

ONE-POT SYNTHESIS OF PYRROLES FROM *N*-SILYL-1-AZAALLYL
ANIONS

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Abstract --- Some kinds of pyrroles, 1-pyrrolines,
and 2*H*-pyrroles were synthesized from the *N*-silyl-
1-azaallyl anions and α -diketones by an one-pot
reaction.

Recently, the application of organosilicone reagents to organic synthesis has been strikingly developed, and many new reactions and reagents have been reported.¹⁻³ One of these reagents, an α -silyl carbanion has been extensively used in syntheses of alkenes.⁴ In the course of our investigation on the reaction of α -silyl carbanion with carbonyl compounds⁵ or their analogs,⁶ we previously reported the preparation of an *N*-silyl-1-azaallyl anion (3a) from benzonitrile (2) and the α -silyl carbanion of the corresponding alkylsilanes (1) (Eq. 1).⁷⁻⁹

The utility of 1-azaallyllithium reagents in alkylation,¹⁰ hydroxyalkylation,¹¹ α -iminoalkylation,¹² synthesis of *N*-alkenylcarbamates¹³ and synthesis of *N*-heterocyclic compounds^{14,15} has been demonstrated by many workers, and the 1-azaallyllithium reagents resemble 2-azaallyllithium reagents very closely in their utility.¹⁶

stituents (see Table 1). For example, the *N*-silyl-1-aza-allyl anion (3a) reacted with benzil (4a) to give 2,3,5-triphenyl-4-(2-pyridyl)pyrrole (5a) in quantitative yield. When the 3-methyl-5-isoxazolyl derivative (3b) was employed, the yield of the pyrrole (5b) strikingly decreased (48%).

This low yield of 5b does not result from the lower reactivity of the silane (1b) than that of 1a, but it may result from the instability of 3b.⁹

Enolizable α -diketones such as 1-phenylpropane-1,3-dione (4b) or dimethylglyoxal (4c), and cyclic α -diketone such as cyclohexane-1,2-dione (4e) or camphorquinone (4f) were not suitable for this reaction. Especially, the reaction of 4c with 3a was very complex and the yield of the corresponding pyrrole (5d) was low (34%, yield of the isolated pure product). In the case of cyclic α -diketones (4e) and (4f), the reaction was so complex that any product was hardly isolated from the reaction mixture.

The reaction of 3a with phenylglyoxal (4d) gave the corresponding 2*H*-pyrrole (7e) in 21% yield instead of the pyrrole (5e) under the same conditions. The compound (7e) should be a product of incomplete reduction of a carbon-nitrogen double bond of an intermediate 4,5-dihydroxy-4,5-diphenyl-1-pyrroline (6e) in this cyclization reaction. Accordingly, the reduction conditions were optimized, and the result was shown in Table 2. The reducing power of SBH was so weak even under reflux that the carbon-nitrogen

Table 1. Yields of 5a ~ 5g

5	Yield (%) ^{a)}
5a	100
5b	48
5c	65 ^{b)}
5d	(34)
5e	0 ^{c)}
5f	0
5g	0

a) Yield determined by ¹H-nmr and yield of the pure product isolated in parentheses.

b) A small amount of the 3-methyl isomer was observed.

c) Compound 7b was obtained in 21% yield instead of 5e.

Table 2. Reduction conditions for the synthesis of 5e

Method	Reductant	Conditions ^{a)}	Yield (%) ^{b)}	
			<u>5e</u>	<u>7b</u>
A	NaBH ₄	room temp. 4h	0	21
B	NaBH ₄	reflux 4h	0	26
C	LiAlH ₄	room temp. 4h	0	33
D	LiAlH ₄	reflux 4h	21	31
E	LiAlH ₄	reflux 12h	44	20

a) Solv: THF. b) Determined by ¹H-nmr.

double bond of 7e was hardly reduced to give 5e followed by acid-catalized dehydration reaction (see method B). Therefore, lithium aluminum hydride (LAH) was used instead of SBH. Although LAH was more powerful than SBH in their reducing ability, it did not give 5e at room temperature (method C). It, however, gave 5e in 21% yield under reflux for 4 h together with 31% of 6e (method D). A prolonged reaction period increased the yield of 5e (44%) accompanied with a somewhat diminished yield of 7e (20%) as shown in Table 2 (method E).

