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Site-Selectivity in the Cyanation of 3-Substituted Pyridine 1-Oxides with Trimethylsilanecarbonitrile

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The cyanation of 3-halo-, 3-methoxy-, and 3-dimethylaminopyridine 1-oxide with trimethylsilanecarbonitrile gave predominantly the corresponding 3-substituted 2-pyridinecarbonitriles. The deoxygenation of nitropyridine 1-oxides to nitropyridines with the same reagent is also described.

Keywords——site-selective reaction; trimethylsilanecarbonitrile; pyridine 1-oxide; 2-pyridinecarbonitrile; nitropyridine 1-oxide; deoxygenation; aromatic amine N-oxide; cyanation

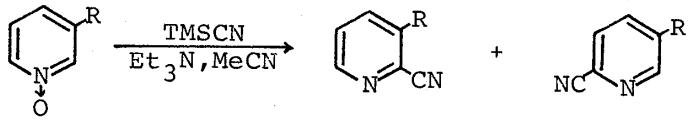
It is well known that many pyridine 1-oxides, except for 4-chloropyridine 1-oxide[1] and trifluoromethylpyridine 1-oxide,[2] are not susceptible to the Reissert–Henze reaction, unlike quinoline 1-oxides.[1,3] When pyridine 1-oxides are converted to 1-methoxypyridinium iodides, the quaternary bases readily react with potassium cyanide in aqueous dioxane.[4] This reaction, however, is not convenient for the preparation of cyanopyridines, giving a mixture of 2- and 4-pyridinecarbonitriles.

Recently, two groups have reported the cyanation of pyridine 1-oxides with trimethylsilanecarbonitrile (TMSCN). Namely, Vorbrüggen *et al.*[5] described the reaction of pyridine 1-oxides with TMSCN in the presence of triethylamine in acetonitrile (method A) and with trimethylchlorosilane and sodium cyanide in dimethylformamide (method B) at 100—110 °C. On the other hand, Fife *et al.*[6] reported the reaction of pyridine 1-oxides with TMSCN in the presence of *N,N*-dimethylcarbamoyl chloride in dichloromethane at room temperature (method C). These reactions are synthetically valuable, bacause of the exclusive formation of α-pyridinecarbonitriles. For example, the reaction of pyridine 1-oxide itself gave 2-pyridinecarbonitrile as the sole product. Furthermore, the reaction of 3-hydroxypyridine 1-oxide afforded 3-hydroxy-2-pyridinecarbonitrile by methods A, B, and C, and that of 3-carboxypyridine 1-oxide gave 6-cyano-3-pyridinecarboxylic acid by method B without the formation of positional isomers.

We applied these methods to the synthesis of diazine(pyridazine, pyrimidine, and pyrazine)carbonitriles and found Vorbrüggen's method A to be more convenient than Fife's method C.[7] Thus, in order to utilize the reaction for the preparation of monosubstituted 2-pyridinecarbonitriles, we investigated the site-selectivity in the reaction of various pyridine 1-oxides under the conditions of method A. In the present paper, the exclusive formation of 3-halo-2-pyridinecarbonitriles is described, together with the deoxygenation of nitropyridine 1-oxides, which was observed during the investigation.

When 3-fluoropyridine 1-oxide (**1a**) was treated with TMSCN by method A, 3-fluoro-2-pyridinecarbonitrile (**2a**) was obtained in 83% yield. Gas-chromatographic (GC) analysis of the crude product revealed no formation of positional isomers, *e.g.* 5-fluoro-2-pyridinecarbonitrile (**3a**). The structure **2a** can be easily discriminated from **3a** by proton magnetic resonance (^{1}H-NMR) spectrometry. Although the reactions of 3-chloro- (**1b**) and 3-

bromopyridine 1-oxide (**1c**) under the same conditions gave mixtures of positional isomers, the yields of the 5-halo-2-pyridinecarbonitriles (**3b, c**) were negligible. The main products, 3-chloro- (**2b**) and 3-bromo-2-pyridinecarbonitrile (**2c**), were easily purified by silica-gel column chromatography. Furthermore, it should be mentioned that complete site-selectivity was also observed in the reaction of 3-methoxy- (**1d**) and 3-dimethylaminopyridine 1-oxides (**1e**) to give 3-methoxy- (**2d**) and 3-dimethylamino-2-pyridinecarbonitriles (**2e**) in good yields.



