6)−S(1)−N(2)	108.77(13)	C(5)−N(1)−S(1)	116.5(2)
C(4)−N(2)−C(1)	110.9(2)	C(4)−N(2)−S(1)	117.3(2)
C(1)−N(2)−S(1)	113.6(2)	C(10)−N(4)−C(5)	118.6(2)
C(10)−N(6)−S(1)	116.7(2)	N(4)−C(10)−N(6)	127.8(3)

frit and the volatiles removed in vacuo. The residue is extracted with hexane (10 mL) and kept at 0 °C for 6 h giving yellow crystals of $[(Me_2N)CN]_2(ClSN)$ (**1**) (0.38 g, 70%). Mp: 115 °C (decomp). IR (cm^{-1}) 1560 s (br), 1460 s, 1370 m, 1245 w, 1190 m, 1155 m, 1050 m, 940 m, 920 m, 860 w, 810 w, 750 m. NMR: ^{1}H, δ 3.13 (s, 12H, NMe), ^{13}C, δ 38.05 (CH_3), 158.29 (NCN). Anal. Calcd for $C_6H_{12}N_5SCl$: C, 32.50; H, 5.46; N, 31.59. Found: C, 32.42; H, 5.58; N, 31.55.

Reaction of $(ClCN)_2(ClSN)$ with Triethylamine in 1:4 Molar Ratio in Toluene. Trichlorothiatriazine (0.25 g, 1.22 mmol) in a 50 mL round-bottomed flask is dissolved in dry toluene (25 mL). Triethylamine (0.49 g, 4.84 mmol) is added over a period of 5 min upon which the solution is found to turn yellow with the formation of a white solid. The mixture is then heated at 50 °C for 24 h during which the color of the solution turned brown. The reaction mixture is filtered using a frit, and all volatiles are removed in vacuo. The residue obtained is extracted with hexane (20 mL), and kept at room temp. After 2 weeks, formation of colorless crystals is observed the amount of which is found to increase upon exposure to air. The compound is identified as $[(Et_2N)CN]_2[S(O)NH]$ (**2**) (0.18 g, 57%). Mp: 130 °C. IR (cm^{-1}) 3350 w, 3170 m, 1630 m, 1530 vs, 1450 s, 1320 s, 1290 s, 1220 w, 1180 s, 1050 vs, 1000 s, 830 m, 810 m, 780 m, 750 m cm^{-1}. NMR: ^{1}H, δ 1.07 (t, 12H, CH_3), 3.44 (q, 8H, NCH_2), 6.50 (s, br, 1H, NH); ^{13}C, δ 13.35 (s, CH_3), 42.04 (s, CH_2),156.40 (s, NCN). MS(EI) [m/e (species) intensity]: 259 (M^+) 8; 241 ($M^+ - OH$) 66; 98 (C_2N_3S) 35, 72 (NEt_2) 100. Anal. Calcd for $C_{10}H_{21}N_5OS$: C, 46.31; H, 8.16; N, 27.00. Found: C, 46.38; H, 8.05; N, 27.15.

Reaction of $(ClCN)_2(ClSN)$ with Triethylamine in 1:4 Molar Ratio in Diethyl Ether. Trichlorothiatriazine (0.30 g, 1.47 mmol) is treated with triethylamine (0.59 g, 5.83 mmol) in diethyl ether (25 mL) at 30 °C as described for the preparation of **1**. After 6 h the reaction mixture is worked up, and the residue extracted with hexane (5 mL) and kept at room temperature. After 10 days, formation of colorless crystals was observed, the amount of which was found to increase upon exposure to air (0.21 g, 55%). The physical and spectral properties of the compound are identical to those of **2**.

Reaction of $(ClCN)_2(ClSN)$ with Triethylamine and Water in 1:5:1 Molar Ratio. A mixture of trichlorothiatriazine (0.24 g, 1.17 mmol) and triethylamine (0.48 g, 4.74 mmol) is reacted in toluene (25 mL) as described for the preparation of **2**. After 24 h the reaction mixture is filtered, volatiles removed in vacuo and the residue extracted with hexane (10 mL). To this is added 1 molar equiv of a 1:1 mixture of triethylamine and water at room temperature upon which formation of colorless crystals is observed whose physical and spectral characteristics are identical as those of **2** (0.16 g, 53%).