Synthesis of 1-pyrrolines (6) and 2H-pyrroles (7) and their transformation to pyrroles (5). --- The reaction of 3a with 4a was quenched with water without SBH-reduction to give 4,5-dihydroxy-4,5-diphenyl-1-pyrroline (6a) in 54% yield (eq. 3, Table 3). The anion (3a) analogously reacted with 4c to afford the corresponding 1-pyrroline derivative (6b) in 27% yield. On the other hand, 2-hydroxy-2,3,5-triphenyl-4-(2-pyridyl)-2H-pyrrole (7a) was obtained in 87% yield when the reaction of 3a with 4a was quenched with concentrated hydrochloric acid instead of water. The analogous reaction of 3a with 4c (or 3c with 4a) afforded the corresponding 2H-pyrroles (7b, 7c) in 21 and 19% yields, respectively. The poor yield of 7b is attributable to

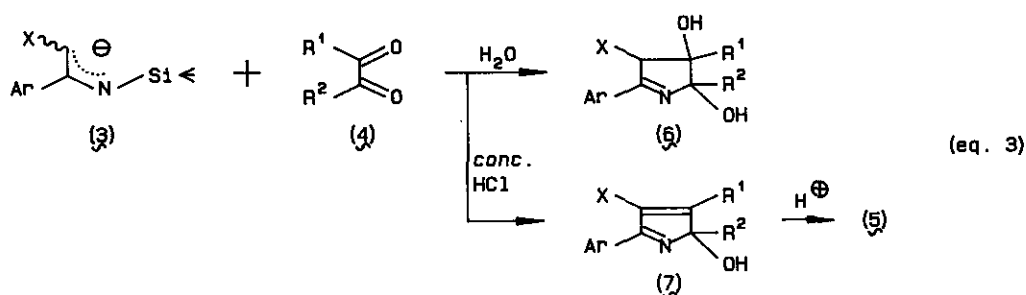


Table 3. synthesis of 6 and 7
from N-silyl-1-azaallyl anions (3)

Products	X	Ar	R ¹	R ²	Yield (%)
<u>6a</u>	2-Py	Ph	Ph	Ph	54
<u>6b</u>	2-Py	Ph	Me	Me	27
<u>7a</u>	2-Py	Ph	Ph	Ph	87
<u>7b</u>	2-Py	Ph	Ph	H	21
<u>7c</u>	<i>t</i> -BuOCO	2-Py	Ph	Ph	19

the instability of 4c, whereas that of 7c may be attributable to the lower reactivity of 3c. Indeed, an appreciable amount of *t*-butyl 3-oxo-3-(2-pyridyl)propanoate, which was formed from the unreacted anion (3c) by hydrolysis, was recovered from the reaction mixture.

The compound (7a) was transformed into the corresponding pyrrole (5a) in 92% yield on reduction with SBH followed by acidification with concentrated hydrochloric acid.¹⁷ This interconversion of 7a to 5a should demonstrate that 7a is an intermediate in the formation of 5a as shown below.

