

Reactions of Chloramine with Methylpyridines. Synthesis and Crystal Structure of *N*-Amino-3,5-dimethylpyridinium Chloride

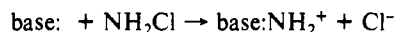
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Received February 27, 1990

The reactions of 2,4-, 2,3-, and 3,5-lutidines and 2,4,6-collidine with ether solutions of chloramine were examined. Only in the case of 3,5-lutidine was an amination product obtained. In the other cases ammonium chloride and the hydrochlorides of the respective nitrogen bases were the only solids isolated. The crystal structure of the amination product was determined by X-ray diffraction and shown to be *N*-amino-3,5-dimethylpyridinium chloride, C₇H₁₁N₂Cl. Crystals are triclinic, space group *P*1̄, with *a* = 7.663 (1) Å, *b* = 8.241 (2) Å, *c* = 8.266 (2) Å, α = 116.75 (2)°, β = 115.39 (2)°, γ = 91.85 (2)°, and *Z* = 2. The changes in N-N and C-N distances and C-N-C bond angles produced by the amination of 3,5-lutidine are discussed in terms of the changes in hybridization of the bonding orbitals of the heterocyclic nitrogen.

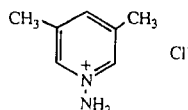
Introduction

Numerous investigations have examined the use of chloramine as an aminating agent for a variety of nucleophilic substances, notably molecules containing nitrogen or phosphorus donor atoms.¹ The result has been the development of syntheses for a variety of hydrazine and aminophosphine derivatives, as well as a series of triazanium chlorides. The latter were a new class of compounds containing a chain of three saturated nitrogen atoms disubstituted on the middle nitrogen atom.² Kinetic studies indicated that the reactions follow an S_N2 mechanism in accordance with the following equation:



However, little work on the chloramination of nitrogen-heterocyclic aromatic compounds has been reported to date. An early paper contained a brief statement that, in attempts to chloramine pyridine and 2-methylpyridine, the only solid product isolated was ammonium chloride.³ Shortly thereafter, the formation of 2-aminoquinoline or 2-aminopyridine in small yields by the reaction of gaseous chloramine with liquid quinoline or pyridine was reported.⁴ The probable formation of the 8-amino derivatives of theobromine and caffeine by analogous chloraminations was also suggested. Since this short note, no further studies of chloraminations of heteroaromatic compounds have appeared. However, various substituted *N*-aminopyridinium cations have been reported as products of the reaction of heterocyclic nitrogen bases with *O*-(mesitylsulfonyl)hydroxylamine.⁵

In view of the broad applicability of the chloramination reaction with various nucleophiles, the unanswered questions concerning the reactions of chloramine with nitrogen heterocycles merited further investigation. In the present study, the reactions of chloramine with 2,3-lutidine, 2,4-lutidine, 2,6-lutidine, 3,5-lutidine, and 2,4,6-collidine were examined. In the case of 3,5-lutidine a solid amination product was isolated in high yield and its structural formula was shown to be



by an X-ray crystal structure study. The only solids isolated in the other cases were ammonium chloride and the respective pyridinium chlorides.

Experimental Section

Materials. 2,3-, 2,4-, 2,6-, and 3,5-lutidines and 2,4,6-collidine were obtained from Aldrich Chemical Co. and used as obtained. Chloramine was prepared by the gas-phase reaction of chlorine-nitrogen mixtures with gaseous ammonia in a Sisler-Mattair type reactor.⁶ Solutions of

Table I. Products of the Reactions with Chloramine

	mp, °C	% C	% H	% N
2,6-lutidine	218-219	58.95	7.03	9.68
2,4-lutidine	208-210	58.76	7.10	10.01
2,3-lutidine	202-204	59.01	7.05	9.93
lutidine·HCl (theory)		58.53	7.03	9.76
2,4,6-collidine	230-231	58.30	7.60	8.71
collidine·HCl (theory)		60.95	7.67	8.88
3,5-lutidine	227-229	53.00	7.32	17.39
lutidine·NH ₂ Cl (theory)		53.00	6.99	17.66

