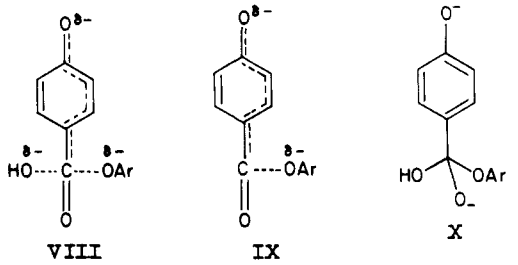

VIII IX X

anism between the two extremes IX and X. The conjugate base of the ester reacts with hydroxide ion through a path involving a tetrahedral intermediate (X) which is more energetically favorable than that represented by (VIII).

At the standard state of 1 M for reactants and hydroxide ion there is significant reaction through both k_a and k_b routes of hydrolysis (structures IX and X, respectively). Changing the pK of the leaving group will only alter the likelihood that the path taken will be one of the two as shown in Figure 3 (A). Change in leaving group basicity cannot lead to the concerted pathway (VIII) taking the major part of the reaction flux.

A preliminary investigation indicates that the *o*-oxo ketene is not formed in either 4-nitrophenyl 2-hydroxy-5-nitrobenzoate or 2,4-dinitrophenyl salicylate hydrolysis. The major competitor of the $B_{Ac}2$ mechanism is the Smiles[14] rearrangement in these cases. The efficiency of other para electron-releasing groups in assisting the S_N1 mechanism was tried; the ester with a 4-amino group has a $B_{Ac}2$ mechanism for its alkaline hyrolysis (Figure 2) indicating that the relatively high pK of the amine does not provide sufficient of the conjugate base for the dissociative mechanism to compete. The 4-acetamido group, although possessing a more acidic nitrogen, does not promote an E1cB mechanism in the hydrolysis of 2,4-dinitrophenyl 4'-acetamidobenzoate.[22]

Acknowledgment. We thank S.E.R.C. (United Kingdom) and CNR (Italy) for the support of this work and N.A.T.O for a travel grant (RF 115.80). Part of this work was carried out during tenure of a Ciba-Geigy Senior Fellowship (A.W.).

Registry No. $PhNH_2$, 62-53-3; $PhNHC(O)$-*p*-C_6H_4OH, 14121-97-2; HO-*p*-$C_6H_4C(O)OPh$, 17696-62-7; HO-*p*-$C_6H_4C(O)$-O-*p*-C_6H_4Cl, 50687-75-7; HO-*p*-$C_6H_4C(O)O$-*p*-C_6H_4CN, 70568-47-7; HO-*p*-$C_6H_4C(O)O$-*p*-$C_6H_4NO_2$, 38597-39-6; ^-O-*p*-$C_6H_4C(O)O$-2,4-$(NO_2)_2C_6H_3$, 94324-03-5; H_2O, 7732-18-5; 2,4-dinitrophenyl 2-hydroxybenzoate, 94324-02-4; 2,4-dinitrophenol, 51-28-5; salicyloyl chloride, 1441-87-8; 2-nitro-4-chlorophenyl 4-hydroxybenzoate, 93749-96-3; 2-chloro-4-nitrophenyl 4-hydroxybenzoate, 93749-97-4; 2,5-dinitrophenyl 4-hydroxybenzoate, 93749-98-5; 2,4-dinitrophenyl 4-hydroxybenzoate, 83187-56-8; 2,6-dinitrophenyl 4-hydroxybenzoate, 93749-99-6; 2,4-dinitrophenyl 4-methoxybenzoate, 24642-86-2; 2,4-dinitrophenyl 4-aminobenzoate, 94324-04-6; 2,4-dinitrophenyl 3-methylbenzoate, 36106-78-2; 2,4-dinitrophenyl 3-chlorobenzoate, 37156-55-1; 2,4-dinitrophenyl 3-methoxybenzoate, 36106-79-3; 2,4-dinitrophenyl 4-nitrobenzoate, 7622-07-3; 2,4-dinitrophenyl 3-nitrobenzoate, 36106-83-9; 2,4-dinitrophenyl 3,5-dinitrobenzoate, 94324-05-7; 2,4-dinitrophenyl benzoate, 1523-15-5; 4-carbonyl-2,5-cyclohexadienone, 94324-06-8.

