

fides in DMF in the presence of piperidine (sixfold) gave no detectable amounts of sulfenamides, resulting in recovery of the starting materials.

Registry No.—6, 1155-00-6; 7, 66552-58-7; carbon disulfide, 75-15-0.

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Identification of 2,5-Dihydropyridine Intermediates in the Reactions of 2-Alkyl(phenyl)-1-lithio-1,2-dihydropyridines with Alkyl Halides

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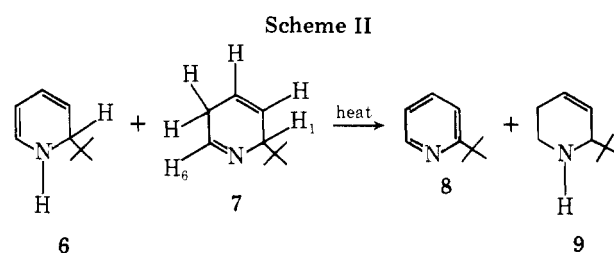
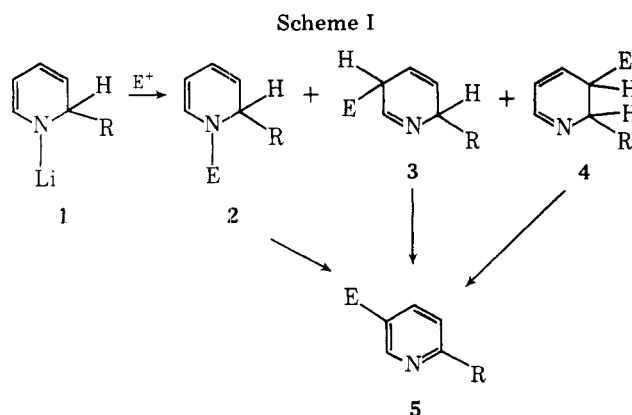
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A series of 2,5-disubstituted 2,5-dihydropyridines (**10**) have been prepared from 2-alkyl(phenyl)-1-lithio-1,2-dihydropyridines (**1**) and alkyl halides and have been characterized by their IR and NMR spectra. Each 2,5-dialkyl-2,5-dihydropyridine (**10a-d**) decomposes on exposure to air or when heated to a mixture containing the corresponding 2,5-dialkylpyridine (**11a-d**) and the 2,5-dialkyl-1,2,5,6-tetrahydropyridine (**12a-d**). However, decomposition of a 5-alkyl-2-phenyl-2,5-dihydropyridine (**10d,f**) gives only the 5-alkyl-2-phenylpyridine (**11e,f**). The 2,5-dihydropyridines (**10**) are converted to the corresponding tetrahydropyridines (**12**) by lithium aluminum hydride reduction.

There has been little direct evidence for the existence of unstable 2,5-dihydropyridines.¹ However, they have been proposed as intermediates in reactions which include the sodium borohydride reduction of pyridinium salts,^{2,3} the synthesis of 8-azasteroids,⁴ the dehydrogenation of a 1,4-dihydropyridine,⁵ and the reactions of lithium tetrakis(*N*-dihydropyridyl)aluminum with alkyl halides and bromine.⁶

The reactions of 1-alkyl(aryl)-1,2-dihydropyridines (**1**) with electrophiles can, in theory, lead to 1,2-, 2,5-, and 2,3-dihydropyridines as shown in Scheme I. The stable acylation products^{7,8} of complex **1** (R = phenyl) are 1,2-dihydropyridines (**2**) which result from *N*-acylation and 2,5-disubstituted pyridines (**5**) which involve *C*-acylation. The latter are as-



sumed to form from decomposition of 2,5-dihydropyridine intermediates (**3**). Alkylation^{8,9,10} of complex **1** (R = phenyl) by the use of alkyl halides leads to 5-alkyl-2-phenylpyridines (**5**) which also presumably are formed on the decomposition of 2,5-dihydropyridines (**3**). Products obtained from the reaction of **1** with bromine,⁹ cyanogen bromide,¹¹ benzophenone,¹² and phenyl disulfide¹³ also are assumed to involve 2,5-dihydropyridine precursors.