a: R=F **b**: R=Cl **c**: R=Br **d**: R=OMe
e: R=NMe_2 **f**: R=Me **g**: R=Et **h**: R=Ph
i: R=$CONEt_2$ **j**: R=COOEt **k**: R=CN

Chart 1

TABLE I. The Cyanation of 3-Substituted Pyridine 1-Oxides

Pyridine 1-oxide	R	Reaction time (h)	Isolated yield (%)		Ratio determined by GC (%)	
			2	**3**	**2**	**3**
1a	F	6	83	0	100	0
1b	Cl	6	85	6	95	5
1c	Br	4	86	9	91	9
1d	OMe	6	73	0	100	0
1e	NMe_2	10	83	0	100	0
1f	Me	10	93[a]		72	28
1g	Et	24	94[a]		58	42
1h	Ph	8	26	58	34	66
1i	$CONEt_2$	2	53	28	63	37
1j	COOEt	3	36	51	39	61
1k	CN	0.5	36[b]	14[b]	72	28

a) Mixture of **2** and **3**. *b*) Total yield of **2k** and **3k** was 81%.

Throughout the reactions described above, the presence of the lone-pair electrons on the 3-substituents appears to be a common factor controlling the site-selectivity. The exact role of the lone-pair electrons is not clear at present, but as illustrated in Chart 2, a mechanism including the interaction of the 3-substituents and TMSCN can explain the introduction of the cyano group from the same side as the substituents.

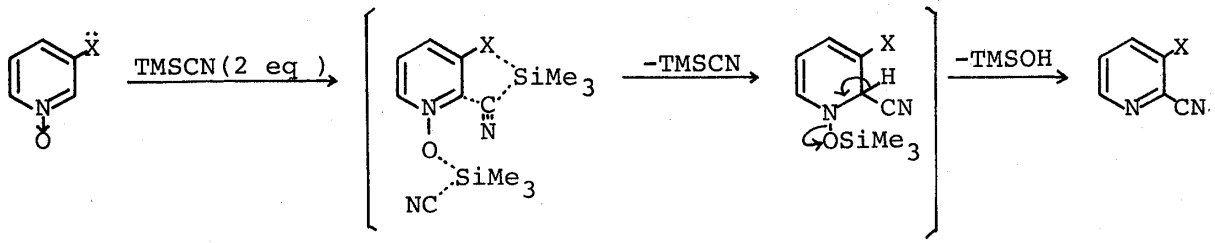


Chart 2

On the other hand, the cyanation of 3-methyl- (**1f**), 3-ethyl-(**1g**), 3-phenyl- (**1h**), 3-diethylcarbamoyl- (**1i**), 3-ethoxycarbonyl- (**1j**), and 3-cyanopyridine 1-oxide (**1k**) under the same conditions resulted in the formation of mixtures of the corresponding 2- and 6-cyano derivatives, though the isomer ratio depended on the kind of substituent. As mentioned before, Vorbrüggen *et al.*[5] obtained 6-cyano-3-pyridinecarboxylic acid from the reaction of 3-carboxypyridine 1-oxide by method B, and they briefly discussed the steric role of the carboxylic group in controlling the orientation. Based on the results listed in Table I, however, the steric and electronic effects of the 3-substituents are considered not to play an important role in determining the orientation.

During the present investigation, deoxygenation of nitropyridine 1-oxides (**4a—c**) was also observed. When 3-nitropyridine 1-oxide (**4b**) was allowed to react with TMSCN under

