Table II. ^{1}H NMR Characterizing Chemical Shifts for 2,4-Diphenylthiopyrylium Ion (2) and Related 2*H*-Thiopyran Adducts with Amines

compd	solvent	chemical shift, δ H-3	H-5	H-6	$J_{3,5}$, Hz	$J_{5,6}$, Hz	$J_{3,6}$, Hz
2	CD_3CN	9.07	8.95	9.84	1.5	9.0	0

compd	solvent	chemical shift, δ H-2	H-3	H-5	$J_{2,3}$, Hz	$J_{2,5}$, Hz	$J_{3,5}$, Hz
2 + diethylamine (4)	CD_3CN	5.35	5.85	6.85	6.7	0	0.5
2 + butylamine (5)	CD_3CN	5.25	5.80	6.85	7.5	0	0.5

The formation of 2*H*-thiopyran adduct **4** is observed in the reaction of **2** with diethylamine in CD_3CN by ^{1}H and ^{13}C NMR spectroscopy. The ^{13}C NMR spectrum obtained upon addition of 2 equiv of diethylamine to a solution of 300 mg of **2** in 2 mL of CD_3CN shows a strong upfield shift of the hydrogen-bearing α-carbon atom (from δ 154.2 to 65.3), because of the neutralization of the positive charge and the change of hybridization from sp^2 to sp^3. In off-resonance-decoupling experiments this signal is detected as a doublet. The corresponding ^{1}H NMR chemical shift values are reported in Table II.

The ^{1}H NMR spectrum obtained for the corresponding reaction with butylamine in CD_3CN shows the presence of the signals of the 2*H* adduct **5** (see Table II) together with the signals of another compound (δ 4.83, d, J = 6.7 Hz; δ 6.05, slightly broadened doublet, J = 6.7 Hz; δ 6.96, slightly broadened singlet). The latter signals undergo a slow increase with time, whereas those of the 2*H* adduct show a corresponding decrease. The ^{13}C NMR spectrum of this reaction mixture is rather complicated. However, a distinctive feature is the presence of a weak signal at δ 214.3, which may be attributed to a thiocarbonyl group, suggesting the presence of ring opening to a divinylogous thioamide structure for this compound. The final product of this reaction is 1-butyl-2,4-diphenylpyrydinium ion as formed according to an already known reaction course.[7]

The behavior of thiopyrylium ions **1** and **2** toward amines reported here is in contrast with that of the unsubstituted thiopyrylium ion, which reacts with primary and secondary amines to yield open-chain cations,[6] and with that of the corresponding 2,4,6-triphenyl-[8] and 2,4-diphenylpyrylium ions,[9] where only the open-chain divinylogous amide or the final 1-substituted pyridinium ions are detected.

2*H*-Pyran adducts obtained from amines can be indeed observed in specific cases only, e.g., from sterically hindered[10] or 4-dialkylamino-substituted pyrylium ions.[11] Thus the ring-opening step is strongly affected by the substituents on the ring. Moreover, the presence of a sulfur atom seems to be a main factor in strongly depressing the rate of this step.

Experimental Section

^{1}H NMR measurements were carried out on a JEOL C60-HL instrument. ^{13}C NMR measurements were carried out on a Varian CFT-20 instrument. The temperature of the probe was kept at 25 ● 1 °C. The chemical shift values are quoted in δ units relative to Me_4Si. Me_2SO-d_6 and CD_3CN were standard grade solvents.

2,4,6-Triphenylthiopyrylium (1) perchlorate was available from a previous work.[5]

2,4-Diphenylthiopyrylium (2) perchlorate was prepared according to a literature procedure.[7]

Registry No. 1 ClO_4^-, 2930-37-2; 2 ClO_4^-, 30235-02-0; 3, 82338-23-6; 4, 82388-24-7; 5, 82388-25-8; diethylamine, 109-89-7; butylamine, 109-73-9.

(7) Graphakos, B. J.; Katritzky, A. R.; Lhommet, G.; Reynolds, K. *J. Chem. Soc., Perkin Trans. 1* **1980**, 1345.

(8) Katritzky, A. R.; Brownlee, R. T. C.; Musumarra, G. *Tetrahedron* **1980**, *36*, 1643.

(9) Doddi, G., unpublished results.

(10) (a) Fisher, G. H.; Zimmermann, T. *Z. Chem.* **1981**, *21*, 282. (b) Katritzky, A. R.; Lloyd, J. M.; Patel, R. C. *J. Chem. Soc., Perkin Trans. 1* **1982**, 117.

(11) Van Allan, J. A.; Reynolds, G. A.; Petropoulos, C. C. *J. Heterocycl. Chem.* **1972**, *9*, 783.

Flash Vacuum Pyrolysis of Substituted Pyridine *N*-Oxides and Its Application to Syntheses of Heterocyclic Compounds[1]

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Flash vacuum pyrolysis of 2-picoline *N*-oxide gave 2-picoline, pyridine, 2-ethylpyridine, 2-vinylpyridine, 2-pyridylmethanol, bis(2-pyridyl)methane, 1,2-bis(2-pyridyl)ethane, and 1,2-bis(2-pyridyl)ethylene. These reactions are explained by intermediary participation of the 2-picolyl radical. Flash vacuum pyrolysis of methyl-substituted 2-benzylpyridine *N*-oxides led to methyl-substituted pyrido[1,2-*a*]indoles or to benzo[*g*]quinoline in moderate yields.

Although photochemical reactions of *N*-oxides of pyridine derivatives have been widely investigated,[2] little is known concerning the behavior of thermally excited molecules of these compounds. Flash vacuum pyrolysis

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Table I. FVP of Pyridine and Picoline N-Oxides (1)[a]

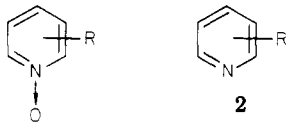
N-oxides	temp, °C	recovery of 1, %	product (yield, %)
1a	650	60	2a (26)
1a	800	8	2a (75), volatile products[b]
1b	650	tr	2b (12), other products[c]
1b	800	0	2b (17), other products[d]
1c	650	68	2c (15)
1c	800	tr	2a (2), 2c (4), volatile products[b]
1d	650	91	2d (6)
1d	800	15	2d (24), 3 (22),[e] volatile products[b]

[a] All runs in this table were carried out under 0.1–1 mmHg of pressure (without carrier). [b] See footnote 4. [c] Same products as in FVP at 800 °C were formed. [d] Products and yields are listed in Table II. [e] Reference 27.

(FVP) offers a simpler reaction system than conventional solution methods or pyrolysis of neat liquid.[3] We here report on the results of FVP of several pyridine N-oxides.

Results and Discussion

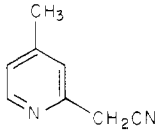
FVP of the N-oxides of pyridine and three picolines (**1a–d**) revealed significant differences among these closely related compounds (Table I).



