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Reactions of 1,4-Bis(trimethylsilyl)-1,4-dihydropyridines with Carbonyl Compounds: A New Method for Regioselective Synthesis of 3-Alkylpyridines

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A new method for the alkyl group introduction at the 3-position of pyridienes is described: Reductive disilylation of pyridine, its 2-methyl, 3-methyl, and 4-methyl derivatives affords the corresponding 1,4-disilyl-1,4-dihydropyridines. In the presence of a catalytic amount of tetrabutylammonium fluoride, these dihydropyridines smoothly react with a variety of aldehydes and ketones to give 3-alkylpyridines.

Although direct substitution at the carbon atom of pyridine has been an attracting theme for a long time, no effective method was reported until a recent year. Compared with benzene as an isoelectronic hydrocarbon counterpart, electrophilic substitution at the ring of pyridine is awfully sluggish.[1] Especially so if a carbon electrophile is used. Quaterization occurs at the ring nitrogen, under the reaction conditions, so that the nucleophilicity of pyridine ring is lowered. Substituted pyridines have been mostly synthesized according to the conventional methods such as a ring synthesis[1,2] and a chain elongation at the preexisting functional groups.[3]

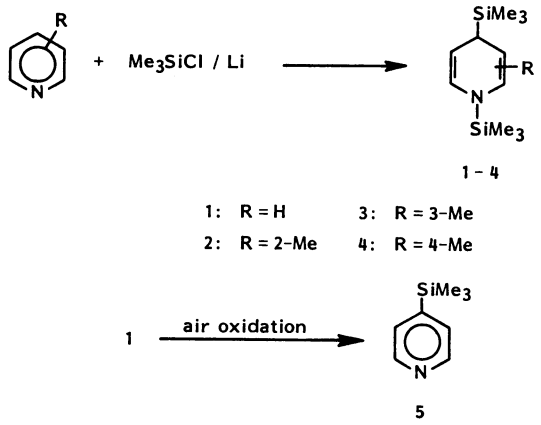
Two new methods have merged recently: One is the reaction of lithiopyridines with an electrophile, which can be generated in a regioselective manner by the aid of a directing group.[4] The other is the nucleophilic addition of organometallics with pyridines in the presence or absence of a pyridine-activating agent.[5] These reactions are performed on the aromatic ring of pyridines, and the pyridines substituted only at the 3-position are hardly accessible.

When the aromatic ring of pyridine is formally reduced by a metal hydride or its equivalent, *N*-metalated dihydropyridines are formed.[6] 1,4-Bis(trimethylsilyl)-1,4-dihydropyridine (**1**), which is available by a reductive disilylation of pyridine and is not so unstable as to exclude its isolation,[7] belongs to this family. So far no synthetic application of **1** has been reported. Since **1** carries an *N*-silylated cyclic enamine moiety,[8] its reaction with electrophiles is expected to occur regioselectively at the 3-position of pyridine.

The present article describes a new synthetic method of 3-alkylpyridines from pyridines.[9] Fluoride-catalyzed reactions of 1,4-bis(trimethylsilyl)-1,4-dihydropyridine (**1**) with a variety of carbonyl compounds produce 3-alkylpyridine derivatives. This method can be extended to several alkyl-substituted pyridines.

Results and Discussion

1,4-Disilyl-1,4-dihydropyridine **1** was synthesized by the known method starting with pyridine, chlorotrimethylsilane, and lithium powder in dry THF.[7] Though isolable by distillation under vacuum, **1** was found extremely air-sensitive. Oxidation starts once **1** is exposed to air, and it becomes contaminated by 4-trimethylsilylpyridine (**5**). The purification by distillation caused its partial oxidation, and the purity of **1** was only slightly higher than 90%. For its safety use, **1** may be stored in a bottle which is capped with a rubber septum and filled with dry nitrogen. A syringe is used to take **1** out of the bottle.



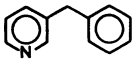
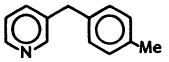
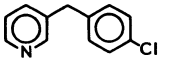
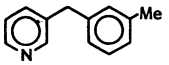
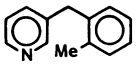
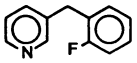
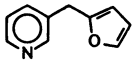
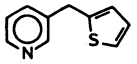
Scheme 1.

This preparation method was successfully applied to 2-methyl-, 3-methyl-, and 4-methylpyridines to give the corresponding 1,4-bis(trimethylsilyl)-1,4-dihydropyridines **2**—**4** in fair yields (Scheme 1). Again they are all air-sensitive.

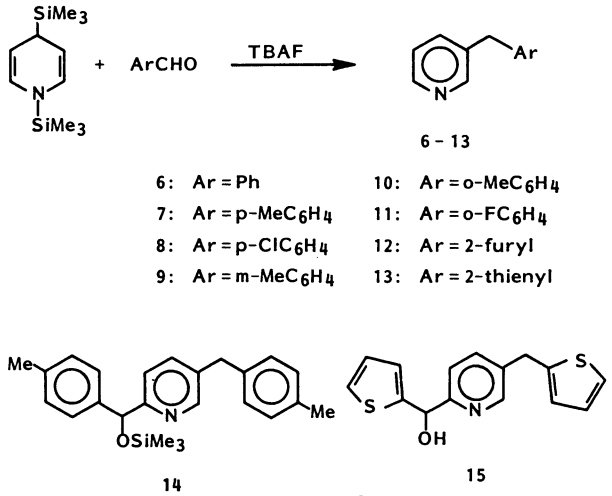
An equimolar mixture of **1** and benzaldehyde in dry THF was treated, at room temperature and under an inert atmosphere, with a catalytic amount (10 mol%) of tetrabutylammonium fluoride (TBAF). After usual hydrolytic work-up and column chromatography over silica gel, 3-benzylpyridine (**6**) was obtained in 72% yield (Scheme 2). The fluoride catalyst could not be replaced by a Lewis acid, titanium(IV) chloride, most of the benzaldehyde being recovered (1 h at room temperature in dry dichloromethane).

The Friedel-Crafts acylation of benzene with 3-pyridinecarbonyl chloride followed by the carbonyl reduction is the major route for preparing **6**.[10] However, the Friedel-Crafts reaction can not be an effective preparation method for 3-benzylpyridines bearing an *o*- or *m*-substituent. Accordingly, benzaldehydes hav-

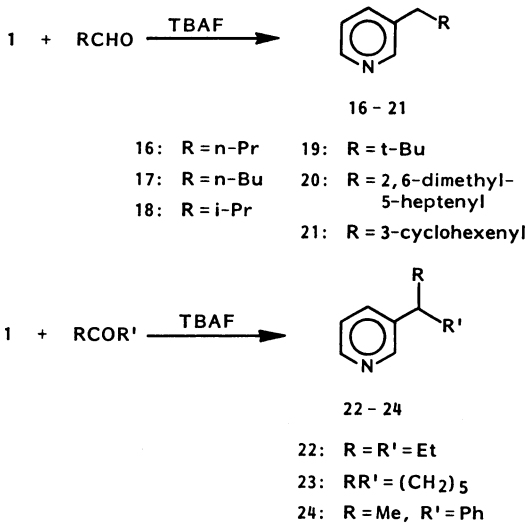
Table 1. Reaction of **1** with Aromatic Aldehydes Leading to 3-Substituted Pyridines **6**—**13**[a]

Ar-CHO	Time/h	Product		Yield/%[b]
PhCHO	15		**6**	72
p-MeC_6H_4CHO	14		**7**	64[c]
p-ClC_6H_4CHO	15		**8**	62
m-MeC_6H_4CHO	18		**9**	75
o-MeC_6H_4CHO	12		**10**	70
o-FC_6H_4CHO	17		**11**	53
2-Furyl-CHO	13		**12**	53
2-Thienyl-CHO	16		**13**	58[d]

a) All the reactions were carried out at room temperature in dry THF under argon. b) Isolated yield based on the aldehydes. c) Accompanied by 34% of **14**. d) Accompanied by 28% of **15**.