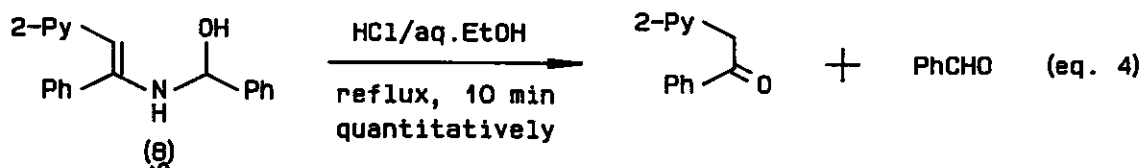
The structures of the compounds (5, 6, and 7) were determined by their spectroscopic properties and by microanalyses (see Experimental). For example, the ir spectrum of 5a suggested the presence of pyrrolic NH group at 3400 cm⁻¹, and the ¹H-nmr spectrum of 5a showed a characteristic broad signal at δ 8.57 for the NH proton of the pyrrole ring together with two

kinds of strong singlet-like phenyl signals at δ 6.90 and 7.00 (integral ratio, 2 : 1) complicated by the ABCD spin system for the 2-pyridyl protons (δ 6.55 - 8.2). Furthermore, the mass spectrum of 5a showed a molecular ion peak at m/z 372 (molecular weight of 5a; $C_{27}H_{20}N_2 = 372.45$).

Lutz and Boykin²¹ have reported that 2-hydroxy-2,3,4,5-tetraphenyl-2H-pyrrole easily rearranges to 2,3,4,4-tetraphenyl-2-pyrrolin-5-one by the action of an acid or a base. Therefore, 2,4,4-triphenyl-3-(2-pyridyl)-2-pyrrolin-5-one is an alternative structure for 7a. The ir spectrum of 7a, however, suggested the presence of both the hydroxy (3350 and 3050 cm^{-1}) and imino groups (1605 cm^{-1}), and suggested the absence of the carbonyl group. In addition, the three signals assignable to the sp^3 -carbons at δ 66.75(C-H), 85.54(C-OH), and 102.80(C-OH), appeared in the ^{13}C -nmr spectrum of the corresponding precursor compound (6a), diminished to one sp^3 -carbon signal at δ 104.57(C-OH) in the ^{13}C -nmr spectrum of the compound (7a); and there was no carbonyl carbon signal for the 2-pyrrolin-5-one structure in this spectrum. These results, mentioned above, established the structure of the 2H-pyrrole for 7a. Furthermore, this 2H-pyrrole structure is also supported by the fact that 7a is quantitatively converted to the corresponding pyrrole.¹⁷

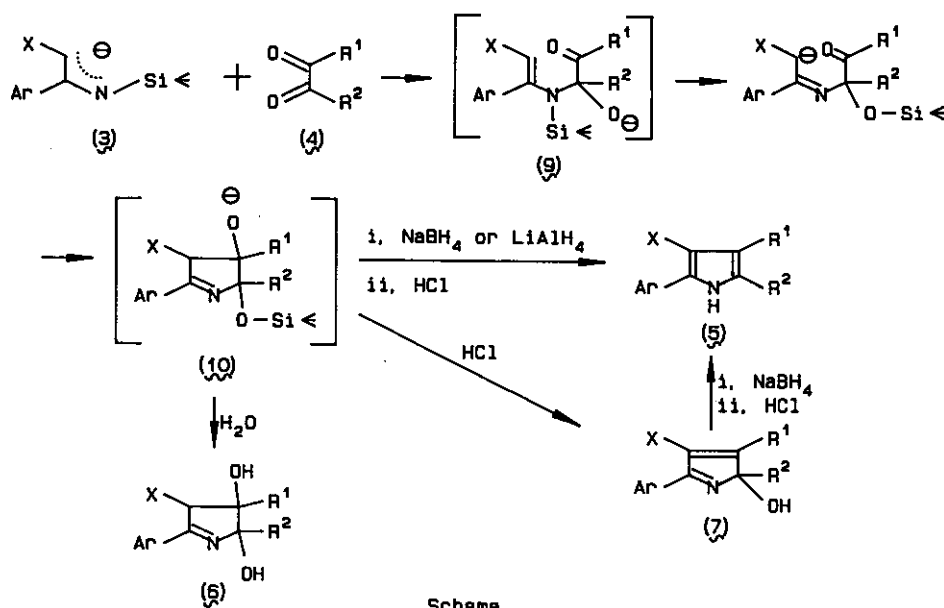
As previously reported,¹⁴ the *N*-silyl-1-azaallyl anion (3) (or the corresponding *N*-silylenamine) is equivalent to a primary enamine which is an ambident nucleophile possessing nitrogen and carbon atoms as the reaction center. Another *N*-silyl-1-azaallyl anion, derived from 2-trimethylsilyl-1,3-oxathiane and 2a, reacts with methyl iodide at the 3-positioned carbon atom (the C-addition),^{19, 20} whereas the *N*-silyl-1-aza-allyl anion (3a) reacts with ethyl chloroformate at the nitrogen atom to form the corresponding ethyl carbamate²¹ (*N*-addition). Therefore, in order to clarify which of the nitrogen atom or the carbon atom of the anion (3) attacks the carbonyl carbon of 4, the *N*-silyl-1-azaallyl anion (3a) was treated with