Table II. Crystallographic Data for *N*-Amino-3,5-dimethylpyridinium Chloride

C ₇ H ₁₁ N ₂ Cl	fw = 158.64
<i>a</i> = 7.663 (1) Å	<i>P</i> 1̄ (No. 2)
<i>b</i> = 8.241 (2) Å	<i>T</i> = 27 °C
<i>c</i> = 8.266 (2) Å	λ = 1.541 78 Å
α = 116.75 (2)°	ρ(calcd) = 1.30 g cm ⁻³
β = 115.39 (2)°	μ = 35.8 cm ⁻¹
γ = 91.85 (2)°	<i>R</i> (<i>F</i>) = 0.069
<i>V</i> = 404.35 (2) Å ³	<i>R</i> _w (<i>F</i>) = 0.077
<i>Z</i> = 2	

chloramine in ether were prepared by passing the effluent gas from the reactor into anhydrous ether and pouring the resulting solution through the column of anhydrous copper sulfate to remove the ammonia.⁷

Method. The reactions with all the pyridine derivatives were carried out at 0 °C by stirring the pyridine derivative with an ether solution of a slight excess of chloramine. The reaction with 2,6-lutidine is typical: One-hundredth (0.01) mole of 2,6-lutidine was mixed with 40 mL of 0.3 M chloramine solution in ether (0.012 mol of NH₂Cl, 20% excess) at 0 °C, and the mixture was stirred for 8 h and allowed to stand overnight. The white precipitate that formed was filtered off and shown to be ammonium chloride (mp > 300 °C). The filtrate was evaporated to a volume of 10 mL by passing dry nitrogen over it for a period of 2 h and then allowed to stand overnight in the refrigerator. Yellow crystals formed but were shown by melting point determination (218-219 °C) and elemental analysis to be the hydrochloride of 2,6-lutidine. No other solid product was obtained. An authentic sample of the hydrochloride of 2,6-lutidine was prepared from 2,6-lutidine and dry HCl for comparison to confirm this conclusion.

Experimental Results. Analogous results were obtained in the reactions of chloramine with 2,4- and 2,3-lutidines and with 2,4,6-collidine, the only solid products isolated being ammonium chloride and the hydrochlorides of the respective nitrogen bases. The analyses and melting points of the hydrochlorides are listed in Table I.

Different results were obtained in the reaction with 3,5-lutidine. In this case concentration of the final filtrate resulted in the formation of pale yellow crystals that, after recrystallization from a 2:1 mixture of acetone and chloroform, melted at 227-229 °C. Anal. Calcd for C₇H₁₁N₂Cl: C, 52.97; H, 6.99; N, 17.66. Found: C, 53.00; H, 7.32; N, 17.39. These data indicate the amination of the lutidine by chloramine. The weight of this product corresponded to a yield of 75.4% of theoretical.

Crystal Structure Determination. To establish unequivocally the identity of the above amination product, the structure was determined

- (1) A good review of chloramination can be found in: Frazier, S. E.; Sisler, H. H. *Chloramination Reactions*; Dowden, Hutchinson & Ross, Inc.: Stroudsburg, PA, 1977.
- (2) Utvary, K.; Sisler, H. H. *Inorg. Chem.* **1968**, *7*, 698.
- (3) Omietanski, G.; Sisler, H. H. *J. Am. Chem. Soc.* **1956**, *78*, 1211-3.
- (4) Brooks, B. E.; Rudner, B. J. *Am. Chem. Soc.* **1956**, *78*, 2339-40.
- (5) Tamura, Y.; Minanikura, J.; Ikeda, M. *Synthesis* **1977**, 1-17.
- (6) Sisler, H. H. *J. Am. Chem. Soc.* **1954**, *76*, 3906-9.