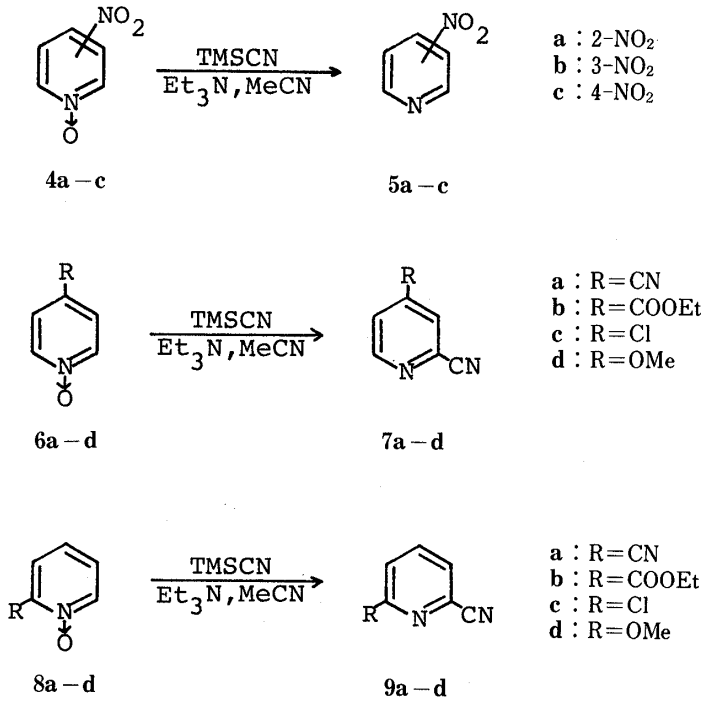


Chart 3

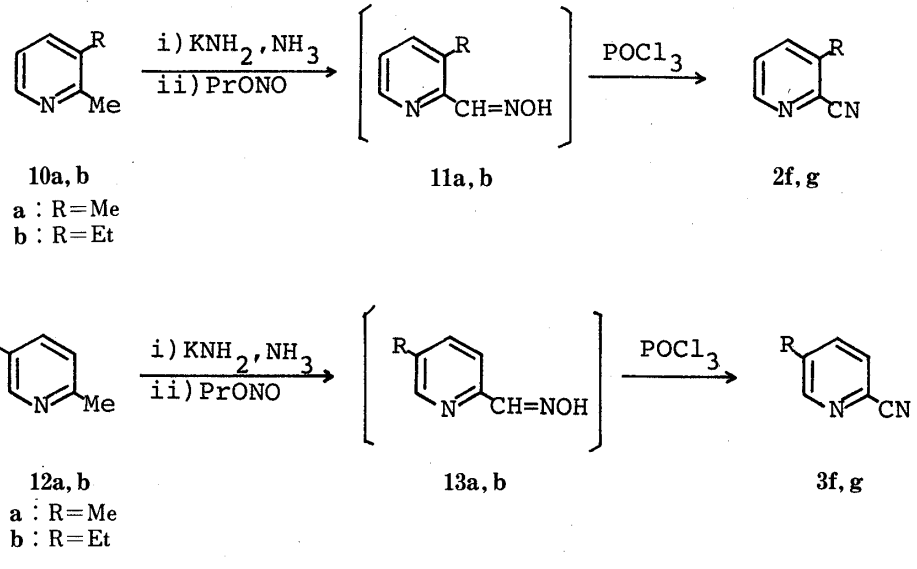


Chart 4

TABLE II. 2-Pyridinecarbonitriles

No.	bp (mmHg) or [mp] (°C)	IR ($CHCl_3$) cm^{-1} C≡N	^{1}H-NMR ($CDCl_3$) δ (ppm)	Formula	Analysis (%) Calcd (Found) C	H	N
2a	120—125 (17)	2240	7.5—7.8 (2H, m) 8.5—8.7 (1H, m)	$C_6H_3FN_2$	59.02 (58.72	2.48 2.23	22.95 22.82)
2b	100 (3)	2240	7.47 (1H, dd, J=8.0, 4.0 Hz) 7.87 (1H, dd, J=8.0, 2.0 Hz) 8.57 (1H, dd, J=4.0, 2.0 Hz)	$C_6H_3ClN_2$	52.01 (51.76	2.18 2.05	20.22 19.94)
3b	[106—108] 110 (3)	2240	7.6—8.0 (2H, m) 8.72 (1H, d, J=2.0 Hz)	$C_6H_3ClN_2$	52.01 (52.31	2.18 1.94	20.22 20.38)
2c	120 (3)	2240	7.49 (1H, dd, J=8.0, 4.0 Hz) 8.11 (1H, dd, J=8.0, 2.0 Hz) 8.69 (1H, dd, J=4.0, 2.0 Hz)	$C_6H_3BrN_2$	39.37 (39.79	1.65 1.63	15.31 15.43)
3c	100—110 (3)	2240	7.57 (1H, d, J=8.0 Hz) 7.98 (1H, dd, J=8.0, 2.0 Hz) 8.77 (1H, d, J=2.0 Hz)	$C_6H_3BrN_2$	39.37 (39.37	1.65 1.60	15.31 15.07)
2d	[111—112][a]	2240	3.98 (3H, s) 7.4—7.7 (2H, m) 8.28 (1H, dd, J=4.0, 2.0 Hz)				
2e	165—170 (15)	2230	3.12 (6H, s) 7.2—7.4 (2H, m) 8.0—8.2 (1H, m)	$C_{14}H_{12}N_6O_7$[b] (Picrate)	44.68 (44.70	3.21 3.13	22.34 22.59)
2f	120 (15) 85—87[c]	2240	2.57 (3H, s) 7.42 (1H, dd, J=8.0, 4.0 Hz) 7.75 (1H, dd, J=8.0, 1.0 Hz) 8.50 (1H, dd, J=4.0, 1.0 Hz)				