Supplementary Material Available: Analytical data (1 page). Ordering information is given on any current masthead page.

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On the Amination of Halogenonitropyridines

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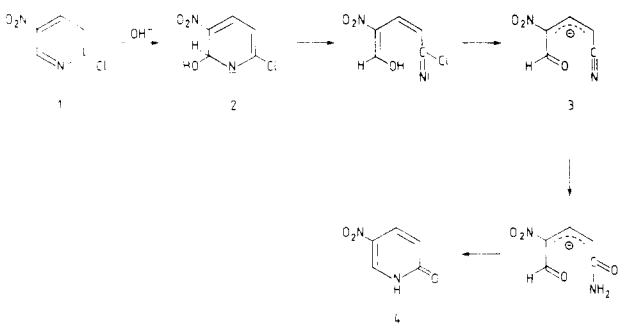
Evidence is presented, based on ^{15}N-labeling experiments and ^1H NMR spectroscopy, that the conversion of 2-chloro-5-nitropyridine (1) into 2-amino-5-nitropyridine by treatment with potassium amide/liquid ammonia proceeds to about 75% according to a sequence of reactions involving addition of the amide ion to C-6, ring-opening, and ring-closure [S_N(ANRORC) mechanism]. On the contrary, 2-chloro-3,5-dinitropyridine (11) is nearly quantitatively aminated by liquid ammonia (containing no potassium amide) into 2-amino-3,5-dinitropyridine according to an S_N(AE) process, thus no ring-opening being involved. As shown by NMR spectroscopy, the position of addition of liquid ammonia to 11 is temperature dependent. At −60 °C the addition takes place at C-4, while at −40 °C the addition at C-6 is strongly favored. Apparently the addition at C-4 is kinetically controlled; the addition at C-6 leads to the thermodynamically more stable adduct. Amination of 11 with liquid ammonia in the presence of potassium permanganate yields mainly 2,6-diamino-3,5-dinitropyridine.

The nucleophilic displacement of halogen in heteroaryl halides can occur according to a number of different pathways. It has been shown that amination of many halogenopolyazaaromatics by potassium amide/liquid ammonia often involves an S_N(ANRORC) mechanism, describing a reaction sequence, which starts by Addition of the Nucleophile (usually at a position meta to the leaving group), and is followed by Ring Opening and Ring Closure.[1]

The occurrence of an S_N(ANRORC) mechanism in nucleophilic substitutions of halogenopyridines has not hitherto been observed. It has been reported that 2-bromopyridine on amination with potassium amide/liquid ammonia does not react with ring opening but gives 2-aminopyridine exclusively according to the S_N(AE) process.[2,3]

Scheme I



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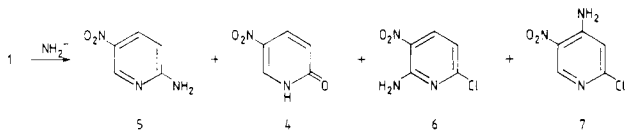
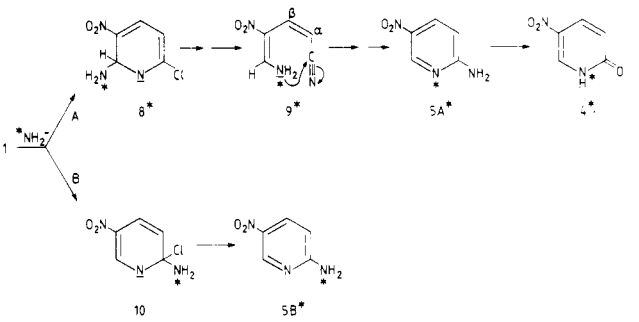
0022-3263/85/1950-0484$01.50/0