Scheme 2.



Scheme 3.

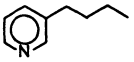
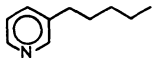
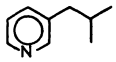
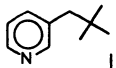
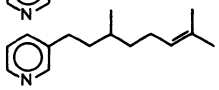
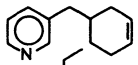
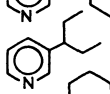
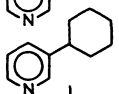
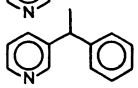
ing a variety of substitution patterns were employed to the reaction, and 3-(substituted benzyl)pyridines **7**—**11** were obtained in good yields (Scheme 2 and Table 1). Heteroaromatic aldehydes such as 2-furan- and 2-thiophenecarbaldehydes also reacted with **1** as well to produce **12** and **13**.

In most cases, 3-alkylpyridines **6**—**13** were the sole products. However in the reactions with *p*-methylbenzaldehyde and 2-thiophenecarbaldehyde, the major products **7** and **13** were accompanied by minor products **14** and **15**, respectively. They were assigned to be 2,5-disubstituted pyridine structures in which two molelules of the aldehydes had been incorporated at the 2- and 5-positions. Their formation indicates that not only the *N*-silyl group but also the 4-silyl moiety has participated in the reaction. This will be discussed later.

Similar reactions of **1** with aliphatic aldehydes required an elevated reaction temperature. Thus, **1** reacted with aldehydes carrying a primary, secondary, and tertiary alkyl group, under reflux in dry THF, to afford 3-alkylpyridines **16**—**19** (Scheme 3 and Table 2). Aldehydes bearing a carbon-carbon double bond could be employed without any trouble. The corresponding 3-alkylpyridines **20** and **21** were obtained. Further applications to the reactions with ketones were also successful to giving **22**—**24**.

The site of substitution was clearly determined to be the 3-position on the basis of spectral data. As an example, **18** shows an unsymmetrical substitution pattern with two vacant α-positions in the ^1H NMR spectrum: δ 7.06 (1H, dd, 5-H), 7.31 (1H, dt, 4-H), and

Table 2. Reaction of **1** with Aliphatic Aldehydes or Ketones Leading to 3-Substituted Pyridines **16—24**[a]

Aldehyde or ketone	Time/h	Product		Yield/%[b]
n-PrCHO	10		**16**	26
n-BuCHO	6		**17**	39
i-PrCHO	7		**18**	77
t-BuCHO	8		**19**	62
3,7-Dimethyl-6-octenal	10		**20**	61
3-Cyclohexene-1-carbardehyde	10		**21**	54
3-Pentanone	10		**22**	37
Cyclohexanone	5		**23**	71
Acetophenone	5		**24**	15

a) All the reactions were carried out under reflux in dry THF under argon. b) Isolated yield based on the carbonyl compounds.

8.2—8.4 (2H, m, 2- and 6-H). Its ^{13}C NMR spectrum confirmed the 3-substitution, in which a singlet signal appeared at δ 136.64 (3-C) and two doublets at 147.11 and 150.38 (2- and 6-C).[11]

The most practical route to 3-alkylpyridines available so far is a chain elongation of 3-methyl- or 3-ethylpyridines via α-metalated intermediates.[12] Our present method implies even more important synthetic values since 3-alkylpyridines substituted by a variety of alkyl groups are readily accessible, in a simple procedure under mild conditions, by the employment of appropriate carbonyl compounds.

Figure 1 illustrates a possible mechanism for the reaction of **1** with *p*-methylbenzaldehyde. The silyl moiety on the nitrogen is selectively eliminated by an attack of fluoride anion to form 3-azapentadienyl anion intermediate **A**. This anion adds to the aldehyde at the 3-position to form adduct **B**. The other addition onto the nitrogen might occur as well. Even if so, the resulting adduct would not find any stabilization path, undergoing a reversible retro addition going back to the starting **A**. The elimination of silanol from **B** leads to **C**. Subsequent fluoride-induced desilylation of **C** forms the methanide **D** stabilized by two aryls. **D** is then quenched with water to give 3-(*p*-methylbenzyl)-pyridine (**7**). If the desilylation of **C** is immediately followed by attack of the second molecule of the aldehyde, the 2,5-disubstituted pyridine **14** is produced as a side-product.

Similar reactions of other 1,4-disilyl-1,4-dihydropyridines **2—4** were next examined. In these cases,

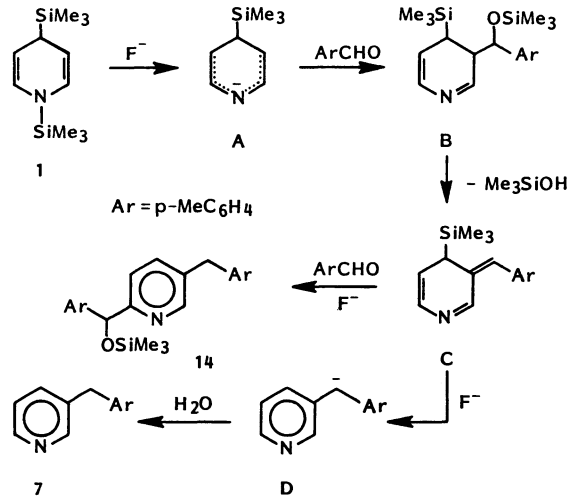
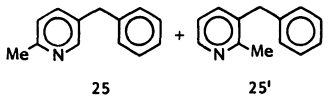
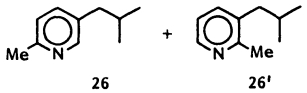
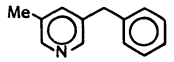
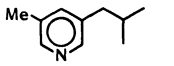
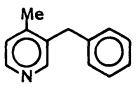
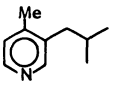


Fig. 1. A mechanism for the reaction of **1** with *p*-methylbenzaldehyde.