3f	125 (15) 72—74[d]	2240	2.45 (3H, s) 7.5—7.8 (2H, m) 8.55 (1H, s)				
2g	110—115 (15)	2240	1.33 (3H, t, J=7.0 Hz) 2.89 (2H, q, J=7.0 Hz) 7.43 (1H, dd, J=8.0, 4.0 Hz) 7.75 (1H, dd, J=8.0, 2.0 Hz) 8.50 (1H, dd, J=4.0, 2.0 Hz)	$C_{18}H_{16}N_6O_5$[e] (Picrolonate)	54.54 (54.81	4.07 4.06	21.21 21.41)
3g	125 (18)[f]	2240	1.27 (3H, t, J=7.0 Hz) 2.74 (2H, q, J=7.0 Hz) 7.5—7.8 (2H, m) 8.55 (1H, s)				
2h	[125—126][g]	2240	7.4—7.7 (6H, m) 7.90 (1H, dd, J=8.0, 2.0 Hz) 8.70 (1H, dd, J=2.0, 4.0 Hz)	$C_{12}H_8N_2$	79.98 (80.18	4.48 4.68	15.55 15.60)
3h	[93—94][h]	2240	7.4—7.8 (6H, m) 8.05 (1H, dd, J=8.0, 2.0 Hz) 8.97 (1H, d, J=2.0 Hz)	$C_{12}H_8N_2$	79.98 (80.22	4.48 4.56	15.55 15.55)
2i	[72—73][i]	2240	1.13 (3H, t, J=7.0 Hz) 1.30 (3H, t, J=7.0 Hz) 3.25 (2H, q, J=7.0 Hz) 3.65 (2H, q, J=7.0 Hz) 7.4—7.9 (2H, m) 8.72 (1H, dd, J=4.0, 2.0 Hz)	$C_{11}H_{13}N_3O$	65.00 (64.93	6.45 6.68	20.68 20.66)
3i	[82—83][j]	2240	1.20 (6H, t, J=7.0 Hz) 3.30 (4H, q, J=7.0 Hz) 7.8—8.1 (2H, m) 8.7—8.8 (1H, m)	$C_{11}H_{13}N_3O$	65.00 (64.97	6.45 6.61	20.68 20.69)
2j	130 (3)	2240	1.50 (3H, t, J=7.0 Hz) 4.51 (2H, q, J=7.0 Hz)	$C_9H_8N_2O_2$	61.36 (61.62	4.58 4.66	15.90 15.95)

TABLE II. (continued)