Scheme II



Scheme III



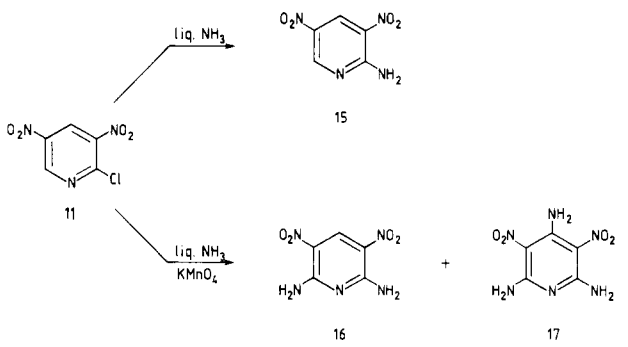
Some years ago Reinheimer et al. reported the occurrence of an S_N(ANRORC) mechanism in the hydroxydechlorination of 2-chloro-5-nitropyridine (1) by treatment (Scheme I) with an excess of base in Me_2SO.[4] It was convincingly shown that the formation of 5-nitropyridin-2(1*H*)-one (4) involves the intermediacy of the (isolable) formylcyanonitropropenide salt (3), being formed by ring opening of the initially formed Meisenheimer adduct 2. The conversion of 3 into 4 takes place only with an excess of hydroxide ions.

The fact that base treatment of compound 1 leads to ring opening induced us to study the amination of 1 with ^{15}N-labeled potassium amide/liquid ammonia. If ring opening occurs in this reaction, incorporation of nitrogen-15 into the pyridine ring will take place. As an extension of this work we included in our research the amination of 2-chloro-3,5-dinitropyridine (11).

Amination of 2-Chloro-5-nitropyridine (1). On treatment of 1 equiv. of 2-chloro-5-nitropyridine (1) with 2 equiv. of potassium amide, dissolved in liquid ammonia, at −33 °C for 1 h a mixture of compounds is formed (Scheme II). This mixture contains as main products 2-amino-5-nitropyridine (**5**, 40%) and 5-nitropyridin-2-(1*H*)-one (**4**, 12%), together with small quantities (<3%) of 2-amino-6-chloro-3-nitropyridine (**6**) and 4-amino-2-chloro-5-nitropyridine (**7**); in addition 15% of starting material is recovered. When the amination is carried out with ^{15}N-labeled potassium amide/liquid ammonia, 75% ^{15}N incorporation into the nitrogen of the pyridine ring in **5** was found. This result was established by mass spectrometric determinations of the excess of nitrogen-15 in **5A*** (9.4%) and in 5-nitropyridin-2(1*H*)-one (**4***) (7.1%), the last-mentioned compound being obtained from **5A*** by diazotization (Scheme III). These results unequivocally prove that the amination of 1 involves a ring-opening–ring-closure sequence (route A, percent S_N(ANRORC) = 7.1/9.4 × 100 = 75%). It starts by the initial formation of a C-6 adduct **8*** and ring opening of **8*** into the aminocyano compound **9***, which on cyclization gives **5A***.

The remaining 25% of **5** results from a reaction of 1 according to the more classical Addition–Elimination mechanism (route B), involving intermediate **10** (percent S_N(AE) = 25%).

Scheme IV



To substantiate further the involvement of the S_N(ANRORC) mechanism in the amination of 1 into **5** we tried to obtain additional ^1H NMR evidence. When 1 is dissolved in liquid ammonia, containing potassium amide at −33 °C, the ^1H NMR spectrum exhibits besides the signals of substrate 1 and product **5** a singlet at δ 9.97 and two pairs of doublets, one at δ 6.99 (J = 13 Hz) and δ 5.16 (J = 13 Hz) the other one at δ 7.32 (J = 9 Hz) and δ 5.32 (J = 9 Hz). The chemical shifts of these signals combined with the magnitude of the coupling constants suggest the presence of open-chain compound **9**. This compound can be present in the cis and trans orientation around the α-β bond, as suggested by the pair of doublets. These data are in good agreement with the ones, reported by Reinheimer.[4]