1 2

a, R = H
b, R = 2-CH_3
c, R = 3-CH_3
d, R = 4-CH_3

FVP of **1a**, **1c**, and **1d** at 650 °C gave only the deoxygenated analogues **2a**, **2c**, and **2d**, with 60–91% of the starting materials recovered. At 800 °C these same products were accompanied by unidentified low molecular weight products,[4] with almost complete conversion of starting materials. FVP of **1d** at 800 °C also gave 22% of 2-cyanomethyl-4-picoline (**3**), formed by a pathway that



3

is not clear. In contrast to these results, **1b** was completely converted by FVP at 650 °C (and at 800 °C) and yielded only products containing the pyridine ring in the molecule, without fragmentation to the volatile, low molecular weight products that were formed from the other N-oxides.

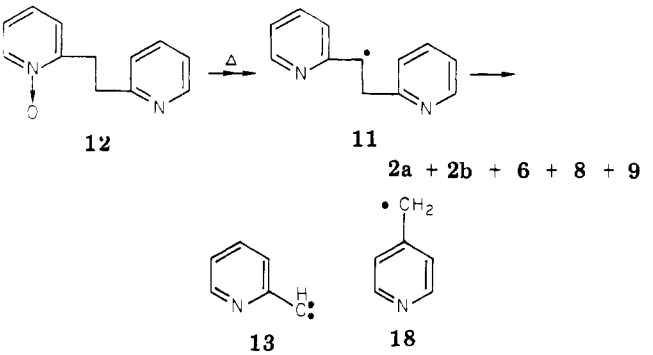
In light of these observations, we investigated the FVP of **1b** in more detail. The results are given in Table II.

When the temperature was 550 °C or above, decomposition of **1b** was observed, whereas the oxide was recovered almost quantitatively at 500 °C. This boundary temperature was essentially the same regardless of the kind of the carrier gas, as well as in the absence of a carrier.

In these pyrolyses, pyridine (**2a**), 2-picoline (**2b**), 2-pyridylmethanol (**4**), 2-ethylpyridine (**5**), 2-vinylpyridine (**6**), bis(2-pyridyl)methane (**7**), 1,2-bis(2-pyridyl)ethane (**8**), and 1,2-bis(2-pyridyl)ethylene (**9**) were always produced. The proportions of these products were essentially independent of temperature or carrier, although an increase in the proportion of **2b** was observed when methanol (whose hydrogen atoms are usually labile in radical reactions) was used as the carrier. Among these products, **2a**, **2b**, and **4–8** were quite thermally stable; FVP of the each compound under similar conditions (800 °C) resulted in almost quantitative recovery of the starting material.[5]

Compounds **5–9** are obviously formed by intermolecular reactions. Ionic intermediates seem unlikely in a nonpolar, vapor-phase reaction at low pressure, and the participation of the 2-picolyl radical (**10**) is more likely. We propose the reaction pathways outlined in Scheme I.

The formation of **8** is simply explained by dimerization of radical **10**. Formation of **2a**, **2b**, **6**, and **9** can be rationalized by reactions of the dipyridylethyl radical **11**. FVP of 1,2-bis(2-pyridyl)ethane N-oxide (**12**) should produce the radical **11**, and in fact FVP of **12** gave **2a**, **2b**, **6**,



12 11 2a + 2b + 6 + 8 + 9

13 18

8, and **9** (11%, 11%, 39%, 7%, and 20%, respectively). Formation of **2a** can also occur by thermal cleavage of **10**, and the formation of **4**, **5**, and **7** can be accounted for by successive radical processes, although a detailed mechanistic explanation is difficult. Formation of **9** by dimerization of pyridyl carbene **13** appears unlikely because products that should result from **13**[6] such as aniline or cyanocyclopentadiene were not detected. In addition, deoxygenation by heterolytic cleavage of the N–O bond may be in part responsible for formation of **2b**.[7] The formation of **5–9**, and especially the preferential generation of the dimer **8**, indicates a significant lifetime for the radical **10**.[8]

Moreover, the formation of 2-benzylpyridine (**14**) in FVP of **1b** with benzene carrier suggests a coupling of **10** with benzene, and formation of 2-phenethylpyridine (**16**) with toluene carrier supports a coupling between **10** and the benzyl radical formed from toluene.

Picolyl radicals **10** and **18** have been of interest as het-

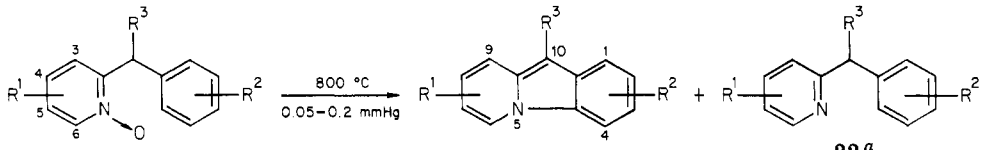
(1) Parts of this work were preliminarily published in our communications: *Chem. Pharm. Bull.* **1981**, *29*, 1481; *Chem. Lett.* **1981**, 1737.
(2) For example: Katritzky, A. R.; Lagowski, J. M. "Chemistry of the Heterocyclic N-Oxides"; Academic Press: New York, 1971. Ochiai, E. "Aromatic Amine Oxides"; Elsevier, Amsterdam, 1967.
(3) For example: Brown, R. F. C. "Pyrolytic Methods in Organic Chemistry"; Academic Press: New York, 1980.
(4) Separation and identification of these compounds were unsuccessful because of their low boiling points (≤room temperature).
(5) FVP of **9** was unusual in that ca. 22% of **9** was decomposed to give 19% of **2b** (at 800 °C), and the mechanism is inexplicable here.
(6) Crow, W. D.; Paddon-Row, M. N.; Sutherland, D. S. *Tetrahedron Lett.* **1972**, 2239. Crow, W. D.; Khan, A. N.; Paddon-Row, M. N.; Sutherland, D. S. *Aust. J. Chem.* **1975**, *28*, 1741; 1755; 1763.
(7) This concept may be applicable to deoxygenation of **1a**, **1c**, and **1d**, as well as that of 2-benzylpyridine N-oxides described later.
(8) However, these intermolecular reactions might be completed in the hot zone, because when vapor of methanol or benzene was introduced during the FVP from an inlet attached to a position just after the hot zone, the formation of **8** was not retarded, the yields of described products were practically unaltered, and cross-coupled compounds (described later) were not detected.

Table II. FVP of 2-Picoline *N*-Oxide (1b)

conditions			products, %									recovery of 1b, %
carrier	temp, °C	pressure, mmHg	2a	2b	4	5	6	7[a]	8[b]	9[b]	others	
absent	800	0.1-1	24	17	3	4	7	8	26	11	tr	0
N_2	500	1-5	0	0	0	0	0	0	0	0	0	[e]
N_2	550	1-5	4	6	5	2	2	2	10	2	tr	63
N_2	650	1-5	10	13	8	4	4	7	33	15	tr	tr
N_2	800	1-5	23	13	2	3	5	11	27	9	tr	0
CH_3OH	800	1-5	6	31	10	tr	tr	3	45	1	tr	0
PhH	800	1-5	14	17	8	tr	tr	7	27	2	**14** (8%)[c] + **15**[c]	0
$PhCH_3$	800	1-5	15	16	7	2	2	5	34	5	**16** (17%)[d] + **17**[c]	0

[a] Reference 23. [b] Reference 24. [c] Reference 25. [d] Reference 26. [e] Quantitative.