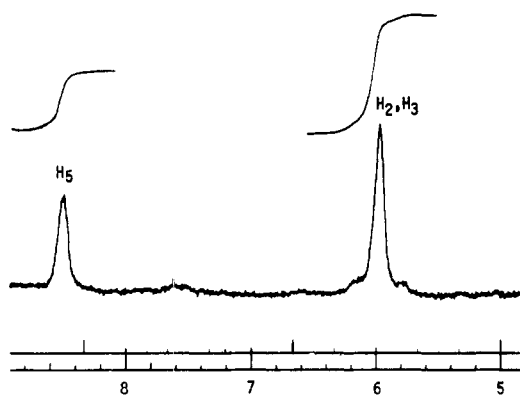
The first direct evidence for a 2,5-dihydropyridine, formed in the reaction of 2-*tert*-butyl-1-lithio-1,2-dihydropyridine (**1a**) with methanol, was reported¹⁴ from this laboratory. This reaction gave dihydropyridines **6** and **7** which were decomposed by heat to 2-*tert*-butylpyridine (**8**) and 2-*tert*-butyl-1,2,5,6-tetrahydropyridine (**9**).

Results and Discussion

We have now identified the 2,5-dihydropyridines (**10**) obtained from the reactions of pyridine-alkyllithium complexes (**1**) with methyl and ethyl halides (Table I). Structural as-

Table I. Pyridine-Alkylolithium Complexes (1), 2,5-Dihydropyridines (10), and Vinyl Proton Absorptions of 2,5-Dihydropyridines

no.	registry no.	R	no.	R	R'	registry no.	chemical shifts for vinyl protons of 10, δ	
							H ₅	H ₂ , H ₃
1a	42540-75-0	<i>t</i> -Bu	10a	<i>t</i> -Bu	CH ₃	66562-50-3	8.45	6.00
1b	20180-25-0	<i>n</i> -Bu	10b	<i>t</i> -Bu	C ₂ H ₅		8.09	5.80
ac	24724-75-2	phenyl	10c	<i>n</i> -Bu	CH ₃		8.05	5.73
			10d	phenyl	CH ₃	66562-51-4	8.30	5.92
			10e	phenyl	C ₂ H ₅	66562-52-5	8.15	5.87

Figure 1. NMR spectrum of the vinyl proton absorptions of 2-*tert*-butyl-5-methyl-2,5-dihydropyridine (10a).

signments for these 2,5-dihydropyridines are based on their NMR and IR spectra, their decomposition products, and their facile reduction (lithium aluminum hydride) to the corresponding tetrahydropyridines (12). A series of pyridine-alkylolithium complexes (1) were prepared as yellow crystalline solids from pyridine and the appropriate alkylolithium compound. The reaction of each complex (1) with methyl iodide or ethyl bromide gave a 2,5-dialkyl(aryl)-2,5-dihydropyridine (10).

The NMR spectrum of 2-*tert*-butyl-5-methyl-2,5-dihydropyridine (10a) is representative of those obtained for other 2,5-dialkyl-2,5-dihydropyridines. It showed a broad absorption at δ 8.45 (1 H) assigned to H₅, a broad absorption at δ 6.00 (2 H) assigned to H₂ and H₃, and a multiplet at δ 4.40 (1 H) assigned to H₄. Other absorptions of 10a were obscured by those of the solvent. The vinyl proton absorptions for 10a are shown in Figure 1. A summary of vinyl proton absorptions for all 2,5-dialkyl-2,5-dihydropyridines (10) is given in Table I.

The reactions of complexes 1a-c with alkyl halides could also give 1,2-dialkyl-1,2-dihydropyridines as a result of *N*-alkylation. However, the general absorption patterns reported¹ for the NMR spectra of alkyl-substituted 1,2-dihydropyridines differ substantially in the vinyl proton region from patterns observed in the NMR spectra obtained in these studies. Thus these reactions gave no detectable amounts of the 1,2-dihydropyridines.

The NMR spectra of some solutions containing 2,5-dihydropyridines showed additional absorptions of much lower intensity near those reported for vinyl protons H₂, H₃, and H₅.

These absorptions suggest the presence of stereoisomeric 2,5-dihydropyridines in some of these mixtures. This aspect of the structures of the 2,5-dihydropyridines formed in the reactions of complex 1 with alkyl halides is currently under investigation.