A variation of this reaction with 1 molar equiv of water in the absence of triethylamine in toluene gives a white precipitate which is sensitive to air and moisture and is insoluble in common organic solvents. Analysis of this compound showed the absence of sulfur. IR (cm^{-1}) 2200 m, 1650 s, 1575 s, 1285 m, 1215 w, 990 s, 720 w. MS (ES$^+$) [m/e, (intensity)]: 284 (100); 270 (18); 102 (68). Anal. Found: C, 14.34; H, 1.72; N, 24.50.

Reaction of $(ClCN)_2(ClSN)$ with Morpholine in 1: 6 Molar Ratio. $(ClCN)_2(ClSN)$ (0.65 g, 3.18 mmol) and morpholine (1.66 g, 19.05 mmol) are reacted in toluene (25 mL) under conditions similar to those described for preparation of **2**. The solution which is initially yellow becomes colorless with the formation of a white solid on completion of addition of morpholine. After 24 h at 55 °C, it is filtered and the white solid obtained on removing the volatiles is extracted with a

mixture of hexane and toluene (50/50 v/v, 20 mL). This is maintained at 4 °C for 3 weeks upon which colorless crystals of $[(OC_4H_8N)CN]_2[(OC_4H_8N)SN]$ (**3**) are found to form (0.90 g, 79%). Mp: 120 °C. IR (cm^{-1}): 1550 s, 1510 vs, 1485 s, 1440 s, 1410 w, 1340 s, 1290 w, 1250 vs, 1185 w, 1110 vs, 1035 vs, 990 m, 900 m, 850 m, 815 w. NMR: ^1H, δ 2.90 (t, 4H, $SNCH_2$), 3.70 (m, 20H, $CNCH_2$,OCH_2);^{13}C, δ, 42.91 (s, $CNCH_2$), 43.45 (s, $SNCH_2$), 65.59 (s, CH_2OCH_2), 65.95 (s, CH_2OCH_2), 161.16 (s, NCN). MS (EI) [*m*/*e* (species) intensity]: 355 ($M^+ - 1$) 1; 184 ($M^+ - OC_4H_8N$) 4; 100 ($C_2H_2N_3S$) 25, 86 (OC_4H_8N) 50, 57 (100). Anal. Calcd for $C_{14}H_{24}N_6O_3S$: C, 47.17; H, 6.79; N, 23.58. Found: C, 47.00; H, 6.71; N, 23.72.

Reaction of 1 with Morpholine in 1:2 Molar Ratio. Morpholine (0.34 g, 3.90 mmol) and **1** (0.43 g, 1.94 mmol) are reacted in toluene (25 mL) under conditions described for preparation of **2**. The bright yellow solution of **1** becomes colorless with the formation of a white solid on completion of addition of morpholine. After stirring the reaction mixture at 80 °C for 12 h, it is filtered, volatiles are removed in vacuo, and the residue is extracted with hexane (10 mL). A pale greenish white solid is found to form which on recrystallization gives colorless crystals of $[(Me_2N)CN]_2[NS(NC_4H_8O)]$ (**4**) (0.25 g, 47%). Mp: 123 °C. IR (cm^{-1}) 1500 s (br), 1360 s (br), 1260 w, 1220 w, 1155 vw, 1115 m, 1050 s, 930 m, 900 w, 865 w, 830 w, 760 m, 685 m. NMR: ^1H, δ 2.90 (m, 4H, $SNCH_2$), 3.75 (m, 4H, OCH_2), 3.1 (s, 12H, NCH_3);^{13}C, δ 35.10 (s, NCH_3), 42.70 (s, $SNCH_2$), 65.70 (s, CH_2OCH_2), 161.00 (s, NCN). MS (EI) [*m*/*e* (species) intensity]: 270 ($M^+ - 2$) 3; 228 ($M^+ - NC_2H_6$), 18; 186 ($M^+ - OC_4H_8N$) 43; 112 (C_2N_4S) 100. Anal. Calcd for $C_{10}H_{20}N_6OS$: C, 44.10; H, 7.40; N, 30.86. Found: C, 44.26; H, 7.55; N, 30.75.

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Supporting Information Available: For compounds **1**, **2**, and **3** tables listing detailed crystallographic data, atomic positional parameters, bond lengths and angles, equivalent isotropic and anisotropic displacement coefficients, hydrogen atom coordinates, and isotropic displacement coefficients. This material is available free of charge via the Internet at http://pubs.acs.org.

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