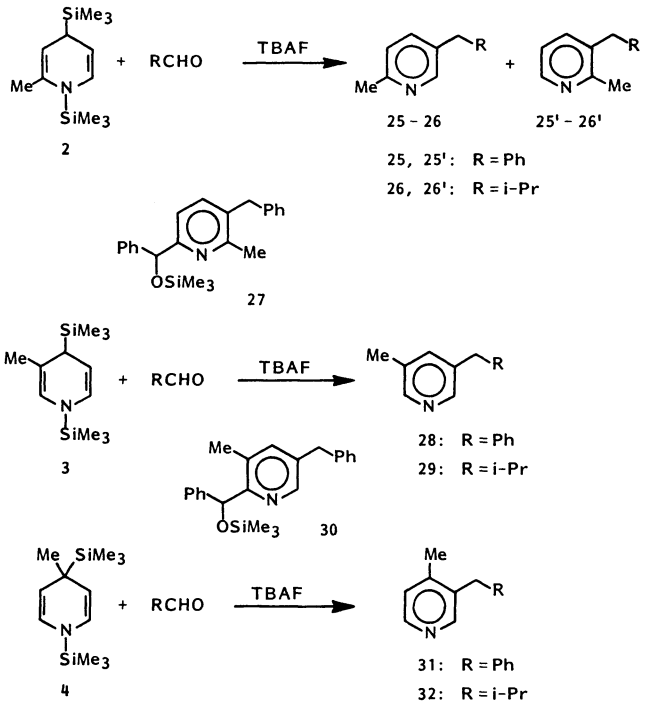
benzaldehyde and 2-methylpropanal were employed as representatives of aromatic and aliphatic aldehydes, respectively. The results are summarized in Table 3.

2-Methyl-1,4-disilylpyridine **2** furnished mixtures of 2,5-and 2,3-disubstituted pyridines **25—26** and **25′—26′**, respectively (Scheme 4 and Table 3). Although the 2,5-disubstituted regioisomers **25—26** were major products, their preference over the others was not so big as expected (**25**:**25′**=**6**:4; **26**:**26′**=6:4 (by ^{1}H and/or ^{13}C NMR)). No persuasive explanation for the comparable regioisomeric ratio is available. It is readily understood on the basis of steric demand that only the

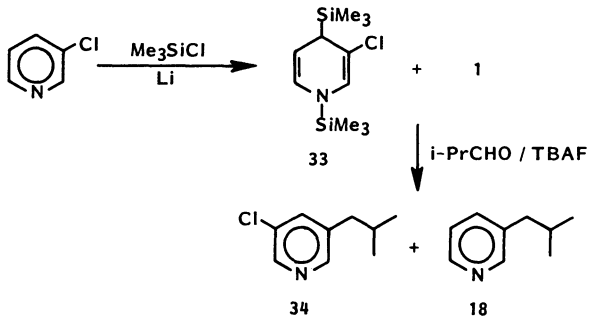
Table 3. Reaction of Dihydropyridines **2**—**4** with Aldehydes Leading to **25**—**32**

Dihydropyridine	Aldehyde	Reaction conditions	Time/h	Product	Yield/%[a]
2	PhCHO	room temp. in THF	14	 **25** **25'**	45[b] (**25**:**25'**=6:4)
2	*i*-PrCHO	reflux in THF	10	 **26** **26'**	77 (**26**:**26'**=6:4)
3	PhCHO	room temp. in THF	16	 **28**	67[c]
3	*i*-PrCHO	reflux in THF	10	 **29**	77
4	PhCHO	room temp. in THF	15	 **31**	31
4	*i*-PrCHO	reflux in THF	10	 **32**	37

a) All isolated yields based on the aldehydes. b) Accompanied by 22% of **27**. c) Accompanied by 17% of **30**.



Scheme 4.



Scheme 5.

intermediate leading to **25'** could further react with the second molecule of benzaldehyde to give **27**.

In the reactions of 3-methyl-1,4-disilylpyridine (**3**), the 5-position is the only place where the nucleophilic addition can occur. For example, 3,5-disubstituted pyridines **28** and **29** were obtained as single isomers in excellent yields. As anticipated, the second addition took place at the place adjacent to the sterically less bulky 3-methyl moiety to give **30**.

4-Methyl-1,4-disilylpyridine (**4**) also demonstrated the 3-substitution providing **31** and **32**, but the yields were relatively diminished (Scheme 4 and Table 3).

Thus, these facile methods of alkyl group introduction could be successfully applied to methylpyridines with all possible substitution patterns. Pyridines with other alkyl group(s) will be utilized as well if the corresponding 1,4-dihydropyridines are obtainable.

Reductive disilylation of 3-chloropyridine was carried out under similar conditions (Scheme 5). The product isolated by vacuum distillation was found to be a mixture of 3-chloro-1,4-bis(trimethylsilyl)-1,4-dihydropyridine (**33**) and **1** (by ^{1}H NMR). As their separation was rather difficult, this mixture was subjected to the reaction with 2-methylpropanal in the presence of TBAF. A mixture of 3-chloro-5-(2-methylpropyl)pyridine (**34**) and 3-(2-methylpropyl)pyridine (**18**) was obtained, indicating that the alkyl group introduction via the disilylation method seems not so fruitful for halogen-substituted pyridines.

Experimental

General. Meting points were determined on a Yanagimoto melting point apparatus and are uncorrected. IR spectra were taken with a JASCO IRA-1 or a JASCO A-702 spectrometer. ^{1}H NMR spectra were recorded on a Hitachi R-40

(90 MHz) or a JEOL FX-100 instrument (100 MHz) and ^{13}C NMR on a JEOL FX-100 spectrometer at 25.05 MHz. Chemical shifts are expressed in parts per million downfield from tetramethylsilane as an internal standard. Mass spectra were measured with a JEOL-01SG-2 spectrometer at 70 eV of ionization energy. GC-Mass spectra as well as high resolution mass spectra were also obtained on the same instrument. Elemental analyses were performed on a Hitachi 026 CHN analyzer. Thin-layer chromatography (TLC) was accomplished on 0.2 mm precoated plates of silica gel 60 F-254 (Merck) or of aluminum oxide 60 F-254 type-E (Merck). Visualization was made with ultraviolet light (254 and 365 nm), iodine, molybdophosphoric acid (5% in ethanol), or *p*-anisaldehyde (5% in ethanol containing 5% of sulfuric acid). For preparative column chromatography, Wakogel C-200, C-300 (Wako), and Silicagel 60 (Merck) were employed. Flash chromatography was carried out on an EYELA EF-10 apparatus using a column (20×180 mm) packed with Silicagel 60 (Merck, size: 0.04—0.063 mm). Preparative high-performance liquid chromatography(HPLC) was performed on a Kusano KHLC-201 apparatus with a UV-detector Uvilog-III using a column (22×300 mm) packed with silica gel (Wakogel LC-50H). Gas liquid chromatography (GLC) was accomplished on a Yanaco G-2800 gas chromatograph (Yanagimoto) with an ionization flame detector using a glass column (SE-30, 3×2000 mm) or a glass capillary column (Silicone GE, SE-30, 0.25×50000 mm). Micro vacuum distillation was carried out on a Sibata GTO-250R Kugelrohr distilling apparatus. Solvents were evaporated with a Tokyo Rikakikai rotary evaporator type-V at about 50 °C unless otherwise stated.