Signals characteristic for the presence of the σ-adduct 2-amino-6-chloro-3-nitropyridinide (**8**) could not be detected in the ^1H NMR spectrum. It indicates that the rate of ring opening of **8** is relatively faster than its rate of formation. Indirect evidence for the intermediacy of **8** is provided by the result that the yield of compound **6** is increased from <3% to about 10% when 1 is added to a solution of potassium amide *and* potassium permanganate in liquid ammonia. Potassium permanganate present in the liquid ammonia is able to oxidize **8** partly into **6** and thus prevents that all molecules of σ-adduct **8** undergo ring opening. We observed that the yield of the 4-amino compound **7** is also increased (up to about 6%) when the amination of 1 is carried out in the presence of potassium permanganate. It shows that compound 1 is also able to undergo addition at C-4, although to a limited extent.

In conclustion, from our work it is evident that compound 1 features a remarkable multisided addition pattern toward the amide ion: addition at C-2, leading to **5** [S_N(AE)^{ipso}], addition at C-4, yielding the Chichibabin product **7** [S_N(AE)^{ipso}], and addition at C-6, leading to another Chichibabin product **6** [S_N(AE)^{ipso}] and to **5** [S_N(ANRORC)^{ipso}]. Based on the yield of products obtained in the amination, the addition sequence is C-6 > C-2 > C-4. These results are very different from those obtained with 2-bromopyridine, which only undergoes an exclusive aminodebromination at C-2 [S_N(AE)^{ipso}].[2]

Amination of 2-Chloro-3,5-dinitropyridine (11). Amination of 11 with potassium amide in liquid ammonia at −33 °C yields only tarry products, but with liquid ammonia (containing no potassium amide) a quantitative yield of 2-amino-3,5-dinitropyridine (**15**) was obtained (Scheme IV). When the amination was carried out with liquid ammonia, being ^{15}N labeled, no incorporation of the nitrogen-15 into the pyridine ring was observed, nitrogen-15 being exclusively present on the amino group at position 2. This was proved by conversion of the ^{15}N-labeled amino compound (**15***) into the corresponding pyridin-2(1*H*)-one by acid treatment and measuring the ^{15}N content in the pyridone obtained. No ^{15}N labeling was

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Table I. ^1H and ^{13}C Chemical Shifts (ppm) and Coupling Constants (Hertz) of 11 in Deuteriochloroform and in Liquid Ammonia

solvent	H-4	H-6	$J_{4,6}$	C-4	C-6	$^1J_{C_4H}$	$^1J_{C_6H}$
$CDCl_3$	9.08	9.50	3.3	130.0	147.3	178	198
NH_3[a]	8.30	5.37	1.5	130.8	66.8	168	159
	$\Delta\delta$ = 0.78	$\Delta\delta$ = 4.13		$\Delta\delta$ = −0.8	$\Delta\delta$ = 80.5		
NH_3[b]	5.28	7.85	0.9				
	$\Delta\delta$ = 3.80	$\Delta\delta$ = 1.65					

[a] Spectra at −40 °C. [b] Spectrum at −60 °C.

Table II. ^1H and ^{13}C Chemical Shifts (ppm) and Coupling Constants (Hertz) of 15 in Dimethyl-d_6 Sulfoxide and in Liquid Ammonia

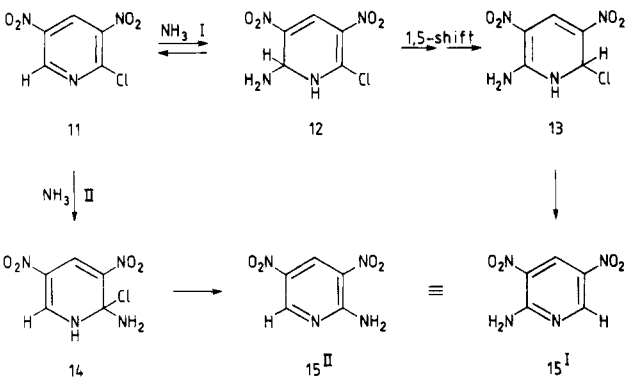
solvent	H-4	H-6	$J_{4,6}$	C-4	C-6	$^1J_{C_4H}$	$^1J_{C_6H}$
Me_2SO-d_6	8.97	9.18	3.3	131.3	151.4	174	190
NH_3[a]	5.32	8.27		46.1	153.9	146	176
	$\Delta\delta$ = 3.65	$\Delta\delta$ = 0.91		$\Delta\delta$ = 85.2	$\Delta\delta$ = −2.5		