No.	bp (mmHg) or [mp] (°C)	IR ($CHCl_3$) cm^{-1} C≡N	^{1}H-NMR ($CDCl_3$) δ (ppm)	Formula	Analysis (%) Calcd (Found) C	H	N
			7.71 (1H, dd, J=8.0, 4.0 Hz)				
			8.48 (1H, dd, J=8.0, 2.0 Hz)				
			8.87 (1H, dd, J=4.0, 2.0 Hz)				
3j	125 (3)	2240	1.46 (3H, t, J=7.0 Hz)	$C_9H_8N_2O_2$	61.36	4.58	15.90
			4.53 (2H, q, J=7.0 Hz)		(61.58	4.72	16.05)
			7.86 (1H, d, J=8.0 Hz)				
			8.51 (1H, dd, J=8.0, 2.0 Hz)				
			9.35 (1H, d, J=2.0 Hz)				
2k	125 (3)	2240	7.75 (1H, dd, J=8.0, 4.0 Hz)				
	77—79[k]		8.22 (1H, dd, J=8.0, 2.0 Hz)				
			8.96 (1H, dd, J=4.0, 2.0 Hz)				
3k	110 (3)	2240	7.83 (1H, d, J=7.0 Hz)				
	110—112[l]		8.17 (1H, dd, J=7.0, 2.0 Hz)				
			8.96 (1H, d, J=2.0 Hz)				
7a	[89—90][m]	2240	7.80 (1H, d, J=5.0 Hz)				
			7.92 (1H, s)				
			8.95 (1H, d, J=5.0 Hz)				
7b	180 (14)	2240	1.43 (3H, t, J=7.0 Hz)	$C_9H_8N_2O_2$	61.36	4.58	15.90
	[42—44]		4.45 (2H, q, J=7.0 Hz)		(61.42	4.73	16.05)
			8.0—8.3 (2H, m)				
			8.89 (1H, d, J=5.0 Hz)				
7c	[84—85][n]	2240	7.54 (1H, dd, J=2.0, 5.0 Hz)				
			7.71 (1H, d, J=2.0 Hz)				
			8.67 (1H, d, J=5.0 Hz)				
7d	[117—119][o]	2240	3.91 (3H, s)	$C_7H_6N_2O$	62.68	4.51	20.89
			7.02 (1H, dd, J=3.0, 6.0 Hz)		(62.43	4.49	20.92)
			7.26 (1H, d, J=3.0 Hz)				
			8.53 (1H, d, J=6.0 Hz)				
9a	[123—124][p]	2240	7.8—8.3 (3H, m)				
9b	[71—72][q]	2240	7.7—8.4 (3H, m)	$C_9H_8N_2O_2$	61.36	4.58	15.90
					(61.08	4.63	16.02)
9c	[87—88][r]	2240	7.5—8.0 (3H, m)	$C_6H_3ClN_2$	52.01	2.18	20.22
					(51.96	2.00	20.24)
9d	115—120 (19)	2240	3.92 (3H, s)	$C_7H_6N_2O$	62.68	4.51	20.89
	[63—65]		6.8—7.4 (2H, m)		(62.68	4.81	21.13)
			7.68 (1H, dd, J=8.0, 7.5 Hz)				

a) Colorless needles from AcOEt, lit.[24] mp 110—113 °C. *b*) Yellow needles from EtOH, mp 104—105 °C. *c*) Lit.[25] mp 87—90 °C. *d*) Lit.[25] mp 73—75 °C. *e*) Yellow plates from EtOH, mp 99 °C (dec.). *f*) Lit.[26] bp 132 °C (20 mmHg). *g*) Colorless scales from CH_2Cl_2–hexane. *h*) Pale yellow needles from CH_2Cl_2–hexane. *i*) Colorless needles from ether–hexane. *j*) Colorless plates from ether–hexane. *k*) Lit.[24] mp 80—82 °C. *l*) Lit.[24] mp 111—112 °C. *m*) Colorless scales from ether–hexane, lit.[27] mp 90—91 °C. *n*) Colorless needles from hexane, lit.[27] mp 85—86 °C. *o*) Pale yellow needles from hexane. *p*) Colorless needles from C_6H_6, lit.[27] mp 126—127 °C. *q*) Colorless scales from ether. *r*) Colorless scales from hexane.

the conditions of method A, 3-nitropyridine (**5b**) was obtained, instead of the expected 3-nitropyridinecarbonitriles. Similarly, 2-nitro- (**4a**) and 4-nitropyridine 1-oxide (**4c**) reacted with TMSCN to give 2-nitro- (**5a**) and 4-nitropyridine (**5c**),[7] respectively. In these cases, no formation of cyanopyridines, including cyanopyridine 1-oxides, was observed.