benzaldehyde under the same conditions to afford the *N*-adduct, 1-phenyl-1-(phenylhydroxymethyl)amino-2-(2-pyridyl)ethene (8), in 75% yield as yellow crystals. It is difficult to determine the structure of 8 by its spectral properties. On treatment with hydrochloric acid, however, the adduct (8) quantitatively gave 2-phenacylpyridine and benzaldehyde (eq. 4). This result confirms the structure of 8. On the other hand, 4d undergoes selective cross aldol condensation with silyl enol ethers at the more reactive formyl group.²² Similarly, the formyl group of 4d must have exclusively reacted with nitrogen atom of 3a to afford 5e or 5e regioselectively.



In conclusion, the *N*-silyl-1-azaallyl anions (3) react with the α -diketones to give the *N*-adducts (9), which undergo an intramolecular addition-cyclization reaction to give an intermediate (10) as shown in Scheme. The formation of 10 was confirmed by the isolation of 6 after quenching the reaction mixture with water. As described above, the carbon-nitrogen double bond of 10 or 7 was reduced with SBH or LAH to give 5 followed by an acid-catalyzed dehydration reaction.

Finally, a reaction of 4a with an 1-azaallyl anion, generated from 2-picoline and 2a, was compared with that of 4a with 3a under the same conditions in order to evaluate the role of the silyl group in the reaction. In spite of a high yield of the 1-azaallyl anion from 2-picoline and 2a,^{7, 23} the yield of 5a was poor (38%) in the former reaction, in contrast to the quantitative yield of 5a in the latter reaction. These are explained as follows. Firstly, the silyl group adjacent to the negatively charged nitrogen atom stabilizes the anion (3) through $(\sigma^*-\text{p})_{\pi}$ overlap between the antibonding σ^* level of the C-Si bond with the adjacent filled



p-orbital of the nitrogen anion.⁸ Secondly, the silyl group is easily eliminated from 10 as trimethylsilanol.

EXPERIMENTAL

All mps (Mitamura micro-melting point apparatus) and bps are uncorrected. Uv spectra were recorded on a JASCO UVDEC-505 spectrophotometer for solutions in EtOH, and ir spectra were taken on a Hitachi Model 260-50 or JEOL JIR-5300 spectrophotometer. ¹H-Nmr were determined with a JEOL PMX-60SI or JNM FX-90Q spectrometer for solutions in CDCl₃ or CD₃OD as shown below. Chemical shifts are reported in δ values (internal standard Me₄Si). Mass spectra were recorded with a Hitachi M-80 double-focussing mass spectrometer at 70 eV. Elemental analyses were performed at the Institute of Physical and Chemical Research.

Materials. --- 2-(Trimethylsilylmethyl)pyridine⁷ (1a) and 3-methyl-5-trimethylsilylmethylisoxazole⁹ (1b), 1-phenyl-1,2-propanedione²⁴ (4b), 1,2-cyclohexanedione²⁵ (4e) and camphorquinone²⁶ (4f) were respectively prepared by a method reported previously.

Synthesis of the pyrroles (5a - 5d); General procedure. --- All pyrroles

(5) were prepared according to the procedure given below. As an example, the synthesis of the pyrrole (5a) was described.