(7) Gilson, I. T.; Sisler, H. H. *Inorg. Chem.* **1965**, *4*, 273-5.

Table III. Positional Parameters ($\times 10^4$) for N-Amino-3,5-dimethylpyridinium Chloride

	x	y	z	$U, \text{\AA}^2$
Cl	1715 (2)	2597 (2)	4930 (2)	56 (1)
N(1)	3842 (5)	7643 (5)	6261 (6)	41 (2)
N(1a)	2052 (6)	6360 (6)	4455 (6)	51 (2)
C(2)	4237 (7)	9471 (7)	6744 (7)	44 (3)
C(3)	5974 (7)	10762 (7)	8443 (7)	42 (3)
C(3a)	6426 (7)	12801 (7)	8995 (8)	53 (3)
C(4)	7350 (7)	10166 (6)	9672 (7)	43 (3)
C(5)	6937 (6)	8295 (6)	9156 (7)	39 (3)
C(5a)	8410 (7)	7619 (7)	10473 (8)	53 (3)
C(6)	5174 (7)	7056 (6)	7439 (7)	41 (3)

^a Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

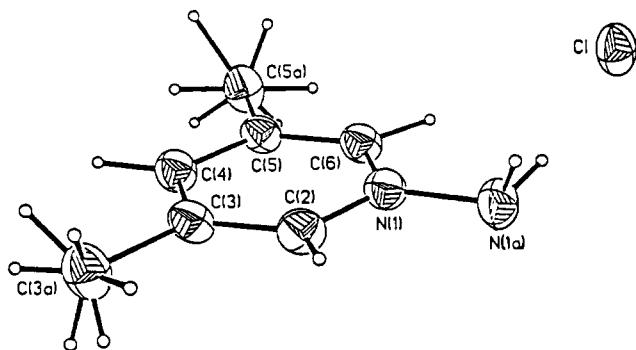


Figure 1. View of N-amino-3,5-dimethylpyridinium chloride showing the atomic numbering and thermal ellipsoids. The disordered hydrogen atoms on C(3a) and C(5a) are indicated by two sets of H atoms. The Cl^- ion is in the correct relative position found in the crystal to show the $\text{N}-\text{H}\cdots\text{Cl}$ hydrogen bond.

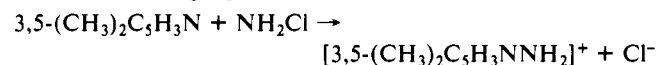
by X-ray diffraction. A well-shaped crystal of $0.15 \times 0.2 \times 0.2$ mm size was used for intensity measurements on a Nicolet PI diffractometer with Ni-filtered $\text{Cu K}\alpha$ radiation. Reflections were collected in the 2θ range 1.5 – 112.0° by using the θ – 2θ scan mode and a variable scan speed (1.90 – $29.30^\circ \text{ min}^{-1}$). Two check reflections measured after every 50 reflections showed an intensity variation of $\pm 5\%$. Of 1193 reflections measured, 1004 with $F > 2.5\sigma$ were used in calculations. Pertinent data are listed in Table II.

The structure was solved by the heavy-atom method. The difference maps showed positions of all H atoms bonded to the ring and the NH_2 group and indicated CH_3 groups having H atoms in two orientations (rotated by 60°). Because not all methyl hydrogen atoms gave suitable bond angles, coordinates of three of them were calculated by assuming tetrahedral geometry around the carbon atoms.

Non-hydrogen atoms were refined with anisotropic thermal factors. The parameters of the H atoms were included in the structure factor calculations but they were not refined. The isotropic temperature factor of 0.05\AA^2 was assigned to all H atoms. The final refinement of all parameters converged at $R = 0.069$ and $R_w = 0.037$ where $w = \sigma^{-2}$. The residual peaks in the final difference map were in the range from -0.54 to 0.66 e \AA^{-3} . All calculations were carried out with the SHELXTL system (Nicolet, 1986). Crystal data are summarized in Tables II–IV. The structure is illustrated in Figure 1.