Acylation of complex 1a with acetyl chloride gave, as expected,^{8,9} 1,2-dihydropyridine 13 which was sufficiently stable to be collected by preparative GLC at 150 °C.

The reactions of lithium tetrakis(*N*-dihydropyridyl)aluminate⁶ and complex 1c⁹ with bromine have been reported to give 3-bromopyridine and 5-bromo-2-phenylpyridine, respectively. However, treatment of complex 1a with either bromine or pyridinium perbromide gave no detectable amount of 5-bromo-2-*tert*-butylpyridine but did afford 6,6'-di-*tert*-butyl-3,3'-dipyridyl (16). The formation of dipyridyl 16 may involve 2,5-dihydropyridine intermediates 14 and 15 (Scheme III). Experiments aimed at identification of these intermediates are currently underway. Dipyridyls also have been reported^{10,11} in the reactions of complexes 1b and 1c with other halogenating agents.

Workup and analysis of a sample of each 2,5-dialkyl-2,5-dihydropyridine (10a-c) revealed that each had decomposed to a mixture containing the corresponding 2,5-dialkylpyridine (11a-c) and the 2,5-dialkyl-1,2,5,6-tetrahydropyridine (12a-c). The relative percentage of dialkyltetrahydropyridine (12) in each reaction was less than that of the dialkylpyridine (11). The tetrahydropyridine may have been formed by transfer of a hydride ion from one 2,5-dihydropyridine mol-

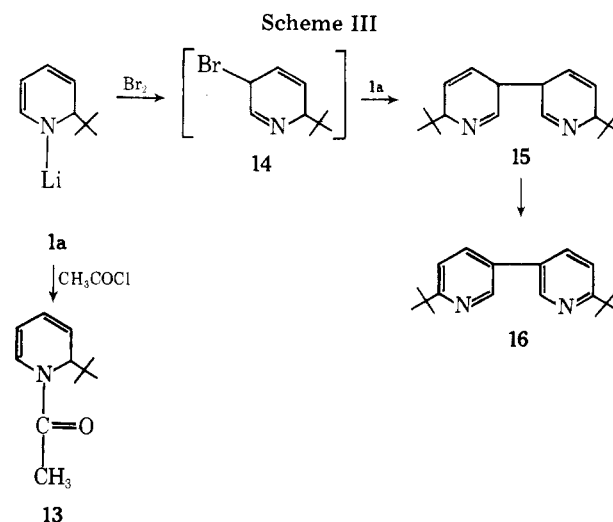
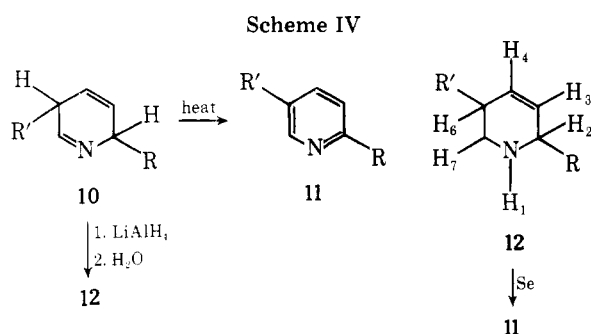


Table II. Vinyl Proton Absorptions and Elemental Analyses of Tetrahydropyridines 12a-e

compd	registry no.	vinyl protons, δ	elemental analysis					
			calcd			found		
			C	H	N	C	H	N
12a	66562-53-6	5.62	78.37	12.49	9.14	78.25	12.61	9.29
12b		5.65 ^a	78.97	12.96	8.37	78.89	12.84	8.13
12c		5.60 ^b	78.43	12.42	9.15	78.40	12.37	9.17
12d	66562-54-7	5.70	83.24	8.67	8.09	83.40	8.60	8.01
12e	66562-55-8	5.70	83.42	9.09	7.49	83.52	9.03	7.49

^aTwo broad absorptions, approximate ratio 5:1. ^bTwo broad absorptions, approximate ratio 2:1.



ecule to the C=N moiety of another. Compounds 11 and 12 generally could not be separated cleanly by distillation or preparative GLC. In each case a pure sample of the 2,5-dialkylpyridine (11) for spectral and elemental analyses was obtained from these mixtures by selenium oxidation of 12 to 11. A pure sample of the 2,5-dialkyl-1,2,5,6-tetrahydropyridine (12) was prepared by the hydride reduction of the 2,5-dialkyl-2,5-dihydropyridine (10). These reactions are shown in Scheme IV. Decomposition of each 5-alkyl-2-phenyl-2,5-dihydropyridine (10d and 10e) gave only the 5-alkyl-2-phenylpyridine (11d and 11e). A summary of the data obtained from these reactions is given in Table II.