[a] Spectra at −40 °C.

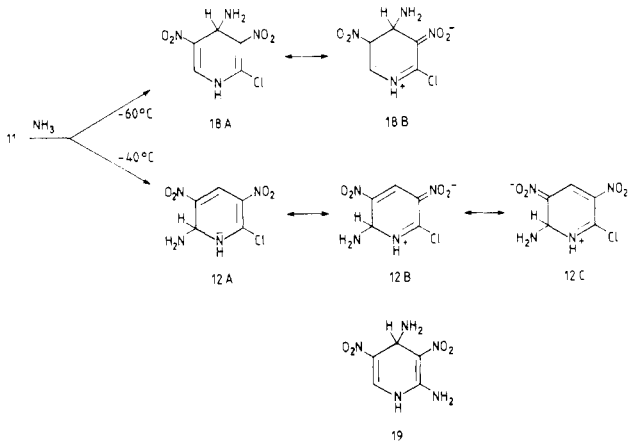
found. This result clearly indicates that no ring opening is involved in the amination. Treatment of **11** with liquid ammonia, containing potassium permanganate, gives a quite different result. No formation of **15** but of 2,6-diamino-3,5-dinitropyridine (**16**, 70%) together with some 2,4,6-triamino-3,5-dinitropyridine (**17**, 5%) was observed. It is evident that in the formation of both products **16** and **17** an addition of ammonia to C-6 of the pyridine ring and subsequent oxidation of the adduct must be involved leading to the introduction of the amino group at C-6. The introduction of the amino group at C-4 (i.e., **17**) suggests the intermediacy of a C-4 adduct although this addition reaction occurs to a limited extent. In order to substantiate the addition of ammonia to C-6 in **11** we measured the ^1H and ^{13}C NMR spectra of a solution of **11** in liquid ammonia at −40 °C and observed (see Table I) that H-6 and C-6 have undergone considerable upfield shifts ($\Delta\delta$(H-6) = 4.13 ppm and $\Delta\delta$(C-6) = 80.5 ppm). These upfield shifts show that at C-6 addition has taken place (i.e., **12**); the values are in good agreement with the ones reported for similar adducts.[5] These signals could be unequivocally assigned to C-6 adduct **12** on the basis of comparison of the spectra with those of 6-deuterio-2-chloro-3,5-dinitropyridine in $CDCl_3$ and liquid ammonia. After 1 h at −40 °C no change of the ^1H NMR spectrum has taken place; no indication for the formation of **15** was observed and in addition no trace of a C-4 adduct was found. These results bring forward the interesting question whether **15** is formed via route II involving **14** or via **12** (route I) which via a 1,5-sigmatropic suprafacial hydrogen shift and subsequent elimination of hydrogen chloride (Scheme V) would also give **15** (i.e., 15^I). Reaction course I can be considered as a tele amination [$S_N(AE)^{tele}$]; several examples of tele reactions in pyridines and naphthyridines have been reported.[6,7]

Further investigations on σ-adduct formation between **11** and liquid ammonia have shown that the addition pattern is temperature controlled (Scheme VI). Whereas, as we have seen, at −40 °C addition takes place at C-6, at lower temperature (−60 °C) addition is found to occur at C-4; i.e., **18** is formed ($\Delta\delta$(H-4) = 3.80 ppm, see Table I). At an intermediate temperature (−50 °C) both adducts are formed; the ^1H NMR spectrum exhibits signals of adduct **12** at δ 8.40 and δ 5.45 and of adduct **18** at δ 7.90 and δ 5.30 (ratio **12**:**18** = 3:1). Apparently at −60 °C the formation

Scheme V



Scheme VI



of **18** is kinetically controlled, but at somewhat higher temperature the thermodynamically more stable C-6 adduct **12** is favored. The higher stability of **12** compared to **18** is probably due to its more extended conjugate resonance system **12A** ⇄ **12B** ⇄ **12C**.