Table III. FVP of 2-Benzylpyridine *N*-Oxides (20)[a]



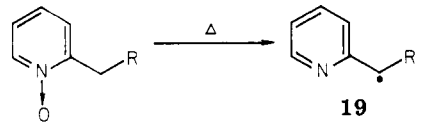
20 **21**[a] **22**[a]

20					21 (yield), %		22	others
	R^1	R^2	R^3	mp, °C	NMR	isolated	(yield), %	(yield), %
a	H	H	H	98-99[b]	74	63	11[b]	
b	H	*o*-CH_3	H	158.5-159[c]	tr	0	19[d]	35[e]
c	H	*m*-CH_3	H	121.5-122[b,c]	25	23[f]	20[b]	
					16	0[g]		
d	H	*p*-CH_3	H	54.5-56[b]	69	52	11[b]	
e	H	H	CH_3	101-102	13	11	8[h]	41[i]
f	3-CH_3	H	H	84.5-85.5	10	6	10[j]	51[e]
g	4-CH_3	H	H	67-68	51	40	16[j]	
h	5-CH_3	H	H	99-99.5	43	37	28[k]	
i	6-CH_3	H	H	67-67.5	42	33	19[j]	

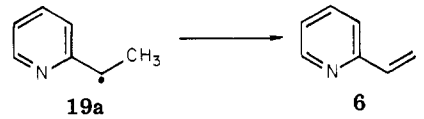
[a] R^1, R^2, R^3 are in the same relative positions as in **20**. [b] Reference 14. [c] Picrate. [d] Reference 15. [e] Benzo[*g*]quinoline (**23**). [f] 2-Methylpyrido[1,2-*a*]indole (**21c**). [g] 4-Methylpyrido[1,2-*a*]indole. [h] Reference 16. [i] 1-(2-Pyridyl)-1-phenylethylene (**25**). [j] Reference 21. [k] Bp 133 °C (bath temperature, 0.1 mmHg), picrate mp 129.5-130 °C.

eroaromatic isoelectronic analogues of the benzyl radical, and their nitrogen atoms are believed to be responsible for their stability because of conjugation.[9] These radicals have been presumed to be intermediates in the reactions of **1b** and **1d** with acid anhydrides.[2] Although the radical **18** (formed via "anhydro base") was shown to be present in the reaction of **1d** with acetic anhydride by CIDNP,[10] presence of the radical **10** has been considered unlikely[2,11] in a similar reaction of **1b**.

We wished to explore the pyrolysis of pyridine *N*-oxides as a route to heteroaromatic compounds. For confirmation of the formation of (2-pyridyl)methyl radicals (**19**) from



20 **19**



19a **6**

the corresponding *N*-oxides (**20**) in FVP, 2-ethylpyridine *N*-oxide was pyrolyzed at 800 °C to give pyridine (**2a**) and 2-vinylpyridine (**6**) as the major products (20% and 45%, respectively), suggesting the existence of radical **19a** in the FVP.

From these observations, it was expected that an intramolecular radical reaction could occur when an *N*-oxide of type **20** possesses a reactive site in its side chain R. Accordingly, 2-benzylpyridine *N*-oxides (**20a–i**) were subjected to FVP at 800 °C with the results listed in Table III.

From all these 2-benzylpyridine *N*-oxides except **20b** (*o*-methylbenzyl), **20e** (1-phenethyl), and **20f** (3-methylpyridyl), the principal product was the corresponding pyrido[1,2-*a*]indole **21**, accompanied by a lesser amount of the 2-benzylpyridine **22**. In the FVP of **20c**, both 2-methyl- (**21c**) and 4-methylpyrido[1,2-*a*]indoles were identified in the product by NMR, but only the former could be isolated. *N*-Oxides **20b**[12] and **20f**, with methyl groups adjacent to the benzyl bridge, gave benzo[*g*]quinoline (**23**) as the principal product. Reaction pathways for the formation of **21**[13] and **23** by way of radicals **24** are

(9) For example: Failes, R. L.; Joyce, J. T.; Watton, E. C. *J. Chem. Soc., Faraday Trans. 1* **1973**, *69*, 1487. Nanda, D. N.; Narasimhan, P. T. *Int. J. Quantum Chem.* **1974**, *8*, 451. Pittman, C. U., Jr.; Smith, M. R.; Nichols, G. D.; Wuu, S. K.; Kispert, L. D. *J. Chem. Soc., Perkin Trans 2* **1975**, 1581 and references therein.

(10) Iwamura, H.; Iwamura, M.; Imanari, M.; Takeuchi, M. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 3486 and references therein.

(11) Iwamura, H.; Iwamura, M.; Nishida, T.; Miura, I. *Tetrahedron Lett.* **1970**, 3117; *J. Am. Chem. Soc.* **1970**, *92*, 7474.

(12) In the FVP of **20b**, isolation of 1-methylpyrido[1,2-*a*]indole was unsuccessful, although its existence in the reaction mixture was suggested by NMR and TLC.

(13) The reaction is in contrast to reaction of phenyl(2-pyridyl)carbene, which gives carbazole almost quantitatively: Mayor, C.; Wentrup, C. *J. Am. Chem. Soc.* **19755**, *97*, 7467.

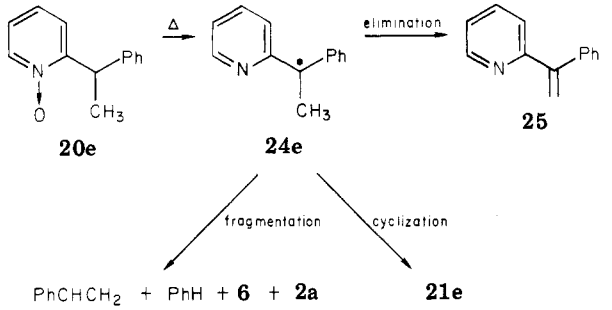
(14) Oae, S.; Tamagaki, S.; Negoro, T.; Kozuka, S. *Tetrahedron* **1970**, *26*, 4051.

(15) Moser, K. B.; Bradsher, C. K. *J. Am. Chem. Soc.* **1959**, *81*, 2547.

(16) Sury, E.; Hoffmann, K. *Helv. Chim. Acta* **1954**, *37*, 2133.

suggested in Scheme II.