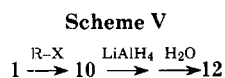
The 2,5-dialkyl(phenyl)-2,5-dihydropyridines (10) obtained from the reactions of complex 1 with alkyl halides were expected to undergo hydride reduction at the C=N bond; accordingly, each was treated with lithium aluminum hydride. On reduction, 2,5-dihydropyridines 10a, 10d, and 10e each gave a single tetrahydropyridine according to GLC and NMR analyses. However, the NMR spectrum of each of the reduction products of 2,5-dihydropyridines 10b and 10c suggested the presence of two stereoisomeric tetrahydropyridines.

The hydride reductions described above generally gave high yields of tetrahydropyridines, and the reaction sequence shown in Scheme V may serve as a convenient synthesis of a variety of 2,5-dialkyl-1,2,5,6-tetrahydropyridines (12).

Experimental Section

General. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Nuclear magnetic resonance spectra were obtained on Varian T-60 and HA-100 instruments. Analyses of reaction product mixtures and relative percentage yields of products were obtained on a Varian Aerograph 90-P3 gas chromatograph equipped with a 20 ft \times $\frac{3}{8}$ in. column composed of 30% SE-30 on Chromosorb W (60/80 mesh). Infrared spectra were recorded on a Perkin-Elmer 621 instrument. *tert*-Butyllithium in pentane was obtained from Lithium Corporation of America. Other alkylolithium compounds were prepared by standard procedures.

2-*tert*-Butyl-1-lithio-1,2-dihydropyridine (1a).¹⁴ In a nitrogen-flushed drybox, 0.06 mol of *tert*-butyllithium was added to a 25 \times 200 mm test tube. The test tube was sealed with a serum cap, removed from the drybox and cooled to about -70° in a dry ice-isopropyl alcohol bath. A solution of 0.04 mol of pyridine in about 10 mL



of dry pentane was added slowly over a period of about 10 min by use of a syringe. The mixture was shaken vigorously after each addition. Complex 1a began crystallizing as a yellow solid in about 1 h. The mixture was generally allowed to stand at -70° C overnight to assure maximum crystallization.

2-*n*-Butyl-1-lithio-1,2-dihydropyridine (1b)¹⁵ was prepared according to the procedure described for 1a. Complex 1b was obtained from pyridine and butyllithium in hexane as a yellow solid. NMR (ethyl ether): δ 6.70 (1 H, d, H₅), 5.95 (1 H, m, H₃), 4.87 (1 H, t, H₁), 4.43 (2 H, m, H₂ and H₄).

1-Lithio-2-phenyl-1,2-dihydropyridine (1c)¹⁷ was prepared according to the procedure described previously for complex 1a except that 0.04 mol of pyridine was added to 0.08 mol of phenyllithium¹⁸ in ethyl ether which had been cooled to 0° C in an ice-water bath. The mixture was allowed to stand at room temperature until the yellow complex 1c crystallized. The mixture was generally refrigerated overnight to insure maximum crystallization. An NMR spectrum obtained for complex 1c in tetramethylethylenediamine with Me₄Si as the internal standard agreed with that previously reported.¹⁷

2-*tert*-Butyl-5-methyl-2,5-dihydropyridine (10a) was used to remove the supernatant liquid from complex 1a. The complex was washed by injecting 10 mL of dry ethyl ether or pentane into the test tube, shaking the mixture, allowing the solid to settle, and withdrawing the liquid. This procedure was repeated. A mixture of complex 1a and about 20 mL of dry ethyl ether was slowly added by use of a syringe. As the components reacted, the solid complex dissolved. The mixture was allowed to stand at 0° C for 2-3 h. The resultant clear, yellow solution was transferred with a syringe to a small round-bottomed flask which had been flushed with nitrogen, fitted with a serum cap, and cooled in an ice-water bath. The flask was placed on a rotary evaporator, and the mixture was concentrated at 0° C. A sample of the concentrate was transferred with a syringe to an NMR tube, Me₄Si was added, and an NMR spectrum of complex 1a in ethyl ether was obtained: δ 8.45 (1 H, br s, H₅), 6.00 (2 H, br s, H₂, H₃), 4.40 (1 H, m, H₄). IR: 1715, 1675, 1640 cm⁻¹.

