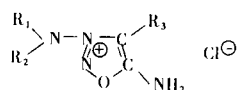

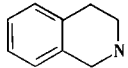
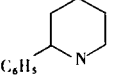
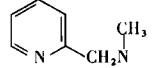
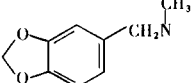


TABLE I



		R ₃	Yield %	M.p., °C	Crystallization Solvent	Formula (6) HCl
1		H	79	178	A	C ₄ H ₈ N ₄ O
2		H	64	135	A	C ₆ H ₁₂ N ₄ O
3		H	49	144-145	A	C ₆ H ₈ N ₄ O
4		H	56	94-96	C	C ₆ H ₁₂ N ₄ O
5		CH ₃	71	110-112	A	C ₇ H ₁₄ N ₄ O
6		C ₂ H ₅	72	94-96	C	C ₁₀ H ₁₆ N ₄ O
7		C ₆ H ₅ , CH ₂ CH ₂	74	113-114	C	C ₁₆ H ₂₀ N ₄ O
8		H	35	182	A	C ₆ H ₁₀ N ₄ O
9		H	53	162-163	A	C ₇ H ₁₂ N ₄ O
10		H	48	153-154	A	C ₈ H ₁₄ N ₄ O
11		H	67	180	A	C ₆ H ₁₀ N ₄ O ₂
12		H	59	187-188	D	C ₇ H ₁₃ N ₃ O [2HCl]
13		H	41	160	A	C ₁₀ H ₁₂ N ₄ O
14		H	62	171	A	C ₁₁ H ₁₄ N ₄ O
15		H	32	138-140	A	C ₁₁ H ₁₄ N ₄ O
16		H	52	154	C	C ₁₂ H ₁₆ ClN ₄ O
17		H	52	158-159	A	C ₁₆ H ₁₆ N ₄ O

TABLE I (Continued)

		R ₃	Yield %	M.p., °C	Crystallization Solvent	Formula HCl
18		H	52	155	A	C ₁₁ H ₁₂ N ₂ O
19		H	41	173-174	A	C ₁₃ H ₁₆ N ₂ O
20		H	38	155	B	C ₉ H ₁₁ N ₂ O [2HCl]
21		H	49	154	A	C ₁₁ H ₁₂ N ₂ O ₃

A = Methanol/ether. B = Ethanol/ether. C = Isopropanol/ether. D = Ethanol.

TABLE II





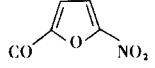


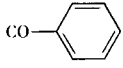

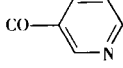

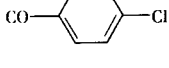


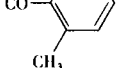
		R ₃	R ₄	Yield %	M.p., °C	Crystallization Solvent	Formula HCl
22		H	COCH ₃	76	173	A	C ₆ H ₁₀ N ₄ O ₂
23		H	COOC ₂ H ₅	69	155	C	C ₇ H ₁₂ N ₄ O ₃
24		H		61	218-219	A	C ₉ H ₉ N ₅ O ₃ (free base)
25		H	COCH ₂ CH ₂ C ₆ H ₅	71	153-154	A	C ₁₃ H ₁₆ N ₄ O ₂
26		H		81	178	A	C ₁₁ H ₁₂ N ₄ O ₂
27		H		57	198-199	A	C ₁₀ H ₁₁ N ₅ O ₂ [2 HCl]
28		H		76	184-185	A	C ₁₁ H ₁₁ ClN ₄ O ₂
29		H	COCH ₂ C[CH ₃] ₃	56	180-181	A	C ₁₀ H ₁₈ N ₄ O ₂
30		H		63	160-162	D	C ₁₂ H ₁₄ N ₄ O ₂

TABLE II (Continued)

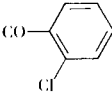
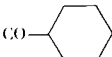

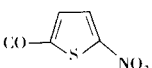
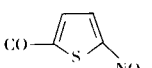