General Procedure for Reductive Disilylation of Pyridines Leading to 1,4-Bis(trimethylsilyl)-1,4-dihydropyridines 1—4. The Sulzbach's method[7] was applied with a minor modification. All the procedure has to be carried out in an inert atmosphere, or air-sensitive dihydropyridines **1—4** are readily oxidized into 4-trimethylsilylpyridines. Detail of the reductive disilylation of pyridine is described below as a typical procedure: To a suspension of lithium powder (2.08 g, 300 mmol) in freshly distilled dry THF (30 ml) was added chlorotrimethylsilane (38.1 ml, 300 mmol) at −10 °C. Pyridine (100 mmol) in dry THF (25 ml) was added dropwise by use of a syringe in a period 30 min. After the completion of addition, the mixture was allowed to stir at 0 °C for 1 h. The precipitate was filtered off by the aid of the pressure of dry nitrogen. The filtrate was condensed in vacuo and then distilled under a reduced pressure to give **1** (7.64 g, 34%) which was contaminated by a small amount of **5** (purity 90%). The receiver flask containing distilled **1** was filled with dry nitrogen and capped with a rubber septum. To the septum was attached a needle which was connected to a balloon filled with dry nitrogen. In this way, **1** can be safely stored at room temperature at least for a week. A syringe may be used in order to take **1** out of the flask.

Similar procedures were applied to 2-methyl-, 3-methyl-, and 4-methylpyridine to give the corresponding dihydropyridines **2—4**. When **1** was exposed to dry air and chromatographed over silica gel with hexane-diethyl ether (10 : 1 vol/vol), 4-trimethylsilyl-pyridine (**5**) was obtained.

1,4-Bis(trimethylsilyl)-1,4-dihydropyridine (1): Yield 34%; colorless air-sensitive liquid; bp 45—50 °C/33 Pa; ^1H NMR ($CDCl_3$) δ=−0.11 (9H, s, 4-Me_3Si), 0.11 (9H, s, 1-Me_3Si), 2.25 (1H, t, J=6.9 Hz, 4-H), 4.35 (2H, dd, J=9.0 and 6.9 Hz, 3- and 5-H), and 5.70 (2H, d, J=9.0 Hz, 2- and 6-H).

2-Methyl-1,4-bis(trimethylsilyl)-1,4-dihydropyridine (2): Yield 27%; colorless air-sensitive liquid; bp 70—75 °C/320 Pa; ^1H NMR ($CDCl_3$) δ=− 0.11 (9H, s, 4-Me_3Si), 0.08 (9H, s, 1-Me_3Si), 1.62 (3H, s, 2-Me), 1.89 (1H, t, J=6.9 Hz, 4-H), 4.0—4.3 (2H, m, 3- and 5-H), and 5.61 (1H, d, J=9.0 Hz, 6-H).

3-Methyl-1,4-bis(trimethylsilyl)-1,4-dihydropyridine (3): Yield 37%; colorless air-sensitive liquid; bp 74—77 °C/200 Pa; ^1H NMR ($CDCl_3$) δ=0.08 (9H, s, 4-Me_3Si), 0.17 (9H, s, 1-Me_3Si), 1.53 (3H, s, 3-Me), 2.07 (1H, d, J=6.9 Hz, 4-H), 4.30 (1H, dd, J=9.0 and 6.9 Hz, 5-H), 5.52 (1H, s, 2-H), and 5.72 (1H, d, J=9.0 Hz, 6-H).

4-Methyl-1,4-bis(trimethylsilyl)-1,4-dihydropyridine (4): Yield 25%; colorless air-sensitive liquid; bp 70—75 °C/333 Pa; ^1H NMR ($CDCl_3$) δ=−0.12 (9H, s, 4-Me_3Si), 0.06 (9H, s, 1-Me_3Si), 1.86 (3H, s, 4-Me), 3.87 (2H, d, J=9.0 Hz, 3- and 5-H), and 5.53 (2H, d, J=9.0 Hz, 2- and 6-H).

4-Trimethylsilylpyridine (5): Pale yellow liquid; IR (neat) 1250 and 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.07 (9H, s, Me_3Si), 7.05 (2H, d, J=6.5 Hz, 3- and 5-H), and 8.55 (2H, d, J=6.5 Hz, 2- and 6-H); ^{13}C NMR ($CDCl_3$) δ=1.82 (q, Me_3Si), 128.05 (d, 3- and, 5-C), 148.54 (d, 2- and 6-C), and 150.18 (s, 4-C); MS *m/z* (rel intensity, %) 151, (M^+, 36), 137 (13), 136 (base peak), 83 (11), and 73 (10). HRMS Found: *m/z* 151.0796. Calcd for $C_8H_{13}NSi$: M, 151.0817.

General Procedure for Fluoride-Catalyzed Reaction of 1 with Aromatic Aldehydes Leading to 6—13. The reaction of **1** with benzaldehyde is described below as a typical procedure: Under an argon atmosphere, **1** (purity 90%, 0.287 g, 1.15 mmol) was added, by use of a syringe, to the solution of benzaldehyde (0.117 g, 1.1 mmol) in dry THF (5 ml). A solution of TBAF in THF (1M solution, 0.1 ml, 0.1 mmol) was slowly added also by the aid of a syringe. The mixture was stirred at room temperature under argon for 15 h and poured into saturated sodium hydrogencarbonate solution. The product was extracted with diethyl ether (20 ml), the ether washed with brine, dried over magnesium sulfate, and then evaporated in vacuo. The residue was chromatographed over silica gel (10 g) by using hexane-diethyl ether (5 : 1 vol/vol) to give **6** (0.134 g, 72%) as a pale yellow liquid.

Other seven aromatic aldehydes were treated in a similar way. The reaction times and the yields of 3-alkylpyridines **6—13** are listed in Table 1.

3-Benzylpyridine (6): Pale yellow liquid; mp (picrate) 100—101 °C; IR (neat) 1600, 1575, 1495, 1480, 1450, 1420, and 1025 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.92 (2H, s, CH_2), 7.0—7.5 (7H, m, ArH), and 8.3—8.5 (2H, m, 2- and 6-H); ^{13}C NMR ($CDCl_3$) δ=28.65 (t, CH_2), 123.34, 126.41, 127.53, 128.35, 128.59, 128.74, 136.25 (d), 139.66, 147.46 (d, 6-C), and 149.99 (d, 2-C); MS *m/z* (rel intensity, %) 169 (M^+, base peak), 168 (77), 167 (20), 91 (20), 83 (11), and 65 (16). Found (picrate): C, 54.44; H, 3.62; N, 14.27%. Calcd for $C_{18}H_{14}N_4O_7$: C, 54.28; H, 3.54; N, 14.07%.

3-(*p*-Methylbenzyl)pyridine (7): Yellow liquid; mp (picrate) 111—114 °C; ^1H NMR ($CDCl_3$) δ=2.26 (3H, s, *p*-Me), 3.86 (2H, s, CH_2), 6.9—7.2 (5H, m, ArH), 7.35 (1H, m, ArH), and 8.3—8.5 (2H, m, 2- and 6-H); MS *m/z* (rel intensity, %) 183 (M^+, base peak), 182 (46), 168 (34), 167 (13), 105 (15), 91 (12), and 77 (14). Found (picrate): C, 55.40; H, 3.84; N, 13.77%. Calcd for $C_{19}H_{16}N_4O_7$: C, 55.34; H, 3.91; N, 13.59%.

