**General Procedure for the Reactions of Nitrones with Phosphonates.** A 50% dispersion of sodium hydride in mineral oil (0.5 g, 0.01 mol) was washed with petroleum ether (bp 40–60 °C, 3 × 10 mL) in an inert atmosphere. After evaporation of the residual petroleum ether, 10 mL of DME (freshly distilled from lithium aluminum hydride) was injected, followed by 0.01 mol of phosphonate dissolved in 5 mL of DME with cooling. After the liberation of hydrogen ceased, 0.01 mol of the nitrone dissolved in 5 mL of DME was introduced. The reaction mixture was stirred under the conditions (time and temperature) indicated in the tables. DME was evaporated in vacuo, and the residue was placed on a short alumina column. Elution of the column by chloroform gave mixtures of starting nitrone with aziridine and enamine products. These mixtures were separated by preparative thin-layer chromatography (alumina $GF_{254}$, 1 mm) by development with mixtures of chloroform–petroleum (bp 40–60 °C). The physical constants of products **8–15** were reported previously.[4,5] The yields are given in the tables. Further elution of the columns by methanol gave the cyclic phosphates **20** or **21** which were isolated by the evaporation of the solvent.

***trans*-1-Methyl-2-cyano-3-phenylaziridine (22).** This compound was obtained from the reaction of nitrone **7** with phosphonate **2** in refluxing DME for 48 h. The product was isolated in the usual manner: IR (neat film) 2220 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.43 (5 H, m), 2.86 (1 H, d, $J$ = 3 Hz), 2.73 (3 H, br s), 2.51 (1 H, d, $J$ = 3 Hz, lit.[20]).

**4,5-Dimethyl-2-hydroxy-2-oxo-1,3,2-dioxaphospholane (20):** IR (Nujol) 3300, 1640, 1210, 1120, 1080, 975 $cm^{-1}$; $^1H$ NMR ($D_2O$) $\delta$ 4.33–3.66 (2 H, m), 1.38–1.30 (6 H, singlets); $^{31}P$ NMR ($D_2O$) 15.6 ppm.[21]

**5,5-Dimethyl-2-hydroxy-2-oxo-1,3,2-dioxaphosphorinane (21):** IR (Nujol) 3300, 2400, 1680, 1620, 1200, 1075, 1060, 1000, 940, 900 $cm^{-1}$; $^1H$ NMR ($D_2O$) $\delta$ 3.93 (4 H, d, $J$ = 12 Hz), 0.97 (6 H, s); $^{31}P$ NMR ($D_2O$) −2.1 ppm; $^{31}P$ NMR (pyridine) −5.15 ppm.[22,23]

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**Registry No.** **1**, 72258-75-4; **2**, 67920-85-8; **3**, 67889-05-8; **4**, 66934-40-5; **5**, 3317-61-1; **6**, 24423-87-8; **7**, 3376-23-6; **8**, 57740-49-5; **9**, 57740-50-8; **10**, 61650-07-5; **11**, 66934-41-6; **12**, 64890-49-9; **13**, 80387-05-9; **14**, 5019-07-8; **15**, 64890-46-6; **18**, 867-13-0; **19**, 2537-48-6; **20**, 50577-87-2; **21**, 873-99-4; **22**, 80375-47-9.

# Ring Transformations in Reactions of Heterocyclic Compounds with Nucleophiles.[1] Conversion of 5-Nitropyrimidine into 2-Substituted 5-Nitropyrimidine and 2-Amino-5-nitropyridines by Amidines[2]