The reactions of 4-cyano- (**6a**), 4-ethoxycarbonyl- (**6b**), 4-chloro- (**6c**), and 4-methyoxypyridine 1-oxides (**6d**), and the 2-substituted analogs (**8a—d**) were tested, in order to examine the scope of the deoxygenation. Since these substrates underwent cyanation to give the

corresponding 2-pyridinecarbonitriles (**7a—d** and **9a—d**), the deoxygenation was concluded to be specific to the nitropyridine 1-oxides.

In addition, authentic specimens of **2f, g** and **3f, g** were prepared by an alternative route, because these compounds could not be isolated by column chromatography after the cyanation of **1f, g**. As shown in Chart 4, the nitrosation[8] of 2,3-dimethyl (**10a**), 3-ethyl-2-methyl- (**10b**), 2,5-dimethyl- (**12a**), and 5-ethyl-2-methylpyridine (**12b**) followed by the dehydration of the resulting 2-aldoximes (**11a, b** and **13a, b**) with phosphoryl chloride gave **2f, g** and **3f, g** unequivocally. The formation ratio of the isomers on cyanation (Table I) was determined by the use of authentic **2f, g** and **3f, g** thus synthesized.

Experimental

All melting points and boiling points are uncorrected. Infrared (IR) spectra were measured with a JASCO IRA-1 spectrometer. ^{1}H-NMR spectra were taken at 60 MHz with a JEOL JNM-PMX 60 spectrometer. Chemical shifts are expressed in δ (ppm) value. The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, dd = double doublet, and m = multiplet.

Starting pyridine 1-oxides were synthesized according to the reported methods, except for 3-methoxy- (**1d**), 3-dimethylamino- (**1e**), and 3-*N,N*-diethylcarbamoylpyridine 1-oxides (**1i**): 3-fluoro- (**1a**),[9] 3-chloro- (**1b**),[9] 3-bromo- (**1c**),[9] 3-methyl- (**1f**),[10] 3-ethyl- (**1g**),[11] 3-phenyl- (**1h**),[12] 3-ethoxycarbonyl- (**1j**),[13] 3-cyano- (**1k**),[14] 2-nitro- (**4a**),[15] 3-nitro- (**4b**),[16] 4-nitro- (**4c**),[17] 4-ethoxycarbonyl- (**6b**),[13] 4-chloro- (**6c**),[18] 4-methoxy- (**6d**),[19] 2-cyano- (**8a**),[20] 2-ethoxycarbonyl- (**8b**),[21] 2-chloro- (**8c**),[22] and 2-methoxypyridine 1-oxides (**8d**).[23] 4-Cyanopyridine 1-oxide (**6a**) is commercially available from Tokyo Kasei Kogyo Co., Ltd.

3-Methoxypyridine 1-Oxide——A solution of 3-bromopyridine 1-oxide (**1c**) (3.5 g, 20 mmol) in MeONa–MeOH [prepared from dry MeOH (100 ml) and Na (2.3 g, 100 mmol)] was heated in a sealed tube at 120 °C for 12 h. After evaporation of the solvent, the residue was diluted with H_2O and extracted continuously with $CHCl_3$ for 24 h. The residue obtained from the $CHCl_3$ extract was recrystallized from AcOEt to give colorless needles, mp 98—100 °C (lit.[14] mp 100—101 °C). Yield 1.37 g (55%). IR (KBr) cm^{-1}: 1240 (N–O). ^{1}H-NMR ($CDCl_3$): 3.83 (3H, s), 6.7—7.3 (2H, m), 7.8—8.0 (2H, m).

3-Dimethylaminopyridine 1-Oxide (1e)——A mixture of **1b** (3.5 g, 20 mmol) and 40% Me_2NH aq. solution (6 ml) was heated in a sealed tube at 120 °C for 24 h. After filtration, the filtrate was concentrated to dryness. The residue was extracted with $CHCl_3$, and the crude product obtained from the $CHCl_3$ extract was distilled to give a colorless liquid, bp 160—165 °C (2 mmHg). Yield 3.41 g (87%). Picrate: yellow needles (EtOH), mp 161—162 °C. IR (KBr) cm^{-1}: 1230 (N–O). ^{1}H-NMR ($CDCl_3$): 2.95 (6H, s), 6.5—6.8 (1H, m), 7.12 (1H, dd, J = 8.0 and 4.0 Hz), 7.4—7.8 (2H, m). *Anal.* Calcd for $C_{13}H_{13}N_5O_8$ (picrate): C, 42.52; H, 3.57; N, 19.07. Found: C, 42.80; H, 3.62; N, 19.00.