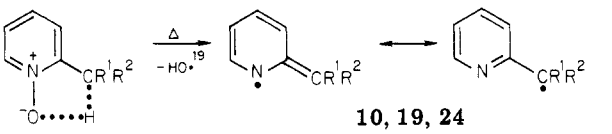
In FVP of **20e**, 1-(2-pyridyl)-1-phenylethylene (**25**) was



the major product, accompanied by pyridine, styrene, 2-vinylpyridine, benzene, 10-methylpyrido[1,2-*a*]indole (**21e**), and **22e**. Formation of these products can also be explained by reaction of intermediary radical **24e**.

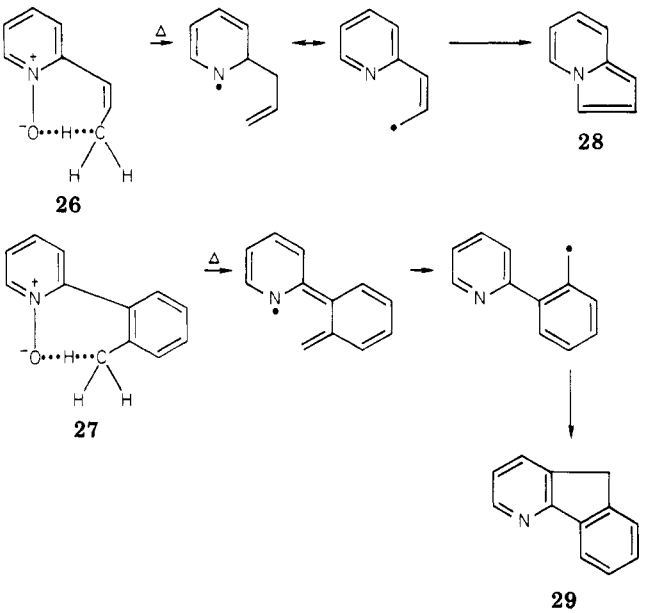
The pyrido[1,2-*a*]indoles **21** are rather unstable, and isolated yields depend on their stability. When they were exposed to air or dissolved in chloroform or dichloromethane, they changed to tarry insoluble materials. Their solutions in hexane, pentane, and carbon disulfide were more stable, and a yellowish fluorescence was commonly observed. Thus, FVP of 2-benzylpyridine *N*-oxides is applicable to the synthesis of methylpyrido[1,2-*a*]indoles,[17] as well as providing a convenient synthesis of benzo[*g*]-quinoline.[18]

Our results imply that the formation of the radicals **10**, **19**, and **24** in the FVP involves some interaction between the oxygen atom and a hydrogen atom attached to the benzyl carbon.



1b and **20**

Additionally, FVP of 2-(1-propenyl)pyridine *N*-oxide (**26**) and 2-(*o*-tolyl)pyridine *N*-oxide (**27**) were examined. Indolizine (**28**, 48%) and 4-azafluorene (**29**, 69%)[20] were the major products in the respective pyrolyses. Similar radical formations may be plausible in these reactions.



Experimental Section

Melting points are uncorrected. Infrared spectra (IR) were recorded on a JASCO A-102 instrument, ultraviolet spectral data (UV) on a Hitachi EPS-3T or 340, ahd nuclear magnetic resonance spectra (NMR) on a Hitachi R-22 (δ in ppm vs. Me_4Si; in $CDCl_3$ unless otherwise noted). Mass spectra (MS) and GC–mass spectra (GC–MS) were recorded on a Hitachi RMS-4H or JEOL JMS-D300. Gas chromatography (GC) was carried out by using a Shimadzu GC-4B instrument with a column (210 cm × 2 mm) packed with 2% SE-30 on Chromosorb-W with the column temperature at 60 °C and the carrier (N_2) at 0.7 kg/cm^2 and 30 mL/min.

Materials. Pyridine *N*-oxides were prepared by oxidation of corresponding pyridines with *m*-chloroperbenzoic acid or with H_2O_2–AcOH.[2] Methyl-substituted 2-benzylpyridines were prepared according to Pridgen's method;[21] melting points of their *N*-oxides are given in Table III.

Pyrolysis Method. Compounds were distilled into a quartz pyrolysis tube (15 cm × 1 cm) from a small flask heated with an air bath or oil bath. The quartz tube was heated with a furnace. Although the "contact times" depend upon reaction conditions, versatile contact times in this work were in the range 0.1–0.001 s.[22] Products were collected in a cold trap (liquid N_2). The collected mixture was distilled at 80 °C under ca. 0.1 mmHg and separated into a residual part (fraction I) and a distillable part (fraction II). Fraction I was chromatographed on alumina (hexane–ether). Fraction II was analyzed by GC and GC–MS and the yields of the volatile products were obtained from GC of the fraction.

Pyrolyses of Picoline *N*-Oxides. Pyrolyses of **1b** were conducted without a carrier at 800 °C, with nitrogen carrier at 500–800 °C, and with benzene, toluene, or methanol carriers at 800 °C. Flow rates of **1b** were 46–66 mg/min and of the organic carriers were 2.9–3.4 mmol/min. Conditions and results are shown in Table II. Products **4**, **7–9**, and **14–17** were separated from fraction I by column chromatography (hexane–ether/alumina) and were purified by crystallization from petroleum ether or by distillation under reduced pressure.

4, bp (bath temperature) 110–115 °C/5 mmHg, was identical with a commercial sample.

7, bp (bath temperature) 95 °C/0.1 mmHg, was identified by comparison of spectral data with those of an authentic sample;[23] NMR δ 4.33 (2 H, s, CH_2), 6.96–7.77 (6H, m, 3-, 3′-, 4-, 4′-, 5-, 5′-H), 8.56 (2 H, dd, J = 2, 6 Hz, 6-, 6′-H); IR (neat) 3020 (m), 1590 (s), 1565 (s), 1475 (s), 1430 (s), 1150 (m), 1050 (m), 1000 (m), 760 cm^{-1} (s).

8: colorless plates (petroleum ether), mp 49.5–50.5 °C;[24] NMR δ 3.24 (4 H, s, CH_2CH_2), 6.97–7.74 (6 H, m, 3-,3′-,4-,4′-,5-, 5′-H), 8.56 (2 H, dd, J = 2, 6 Hz, 6-, 6′-H).

9: colorless needles (petroleum ether) mp 119–120 °C;[24] NMR δ 7.68 (2 H, s, CH=CH), 7.06–7.77 (6 H, m, 3-,3′-,4-,4′-,5-, 5′-H), 8.63 (2 H, dd, J = 2, 6 Hz, 6-, 6′-H).

14,[25] **15**,[25] **16**,[26] and **17**[25] were identified by physical properties and spectral data reported in the literature. Compounds **2**, **5**, and **6** were determined by GC and GC–MS of fraction II.