After the first fraction affording **7** was eluted with hexa-

ne-diethyl ether (10 : 1 vol/vol), the second fraction was followed (5 : 1 vol/vol) giving **14** in 34% yield. **14**: Pale yellow liquid; IR (neat) 1245, 1080, 880, and 840 cm^{-1}. ^1H NMR ($CDCl_3$) δ=0.16 (9H, s, Me_3Si), 2.34 (6H, s, *p*-Me), 3.89 (2H, s, CH_2), 5.89 (1H, s, CH), 7.0—7.6 (10H, m, ArH), and 8.37 (1H, s, 2-H), MS *m/z* (rel intensity, %) 375 (M^+, base peak), 360 (30), 286 (12), 254 (14), 193 (44), 147 (14), 142 (18), 75 (17), and 73 (43). HRMS Found: *m/z* 375.2008. Calcd for $C_{24}H_{29}NOSi$: M, 375.2017.

3-(*p*-Chlorobenzyl)pyridine (8): Pale yellow liquid; mp (picrate) 107—110 °C; IR (neat) 1570, 1515, 1480, 1420, and 1025 cm^{-1}. ^1H NMR ($CDCl_3$) δ=3.83 (2H, s, CH_2), 6.8—7.5 (6H, m, ArH), and 8.2—8.4 (2H, m, 2- and 6-H); MS *m/z* (rel intensity, %) 205, 208 (M^+, 26 and 78), 168 (base peak), 153 (21), and 80 (13). Found (picrate): C, 49.66; H, 3.21; N, 12.83%. Calcd for $C_{18}H_{13}N_4O_7$: C, 49.96; H, 3.03; N, 12.95%.

3-(*m*-Methylbenzyl)pyridine (9): Yellow liquid; mp (picrate) 142—144 °C; IR (neat) 1610, 1575, 1480, 1420, and 1030 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.26 (3H, s, *m*-Me), 3.85 (2H, s, CH_2), 6.8—7.5 (6H, m, ArH), and 8.3—8.5 (2H, m, 2- and 6-H); MS *m/z* (rel intensity, %) 183 (M^+, base peak), 182 (55), 169 (13), 168 (94), 167 (44), 128 (11), 115 (17), 105 (14), 91 (16), 80 (16), 77 (19), and 65 (25). Found (picrate): C, 54.95, H, 3.95; N, 13.67%. Calcd for $C_{19}H_{16}N_4O_7$: C, 55.34; H, 3.91; N, 13.59%.

3-(*o*-Methylbenzyl)pyridine (10): Yellow liquid; mp (picrate) 130—132 °C; IR (neat) 1575, 1480, 1455, 1420, and 1025 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.17 (3H, s, *o*-Me), 3.88 (2H, s, CH_2), 6.9—7.4 (6H, m, ArH), and 8.2—8.5 (2H, m, 2- and 6-H); MS *m/z* (rel intensity, %) 183 (M^+, base peak), 182 (38), 169 (11), 168 (77), 167 (25), and 104 (14). Found (picrate): C, 55.40; H, 4.00; N, 13.61%. Calcd for $C_{19}H_{16}N_4O_7$: C, 55.34, H, 3.91; N, 13.59%.

3-(*o*-Fluorobenzyl)pyridine (11): Yellow liquid; mp (picrate) 97—98 °C; IR (neat) 1590, 1495, 1480, 1450, 1420, 1230, and 1025 cm^{-1}. ^1H NMR ($CDCl_3$) δ=3.92 (2H, s, CH_2), 6.8—7.5 (6H, m, ArH), and 8.2—8.5 (2H, m, 2- and 6-H); MS *m/z* (rel intensity, %) 187 (M^+, base peak), 186 (54), 185 (16), 168 (17), 167 (12), 133 (12), and 109 (18). Found (picrate): C, 52.07; H, 3.23; N, 13.66%. Calcd for $C_{18}H_{13}N_4O_7F$: C, 51.93; H, 3.15; N, 13.46%.

3-(2-Furylmethyl)pyridine (12): Yellow liquid; mp (picrate) 123—125 °C; IR (neat) 1600, 1580, 1500, 1480, 1425, 1250, 1150, 1070, and 1010 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.90 (2H, s, CH_2), 5.97, 6.23 (each 1H, each m, 3- and 4-H of furyl), 7.1—7.5 (3H, m, ArH), and 8.4—8.5 (2H, m, 2- and 6-H); MS *m/z* (rel intensity, %) 159 (M^+, base peak), 158 (16), 131, (11), 130 (76), 81 (20), and 51 (11). Found (picrate): C, 49.56; H, 3.27; N, 14.44%. Calcd for $C_{16}H_{12}N_4O_8$: C, 49.49; H, 3.11; N, 14.43%.

3-(2-Thienylmethyl)pyridine (13): Yellow liquid; mp (picrate) 104—105 °C; IR (neat) 1570, 1480, 1420, 1030, and 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=4.09 (2H, s, CH_2), 6.83, 6.98 (each 1H, each m, 3- and 4-H of thienyl), 7.1—7.6 (3H, m, ArH), and 8.3—8.5 (2H, m, 2- and 6-H); MS *m/z* (rel intensity, %) 175 (M^+, base peak), 174 (49), 130 (12), and 97 (46). Found (picrate): C, 47.65; H, 3.24; N, 13.77%. Calcd for $C_{16}H_{12}N_4O_7S$: C, 47.53; H, 2.99; N, 13.86%.

After the first fraction giving **13** was eluted with hexane-diethyl ether (2 : 1 vol/vol), the second fraction was followed with the same eluent. This fraction afforded **15** (0.127 g, 28%) after treatment with methanol and crystallization from diethyl ether. **15**: Colorless prisms (diethyl ether); mp 98—100 °C; IR (KBr) 3080, 1470, 1430, 1145, 1050, 1030, and 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ=4.10 (2H, s, CH_2), 4.85 (1H, br, OH), 5.94 (1H, s, CH), 6.6—7.3 (7H, m, ArH), 7.45 (1H, m, ArH), and 8.38 (1H, br s, 2-H); MS *m/z* (rel intensity, %) 287 (M^+, 85), 204 (10), 203 (11), 176 (21), 175 (base peak), 174 (22), 173 (11), 149 (28), 147 (11), 113 (19), 111 (11), 97 (71), 85 (33), and 57 (16). Found: C, 52.45; H, 4.61; N, 5.09%. Calcd for $C_{15}H_{13}NOS_2$: C, 62.69; H, 4.56; N, 4.87%.

General Procedure for Fluoride-Catalyzed Reaction of 1 with Aliphatic Aldehydes or Ketones Leading to 16—24. As a typical procedure, the reaction of **1** with 2-methylpropanal is described below: Under argon, **1** (purity 90%, 0.817 g, 3.26 mmol) was added to a solution of 2-methylpropanal (0.35 ml, 3.8 mmol) in dry THF (8 ml). After TBAF (1 M solution in THF, 0.38 ml, 0.38 mmol) was added, the mixture was heated under reflux for 7 h and then poured into saturated sodium hydrogencarbonate. The product was extracted with diethyl ether (30 ml), the ether washed with brine, dried over magnesium sulfate, and finally evaporated in vacuo. The residue was chromatographed over silica gel (20 g) with hexane-diethyl ether (10 : 1 vol/vol) to give **18** (0.34 g, 77%). Other aliphatic aldehydes and ketones were similarly treated. The results are summarized in Table 2.