Conclusion

The results of these experiments demonstrate conclusively that chloramine in anhydrous ether solution free of ammonia reacts with 3,5-lutidine to give the expected hydrazinium-type salt in good yields by the amination of the ring nitrogen in accordance with the following equation:



In contrast, 2,3-, 2,4-, and 2,6-lutidines and 2,4,6-collidine do not appear to undergo this reaction. Instead, ammonium chloride and the hydrochlorides of the respective nitrogen bases are the only products isolated. Since in each of these bases there are one or two methyl groups α to the ring nitrogen, the attribution of these results to spatial interference of the α -methyl groups is an attractive hypothesis. This hypothesis is, of course, speculative. It

Table IV. Selected Distances (\AA) and Angles (deg) for N-Amino-3,5-dimethylpyridinium Chloride

Bond Distances			
N(1)–N(1a)	1.399 (4)	N(1)–C(2)	1.359 (7)
N(1)–C(6)	1.352 (7)	C(2)–C(3)	1.355 (5)
C(3)–C(3a)	1.513 (8)	C(3)–C(4)	1.396 (8)
C(4)–C(5)	1.386 (8)	C(5)–C(5a)	1.518 (8)
C(5)–C(6)	1.358 (5)		
Bond Angles			
N(1a)–N(1)–C(2)	118.1 (4)	N(1a)–N(1)–C(6)	120.6 (4)
C(2)–N(1)–C(6)	121.2 (3)	N(1)–C(2)–C(3)	120.6 (5)
C(2)–C(3)–C(3a)	121.0 (5)	C(2)–C(3)–C(4)	118.5 (5)
C(3a)–C(3)–C(4)	120.5 (3)	C(3)–C(4)–C(5)	120.4 (3)
C(4)–C(5)–C(5a)	121.3 (3)	C(4)–C(5)–C(6)	118.9 (5)
C(5a)–C(5)–C(6)	119.9 (5)	N(1)–C(6)–C(5)	120.5 (5)

Dimensions of the Hydrogen Bonds ^a			
H(11a)···Cl'	2.203 (6)	N(1a)–H(11a)···Cl'	172.9 (4)
H(12a)···Cl	2.381 (6)	N(1a)–H(12a)···Cl	170.7 (4)

^a Cl' at $-x, 1-y, 1-z$.

gains some additional credence, however, from the fact that the presence of methyl groups in the 2-position on the ring should increase the electron density on the ring nitrogen and thus favor rather than impede the amination of the nitrogen by chloramine. Thus, the electronic effect of the α -methyl groups as the explanation of these experimental results is not attractive. However, further research including an examination of solubilities of potential products is necessary to obtain a satisfactory explanation.

There are two interesting features of the N-amino-3,5-dimethylpyridinium ion: the N(1)–N(1a) distance and the change in the dimensions of the ring relative to other pyridines. Unfortunately, there are no other compounds that are strictly analogous for a comparison. The N(1)–N(1a) distance of 1.399 (4) \AA is shorter than the N–N distances observed in 2,2-dimethyltriazanium chloride (1.439 (6) and 1.462 (6) \AA) and in 1,1,1-trimethylhydrazinium chloride (1.463 (3) \AA).⁸ Our shorter N–N distance is, in part, a consequence of the sp^2 hybridization of N(1), which is expected to decrease the N sp^3 radius by about 0.04\AA . A single bond between two sp^2 N atoms has been estimated to be 1.41\AA .⁹ On this basis, the sp^3 N–N single bond would be 1.49\AA , which is close to the value of 1.50\AA .¹⁰ Thus, it would appear that there is some double-bond character in the N(1)–N(1a) bond. However, as can be seen in Figure 1, the two H atoms are not coplanar with the ring as might be expected. Therefore, the N–N bond may be considered to be an essentially single bond with possibly some shortening due to the formal charge. The question of the N–N double-bond character is pertinent to explaining the observed changes in the pyridine ring dimensions.