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The reaction of 5-nitropyrimidine (1) with benzamidine, pivalamidine, acetamidine, propionamidine, α-phenylacetamidine, *O*-methylisourea hydrochlorides, and cyanamide in ethanolic solution in the presence of triethylamine has been investigated. It was found that reaction of 1 with alkyl(aryl) amidines, having no active methylene groups attached to the amidine moiety (pivalamidine, benzamidine), *exclusively* formed the corresponding 2-substituted 5-nitropyrimidines in good yields. With acetamidine and propionamidine, in addition to the formation of the 2-substituted 5-nitropyrimidines, the formation of 2-amino-5-nitropyridines also was observed; with α-phenylacetamidine a 2-amino-5-nitropyridine derivative *exclusively* was obtained. The reaction of 1 with both *O*-methylisourea and cyanamide leads to 2-amino-5-nitropyrimidine. These reactions provide new examples of degenerate ring transformations of the pyrimidine ring system and of the ring transformatin of pyrimidines into pyridines.

It has been firmly established that pyrimidine an its C- and N-substituted derivatives are appropriate systems to undergo transformations to other heterocyclic ring systems by reaction with various nucleophilic reagents.[3-4] Ring transformations occurring with 1,3-ambident nucleophiles are of special interest since displacement of the N(1)–C-(2)–N(2) portion of the pyrimidine ring by either the N–C–N, C–C–N, or C–C–C fragment of the employed nucleophile (forming pyrimidine, pyridine, or benzene ring systems, respectively) has been observed.

Conversion of a pyrimidine ring into a benzene ring has been reported for the first time in the reaction of 5-nitropyrimidine with ketonic reagents[5] and very recently in the treatment of uracil derivatives with various active methylene compounds[6a] and 5-nitro-2(1*H*)-pyrimidinone with acetone.[6b]

The ring conversion of the pyrimidine system into the pyridine system through replacement of the N(1)–C(2) fragment of the pyrimidine ring by the C–C part of the reacting species has been well-established,[5,7-9] but displacement of the N(1)–C(2)–N(3) portion of the pyrimidine by a C–C–N fragment has only recently been observed in the conversion of 1,3-dimethyluracils into the corresponding 5-substituted 2,6-dihydroxypyridines[10] by α-substituted acetamide derivatives in ethanolic sodium ethoxide.

An interesting series of transformations of the pyrimidines are the so-called degenerate ring transformations.[11,12] In these reactions atom N(1) or the fragments N(1)–C(2) or N(1)–C(2)–n(3) of the pyrimidine ring are replaced by the N, N–C or N–C–N moiety of the nucleophile, respectively, thus leading in all three cases to the same pyri-

(1) Part 24 in the series. For part 23, see Dlugosz, A.; Van der Plas, H. C.; Van Veldhuizen, A. *J. Heterocycl. Chem.* manuscript submitted.
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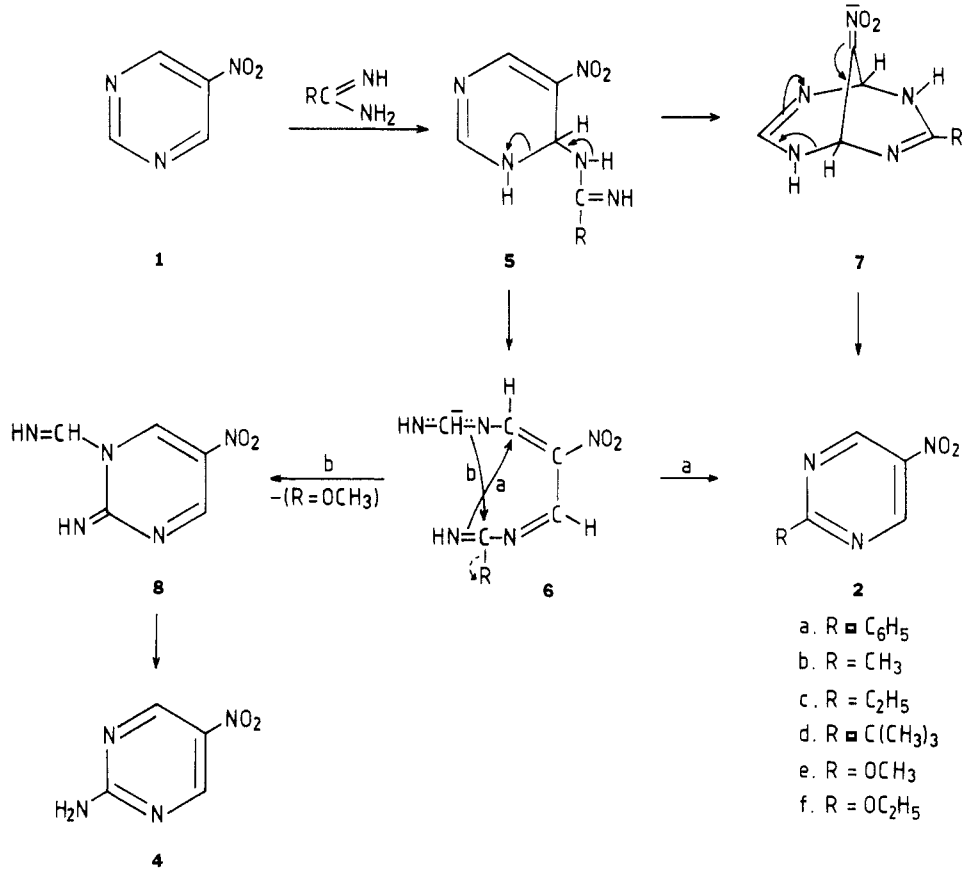
Scheme I