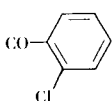

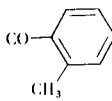

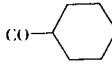


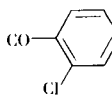


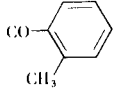

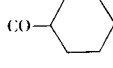
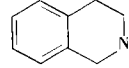
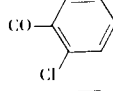
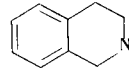
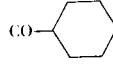
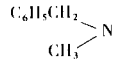
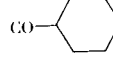
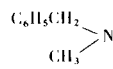
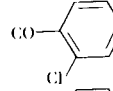
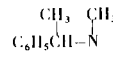
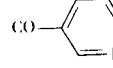
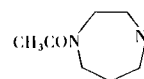
	$\begin{array}{c} R_1 \\ \diagdown \\ N \\ \diagup \\ R_2 \end{array}$	R_3	R_4	Yield, %	M.p., °C	Crystallization Solvent	Formula HCl
31	$\begin{array}{c} CH_3 \\ \diagdown \\ N \\ \diagup \\ CH_3 \end{array}$	H		67	167-168	D	$C_{11}H_{11}Cl_2O_2$
32	$\begin{array}{c} CH_3 \\ \diagdown \\ N \\ \diagup \\ CH_3 \end{array}$	H		59	187	D	$C_{11}H_{18}N_4O_2$
33	$\begin{array}{c} CH_3 \\ \diagdown \\ N \\ \diagup \\ CH_3 \end{array}$	H		48	181-184	B	$C_8H_{12}N_4O_2$
34	$\begin{array}{c} CH_3 \\ \diagdown \\ N \\ \diagup \\ CH_3 \end{array}$	H		57	185-187	A	$C_9H_9N_5O_4S$
35	$\begin{array}{c} CH_2-CHCH_2 \\ \diagdown \quad \diagup \\ N \\ \diagup \quad \diagdown \\ CH_2-CHCH_2 \end{array}$	H	$COCH_3$	36	108-109	C	$C_{10}H_{14}N_4O_2$
36	$\begin{array}{c} CH_2=CHCH_2 \\ \diagdown \quad \diagup \\ N \\ \diagup \quad \diagdown \\ CH_2=CHCH_2 \end{array}$	C_2H_5	$COOC_2H_5$	66	95-96	C	$C_{13}H_{20}N_4O_3$
37	$\begin{array}{c} CH_2-CHCH_2 \\ \diagdown \quad \diagup \\ N \\ \diagup \quad \diagdown \\ CH_2-CHCH_2 \end{array}$	CH_3		53	116-118	A	$C_{14}H_{15}N_5O_4S$
38		H	$COCH_3$	65	173	A	$C_9H_{14}N_4O_2$
39		H	$COOC_2H_5$	72	139-141	B	$C_{10}H_{16}N_4O_3$
40		H	$COOC_2H_5$	76	149-150	A	$C_{15}H_{18}N_4O_2$
41		H		73	158-159	C	$C_{15}H_{17}ClN_4O_2$
42		H		58	140-142	C	$C_{16}H_{20}N_4O_2$
43		H		69	186	C	$C_{15}H_{24}N_4O_2$
44		H	$COCH_3$	62	153-154	C	$C_{10}H_{16}N_4O_2$
45		H		78	168	C	$C_{13}H_{13}ClN_4O_3$

TABLE II (Continued)

		R ₃	R ₄	Yield, %	M.p., °C	Crystallization Solvent	Formula HCl
46		H		74	166-167	A	C ₁₄ H ₁₆ N ₄ O ₃
47		H		61	187	D	C ₁₃ H ₂₀ N ₄ O ₃
48		H		72	142-144	CHCl ₃ (petroleum ether)	C ₁₈ H ₁₄ ClN ₄ O ₂ (free base)
49		H		47	142	CHCl ₃ (ether)	C ₁₈ H ₂₂ N ₄ O ₂
50		H		59	156	C	C ₁₇ H ₂₂ N ₄ O ₂
51		H		57	140-141	A	C ₁₇ H ₁₃ ClN ₄ O ₂
52		H		75	176	A	C ₁₇ H ₁₇ N ₃ O ₂
53		H	COCH ₃	54	179	A	C ₁₁ H ₁₇ N ₃ O ₃

A = Methanol/ether. B = Ethanol/ether. C = Isopropanol/ether. D = Ethanol/petroleum ether.

those carrying a substituent at the 4 position. All titration curves are simple curves. This result is in agreement with the observation that the UV maxima of the monohydrochlorides in ethanol remain unchanged on the addition of perchloric acid. Since acylation of *N*₆ reduces the p*K* values considerably, protonation is taking place at *N*₆ and not at the nitrogen atom attached to position 3. The striking difference of the amide band position in the IR spectra of the acylated 3-aminosydnone imines versus the corresponding salts also points to *N*₆ as site of protonation.