The formation of the N-aminopyridinium ion results in significant changes in the dimensions of the ring. Pyridine in the gas phase has equal C–C bond lengths of 1.392 (1) \AA , the C–N bond lengths are 1.340 (1) \AA , and the C–N–C angle is $116^\circ 50'$.¹¹ In the N-amino-3,5-dimethylpyridinium ion the C–N–C angle is increased to 121.3 (4) $^\circ$ and the C–N distances increase to 1.357 (8) \AA . There is usually very little change in the bond lengths of the pyridine ring on either substitution,^{12,13} coordination to a metal ion,¹⁴ or pyridinium ion formation.^{11,15,16} However, an increase

(8) Giordano, T. J.; Palenik, G. J.; Sisler, H. H. *Inorg. Chem.* **1976**, *15*, 751–4.

(9) Burke-Laing, M.; Laing, M. *Acta Crystallogr.* **1976**, *B32*, 3216–24.

(10) Huheey, J. E. *Inorganic Chemistry*, 3rd ed.; Harper & Row: New York, 1983.

(11) Bak, B.; Nygaard, L. H.; Anderson, J. R. *J. Mol. Spectrosc.* **1958**, *2*, 361–8.

(12) There are over 4000 compounds containing a pyridine in the 1989 release of the Cambridge Structural Database. An analysis of these data is beyond the scope of this report but will be published elsewhere. However, a few representative examples are given in refs 13–16.

(13) Boenigk, D.; Mootz, D. *J. Am. Chem. Soc.* **1988**, *110*, 2135–9.

(14) Steffen, W.; Palenik, G. J. *Inorg. Chem.* **1978**, *17*, 1338–40.

(15) Newkome, G. R.; Theriot, K. J.; Fronczek, F. R. *Acta Crystallogr.* **1985**, *C41*, 1641–4.

(16) Kamenar, B.; Vickovic, I. *Acta Crystallogr.* **1987**, *C43*, 1574–6.

in the C-N-C angle in the pyridine ring occurs in all of the above cases. The changes in the bond angle may be rationalized in terms of an assumption of increased s character in the C-N bonds as predicted by Bent's rules.¹⁷ The changes in the bond lengths appear to be more subtle and appear to depend on the nature of the group bonded to the nitrogen lone pair. However, these

(17) Bent, H. A. *Chem. Rev.* **1961**, *61*, 275-311.

changes may account for the observed increased reactivity of pyridinium ions and related species.

Acknowledgment. We thank the NSF Instrumentation Program for a grant for the purchase of the Nicolet diffractometer.

Supplementary Material Available: Tables of the final thermal parameters, hydrogen atom parameters, and bond distances and angles (2 pages); a listing of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

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Hydrolysis Chemistry of the Chlorophosphazene Cyclic Trimer

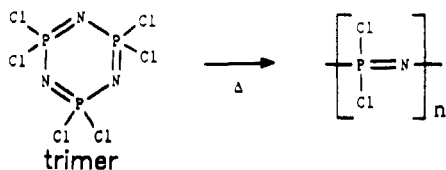
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Received February 28, 1990

The hydrolysis chemistry of the chlorophosphazene (phosponitrile chloride) cyclic trimer has long been of interest because of its possible relevance to polymerization catalysis, as well as the undesirable role of water in the cross-linking of poly(dichlorophosphazene). Hydrolysis of the trimer in THF solutions has been followed through the first 3 equiv of water by using ³¹P NMR as the primary analytical tool. A total of seven products were identified, at least one of which has been previously proposed as a polymerization catalyst. Two of the species are oxo-bridged dimers of two trimer rings that may be useful as model compounds for hydrolytic cross-linking reactions in the polymer.