midine ring system. Nucleophilic displacement of N(1) by nitrogen (of ammonia) and of the N(1)–C(2)–N(3) portion of pyrimidine by the N–C–N fragment of the nucleophile has first been reported by Oostveen et al.[12] in the demethylation of 1-methylpyrimidinium iodide in liquid ammonia and conversion of 1-methylpyrimidinium iodide into 2-phenylpyrimidine and 2-*tert*-butylpyrimidine by treatment with benzamidine and pivalamidine in basic media, respectively. Later Hirota et al.[13,14] showed the occurrence of the same type of ring transformation in the reaction of 1,3-dialkylated uracils with guanidine, urea, and thiourea, leading to cytosine and thiouracil systems.

In the present paper we report on new examples of the transformation of pyrimidines and pyridines and on interesting, new synthetic application of degenerate pyrimidine ring transformations taking place in the reactions of 5-nitropyrimidine (1) with the binucleophilic amidines.

## Results and Discussion

Treatment of 5-nitropyrimidine (1) with benzamidine hydrochloride or pivalamidine hydrochloride in ethanolic solution in the presence of an excess of triethylamine afforded 2-phenyl-5-nitropyrimidine (**2a**) and 2-*tert*-butyl-5-nitropyrimidine (**2d**). However, when 1 was reacted with acetamidine or propionamidine hydrochlorides, besides the expected 2-methyl-5-nitropyrimidine (**2b**) or 2-ethyl-5-nitropyrimidine (**2c**) in comparable yields, 2-amino-5-nitropyridines **3a** and **3b** were isolated from the reaction mixtures. With α-phenylacetamidine only 2-amino-3-phenyl-5-nitropyridine (**3c**) was formed (see Table I for conditions and yields).

Table I. Reaction of 1 Equiv of 5-Nitropyrimidine with an Excess of Amidine Hydrochlorides, *O*-Methylisourea Hydrochloride, and Cyanamide in the Presence of Triethylamine

| RC(=NH)NH$_2$ | equiv of reagent | solvent/rctn (temp, °C) | rctn time, h | products (% yield) |
|---|---|---|---|---|
| R = $C_6H_5$ | 2.2 | ethanol/reflux | 3 | **2a** (84) |
| R = $CH_3$ | 3.5 | ethanol/reflux | 3 | **2b** (46), **3a** (11.5) |
| R = $C_2H_5$ | 3.5 | ethanol/reflux | 3 | **2c** (30), **3b** (33) |
| R = $C(CH_3)_3$ | 3 | ethanol/reflux | 1.5 | **2d** (87) |
| R = $C_6H_5CH_2$ | 2.2 | ethanol/reflux | 3 | **3c** (67) |
| R = $CH_3O$ | 6 | methanol/ambident | 20 | **2e** (29), **4** (49) |
| $NH_2CN$ | 3.5 | ethanol (85-90) | 15 | **4** (64) |

[a] Healed in a sealed tube.