Subsequent pyrolyses of **2b**, **4**, and **8** at 800 °C/1–5 mmHg with nitrogen carrier gave essentially only starting materials. Similar

(17) Although some syntheses of **21** are known, yields are usually low. For the synthesis of unsubstituted pyrido[1,2-*a*]indole, see: (a) Arata, Y.; Ohashi, T.; Uwai, K. *Yakugaku Zasshi* **1955**, *75*, 265. (b) Erner, W. E., U.S. Patent 2886569, 1959; *Chem. Abstr.* **1961**, *53*, 18967f. For 10-methylpyrido[1,2-*a*]indole, see: (c) Robinson, R.; Saxton, J. E. *J. Chem. Soc.* **1952**, 976. (d) Wasserman, H. H.; Waterfield, W. R. *Chem. Ind. (London)* **1961**, 1220.

(18) Reported syntheses of **23** are not simple, and the yields are low: Lal, A. B.; Singh, N. *Chem. Ber.* **1965**, *98*, 2427. Bekhli, A. F.; Kozyreva, N. P. *Khim. Geterosikl. Soedin.* **1968**, 307; *Chem. Abstr.* **1969**, *70*, 47264z.

(19) Most of the oxygen in the FVP was detected as water.

(20) 1,2-Benzoindolizine was not formed in this FVP.

(21) Pridgen, L. N. *J. Heterocycl. Chem.* **1975**, *12*, 443.

(22) See p 41 of ref 3.

(23) Sato, Y. *Chem. Pharm. Bull.* **1957**, *5*, 412.

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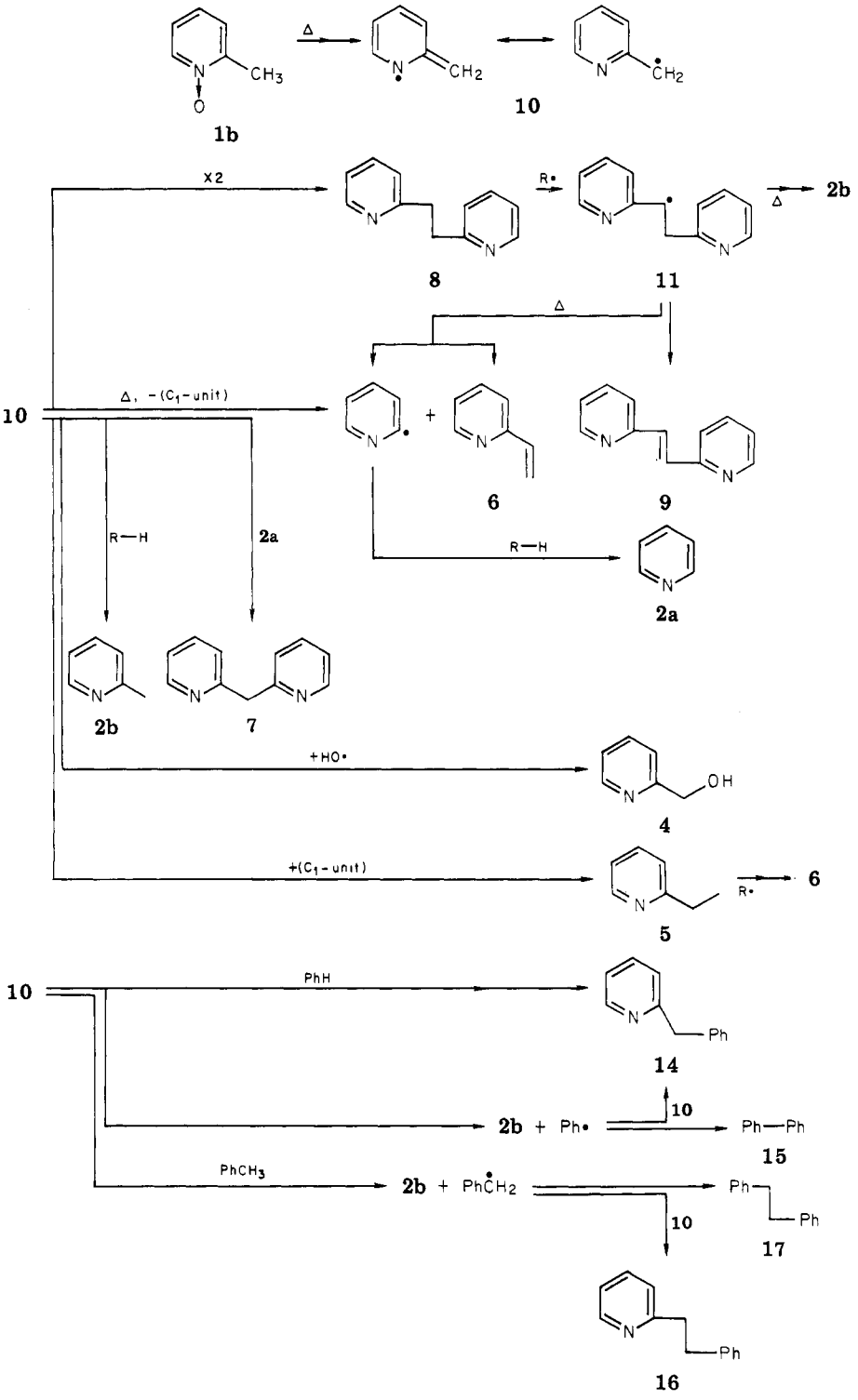
Scheme I[a]



[a] R—H represents a molecule bearing a hydrogen atom that is able to be pulled off, and R· represents a radical involved in the reaction system.

pyrolysis of **9** gave **2a** (trace), **2b** (19%), and **6** (trace), together with starting material **9** (78%).

Pyrolyses of **1c** and **1d** at 800 °C/0.1–1 mmHg without carrier gave primarily pyridine and picolines (Table I). Chromatographic separation (hexane–ether/alumina) of the pyrolysis products of **1d** gave 22% of 2-cyanomethyl-4-picoline (**3**): bp (bath temperature) 194 °C/1 mmHg, picrate mp 88–89 °C;[27] NMR δ 2.41 (3 H, s, CH_3), 3.92 (2 H, s, CH_2), 7.11 (1 H, dd, J = 1, 6 Hz, 5-H), 7.28 (1 H, s, 3-H), 8.48 (1 H, dd, J = 1, 6 Hz, 6-H); IR (neat) 2260, 1610, 1415, 832 cm^{-1} (all strong).