3-Butylpyridine (16): Pale yellow liquid; IR (neat) 2800—3000, 1470, 1420, 1360, and 1020 cm^{-1}, ^1H NMR ($CDCl_3$) δ=0.8—2.6 (9H, m, butyl), 7.14 (1H, dd, *J*=8.1 and 5.0 Hz, 5-H), 7.43 (1H, dt, *J*=8.1, 2.1, and 2.1 Hz, 4-H), and 8.3—8.5 (2H, m, 2- and 6-H).

3-Pentylpyridine (17): Pale yellow liquid; IR (neat) 2800—3000, 1570, 1455, 1420, 1370, and 1020^{-1} cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.7—2.6 (11H, m, pentyl), 7.10 (1H, dd, *J*=8.1 and 5.0 Hz, 5-H), 7.38 (1H, dt, *J*=8.1, 2.1, and 2.1 Hz, 4-H), and 8.2—8.4 (2H, m, 2- and 6-H).

3-(2-Methylpropyl)pyridine (18): Pale yellow liquid; mp (picrate) 111—113 °C; IR (neat) 2800—3000, 1570, 1470, 1420, 1030, and 730 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.82 (6H, d, *J*=7.2 Hz,Me), 1.81 (1H, m, CH), 2.39 (2H, d, *J*=7.2 Hz, CH_2), 7.06 (1H, dd, *J*=8.1 and 4.5 Hz, 5-H), 7.31 (1H, dt, *J*=8.1, 2.1, and 2.1 Hz, 4-H), and 8.2—8.4 (2H, m, 2- and 6-H); ^{13}C NMR ($CDCl_3$) δ=22.17 (q, Me), 29.97 (d, CH), 42.30 (t, CH_2), 123.04 (d, 5-C), 136.34 (d, 4-C), 136.64 (s, 3-C), 147.11 (d, 6-C), and 150.38 (d, 2-C). Found (picrate) C, 49.44; H, 4.46; N, 15.35%. Calcd for $C_{15}H_{16}N_4O_7$: C, 49.45; H, 4.43; N, 15.38%.

3-(2,2-Dimethylpropyl)pyridine (19): Pale yellow liquid; mp (picrate) 125—127 °C; ^1H NMR ($CDCl_3$) δ=0.89 (9H, s, *t*-Bu), 2.46 (2H, s, CH_2), 7.16 (1H, dd, *J*=8.1 and 5.0 Hz, 5-H), 7.38 (1H, dt, *J*=8.1, 2.0, and 2.0 Hz, 4-H), and 8.3—8.5 (2H, m, 2- and 6-H); ^{13}C NMR ($CDCl_3$) δ=29.06 (q, *t*-Bu), 31.59 (s, *t*-Bu), 47.09 (t, CH_2), 122.59 (d, 5-C), 137.44 (d, 4-C), 137.74 (s, 3-C), 147.13 (d, 6-C), and 151.18 (d, 2-C). Found (picrate) C, 50.64; H, 4.91; N, 14.65%. Calcd for $C_{16}H_{18}N_4O_7$: C, 50.79; H, 4.80; N, 14.81%.

3-(3,7-Dimethyl-6-octenyl)pyridine (20): Yellow liquid; IR (neat) 2850—3000, 1580, 1490, 1460, 1430, 1380, 1020, and 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.8—2.7 (12H, m, Me, CH_2, and CH), 1.60, 1.68 (each 3H, s, $=C(Me)_2$), 5.02 (1H, br t, olefinic), 7.08 (1H, dd, *J*=8.0 and 5.0 Hz, 5-H), 7.37 (1H, dt, *J*=8.0, 2.0, and 2.0 Hz, 4-H), and 8.3—8.5 (2H, m, 2- and 6-H); MS *m/z* (rel intensity, %) 217 (M^+, 17), 149 (13), 134 (12), 107 (19), 106 (base peak), 93 (48), 92 (45), 69 (26), and 66 (27).

3-(3-Cyclohexenylmethyl)pyridine (21): Pale yellow liquid; mp (picrate) 101—103 °C; IR (neat) 2850—3030, 1580, 1480, 1425, 1030, 730, and 715 cm^{-1}; ^1H NMR ($CDCl_3$)

δ=0.8—2.1 (7H, m, cyclohexenyl), 2.51 (2H, d, J=7.0 Hz, CH_2), 5.53 (2H, br s, olefinic), 7.08 (1H, dd, J=8.1 and 4.5 Hz, 5-H), 7.35 (1H, dt, J=8.1, 2.0, and 2.0 Hz, 4-H), and 8.2—8.5 (2H, m, 2- and 5-H); MS m/z (rel intensity, %) 173 (M^+, 55), 130 (19), 118 (25), 117 (16), 94 (20), 93 (base peak), 92 (33), 91 (16), 81 (97), 80 (13), 79 (49), 78 (11), 77 (25), and 66 (54). Found (picrate): 53.97; H, 4.60; N, 14.07%. Calcd for $C_{18}H_{18}N_4O_7$: C, 53.73; H, 4.51; N, 13.91%.

3-(1-Ethylpropyl)pyridine (22): Pale yellow liquid; mp (picrate) 112—113 °C; ^{1}H NMR ($CDCl_3$) δ=0.83 (6H, t, Me), 1.57 (4H, m, CH_2), 2.32 (1H, m, CH), 7.13 (1H, dd, J=8.1 and 4.5 Hz, 5-H), 7.32 (1H, dt, J=8.1, 2.1, and 2.1 Hz, 4-H), and 8.3—8.6 (2H, m, 2- and 6-H). Found (picrate) C, 50.63; H, 4.80; N, 14.81%. Calcd for $C_{16}H_{18}N_4O_7$: C, 50.79; H, 4.80; N, 14.81%.

3-Cyclohexylpyridine (23): Pale yellow liquid; mp (picrate) 130—131 °C; IR (neat) 2950, 2850, 1580, 1480, 1450, 1425, 1025, 810 and 720 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=1.0—2.6 (11H, m, cyclohexyl), 7.09 (1H, dd, J=8.1 and 4.5 Hz, 5-H), 7.41 (1H, dt, J=8.1, 2.0, and 2.0 Hz, 4-H), and 8.3—8.5 (2H, m, 2- and 6-H); MS m/z (rel intensity, %) 161 (M^+, base peak), 160 (18), 133 (41), 132 (24), 130 (10), 119 (13), 118 (59), 117 (25), 107 (12), 106 (40), 105 (96), 104 (20), 93 (26), 92 (38), 91 (13), 80 (15), 78 (15), 77 (13), and 65 (20). Found (picrate): C, 52.31; H, 4.65; N, 14.35%. Calcd for $C_{17}H_{18}N_4O_7$: C, 52.31; H, 4.65; N, 14.35%.