The easy accessibility of the 3,5-dinitropyridine ring system for nucleophilic addition is further demonstrated by the fact that 2-amino-3,5-dinitropyridine (**15**), when dissolved in liquid ammonia, easily undergoes addition into the C-4 adduct **19**, as shown by ^1H NMR spectroscopy (see Table II).

Experimental Section

Melting points are uncorrected. The ^1H NMR spectra were recorded on a Hitachi Perkin-Elmer R 24 B spectrometer and a Varian EM 390 spectrometer equipped with a Varian EM 3940 variable-temperature controller. Me_4Si was used as internal

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standard (δ = 0 ppm). In liquid ammonia the solvent peak was used as the standard (δ = 0.95 ppm). The ^{13}C NMR spectra were recorded at 75.460 MHz on a Bruker CXP-300 spectrometer equipped with a B-VT 1000 variable-temperature controller. For measurements in liquid ammonia thick-wall 5- and 10-mm o.d. tubes were used for ^{1}H and ^{13}C NMR spectroscopy, respectively. The latter contained an internal 3-mm capillary with acetone-d_6. This was used both for the lock signal and as internal standard (δ = 29.8 ppm). Spectral parameters: 15000 Hz spectral width, 1.2 s pulse delay. IR spectra were recorded on a Hitachi EPI-G3 spectrometer. Mass spectra were obtained on a AEI MS 902 spectrometer equipped with VG ZAB console and GC–MS analysis was performed on a VG-micromass 7070 F apparatus. Column chromatography was carried out over Merck Silica gel 60 (70-230 mesh ASTM).

Preparation of Starting Materials and Reference Compounds. A. 2-Chloro-5-nitropyridine (**1**),[8] 5-nitropyridin-2-(1*H*)-one (**4**),[9] 2-amino-5-nitropyridine (**5**),[10] 2-amino-6-chloro-3-nitropyridine (**6**),[11] 4-amino-2-chloro-5-nitropyridine (**7**),[12] 2-chloro-3,5-dinitropyridine (**11**),[8] 2-amino-3,5-dinitropyridine (**15**),[13] 2,6-diamino-3,5-dinitropyridine (**16**),[14] and 2,4,6-triamino-3,5-dinitropyridine (**17**)[15] were all prepared according to known synthetic procedures.

B. 2-Chloro-6-deuterio-3,5-dinitropyridine. This compound was synthesized by a sequence of reactions starting with 2-aminopyridine-6-carboxylic acid-*d*, which was prepared by refuxing of 6-aminopicolinic acid in D_2O. Heating of the deuterated acid at about 350 °C in a distillation apparatus yields 2-amino-6-deuteriopyridine, which was purified by column chromatography on silica gel using as eluent chloroform/methanol (10:1). The aminodeuteriopyridine was converted into 6-deuterio-3,5-dinitropyridin-2(1*H*)-one by diazotization and subsequent nitration according to the procedure described by Kozlowska and Plazek.[9] The conversion of this pyridin-2(1*H*)-one into 2-chloro-6-deuterio-3,5-dinitropyridine was performed by treatment with phosphoryl chloride. The deuterium content amounts to 70%.