Treatment of 5-nitropyrimidine (1) with *O*-methylisourea hydrochloride in the presence of triethylamine in methanolic solution lead to formation of 2-methoxy-5-nitropyrimidine (**2e**) and 2-amino-5-nitropyrimidine (**4**). We noticed that when the last-mentioned reaction was carried out in ethanol instead of methanol the initially formed 2-methoxy-5-nitropyrimidine was converted into 2-ethoxy-5-nitropyrimidine (**2f**). It is worth mentioning that when the same nucleophile was reacted with pyrimidinium salts,[12] only 2-aminopyrimidine was obtained, while with *s*-triazine[15] 2-methoxy-*s*-triazine was formed very smoothly. Reaction of 1 with cyanamide in ethanol for 15 h at 85–90 °C in a sealed tube afforded 2-amino-5-nitropyrimidine (**4**) as the main product in a slow reac-

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tion. A longer duration of the reaction or heating in a sealed tube is required in this reaction in order to convert 5-nitropyrimidine completely.

The formation of 2-substituted 5-nitropyrimidines (**2a–2e**) can be considered as a degenerate ring transformation in which the N(1)–C(2)–N(3) fragment of the pyrimidine is replaced by the N–C–N fragment of the amidine. The N–C–N donation properties of amidines have been recognized before and were proved unequivocally in the reaction of a pyrimidinium salt with $^{15}N$-labeled benzamidine in basic media.[12] The formation of **2a–2e** can be described to start by an initial attack of the amidine nitrogen to the highly electron-deficient C(6) in **1**, leading to the 1(3),6-dihydropyrimidine **5**. Whether first ring opening occurs by fission of the N(1)–C(6) bond, leading to an intermediate **6** which on recyclization (route a) gives **2**, or first formation of bicyclic intermediate **7** is still an open question, although there is sufficient evidence for the occurrence of bicyclic intermediates in the reactions of trinitroarenes with nucleophiles.[16,17]

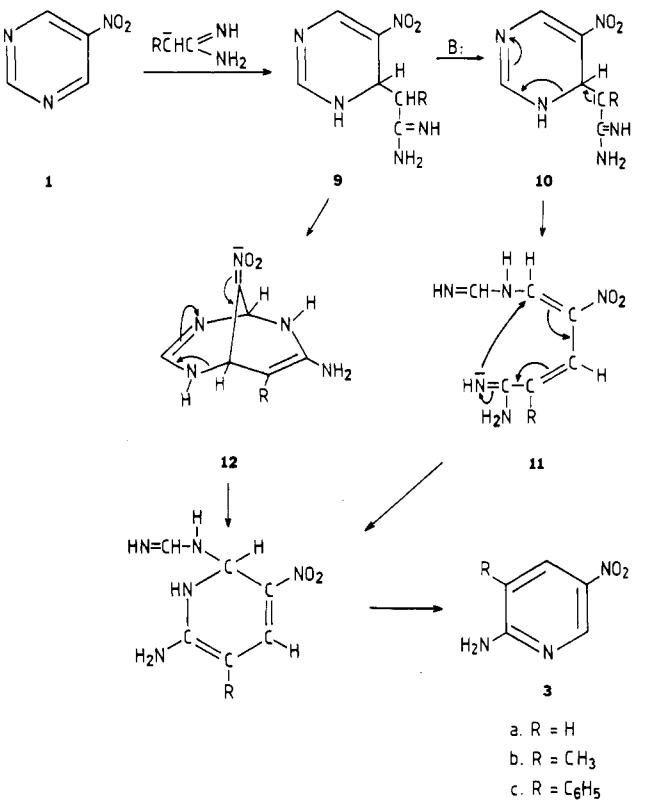
Recyclization of **6** can also occur by attack of the negatively charged nitrogen across the amidine carbon atom (route b in Scheme I), giving **8**. It explains why in the reaction of **1** with *O*-methylisourea hydrochloride 2-amino-5-nitropyrimidine (**4**) is formed, due to loss of a methoxide ion. Product **4** obtained by treatment of **1** with cyanamide is probably formed according to a similar mechanistic pathway. It is evident that in these cases the degenerate ring transformation involves an overall replacement of the two atom N(1)–C(2) fragment of the pyrimidine by the N–C fragment of the nucleophile.