2,4,5-Triphenyl-3-(2-pyridyl)pyrrole (5a): To a THF (50 ml) solution of 2-phenyl-3-(2-pyridyl)-*N*-trimethylsilyl-1-azaallyl anion (3a), generated from 2-trimethylsilylmethylpyridine (1a) (3.3 g, 0.02 mol) and benzonitrile (2a) (2.1g, 0.02 mol) by a method reported previously,^{8,9} diphenylethane-dione (4a) (4.2g, 0.02 mol) in THF (50 ml) was slowly added, and the mixture was stirred for 1 h at -75 °C and then for an additional 2 h at room temperature under oxygen-free dry nitrogen. The reaction mixture was sequentially treated with sodium borohydride (0.95 g, 0.025 mol) for 4 h at room temperature and with conc. HCl (14 ml) for 30 min at room temperature, and finally the solution was neutralized with saturated NaHCO₃ solution and extracted with CHCl₃. The extract gave, after drying (Na₂SO₄) and work-up, a crystalline crude product, which was flash chromatographed on silica gel with CHCl₃ and then with ether to afford 5a in quantitative yield (see Table 1). mp 204.0 - 205.0 °C (from benzene); ir(KBr): 3400cm⁻¹(NH); ¹H-nmr(CDCl₃): δ 8.57(1H, br, NH), 6.37 - 8.16(19H, m, Ph-H and Py-H); ms: *m/z*(%) 372(M⁺, 82), 371(100); Anal. Calcd for C₂₇H₂₀N₂: C, 87.06; H, 5.41; N, 7.52. Found: C, 87.01; H, 5.52; N, 7.32.

(5b): mp 199.3 - 200.3 °C; ir(KBr): 3400cm⁻¹(NH); ¹H-nmr(CDCl₃): δ 8.27(1H, br, NH), 6.99-7.27(15H, m, Ph), 5.34(1H, s, =CH), 2.03(3H, s, CH₃); ms: *m/z*(%) 376(M⁺, 100); Anal. Calcd for C₂₆H₂₀N₂O: C, 82.95; H, 5.36; N, 7.44. Found: C, 82.88; H, 5.28; N, 6.95.

(5c): mp 78.2 - 78.9 °C; ir(KBr): 3400cm⁻¹(NH); ¹H-nmr(CDCl₃): δ 8.03(1H, br, NH), 6.70 - 8.47(14H, m, Ph-H and Py-H), 2.23(3H, s, 2-CH₃);²⁷ ms: *m/z*(%) 310(M⁺, 86), 309(100); Anal. Calcd for C₂₂H₁₈N₂: C, 85.13; H, 5.85; N, 9.03. Found: C, 85.37; H, 5.87; N, 8.58.

(5d): mp 184.5 - 186.1 °C; ir(KBr): 3400cm⁻¹(NH); ¹H-nmr(CDCl₃): δ 8.07(1H, br, NH), 6.43-8.38 (9H, m, Ph-H and Py-H), 2.14 (3H, s, 2-CH₃), 2.01(3H, s, 3-CH₃); ms: *m/z*(%) 248(M⁺, 71), 247(100). Anal. Calcd for C₁₇H₁₆N₂: C, 87.06; H, 5.41; N, 7.52.

82.22; H, 6.50; N, 11.28. Found: C, 82.00; H, 6.48; N, 11.11.

Preparation of 2,4-diphenyl-3-(2-pyridyl)pyrrole (5e) from (3a) and (4d) followed by LiAlH_4 reduction. --- The reaction was performed according to the same method as that for the reaction of 4a (4.2 g, 0.02 mol) with (3a), generated from (1a) (3.3 g, 0.02 mol) and (2a) (2.1 g, 0.02 mol), as shown above. To the reaction mixture in THF (50 ml) was added LiAlH_4 (0.95 g, 0.025 mol) at room temperature, and then the mixture was heated for 12 h under reflux. The reaction mixture was then quenched with conc. HCl (14 ml) at 0 °C followed by neutralization with saturated NaHCO_3 solution. Finally, the mixture was completely extracted with CHCl_3 and dried with Na_2SO_4 to give 5e in 44% yield accompanied with 2-hydroxy-3,5-diphenyl-4-(2-pyridyl)-2H-pyrrole (7b) (20% yield). The results are shown in Table 2 accompanied with the reaction conditions.