Amination of 2-Chloro-5-nitropyridine (1) with Potassium Amide in Liquid Ammonia. 1 (318 mg, (2.0 mmol) was added to a solution of 50 mL of liquid ammonia containing 4.0 mmol of potassium amide. The reaction mixture was then stirred for 1 h at −33 °C after which the reaction was terminated by the addition of ammonium chloride. The ammonia was evaporated and the residue was extraced with three 25-mL portions of chloroform. The chloroform extracts were dried with $MgSO_4$ and the solvent was evaporated off in vacuo. By column chromatography on silica gel using dichloromethane as eluent 40% of **5**, 12% of **4**, and small quantities of **6** and **7** were isolated. Compounds **4**, **5**, **6**, and **7** were identified by mass, NMR, and IR spectroscopy and comparison with authentic specimens.

Amination of 1 with ^{15}N-Labeled Potassium Amide in ^{15}N-Labeled Ammonia. This reaction was carried out in the same manner as described above. ^{15}N-Labeled ammonia was prepared by treatment of ^{15}N-labeled ammonium nitrate, containing an ^{15}N excess in the ammonium group, with a concentrated solution of potassium hydroxide in water at 100 °C for 2 h.[16] The conversion of **5*** into **4*** was performed by the procedure described for unlabeled **5**.[17]

Amination of 1 with Potassium Amide in Liquid Ammonia in the Presence of Potassium Permanganate. This reaction was carried out by adding 1 to a solution of potassium permanganate (2 redox equiv) in liquid ammonia containing the potassium amide. After workup of the reaction mixture 10% of **6** and 6% of **7** were isolated besides 43% of **5** and 5% of **4**.

Amination of 2-Chloro-3,5-dinitropyridine (11) in Liquid Ammonia. 11 (203.5 mg, 1 mmol) was added to 5 mL of dry liquid ammonia at −33 °C. After being stirred for 1 h, 25 mL of methanol were added, and this solution was evaporated to yield 165 mg (90%) of **15**, mp 189–191 °C (lit.[13] mp, 190–192 °C). Amination of 11 in ^{15}N-labeled ammonia was carried out in the same manner to yield **15***.

Conversion of ^{15}N-Labeled 2-Amino-3,5-dinitropyridine (15) into the Corresponding 3,5-Dinitropyridin-2(1*H*)-one. Heating of **15*** with an excess of concentrated hydrochloric acid for 10 h at 140 °C in a sealed tube, and evaporation in vacuo yielded 3,5-dinitropyridin-2(1*H*)-one. The product contained no excess of ^{15}N.

Amination of 11 in Liquid Ammonia in the Presence of Potassium Permanganate. To a solution of potassium permanganate (110 mg, 1 redox equiv) in liquid ammonia was added compound 11 and the solution was allowed to react for 1 h. After workup of the reaction mixture the products **16** and **17** were isolated in respectively 70% and 5% yield. The structures of **16** and **17** were based on NMR, IR, and mass spectra and comparison with authentic specimens.

Acknowledgment. We are indebted to Dr. M. A. Posthumus, Dr. C. A. Landheer, and Mr. C. J. Teunis for mass spectroscopic data and to Dr. H. Holterman and Mr. A. van Veldhuizen for measuring NMR spectra.

Registry No. **1**, 4548-45-2; **4**, 5418-51-9; **4***, 93965-99-2; **5**, 4214-76-0; **5***, 93966-00-8; **6**, 27048-04-0; **7**, 2604-39-9; **11**, 2578-45-2; **15**, 3073-30-1; **15***, 93966-01-9; **16**, 34981-11-8; **17**, 39771-28-3; 2-aminopyridine-6-carboxylic acid-*d*, 93966-02-0; 6-aminopicolinic acid, 23628-31-1; D_2O, 7789-20-0; 2-amino-6-deuteriopyridine, 93966-03-1; 6-deuterio-3,5-dinitropyridin-2(1*H*)-one, 93966-04-2; 2-chloro-6-deuterio-3,5-dinitropyridine, 93966-05-3; potassium amide, 17242-52-3; ammonia, 7664-41-7; ^{15}N-labeled potassium amide, 93966-06-4; ^{15}N-labeled ammonia, 13767-16-3; potassium permanganate, 7722-64-7; 3,5-dinitropyridin-2(1*H*)-one, 2980-33-8.

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