The signals from H₁ and the methyl and *tert*-butyl groups in the NMR spectrum were obscured by absorptions from the solvent. Attempted removal of the last traces of solvent resulted in considerable decomposition of the 2,5-dihydropyridine 10a to aromatic compound 11a and tetrahydropyridine 12a.

2-*tert*-Butyl-5-ethyl-2,5-dihydropyridine (10b) was prepared according to the procedure described for 2,5-dihydropyridine 10a. Because complex 10b proved to be more stable than complex 10a, most reaction solvent could be removed from the sample by rotary evaporation. An NMR spectrum was obtained on a sample of 10b in deuteriochloroform with Me₄Si: δ 8.09 (1 H, br s, H₅), 5.80 (2 H, br s, H₂, H₃), 4.02 (1 H, m, H₄), 3.64 (1 H, br, H₁), 2.41 (2 H, q, CH₃CH₂), 1.60 (3 H, t, CH₃CH₂). IR: 1710 (C=N), 1675 and 1655 cm⁻¹ (C=C).

2-*n*-Butyl-5-methyl-2,5-dihydropyridine (10c) was prepared from complex 1b and methyl iodide according to the procedure described for 2,5-dihydropyridine 10a: NMR δ 8.05 (1 H, br s, H₅), 5.73 (2 H, br s, H₂, H₃), 4.48 (1 H, m, H₁). Absorptions from the methyl and butyl groups were obscured by absorptions from the solvent (pentane).

5-Methyl-2-phenyl-2,5-dihydropyridine (10d) was prepared from complex 1c and methyl iodide by the procedure described for 2,5-dihydropyridine 10a. The methyl iodide-ethyl ether mixture was added to complex 1c in ethyl ether at 0° C: NMR δ 8.30 (1 H, br s, H₅), 7.57 (5 H, s, phenyl), 5.92 (2 H, br s, H₂, H₃). Other absorptions were obscured by those of the solvent.

5-Ethyl-2-phenyl-2,5-dihydropyridine (10e) was prepared from complex 1c and ethyl bromide by the procedure described for 2,5-dihydropyridine 10a. The ethyl bromide-ethyl ether mixture was added to complex 1c in ethyl ether at 0° C. NMR δ 8.15 (1 H, br s, H₅),

5.87 (2 H, br s, H₂, H₃). Other absorptions were obscured by those from the solvent.

1-Acetyl-2-tert-butyl-1,2-dihydropyridine (13) was prepared from complex **1a** and 0.04 mol of acetyl chloride at -70 °C. The mixture was allowed to warm to 0 °C and stand at this temperature for an additional hour. Workup as described above gave a yellow oil which GLC analysis showed to contain a single major product which was collected by preparative GLC as a colorless oil: NMR δ 6.45 (1 H, d, H₅), 6.02 (1 H, m, H₄), 5.60 (1 H, m, H₃), 5.00 (1 H, d, H₁), 2.20 (3 H, s, CH₃), 1.00 (9 H, s, *t*-Bu); IR 1680 (C=O), 1595 and 1575 cm⁻¹ (C=C). Anal. Calcd for C₁₁H₁₇NO: C, 73.76; H, 9.49; N, 7.81. Found: C, 73.59; H, 9.33; N, 7.79.