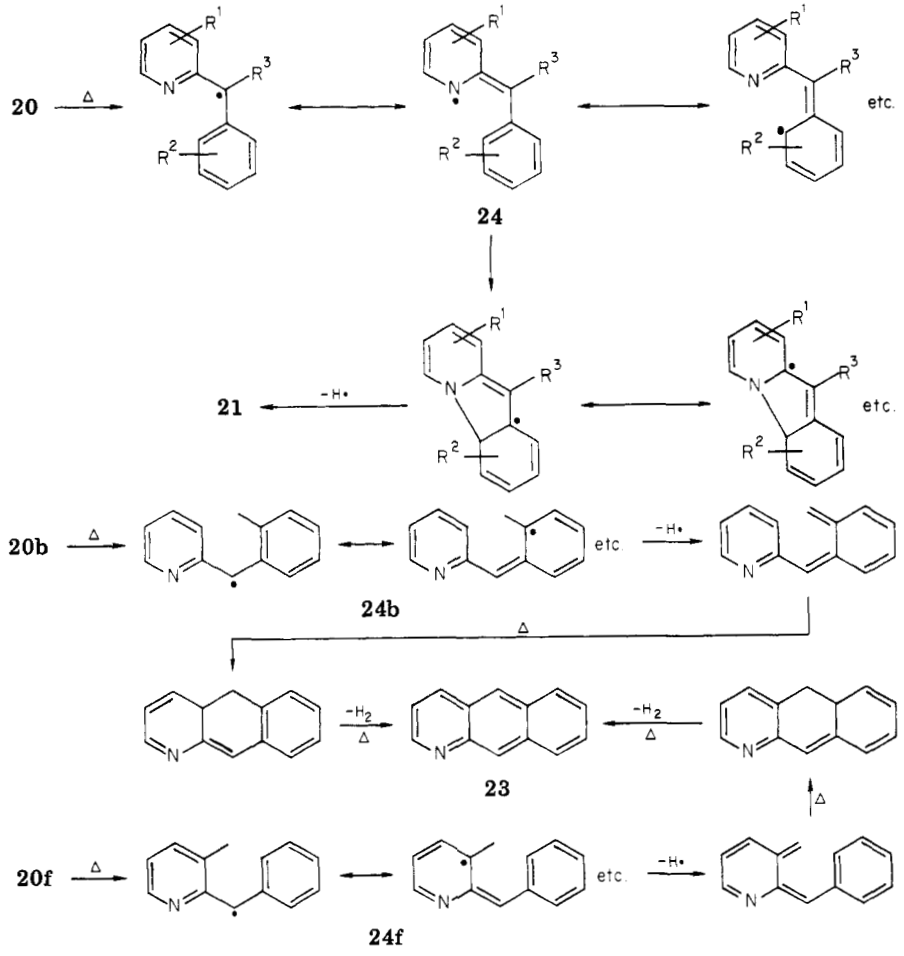
Pyrolysis of 1,2-Bis(2-pyridyl)ethane *N*-Oxide (12). Pyorolysis of **12** at 800 °C/0.05–0.2 mmHg without carrier gave from fraction I 8 (7%) and **9** (20%). From fraction II were isolated **2a** (11%), **2b** (11%), and **6** (39%).

Pyrolysis of 2-Ethylpyridine *N*-Oxide. This compound was pyrolyzed at 800 °C/1–5 mmHg with nitrogen carrier. Fraction II gave **2a** (20%), **2b** (3%), **5** (7%), and **6** (45%).

Pyrolysis of 2-Benzylpyridine *N*-Oxides (20a–i). Pyrolyses of 200–800 mg of **20a–i** were carried out at 800 °C/0.05–0.2 mmHg over periods of about 15 min. The products were isolated by column chromatography (hexane–ether/alumina) of fraction I.

(27) Baker, W.; Buggle, K. M.; McOmie, J. F. W.; Watkins, D. A. M. *J. Chem. Soc.* **1958**, 3594.

Scheme II



Results are shown in Table III.

Pyrido[1,2-*a*]indole (**21a**) was isolated as unstable yellow needles from pentane; mp 174–175 °C (lit.[17a] mp 174 °C); NMR (CS_2) δ 6.36 (1 H, ddd, J = 1, 7, 7 Hz, 7-H), 6.47 (1 H, s, 10-H), 6.74 (1 H, ddd, J = 1, 6.5, 7 Hz, 8-H), 7.00–7.38 (3 H, m, 2-, 3-, 9-H), 7.51–7.76 (2 H, m, 1-, 4-H), 8.16 (1 H, dd, J = 1, 7 Hz, 6-H); IR (KBr) 1622 (m), 1600 (m), 1530 (s), 1515 (s), 1458 (s), 1445 (m), 1345 (s), 1310 (s), 1240 (s), 1225 (s), 1145 (s), 985 (m), 925 (m), 820 (m), 765 (s), 743 (s), 735 (s), 700 cm^{-1} (s); UV (EtOH) λ_{max} 230 (ε 9220), 259 (49 500), 264 (43 300), 276 (sh), 290 (sh), 307 (2760), 318 (3210), 331 (2800), 362 (1480), 382 (2100), 400 (2540), 422 (2220), 448 nm (1000). Anal. Calcd for $C_{12}H_9N$: C, 86.20; H, 5.43; N, 8.38. Found: C, 86.20; H, 5.38; N, 8.12. Benzo[*g*]-quinoline (**23**) was separated as colorless prisms from pentane; mp 112.5–113 °C (lit.[18] mp 113–114 °C);[18,28] NMR (CD_3OD) δ 7.34–7.64 (3 H, m), 7.92–8.13 (2 H, m), 8.43 (1 H, dd, J = 1, 9 Hz), 8.44 (1 H, s), 8.56 (1 H, s), 8.87 (1 H, dd, J = 4, 6 Hz). 2-Methylpyrido[1,2-*a*]indole (**21c**) was isolated as unstable yellow needles from pentane; mp 106–108 °C dec; NMR (CS_2) δ 2.48 (3 H, s, CH_3), 6.32 (1 H, ddd, J = 1, 7, 7 Hz, 7-H), 6.38 (1 H, s, 10-H), 6.72 (1 H, ddd, J = 1, 7, 8 Hz, 8-H), 6.94 (1 H, dd, J = 1, 8 Hz, 3-H), 7.23 (1 H, dd, J = 1, 8 Hz, 9-H), 7.35 (1 H, s, 1-H), 7.51 (1 H, dd, J = 1, 8 Hz, 4-H), 8.09 (1 H, dd, J = 1, 7 Hz, 6-H); IR (KBr) 3040 (m), 1625 (m), 1610 (s), 1595 (m), 1535 (m), 1520 (s), 1490 (m), 1462 (s), 1445 (m), 1413 (m), 1375 (m), 1365 (m), 1345 (s), 1325 (m), 1295 (m), 1255 (m), 1245 (m), 1228 (m), 1173 (m), 1148 (s), 1135 (m), 985 (s), 865 (m), 815 (s), 785 (s), 740 (s), 720 cm^{-1} (s); UV (EtOH) λ_{max} 234 (ε 14 200), 260 (51 500), 265 (sh), 280 (sh), 293 (8890), 308 (3900), 322 (4430), 329 (sh), 335 (sh), 382 (2660), 400 (3060), 422 (2590), 448 nm (sh). Anal. Calcd for $C_{13}H_{11}N$: C, 86.16; H, 6.12; N, 7.73. Found: C, 85.89; H, 6.07; N, 7.97. Although the NMR of the reaction mixture suggested the formation of 4-methylpyrido[1,2-*a*]indole [16%, δ (CS_2) 2.31 (s, CH_3)], it could not be isolated because of its instability toward air and solvents and because of difficulty of its separation from **22c**. 3-Methylpyrido[1,2-*a*]indole (**21d**) was separated as unstable yellow needles from pentane; mp 137.5–138 °C; NMR (CS_2) δ 2.53 (3 H, s, CH_3), 6.30 (1 H, ddd, J = 1, 7, 7 Hz, 7-H), 6.39 (1 H, s, 10-H), 6.68 (1 H, ddd, J = 1, 6.5, 7 Hz, 8-H), 6.96–7.31 (2 H, m, 2-, 9-H), 7.31 (1 H, d, J = 1 Hz, 4-H), 7.44 (1 H, d, J = 6 Hz, 1-H), 8.06 (1 H, dd, J = 1, 7 Hz, 6-H); IR (KBr) 2960 (m), 2920 (m), 1622 (s), 1560 (m), 1530 (s), 1515 (s), 1493 (s), 1458 (s), 1350 (s), 1290 (s), 1260 (s), 1230 (s), 1175 (m), 1150 (m), 1095 (m), 1030 (s), 990 (m), 910 (m), 810 (s), 735 cm^{-1} (s); UV (EtOH) λ_{max} 232 (ε 9300), 259 (45 800), 264 (sh), 280 (sh), 292 (sh), 304 (sh), 318 (3190), 330 (2030), 368 (sh), 382 (1580), 404 (1960), 426 (1650), 451 nm (580). Anal. Calcd for $C_{13}H_{11}N$: C, 86.16; H, 6.12; N, 7.73. Found: C, 86.21; H, 5.94; N, 7.48. 10-Methylpyrido[1,2-*a*]indole (**21e**) was separated as unstable yellow plates from pentane; mp 67.5–68.5 °C (lit.[17d] mp 69 °C); NMR (CS_2) δ 2.50 (3 H, s, CH_3), 6.38 (1 H, ddd, J = 1, 7, 7 Hz, 7-H), 6.76 (1 H, ddd, J = 1, 7, 9 Hz, 8-H), 7.03–7.36 (3 H, m, 2- 3-, 9-H), 7.51–7.70 (2 H, m, 1-, 4-H), 8.18 (1 H, dd, J = 1, 7 Hz, 6-H); IR (KBr) 3040 (m), 2910 (m), 1625 (s), 1605 (s), 1545 (m), 1530 (m), 1515 (s), 1480 (s), 1460 (s), 1405 (m), 1345 (s), 1310 (s), 1260 (m), 1240 (s), 1230 (s), 1150 (m), 1095 (m), 1030 (m), 985 (m), 920 cm^{-1} (m); UV[17d] (EtOH) λ_{max} 228 (ε 9760), 256 (37 700), 261 (40 100), 313 (3250), 320 (3480), 328 (sh), 337 (2650), 382 (1930), 400 (2360), 421 (2390), 446 nm (1740). 1-(2-Pyridyl)-1-phenylethylene (**25**) was separated as a colorless oil of bp 120 °C (bath temperature, 0.5 mmHg); picrate mp 149.5–150.5 °C (lit.[29] mp 151 °C); NMR δ 5.56 (1 H, d, J = 1.5 Hz, =CH), 5.99 (1 H, d, J = 1.5 Hz, =CH), 7.30 (5 H, s, Ph), 7.00–7.62 (3 H, m, 3- 4-, 5-H), 8.61 (1 H, dd, J = 2, 6 Hz, 6-H); IR (neat) 3070 (m), 3050 (s), 3030 (m), 3010 (m), 2930 (m), 1590 (m), 1580 (s), 1565 (s), 1495 (s), 1470 (s), 1425 (m), 1430 (s), 1340 (m), 1150 (m), 1105 (m), 1070 (m), 1050 (m), 1030 (m),