Pyrimidine-to-pyridine ring transformations observed in the reaction of 5-nitropyrimidine with acetamidine, propionamidine, or $\alpha$-phenylacetamidine show that amidines can also serve as a C–C–N donor. This is due to the fact that these amidines are capable of forming carbanions. In these carbanions, the carbon has sufficient negative charge to attack the C(6) position, giving rise to the Michael adduct **9** (Scheme II). This behavior has been commonly observed in nucleophilic reactions of acetamidines with tri- or dinitroarenes.[17] Proton abstraction from the exocyclic $\alpha$ position, accompanied by ring opening, yields an open-chain product **11**, in which by subsequent attack of the terminal amidine nitrogen on C(4) followed by scission of the C(4)–N(3) linkage **3** is produced. With $\alpha$-phenylacetamidine having a more acidic proton in the $\alpha$ position, this reaction pathway is the only one. It cannot be excluded that the formation of **3** can occur via the bicyclic intermediate **12**. An indication for such a possibility is that amidines with electron-deficient benzenes and naphthalenes yield stable bridged products.[17–19] It is evident that these ring transformatins open new and useful synthetic routes to 2-substituted 5-nitropyrimidines. The facile preparation of two previously unknown compounds, i.e., 2-ethyl- and 2-*tert*-butyl-5-nitropyrimidines, exemplifies its usefulness.

## Experimental Section

Melting points are uncorrected. The $^1H$ NMR spectra were recorded on a Varian EM-360 60-MHz spectrophotometer using trimethylsilane ($Me_4Si$) as internal standard. Mass spectra were obtained on a JEOL JMS-D-100 spectrometer.

Scheme II




**1. Preparation of Starting Materials.** 5-Nitropyrimidine (**1**) was prepared by the method described in the literature.[19,20] Amidines were prepared from the corresponding nitriles.[21,22] The amidines were isolated, characterized, and used as hydrochlorides. Cyanamide and *O*-methylisourea hydrochloride were obtained from commerical sources.

**2. Reactions of 5-Nitropyrimidine (1) with the Hydrochlorides of Benzamidine, Acetamidine, Propionamidine, Pivalamidine, α-Phenylacetamidine, and *O*-Methylisourea and with Cyanamide.** 5-Nitropyrimidine (**1**; 62 mg, 0.5 mmol) and the appropriate nucleophile were dissolved in 2 mL of absolute ethanol (or methanol); to this solution was added triethylamine (0.2 mL). The mixture was heated or stirred at room temperature. The equivalents of the nucleophile, the reaction time, the reaction temperature, and the yields of products obtained are summarized in Table I. the melting points, mass spectra, $^1H$ NMR data, and elemental analyses of compounds **2–4** are collected in Table II. The workup of the reaction mixture was strongly dependent on the nucleophiles used. Therefore we described separately the workup of the reaction mixtures obtained.

**a. Reaction Mixture Obtained from 1 with Benzamidine.** During the reaction a precipitate was obtained which was filtered, washed with water and ethanol, and recrystallized from ethanol, giving 85 mg (84%) of 2-phenyl-5-nitropyrimidine (**2a**) as white needles.