(5e): mp 170.0 - 170.5 °C; ir(KBr): 3400cm^{-1} (NH); $^1\text{H-nmr}(\text{CDCl}_3)$: δ 8.30(2H, br, NH and Py-H), 6.60 - 7.50(14H, m, 3-H and Py-H); ms: $m/z(\%)$ 297(15), 296(M^+ , 70), 295(100); HRms: Calcd for $\text{C}_{21}\text{H}_{16}\text{N}_2$ 296.1313. Found: 296.1322.
(7b): mp 225.5 - 226.2 °C; ir(KBr): 3350(OH), 1630(C=C), 1610cm^{-1} (C=N); $^1\text{H-nmr}(\text{CDCl}_3)$: δ 9.50(1H, br), 6.60 - 8.30(15H, m, Ph-H and =CH); ms: $m/z(\%)$ 313(22), 312(M^+ , 100), 180(43); HRms: Calcd for $\text{C}_{21}\text{H}_{16}\text{N}_2\text{O}$ 312.1261. Found 312.1253.

Synthesis of 4,5-dihydroxy-1-pyrrolines (6a - 6h) and 2-hydroxy-4-(2-pyridyl)-2H-pyrroles (7a - 7c); General Procedure. --- All 1-pyrrolines (6) and 2H-pyrroles (7) were prepared according to the following procedures. As examples, the synthesis of 6a and 7a were shown.

4,5-Dihydroxy-2,4,5-triphenyl-3-(2-pyridyl)-1-pyrroline (6a): The reaction was performed by the same method described above for the synthesis of 5a. The reaction mixture of 3a with 4a was quenched with water without reducing with sodium borohydride. The mixture was extracted with CHCl_3 and dried with Na_2SO_4 . The crude product was precipitated from the oily concentrate by adding ether and recrystallized from the mixture of benzene and hexane

to obtain the pure 6a in 54% yield. mp 136.5 - 137.5 °C; ir(KBr): 3480 (OH), 1605cm⁻¹(C=N); ¹H-nmr(CDCl₃): δ 8.14(19H, m, Ph-H and 2-Py-H), 7.50 (1H, s, OH), 4.92(1H, s, CH), 4.40(1H, s, OH), ¹³C-nmr(CDCl₃): δ 66.75, 85.54, 102.80, 122.70, 125.46, 125.99, 126.23, 126.58, 127.05, 127.46, 128.52, 128.93, 129.81, 131.51, 134.80, 138.44, 139.55, 143.02, 148.71, 155.94, 175.07; ms: m/z(%) 388(M-18, 4), 196(33), 195(48), 105(100); Anal. Calcd for C₂₇H₂₂N₂O₂: C, 79.78; H, 5.46; N 6.89. Found: C, 79.71; H, 5.45; N, 6.70.

(6b): mp 151.0 - 152.9 °C; ir(KBr): 3340(OH), 1605cm⁻¹(C=N); ¹H-nmr(CDCl₃): δ 6.65 - 8.23(9H, m, Ph-H and 2-Py-H), 6.51(1H, br s, 5-OH), 4.46(1H, br s, 4-OH), 4.23(1H, s, CH), 1.56(3H, s, 5-CH₃), 1.40(3H, s, CH₃); ms: m/z(%) 282(M⁺, 0.3), 264(7), 197(37), 196(49), 195(100); HRms: Calcd for C₁₇H₁₈N₂O₂ 282.1366. Found 282.1342.