Typical examples of the physical properties of the compounds described are summarized in Table III.

EXPERIMENTAL

The NMR spectra were determined on a Varian A-60 in deuterated DMSO. UV spectra were recorded on a Bausch and Lomb 505 in ethanol solution and the IR spectra on a Perkin-Elmer Infracord 237 B in potassium bromide.

The hydrazines employed as starting materials were either

commercial samples, used without further purification or prepared by nitrosation of the appropriate amine, followed by lithium aluminum hydride reduction.

Preparation of 3-Aminosydnone Imine Hydrochlorides.

To a solution of 0.5 mole of the 1,1-disubstituted hydrazine in 120 ml. of water or water-ethanol, 0.5 mole of potassium cyanide in 70 ml. of water was added under stirring at 5° in the course of 10 minutes, followed by 0.5 mole of aldehyde in the course of one hour. The mixture was stirred for one hour at room temperature, cooled to 5° and 50 ml. of concentrated hydrochloric acid and 0.5 mole of sodium nitrite in 75 ml. of water was added dropwise. The pH of the solution was kept acidic by gradual addition of hydrochloric acid. The nitroso hydrazine was extracted into chloroform. The solution was dried and evaporated to dryness *in vacuo*. The residue was stirred into 10 times its weight of methanol and saturated with hydrogen chloride. The solution was evaporated *in vacuo* at room temperature. The residue was either crystallized or, if impure, chromatographed on silicic acid. On elution with 20-50% methanol in chloroform, the desired product was obtained.

Preparation of Acylated 3-Aminosydnone Imine Hydrochlorides.

The acylation of the 3-aminosydnone imine hydrochloride

TABLE III

		IR (cm ⁻¹)	UV λ max, mμ	ε	NMR (ppm)	pK
1		3180 1680	294 258	10 000 3 800	3N-CH ₃ :3.12 s 4C-H :8.07 s	8.85
22		3155 1712 1625	316 297 243	9 300 10 700 6 600	3N-CH ₃ :3.30 s 4C-H :9.02 s	4.50
6		1675	312	8 600	3N-CH ₃ :3.94 d 4C-CH ₂ :2.78 q	8.20
7		1670	318	6 400	3N-CH ₃ :3.83 d 4α-CH ₂ :2.93 s β-CH ₂ :	8.15
36		1745 1645	335 235	12 900 15 000	3N-CH ₃ :3.96 d 4C-CH ₂ :2.77 q	3.30
13		1670	298 257	8 500 3 500	3N-CH ₃ :3.05 s 3N-CH ₂ :4.68 s 4C-H :8.32 s	
51		1710 1615	330 250	22 000 12 100	3N-CH ₃ :3.37 s 3N-CH ₂ :5.00 s 4C-H :9.45 s	

was achieved by two methods.

Method A.

To a mixture of 150 ml. of acetic anhydride and 150 ml. of pyridine, 3-aminosydnone imine hydrochloride (0.1 mole) was added. The mixture was warmed for a few minutes to 60° and left under exclusion of light for 3 days at room temperature. The crystalline material was removed by filtration through a Büchner funnel and recrystallized.

Method B.

To 120 ml. of pyridine, 3-aminosydnone imine hydrochloride (0.1 mole) was added under stirring. Acyl chloride (0.15 mole) was introduced in small portions at -10°. The mixture was

stirred at room temperature for 3 hours, cooled to 5° and 500 ml. of water was added. The solution was extracted four times with chloroform, the combined extracts were washed with water, dried and evaporated to dryness. The residue was dissolved in the alcohol of choice and hydrogen chloride was introduced at 10° to slightly acidic pH. On addition of ether the crystalline material separated.

Acknowledgment.

We would like to thank Miss M. Gehrig and Mr. J. Furlan for technical assistance and Dr. H. Pook of C. H. Boehringer Sohn, Ingelheim, West Germany, for providing the NMR spectra. The microanalyses were performed by Dr. C. Daesslé, Montreal, and Dr. A. B. Gygli, Toronto.

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Received August 21, 1969

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