6,6'-Di-tert-butyl-3,3'-dipyridyl (16) was prepared from complex **1a** and bromine dissolved in pentane or pyridine perbromide¹⁹ dissolved in tetrahydrofuran by the general procedure described for 2,5-dihydropyridine **10a**. The addition of the brominating reagent to complex **1a** (-70 °C) resulted in immediate formation of a yellow solid. The mixture was shaken frequently. The resultant mixture, a clear yellow solution, was refluxed for 2 h, cooled, and shaken with 25 mL of water. The organic layer was separated and dried (K₂CO₃), and the solvent was removed by rotary evaporation. The residue, microdistilled at 10 mm, gave a mixture which by GLC analysis contained 2-*tert*-butylpyridine, 2-*tert*-butyl-1,2,5,6-tetrahydropyridine, and 6,6'-di-*tert*-butyl-3,3'-bipyridyl (**16**). Bipyridyl **16** was collected by preparative GLC as a yellow solid; mp 121–122 °C; NMR δ 8.40 (2 H, s, C₆-H, C₆'-H), 7.40 (4 H, m, C₃-H, C₄-H, C₃'-H, C₄'-H), 1.25 (18 H, s, *t*-Bu, *t*-Bu'). Anal. Calcd for C₁₈H₂₄N₂: C, 80.61; H, 8.94; N, 10.44. Found: C, 80.69; H, 8.88; N, 10.40.

Decomposition of 2,5-Dihydropyridines. Samples (0.04 mol) of 2,5-dialkyl(aryl)-2,5-dihydropyridines were prepared as described in the previous sections. About 2 mL of water was cautiously added to each sample and the mixture was shaken. The organic layer was separated, the aqueous layer was extracted with three 10-mL portions of ethyl ether, and the combined organic portions were dried (K₂CO₃). The solvent was removed by rotary evaporation, and the residue was distilled at 10 mm of pressure. Each distillate was analyzed by GLC. Decomposition of each 2,5-dialkyl-2,5-dihydropyridine (**10a–d**) gave a mixture containing the 2,5-dialkylpyridine (**11a–d**) and the 2,5-dialkyl-1,2,5,6-tetrahydropyridine (**12a–d**). The relative percentages of **11** and **12** formed by decomposition of **10** were: **10a**, 57:43; **10b**, 74:26; **10c**, 77:23; **10d**, 100:0; **10e**, 100:0. The dialkylpyridines and dialkyltetrahydropyridines obtained in these reactions generally could not be separated completely by distillation or GLC, and the relative percentages reported are approximate. Pure samples of these products were obtained by the procedures described in subsequent sections where the spectral and elemental analyses are also reported.

Decomposition of each 5-alkyl-2-phenyl-2,5-dihydropyridine (**10d** and **10e**) gave only the 5-alkyl-2-phenylpyridine (**11e** and **11f**).

5-Methyl-2-phenylpyridine (11d) was obtained as a yellow solid from decomposition of 2,5-dihydropyridine **10d**: NMR δ 8.45 (1 H, m, H₅), 7.90 (2 H, m, H₂, H₃), 7.40 (5 H, m, phenyl), 2.33 (3 H, s, CH₃); IR 1660, 1600, 1563 cm⁻¹. Anal. Calcd for C₁₂H₁₁N: C, 85.21; H, 6.51; N, 8.28. Found: C, 85.04; H, 6.70; N, 8.26.

5-Ethyl-2-phenylpyridine (11e) was obtained as a yellow solid from decomposition of 2,5-dihydropyridine **10e**: NMR δ 8.15 (1 H, m, H₅), 8.33 (2 H, m, H₂, H₃), 7.73 (5 H, m, phenyl), 3.03 (2 H, q, CH₂CH₃), 1.63 (3 H, t, CH₂CH₃); IR 1647, 1595, and 1560 cm⁻¹. Anal. Calcd for C₁₃H₁₃N: C, 85.25; H, 7.10; N, 7.65. Found: C, 85.18; H, 7.08; N, 7.56.

General Procedure for Preparing Pure 2,5-Dialkylpyridines (11). The crude product containing a 2,5-dialkylpyridine (**11**) and a 2,5-dialkyl-1,2,5,6-tetrahydropyridine (**12**) obtained from decomposition of approximately 0.04 mol of 2,5-dialkyl-2,5-dihydropyridine (**10**) was refluxed with a small excess of selenium (5.0g) in 100 mL of phenyl ether for 36–48 h. The mixture was filtered to remove excess selenium and the filtrate was extracted with five 15-mL portions of 6 N hydrochloric acid. The aqueous layer was separated and made basic with dilute aqueous sodium hydroxide. The aqueous layer was extracted with ethyl ether, the extracts were dried (K₂CO₃), and the ether was removed by rotary evaporation. The residue was analyzed by GLC and samples of 2,5-dialkylpyridines were obtained by preparative GLC as colorless oils.