2-Hydroxy-2,3,5-triphenyl-4-(2-pyridyl)-2H-pyrrole (7a): The reaction mixture of 3a with 4a was treated with conc. HCl instead of water in the synthesis of 6a. The reaction mixture was extracted with CHCl₃ after neutrallization with aq. saturated NaHCO₃ solution. The crude product was precipitated from the oily concentrate by adding ether and recrystallized from the mixture of CHCl₃ and hexane to obtain the pure 7a in 87% yield. mp 156.5 - 158.5 °C; ir(KBr): 3350, 3050(OH), 1635(C=C), 1605cm⁻¹(C=N); ¹H-nmr(CDCl₃): δ 6.67 - 8.35(19H, m, Ph-H and 2-Py-H), 5.25 (1H, br, OH); ¹³C-nmr(CDCl₃): δ 104.57, 122.64, 125.25, 125.44, 127.72, 127.91, 128.30, 128.56, 128.95, 130.32, 131.42, 133.44, 136.56, 138.25, 149.89, 153.86; ms: m/z(%) 389(10), 388(M⁺, 31), 283(18); HRms: Calcd for C₂₇H₂₀N₂O 388.1574. Found 388.1564.

(7c): mp 149.0 - 150.0 °C; ir(KBr) 3400, 3060(OH), 1630(C=C), 1605cm⁻¹(C=N), ¹H-nmr(CDCl₃): δ 6.60 - 8.36(14H, m, Ph-H and 2-Py-H), 5.35(1H, br, OH), 1.46(9H, s, t-Bu); ms: m/z(%) 412(M⁺, 3), 353(27), 352(100); Anal. Calcd for C₂₆H₂₄N₂O₃: C, 75.70; H, 5.87; N, 6.79. Found: C, 75.58; H, 5.90; N, 6.71.

Transformation of 7a to 5a. --- A THF (50 ml) solution of 7a (7.8 g, 0.02 mol) was treated with sodium borohydride (0.95 g, 0.025 mol) for 4 h at room temperature, and then the reaction mixture was successively treated with conc. HCl (14 ml) for 10 min at room temperature and with saturated NaHCO₃ solution to give the pure 5a in 92% yield.

Reaction of 3a with benzaldehyde; Formation of 1-phenyl-1-phenylhydroxy-methylamino-2-(2-pyridyl)ethene (8). --- To a THF (50 ml) solution of 3a, generated from 1a (3.3 g, 0.02 mol) and 2a (2.1 g, 0.02 mol), as shown above, was slowly added benzaldehyde (2.21 g, 0.02 mol) at -75 °C, the mixture was stirred for 1 h at -75 °C, and then for 2 h at room temperature. The reaction mixture was quenched with water (50 ml) at 0 °C, and extracted with CHCl₃ to give 8 (4.5 g, 75%). mp 263.5 - 264.0 °C (recrystallized from methanol); ir(KBr): 3380(OH), 1628cm⁻¹(C=C); ¹H-nmr(CD₃OD): δ 9.10(1H, br, NH in CH₃OH), 6.90 - 8.40(15H, s like signals of Ph-H and =CH complicated with m signals of 2-Py-H), 2.15(1H, s, OH in CH₃OH); ¹³C-nmr(CH₃OH): δ 154.51, 149.58, 143.35, 139.88, 136.47, 133.32, 132.56, 130.56, 130.13, 129.86, 128.61, 126.77, 124.22, 121.62, 93.61, 74.00; ms: m/z(%) 284(M - 18, 32), 207(30), 180(100); HRms: Calcd for C₂₀H₁₆N₂ (M - 18) 284.1312. Found 284.1312.

Hydrolysis of 8 in aq. EtOH. --- The solution of 8 (1.33 g, 0.027 mol) in aq. EtOH (20%, 50 ml) was refluxed for 10 min in the presence of conc. HCl (1 ml) to give 2-phenacylpyridine (4.8 g, 90%, determined by ¹H-nmr) after successive neutralization with NaHCO₃ and extraction with ether.

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