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990 (m), 915 (s), 805 (s), 775 (s), 747 (s), 705 cm^{-1} (s). 9-Methylpyrido[1,2-*a*]indole (**21f**) was separated as unstable yellow plates from pentane; mp 101.5–102.5 °C; NMR (CS_2) δ 2.43 (3 H, s, CH_3), 6.39 (1 H, dd, *J* = 7, 7 Hz, 7-H), 6.50 (1 H, s, 10-H), 6.58 (1 H, ddd, *J* = 1, 7, 7 Hz, 8-H), 7.07–7.42 (2 H, m, 2-, 3-H), 7.60–7.80 (2 H, m, 1-, 4-H), 8.12 (1 H, dd, *J* = 1, 7 Hz, 6-H); IR (KBr) 3050 (m), 2930 (m), 1625 (m), 1605 (m), 1515 (s), 1465 (s), 1350 (s), 1335 (m), 1305 (m), 1248 (m), 1225 (m), 1153 (s), 1118 (m), 1010 (m), 928 (m), 872 (m), 768 (s), 740 cm^{-1} (s); UV (EtOH) λ_{max} 218 (ε 9330), 230 (10 700), 256 (52 500), 260 (sh), 275 (sh), 288 (sh), 304 (2790), 314 (3470), 329 (1950), 355 (sh), 372 (2090), 388 (2630), 410 (2400), 434 nm (1050); high-resolution MS, *m/e* calcd for $C_{13}H_{11}N$, 181.0889, found, 181.0888. 8-Methylpyrido-[1,2-*a*]indole (**21g**) was separated as unstable yellow plates from pentane; mp 151–151.5 °C dec; NMR (CS_2) δ 2.29 (3 H, s, CH_3), 6.20 (1 H, dd, *J* = 2, 7 Hz, 7-H), 6.33 (1 H, s, 10-H), 6.93–7.28 (3 H, m, 2-, 3-, 9-H), 7.68–7.94 (2 H, m, 1-, 4-H), 8.07 (1 H, d, *J* = 7 Hz, 6-H); IR (KBr) 3040 (m), 2905 (m), 1635 (s), 1605 (s), 1520 (s), 1475 (s), 1460 (s), 1375 (m), 1345 (s), 1325 (s), 1240 (s), 1227 (s), 1172 (s), 1030 (m), 1007 (m), 985 (m), 920 (s), 860 (s), 770 (s), 740 (s), 725 (s), 700 cm^{-1} (s); UV (EtOH) λ_{max} 218 (ε 11 100), 230 (13 900), 257 (58 600), 262 (57 600), 277 (sh), 290 (sh), 304 (4390), 315 (5550), 330 (6340), 357 (sh), 378 (2440), 396 (2870), 417 (2360), 445 nm (sh). Anal. Calcd for $C_{13}H_{11}N$: C, 86.16; H, 6.12; N, 7.73. Found: C, 86.19; H, 6.13; N, 7.66. 7-Methylpyrido[1,2-*a*]indole (**21h**) was separated as yellow plates from pentane; mp 137.5–138 °C; NMR (CS_2) δ 2.26 (3 H, s, CH_3), 6.41 (1 H, s, 10-H), 6.58 (1 H, dd, *J* = 2, 9 Hz, 8-H), 6.96–7.28 (3 H, m, 2-, 3-, 9-H), 7.46–7.68 (2 H, m, 1-, 4-H), 7.78 (1 H, d, *J* = 1 Hz, 6-H); IR (KBr) 3050 (m), 2930 (m), 1605 (s), 1540 (s), 1520 (s), 1485 (m), 1460 (s), 1455 (s), 1420 (s), 1340 (s), 1325 (m), 1310 (s), 1265 (m), 1245 (s), 1237 (s), 1175 (s), 1135 (m), 1100 (m), 1035 (m), 1010 (m), 980 (m), 930 (s), 905 (s), 840 (m), 805 (s), 770 (s), 740 (s), 710 cm^{-1} (s); UV (EtOH) λ_{max} 217 (sh), 231 (ε 8710), 259 (49 000), 279 (sh), 292 (sh), 306 (2510), 320 (3020), 332 (1780), 362 (sh), 379 (2000), 399 (2450), 422 (2090), 449 nm (sh). Anal. Calcd for $C_{13}H_{11}N$: C, 86.16; H, 6.12; N, 7.73. Found: C, 86.06; H, 6.01; N, 7.47. 6-Methylpyrido[1,2-*a*]indole (**21i**) was separated as yellow plates from pentane; mp 57–59 °C dec; NMR (CS_2) δ 2.95 (3 H, s, CH_3), 6.13 (1 H, dd, *J* = 1, 6 Hz, 7-H), 6.53 (1 H, s, 10-H), 6.68 (1 H, dd, *J* = 7, 9 Hz, 8-H), 6.94–7.30 (3 H, m, 2-, 3-, 9-H), 7.55 (1 H, dd, *J* = 2, 6 Hz, 1- or 4-H), 8.04 (1 H, dd, *J* = 1, 7 Hz, 4- or 1-H); IR (KBr) 3030 (m), 1630 (s), 1595 (s), 1530 (s), 1473 (m), 1460 (m), 1435 (s), 1405 (s), 1378 (m), 1340 (m), 1305 (s), 1287 (s), 1250 (m), 1215 (s), 1150 (s), 1050 (m), 1032 (m), 1017 (m), 985 (s), 947 (s), 920 (m), 830 (s), 770 (s), 740 (s), 715 (s), 695 cm^{-1} (s); UV (EtOH) λ_{max} 217 (ε 12 900), 252 (68 500), 253 (sh), 260 (47 600), 278 (sh), 291 (sh), 305 (3610), 315 (4870), 330 (8170), 348 (sh), 368 (3270), 386 (3660), 408 (3250), 433 nm (1400). Anal. Calcd for $C_{13}H_{11}N$: C, 86.16; H, 6.12; N, 7.73. Found: C, 86.08; H, 6.23; N, 7.61.