(a) **2-tert-Butyl-5-methylpyridine (11a)**: NMR δ 8.45 (1 H, s, H₅), 7.40 (2 H, m, H₂, H₃), 2.23 (3 H, s, CH₃), 1.00 (9 H, s, *t*-Bu). Anal. Calcd for C₁₀H₁₅N: C, 80.55; H, 10.06; N, 9.38. Found: C, 80.39; H, 9.88;

N, 9.19.

(b) **2-tert-Butyl-5-ethylpyridine (11b)**: NMR δ 8.40 (1 H, s, H₅), 7.25 (2 H, m, H₂, H₃), 2.60 (2 H, q, CH₂CH₃), 1.20 (3 H, t, CH₂CH₃), 1.00 (9 H, s, *t*-Bu). Anal. Calcd for C₁₁H₁₇N: C, 80.99; H, 10.42; N, 8.58. Found: C, 80.77; H, 10.56; N, 8.70.

(c) **2-*n*-Butyl-5-methylpyridine (11c)**: NMR δ 8.38 (1 H, br s, H₅), 7.20 (2 H, m, H₂, H₃), 2.78 (2 H, t, CH₂CH₂CH₃), 2.30 (3 H, s, -CH₃), 1.55 (4 H, m, CH₂CH₂CH₂CH₃), 0.97 (3 H, t, CH₂CH₂CH₂CH₃). Anal. Calcd. for C₁₀H₁₅N: C, 80.54; H, 10.07; N, 9.40. Found: C, 80.46; H, 10.20; N, 9.39.

General Procedure for Preparing 2,5-Dialkyl-1,2,5,6-tetrahydropyridines (12). Pure samples of 2,5-dialkyl-1,2,5,6-tetrahydropyridines, which were formed along with the corresponding aromatic compounds when 2,5-dihydropyridines were decomposed, were prepared according to the following procedure. A 0.04-mol sample of a 2,5-dialkyl-2,5-dihydropyridine (**10**) prepared as previously described was slowly added by use of a syringe to a stirred mixture of 0.02 mol of lithium aluminum hydride in 100 mL of dry ethyl ether at 0 °C. The mixture was allowed to warm to room temperature and was stirred overnight. The reaction was quenched by the slow addition of cold water, and the layers were separated. The aqueous layer was extracted with three 100-mL portions of ethyl ether, and the combined extracts and organic layer were dried (anhydrous K₂CO₃). The crude product obtained on removal of ethyl ether by rotary evaporation was analyzed by GLC.

The NMR spectrum of each of the tetrahydropyridines **12a**, **12d**, and **12e** showed a single broad absorption near δ 5.6 which suggested that a single isomer was present. However, the NMR spectrum of each of the tetrahydropyridines **12b** and **12c** was apparently that of a mixture of two stereoisomeric tetrahydropyridines as suggested by the presence of two broad absorptions near δ 5.6 as well as the presence of two sets of absorptions for other protons in the region δ 3.4–0.9. Detailed analyses of these spectra were not attempted; however, the vinyl proton absorptions and the elemental analyses of the tetrahydropyridines are summarized in Table II.

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Registry No.—*cis*-**10b**, 66562-56-9; *trans*-**10b**, 66562-57-0; *cis*-**10c**, 66562-58-1; *trans*-**10c**, 66562-59-2; **11a**, 56029-43-7; **11b**, 66562-60-5; **11c**, 27012-26-6; **11d**, 27012-22-2; **11e**, 66562-61-6; *cis*-**12b**, 66562-62-7; *trans*-**12b**, 66562-63-8; *cis*-**12c**, 66562-64-9; *trans*-**12c**, 66562-65-0; **13**, 66562-66-1; **16**, 66562-67-2; pyridine, 110-86-1; *tert*-butyllithium, 594-19-4; butyllithium, 109-72-8; phenyllithium, 591-51-5.

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