3-*N,N*-Diethylcarbamoylpyridine 1-Oxide (1i)——A mixture of 3-*N,N*-diethylcarbamoylpyridine (8.9 g, 50 mmol), 30% H_2O_2 aq. solution, and AcOH (50 ml) was heated at 80—90 °C for 5 h. After dilution of the mixture

Table III. Deoxygenation of Nitropyridine 1-Oxides with TMSCN

No.	Yield (%)	Reaction time (h)	bp (mmHg) or [mp] (°C)	^{1}H-NMR ($CDCl_3$) δ (ppm)
5a	59	24	[69—70][a]	7.5—8.5 (3H, m) 8.6—8.8 (1H, m)
5b	20	24	140 (20) [39—41][b]	7.50 (1H, dd, J = 8.0, 5.0 Hz) 7.4—7.6 (1H, m) 8.89 (1H, dd, J = 5.0, 1.5 Hz) 9.40 (1H, d, J = 2.5 Hz)
5c	65	12	[45—46][c] 85 (15)	8.03 (2H, dd, J = 6.0, 2.5 Hz) 8.92 (2H, dd, J = 6.0, 2.5 Hz)

a) Colorless needles from hexane, lit.[28] mp 71 °C.
b) Lit.[29] mp 41 °C.
c) Colorless scales from hexane, lit.[30] mp 47—49 °C.

with H_2O, the solvent was evaporated off. The residue was made alkaline with saturated aq. K_2CO_3 and extracted with $CHCl_3$. The crude product obtained from the $CHCl_3$ extract was recystallized from AcOEt to give colorless prisms, mp 62—63 °C. Yield 7.0 g (72%). Picrate: yellow prisms (EtOH), mp 106—107 °C. IR (KBr) cm^{-1}: 1630 (C=O), 1210 (N–O). ^{1}H-NMR ($CDCl_3$): 1.20 (6H, t, J=7.0 Hz), 3.45 (2H, q, J=7.0 Hz), 7.2—7.3 (2H, m), 8.2—8.4 (2H, m). *Anal.* Calcd for $C_{16}H_{17}N_5O_9$ (picrate): C, 45.39; H, 4.05; N, 16.54. Found: C, 45.45; H, 3.92; N, 16.71.

General Procedure for the Reaction of Pyridine 1-Oxides with TMSCN——A mixture of a pyridine 1-oxide (10 mmol), TMSCN (30 mmol), Et_3N (20 mmol), and MeCN (10 ml) was refluxed for an appropriate time (shown in Table I). After evaporation of the solvent, the residue was made alkaline with 3 N Na_2CO_3 and extracted with CH_2Cl_2. After purification of the CH_2Cl_2 extract by SiO_2 column chromatography, the product was distilled or recrystallized.

General Procedure for the Preparation of 2f,g and 3f,g from 10a,b and 12a,b——A mixture of a 2-methylpyridine (30 mmol) and liq. NH_3-KNH_2 [prepared from liq. NH_3 (100 ml) and K (60 mmol)] was stirred at −33 °C for 2 h. Then, PrONO (60 mmol) was added and the mixture was stirred at −33 °C for 2 h, then quenched with NH_4Cl. The NH_3 was evaporated off, and the residue was extracted with hot acetone. A mixture of the residue obtained from the acetone extract, $POCl_3$ (30 ml), and $CHCl_3$ (30 ml) was refluxed for 1 h. After evaporation of the $CHCl_3$ and excess $POCl_3$, the residue was poured into cold NH_4OH, and extracted with $CHCl_3$. The crude product obtained from the $CHCl_3$ extract was purified by SiO_2 column chromatography using C_6H_6 as an eluent. Distillation of the C_6H_6 eluate gave a pure 2-pyridinecarbonitrile. Yield: **2f** (37%), **3f** (40%), **2g** (27%), and **3g** (42%).

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