3-(1-Phenylethyl)pyridine (24): Pale yellow liquid; mp (picrate) 138—141 °C; IR (neat) 2900—3100, 1570, 1495, 1480, 1445, 1420, 1020, 710, and 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.63 (3H, d, J=6.3 Hz, Me), 4.12 (1H, q, J=6.3 Hz, CH), 7.0—7.5 (7H, m, ArH), and 8.3—8.5 (2H, m, 2- and 6-H); MS m/z (rel intensity, %) 183 (M^+, 47), 169 (14), 168 (base peak), 167 (33), 115 (10), 77 (11), and 51 (12). Found (picrate): C, 54.88; H, 4.01; N, 13.43%. Calcd for $C_{19}H_{16}N_4O_7$: C, 55.34; H, 3.91; H, 13.59%.

Reactions of 2—4 with Benzaldehyde or 2-Methylpropanal Leading to 25—32. The procedures are essentially the same to those described above: The reactions with benzaldehyde was carried out at room temperature and with 2-methylpropanal under reflux. All the results are listed in Table 3.

2-Methyl-5-benzylpyridine (25) + 2-Methyl-3-benzylpyridine (25′): Inseparable mixture (6:4 by ^{1}H NMR and ^{13}C NMR); Pale yellow liquid; ^{1}H NMR ($CDCl_3$) δ=2.43 (3H, s, 2-Me), 3.80, 3.85 (2H, 4:6, each s, CH_2), 6.8—7.4 (7H, m, ArH), and 8.2—8.3 (1H, m, 6-H); ^{13}C NMR ($CDCl_3$) δ=22.08, 23.48 (each q, 6:4, 2-Me), 38.34 (t, CH_2), 120.93 (d), 122.70 (s), 125.99, 128.22, 128.34, 136.32, 136.85 (each d), 146.48, 148.77 (each d, 6-C), 155.58, 156.70 (each s, 2-C); MS m/z 183 (M^+). Found (picrate, mp 143—146 °C): C, 55.22; H, 4.02; N, 13.77%. Calcd for $C_{19}H_{16}N_4O_7$: C, 55.34; H, 3.91; N, 13.59%.

The first fraction affording **25+25′** (hexane-diethyl ether (5:1 vol/vol)) was followed by the second fraction which gave **27** (0.145 g, 22%): Colorless liquid; IR (neat) 2900—3100, 1570, 1490, 1445, 1400, 1245, 1090, 1060, 890, and 840 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.06 (9H, s, Me_3Si), 2.30 (3H, s, 2-Me), 3.83 (2H, s, CH_2), 5.77 (1H, s, CH), 6.9—7.4 (12H, m, ArH); MS m/z (rel intensity, %) 361 (M^+, 36), 281 (10), 179 (29), 91 (12), 77 (15), 75 (24), 73 (38), and 43 (base peak).

2-Methyl-5-(2-methylpropyl)pyridine (26) + 2-Methyl-3-(2-methylpropyl)pyridine (26′): Inseparable mixture (6:4 by ^{13}C NMR); Pale yellow liquid; ^{1}H NMR ($CDCl_3$) δ=0.88 (6H, d, Me), 1.82 (1H, m, CH), 2.3—2.5 (5H, m, 2-Me and CH_2), 6.9, 7.2, and 8.2 (each 1H, m, ArH); ^{13}C NMR ($CDCl_3$) δ=21.72, 22.02 (each q, 2-Me and Me), 28.42, 29.59 (d, 6:4, CH), 41.57 (t, CH_2), 120.41, 122.11 (each d), 124.21 (s), 136.27, 136.73 (each d), 146.07, 149.18 (each d, 6-C), 155.05, and 156.23 (each s, 2-C). Found (picrate, mp 114—116 °C): C, 50.74, H, 4.75; N, 15.25%. Calcd for $C_{16}H_{18}N_4O_7$: C, 50.79; H, 4.80; N, 14.81%.

3-Benzyl-5-methylpyridine (28): Pale yellow liquid; mp (picrate) mp 149—151 °C; IR (neat) 2950—3100, 1605, 1580, 1505, 1460, 1450, 1040, 730, and 710 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.15 (3H, s, 5-Me), 3.79 (2H, s, CH_2), 6.9—7.3 (6H, m, ArH), and 8.13 (2H, br s, 2- and 6-H); MS m/z (rel intensity, %) 183 (M^+, 57), 182 (48), 168 (20), 167 (16), 128 (21), 115 (49), 91 (51), 89 (27), 78 (22), 77 (45), 65 (73), and 39 (base peak). Found (picrate): C, 55.22; H, 3.94; N, 13.66%. Calcd for $C_{19}H_{16}N_4O_7$: C, 55.34; H; 3.91; N, 13.59%.

The first farction containing **28** was followed by the second fraction (both eluted with hexane-diethyl ether (5:1 vol/vol)) which gave **30** (0.074 g, 17%): Pale yellow liquid; IR (neat) 2900—3100, 1600, 1500, 1450, 1410, 1255, 1090, 1060, 890, 840, and 730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.06 (9H, s, Me_3Si), 2.19 (3H, s, 3-Me), 3.83 (2H, s, CH_2), 5.98 (1H, s, CH), 6.9—7.4 (11H, m, ArH), and 8.17 (1H, br s, 6-H); MS m/z (rel intensity, %) 361 (M^+, 41), 346 (15), 272 (14), 270 (14), 181 (15), 180 (18), 179 (43), 115 (15), 91 (36), and 73 (base peak).

3-Methyl-5-(2-methylpropyl)pyridine (29): Pale yellow liquid; mp (picrate) 140—142 °C; IR (neat) 2900—3050, 1580, 1470, 1440, 1390, 1370, 740, and 720 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.85 (6H, d, J=8.0 Hz, Me), 1.81 (1H, m, CH), 2.23 (3H, s, 5-Me), 2.37 (2H, d, J=8.0 Hz, CH_2), 7.11 (1H, br s, 4-H), and 8.09 (2H, br s, 2- and 6-H); ^{13}C NMR ($CDCl_3$) δ=18.27 (q, 5-Me), 22.22 (q, Me), 30.02 (d, CH), 42.20 (t, CH_2), 132.30 (s, 3-C), 136.00 (s, 5-C), 136.93 (d, 4-C), and 147.60 (d, 2- and 6-C); MS m/z (rel intensity, %) 149 (M^+, 31), 107 (base peak), 106 (70), 92 (11), 86 (11), 84 (17), 79 (29), 78 (26), and 77 (59). Found (picrate): C, 50.57; H, 4.77; N, 15.03%. Calcd for $C_{16}H_{18}N_{N4}O_7$: C, 50.57; H, 4.80; N, 14.81%.

3-Benzyl-4-methylpyridine (31): Yellow liquid; ^{1}H NMR ($CDCl_3$) δ=2.15 (3H, s, 4-Me), 3.91 (2H, s, CH_2), 6.9—7.3 (6H, m, ArH), and 8.2—8.4 (2H, m, 2- and 6-H); MS m/z (rel intensity, %) 183 (M^+, base peak), 182 (81), 168 (40), 167 (27), 128 (17), 115 (31), 105 (45), 91 (37), 78 (22), and 77 (35). HRMS Found: m/z 183.1055. Calcd for $C_{13}H_{13}N$: M, 183.1047.