Pyrolysis of 2-(1-Propenyl)pyridine *N*-Oxide (26).[30] The principal compound obtained from column chromatography (hexane–ether/alumina) of fraction I was indolizine (**28**) obtained as colorless plates from pentane; mp 71.5–72.5 °C (lit.[31] mp 73–74 °C), 162 mg (48%); NMR[32] δ 6.12–6.77 (4 H, m, 1-,2-,6-, 7-H), 7.14 (1 H, d, *J* = 1 Hz, 3-H), 7.25 (1 H, dd, *J* = 2, 8 Hz, 8-H), 7.73 (1 H, dd, *J* = 1, 8 Hz, 5-H); IR (KBr) 1625 (m), 1520 (m), 1450 (m), 1363 (s), 1318 (s), 1310 (s), 1243 (s), 1220 (m), 1150 (m), 1075 (s), 1035 (m), 765 (s), 735 (s), 715 cm^{-1} (s); UV[33] (H_2O) λ_{max} 232 (ε 36 300), 274 (4590), 280 (5400), 292 (6290), 336 nm (3030).

Pyrolysis of 2-(*o*-Tolyl)pyridine *N*-Oxide (27).[34] 4-Azafluorene (**29**) was obtained as plates from pentane, mp 93–94 °C (lit.[25] mp 95–97 °C, 69%) and 2-(*o*-tolyl)pyridine (11%) were isolated from fraction I. Toluene (11%) and pyridine (trace) were detected in fraction II.

Registry No. **1a**, 694-59-7; **1b**, 931-19-1; **1c**, 1003-73-2; **1d**, 1003-67-4; **2a**, 110-86-1; **2b**, 109-06-8; **2c**, 108-99-6; **2d**, 108-89-4; **3**, 38746-50-8; **4**, 586-98-1; **5**, 100-71-0; **6**, 100-69-6; **7**, 1132-37-2; **8**, 4916-40-9; **9**, 1437-15-6; **12**, 82198-70-7; **14**, 101-82-6; **15**, 92-52-4; **16**, 2116-62-3; **17**, 103-29-7; **20a**, 20531-86-6; **20b** picrate, 82198-71-8; **20c** picrate, 82198-72-9; **20d**, 20531-88-8; **20e**, 80772-89-0; **20f**, 82198-73-0; **20g**, 80772-88-9; **20h**, 80772-87-8; **20i**, 80772-86-7; **21a**, 245-43-2; **21c**, 80772-77-6; **21d**, 80772-76-5; **21e**, 80772-84-5; **21f**, 80772-83-4; **21g**, 80772-82-3; **21h**, 80772-81-2; **21i**, 80772-80-1; **22b**, 36995-45-6; **22c**, 29263-64-7; **22d**, 29335-87-3; **22e**, 14159-54-7; **22f**, 56664-26-7; **22g**, 5191-54-8; **22h**, 63065-67-8; **22h** picrate, 82198-74-1; **22i**, 10131-46-1; **23**, 260-36-6; **25**, 15260-65-8; **26**, 21715-31-1; **27**, 33421-20-4; **28**, 274-40-8; **29**, 244-99-5; 4-methylpyrido[1,2-*a*]indole, 80772-78-7; 2-ethylpyridine *N*-oxide, 4833-24-3; 2-(*o*-tolyl)pyridine, 10273-89-9.

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Stereochemistry of Aroylphosphonate Phenylhydrazones and Their Conversion to 1*H*-Indazole-3-phosphonates

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Reaction of phenylhydrazine and (2,4-dinitrophenyl)hydrazine with dialkyl aroylphosphonates gives exclusively the *Z* isomers of the arylhydrazones **5**. Heating **5** in acetic acid produces an equilibrium mixture of **5** and the *E* isomers **6**. Oxidation of phenylhydrazones **a–g** (either **5** or **6**) with lead tetraacetate leads to azoacetates **7a–g**, which can be cyclized with BF_3–etherate to 1-phenyl-1*H*-indazole-3-phosphonates **8a–g**.

Aroylphosphonates **1**, which are valuable synthetic intermediates,[1] can react with nucleophiles **2** in either of two ways. Nucleophiles with an α heteroatom such as hydroxylamine[1a] and substituted hydrazines[2] condense with the carbonyl group to provide the corresponding oximes or hydrazones. With simple nucleophiles like water,[3a] alcohols,[3b] thiols,[3c] or amines,[1b,3d] acyl derivatives **4** are

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