**b. Reaction Mixture Obtained from 1 with Acetamidine.** The solvent was removed in vacuo and to the residue obtained was added 2 mL of water. A precipitate was obtained, which was filtered and identified by $^1H$ NMR and mass spectrometry as crude 2-amino-5-nitropyridine (**3a**; 8 mg, 11.5%). A mixture

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Table II. Melting Points, Mass Spectral and $^1$H NMR Data, and Elemental Analyses of Compounds 2-4

| compd | mp °C (lit. mp, °C) | mass spectra, *m/e* | $^1$H NMR data ($CDCl_3$), chemical shift ($\delta$) | analyses, % calcd C | calcd H | found C | found H |
|---|---|---|---|---|---|---|---|
| **2a** | 225-226 (222-223.5)[21] | 201 ($M^+$)<br>77 ($C_6H_5^+$) | 9.48 (s, 2 H),<br>8.6-8.4 (m, 2 H)<br>7.5-7.8 (m, 3 H) | 59.70 | 3.48 | 59.96 | 3.62 |
| **2b** | 57-59 (59-60)[19]<br>(59-60)[19] | 139 ($M^+$)<br>93 ($M^+ - NO_2$)<br>52 (93 - $CH_3CN$) | 9.34 (s, 2 H),<br>2.85 (s, 3 H) | 41.73 | 3.60 | 41.81 | 3.53 |
| **2c** | oil | 153 ($M^+$)<br>107 ($M^+ - NO_2$)<br>52 (107 - $C_2H_5CN$) | 9.35 (s, 2 H),<br>3.13 (q, 2 H)<br>1.42 (t, 3 H) | 47.06 | 4.58 | 47.33 | 4.85 |
| **2d** | 56-56.5 | 181 ($M^+$)<br>166 ($M^+ - CH_3CN$)<br>120 (166 - $NO_2$) | 9.38 (s, 2 H),<br>1.42 (s, 9 H) | 53.04 | 6.08 | 53.13 | 6.30 |
| **2e** | 66.5-68 (68)[23] | 155 ($M^+$)<br>125 ($M^+ - CH_2O$)<br>79 (125 - $NO_2$) | 9.25 (s, 2 H),<br>4.11 (s, 3 H) | 38.71 | 3.23 | 39.01 | 3.46 |
| **2f** | 51-53 (52-54)[24] | 169 ($M^+$)<br>125 ($M^+ - C_2H_4O$)<br>79 (125 - $NO_2$) | 9.29 (s, 2 H),<br>4.59 (q, 2 H)<br>1.48 (t, 3 H) | 42.60 | 4.14 | 42.82 | 4.27 |
| **3a** | 187-188 (188)[26] | 139 ($M^+$)<br>93 ($M^+ - NO_2$)<br>66 (93 - HCN) | 9.05 (d, 1 H),<br>8.30 (dd, 1 H)<br>7.70 (br s, 2 H),<br>6.63 (d, 1 H)[a] | 41.73 | 3.60 | 42.01 | 3.62 |
| **3b** | 250-253 (255)[27] | 153 ($M^+$)<br>107 ($M^+ - NO_2$)<br>80 (107 - HCN) | 8.85 (d, 1 H),<br>8.10 (d, 1 H)<br>7.43 (br s, 2 H),<br>2.11 (s, 3 H)[a] | 47.06 | 4.58 | 47.22 | 4.55 |
| **3c** | 176.5-177 | 215 ($M^+$)<br>169 ($M^+ - NO_2$)<br>142 (169 - HCN)<br>77 ($C_6H_5^+$) | 9.00 (d, 1 H),<br>8.14 (d, 1 H),<br>7.44 (s, 5 H),<br>5.60 (br s, 2 H) | 61.40 | 4.19 | 61.67 | 4.17 |
| **4** | 236-238 (236)[25] | 140 ($M^+$)<br>94 ($M^+ - NO_2$)<br>67 (94 - HCN) | 8.98 (s, 2 H),<br>7.35 (br s, 2 H) | 34.29 | 2.86 | 34.43 | 3.01 |