Introduction

The polymerization of the chlorophosphazene (phosponitrile chloride) cyclic trimer to form poly(dichlorophosphazene)

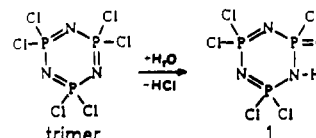


and subsequent derivatization leads to a large class of inorganic polymers with a wide range of properties. These properties include biocompatibility, solvent resistance, thermal stability, and flame retardance.¹ Allcock and Best² proposed that the polymerization of trimer occurs via a ring opening cationic chain growth mechanism. The reaction can be performed either in the melt or in solution.

The melt polymerization reaction, typically carried out at temperatures between 180 and 220 °C, is extraordinarily sensitive to the presence of trace impurities that function as either catalysts, or inhibitors.³ These effects are so extreme that the rate of polymerization varies profoundly from one batch of trimer to another or if two samples of trimer from the same batch are handled slightly differently. The role of water in the polymerization of trimer is very complex and poorly understood. Rigorously purified samples of trimer, obtained from multiple sublimations and recrystallizations, can require weeks to polymerize at 200 °C. Following exposure to atmospheric moisture, however, the polymerization rate is greatly accelerated. At low concentrations, water either acts as a polymerization catalyst or reacts with trimer to generate the active catalytic species. Indeed, Allcock and co-workers³ have raised the question as to whether anhydrous samples of trimer could undergo melt polymerization at all. The eventual polymerization of highly purified trimer has been rationalized as the result of water or other contaminants leaching out of the glass reaction vessels.

One of the mechanisms proposed to explain the catalysis of polymerization is that water facilitates charge separation when a chloride ion dissociates from a trimer ring at elevated temperature. The resulting cation is then assumed to initiate poly-

merization.³ Alternatively, Allcock and co-workers have proposed³ that water catalyzes the polymerization indirectly by the formation of hydrolyzed trimer species (e.g., **1**), which are assumed



to ring open at elevated temperatures to form a charged initiator species. Identification of the products found early in the hydrolysis of trimer was one of the motivations of the present study.

Unfortunately, the role of water in the polymerization of trimer is not entirely favorable. At water contents greater than 1 mol %, an insoluble cross-linked polymer is formed, which can not be derivatized to form useful materials. The structure(s) of the cross-link sites are not known, but they can be expected to involve an oxo bridge between the chains. Hydrolytic cross-linking is somewhat unpredictable; therefore, it complicates the use of water as a polymerization catalyst. As Allcock⁴ has pointed out, the chemistry of phosphazene polymers can frequently be modeled by carrying out analogous reactions on cyclic oligomers. A second motivation for the present study, therefore, was to investigate the possibility of hydrolytic cross-linking reactions (i.e., dimerization of cyclic trimeric units) when the trimer is exposed to water in solution. Such dimers, if formed, could presumably be used to model the cross-links formed by the action of water on poly(dichlorophosphazene).

Previous studies have focused on the later stages of hydrolysis, which ultimately lead to phosphoric acid and ammonium chloride. Those previous investigations employed chromatographic methods, which were complicated by further hydrolysis during the separation.⁵ Because the putative catalytic species are usually envisioned as early products of the hydrolysis, we have used ³¹P

(1) Allcock, H. R. *Science* **1976**, *193*, 1214.

(2) Allcock, H. R.; Best, R. J. *Can. J. Chem.* **1964**, *42*, 447.

(3) Allcock, H. R.; Gardener, J. E.; Smeltz, K. M. *Macromolecules* **1975**, *8*, 36.

(4) Allcock, H. R. *Acc. Chem. Res.* **1979**, *10*, 351.

(5) (a) Pollard, F. H.; Nickless, G.; Warrender, R. W. *J. Chromatogr.* **1962**, *9*, 485. (b) Pollard, F. H.; Nickless, G.; Warrender, R. W. *J. Chromatogr.* **1962**, *9*, 493. (c) Quimby, O. T.; Narath, A.; Lohman, F. H. *J. Am. Chem. Soc.* **1960**, *82*, 1099.

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