4-Methyl-3-(2-methylpropyl)pyridine (32): Yellow liquid; mp (picrate) 106—108 °C; IR (neat) 2900—3000, 1600, 1460, and 1410 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.75 (6H, d, J=8.0 Hz, Me), 1.64 (1H, m, CH), 2.06 (3H, s, 4-Me), 2.24 (2H, d, J=8.0 Hz, CH_2), 6.75 (1H, d, J=5.0 Hz, 5-H), and 7.96 (2H, m, 2- and 6-H); MS m/z (rel intensity, %) 149 (M^+, 30), 135 (35), 107 (base peak), 106 (72), 79 (32), 78 (21), 77 (54), and 53 (25). Found (picrate): C, 50.66; H, 4.77; N, 14.99%. Calcd for $C_{16}H_{18}N_4O_7$: C, 50.79; H, 4.80; N, 14.81%.

3-Chloro-1,4-bis(trimethylsilyl)-1,4-dihydropyridine (33) and 3-Chloro-5-(2-methylpropyl)pyridine (34). A similar procedure as mentioned above was performed by employing 3-chloropyridine (3.0 ml, 31 mmol) in dry THF (6 ml), chlorotrimethylsilane (19 ml, 150 mmol), and lithium powder (1.04 g, 150 mmol) in dry THF (40 ml) to give a mixture of **33** and **1** (1.52 g, bp 65—70 °C/146 Pa, yellow liquid): ^{1}H NMR ($CDCl_3$, the signals of **1** were excluded) δ=−0.08 (9H, s, 4-Me_3Si), 0.10 (9H, s, 1-Me_3Si), 2.26 (1H, d, J=7.5 Hz, 4-H), 4.38 (1H, dd, J=10.5 and 7.5 Hz, 5-H), 5.66 (1H, d, J=10.5 Hz, 6-H), and 5.87 (1H, s, 2-H).

To a solution of thus prepared **33** (0.63 g) and 2-methylpropanal (0.22 ml, 2.43 mmol) in dry THF (5 ml) was added slowly TBAF (1M in THF, 0.22 ml, 0.22 mmol). The mixture was refluxed for 10 h under argon. A similar hydrolytic work-up was followed by a column chromatography over silica gel with hexane-diethyl ether (5 : 1 vol/vol) to give **18** (0.112 g, 34% base on the aldehyde) and then **34** (0.086 g, 21% based on the aldehyde). **34**: Pale yellow liquid; ^{1}H NMR ($CDCl_3$) δ=0.88 (6H, d, J=7.5 Hz, Me), 1.77 (1H, m, CH), 2.35 (2H, d, J=7.5 Hz, CH_2), 7.38 (1H, br s, 4-H), 8.19 (1H, br s, 6-H), and 8.32 (1H, br s, 2-H).

References

1) As reviews: A. J. Boulton and A. McKillop, "Six-membered Rings with One Nitrogen Atom," as Vol. 2A of "Comprehensive Heterocyclic Chemistry," ed by A. R. Katritzky and C. W. Rees, Pergamon Press, Oxford, New York, Toronto, Sydney, Paris, and Frankfurt (1984); P. G. Sammes, "Heterocyclic Compounds," as Vol. 4 of "Comprehensive Organic Chemistry," ed by Sir D. Barton and W. D. Ollis, Pergamon Press, Oxford, New York, Toronto, Sydney, paris, and Frankfurt (1979), pp. 1—84.

2) R. A. Abramovitch and J. G. Saha, *Adv. Heterocycl. Chem.*, **6**, 229 (1966); A. R. Katritzky, "Handbook of Heterocyclic Chemistry," Pergamon Press, Oxford, New York, Toronto, Sydney, Paris, and Frankfurt (1985), pp. 379.

3) P. Doyle and R. R. J. Yates, *Tetrahedron Lett.*, **1970**, 3371; Y. Tamaru, Y. Yamada, and Z. Yoshida, *J. Org. Chem.*, **43**, 3396 (1978); D. L. Comins and N. B. Mantlo, *Tetrahedron Lett.*, **24**, 3683 (1983).

4) A. I. Meyers and R. A. Gabel, *Tetrahedron Lett.*, **1978**, 227; G. W. Gribble and M. G. Saulnier, *ibid.*, **21**, 4137 (1980); J. Epsztajn, Z. Berski, J. Z. Brzezinski, and A. Jozwiak, *ibid.*, **21**, 4739 (1980); F. Marsais, G. L. Nard, and G. Quéguiner, *Synthesis*, **1982**, 235; T. Güngör, F. Marsais, and G. Quéguiner, *ibid.*, **1982**, 499; A. I. Meyers and R. A. Gabel, *J. Org. Chem.*, **47**, 2633 (1982).

5) E. Piers and M. Soucy, *Can. J. Chem.*, **52**, 3563 (1974); C. S. Giam, E. E. Knaus, and F. M. Pasutto, *J. Org. Chem.*, **39**, 3565 (1974); C. S. Giam and K. Ueno, *J. Am. Chem. Soc.*, **99**, 3166 (1977); A. R. Katrizky, J. G. Keay, D. N. Rogers, M. P. Sammes, C. W. F. Leung, and C. M. Lee, *Angew. Chem. Int. Ed. Engl.*, **18**, 792 (1979); K. Akiba, H. Matsuoka, and M. Wada, *Tetrahedron Lett.*, **22**, 4093 (1981); K. Akiba, Y. Iseki, and M. Wada, *ibid.*, **23**, 429 and 3935 (1982); D. L. Comins and A. H. Abdullah, *J. Org. Chem.*, **47**, 4315 (1982); D. L. Comins, *Tetrahedron Lett.*, **23**, 2807 (1983); D. L. Comins and N. B. Mantlo, *ibid.*, **24**, 3683 (1983); K. Akiba, Y. Nishihara, and M. Wada, *ibid.*, **24**, 5269 (1983).

6) C. S. Giam and S. D. Abbott, *J. Am. Chem. Soc.*, **93**, 1294 (1971).

7) R. A. Sulzbach, *J. Organomet. Chem.*, **24**, 307 (1970).

8) W. Ando and H. Tsumaki, *Tetrahedron Lett.*, **22**, 3073 (1982); R. J. P. Corriu, V. Huynh, J. J. E. Moreau, and M. Pataud-Sat, *ibid.*, **23**, 3257 (1982).

9) A part of the present work has been reported as a preliminary communication (O. Tsuge, S. Kanemasa, T. Naritomi, and J. Tanaka, *Chem. Lett.*, **1984**, 1255).

10) F. B. LaForge, *J. Am. Chem. Soc.*, **50**, 2484 (1928); F. J. Villani and M. S. King, *Org. Synth.*, **37**, 6 (1957).

11) The ^{13}C chemical shifts of pyridine is referred to p. 33 of "Handbook of Heterocyclic Chemistry" cited in Ref. 2.

12) E. M. Kaiser and J. D. Petty, *Synthesis*, **1975**, 705; S. V. Kannan and H. Pines, *J. Org. Chem.*, **36**, 2304 (1971).