[a] In $Me_2SO$-$d_6$.

melting point determination of **3a** (purified by sublimation) with an authentic specimen gave no depression. The mother liquor was extracted with chloroform, and the organic layer was separated and dried over $Na_2SO_4$. After evaporation of the solvent the product was isolated by column chromatography (using silica gel and chloroform as eluent) and recrystallized from petroleum ether (40–60 °C), giving 32 mg (46%) of 2-methyl-5-nitropyrimidine (**2b**).

**c. Reaction Mixture Obtained from 1 with Propionamidine.** A precipitate was yielded, which was filtered and identified by $^1$H NMR and mass spectrometry as crude 2-amino-3-methyl-5-nitropyridine (**3b**; 25 mg, 33%) 2-Ethyl-5-nitropyrimidine (**2c**) was isolated from the reaction mixture as an oily product (23 mg, 30%) by a procedure similar to the one described in section b. The compound was purified by repeated column chromatography on silical gel.

**d. Reaction Mixture Obtained from 1 with Pivalamidine.** The solvent was removed in vacuo and to the residual oil was added 2 mL of water. This solution was extracted with chloroform. After the chloroform extracts were dried over $Na_2SO_4$, the solvent was distilled. A white precipitate was obtained, which after recrystallization from the mixture methanol/water (2:1) gave 79 mg (87%) of 2-*tert*-butyl-5-nitropyrimidine (**2d**) as white needles.

**e. Reaction Mixture of 1 with *O*-Methylisourea.** The methanol was removed in vacuo and to the residue was added 2 mL of water. The precipitate was filtered, giving 34.5 g (49%) of 2-amino-5-nitropyrimidine (**4**). The filtrate was extracted with chloroform. After the chloroform extracts were dried over $Na_2SO_4$, the solvent was distilled. The residue was separated by column chromatography (using silica gel and chloroform as eluent), giving 22.5 mg (29%) of 2-methoxy-5-nitropyrimidine (**2e**). **2e** can be converted into 2-ethoxy-5-nitropyrimidine (**2f**) almost quantitatively by being heated in refluxing ethanol in the presence of triethylamine for several hours.

**f. Reaction Mixture of 1 with α-Phenylacetamidine.** After the reaction mixture stood overnight, a precipitate was yielded (107 mg), which was filtered and treated with 5 mL of water. The water solution was extracted with chloroform. The chloroform layer was dried over $Na_2SO_4$ and the solvent removed; 65 mg of 2-amino-3-phenyl-5-nitropyridine (**3c**) was obtained as yellow crystals. From the filtrate an additional 21 mg of **3c** was isolated by addition of 5 mL of water and extraction with chloroform. Collected precipitates recrystallized from methanol: yield, 75 mg (67%) of **3c**.

**g. Reaction Mixture of 1 with Cyanamide.** To the reaction mixture was added 2 mL of water. The precipitate was filtered, washed with water, and crystallized from ethanol, giving 45 mg (64%) of 2-amino-5-nitropyrimidine (**4**).

**Registry No.** 1, 14080-32-1; **2a**, 68906-00-3; **2b**, 14080-34-3; **2c**, 79899-27-7; **2d**, 79899-28-8; **2e**, 14001-69-5; **2f**, 13207-98-2; **3a**, 4214-76-0; **3b**, 18344-51-9; **3c**, 79899-29-9; **4**, 3073-77-6; benzamidine hydrochloride, 1670-14-0; acetamidine hydrochloride, 124-42-5; propionamidine hydrochloride, 3599-89-1; pivalamidine hydrochloride, 18202-73-8; *o*-methylisourea hydrochloride, 5329-33-9; α-phenylacetamidine hydrochloride, 2498-46-6; cyanamide, 420-04-2.