uents at the α position, electronic and steric effects are combined to magnify the substituent influence. An α-methoxy substituent and α-unsaturation have greater acceleration effects on pyrolysis than do α-alkyl substituents but not as great an effect as α-phenyl and α-chloro substituents.

Kooyman et al.[4b] reported a ratio of cyclohexyl trifluoroacetate/cyclohexyl acetate of 19. This very strong effect at the α position of the acid is very significant and most likely is polar rather than steric. The data for isopropyl trichloroacetate are not available but it would appear from the increased rates due to one α-chloro substituent that three chloro substituents would cause an effect even greater than three fluoro substituents because of the combination of both steric and electronic effects.

In summary, therefore, these results demonstrate that substituent effects are more important at the α than at the β position in the acid moiety of esters on their pyrolysis. Multiple branching at the α position by alkyl groups causes a greater steric acceleration effect (compound VII) than similar substitution at the β position (compound VIII).

It is now clear that in pyrolysis, electron-withdrawing groups or electron-releasing groups in the acid moiety at the α position cause rate accelerations.

This suggests that the effects by α-aryl and α-aryl are more than electronic. We proposed that steric effect raise the ground state of the ester effectively reducing the activation free energy. Further evidence to support this concept was found by comparing the activation parameters of the isopropyl esters of trimethyl acetate (VII) and *tert*-butyl acetate (VIII). The entropy of activation ($\Delta S^{\ddagger}$) for VII, where the three methyl groups are located at the α position, showed a less negative value than β-methyl substituent. $\Delta S^{\ddagger}$ for VII was -0.25, while $\Delta S^{\ddagger}$ for VIII was -4.7. The rate ratio for the pyrolysis of these two esters was 1.3. From this we conclude that the more sterically hindered ester (VII) is held in a favorably conformation leading to the cyclic transition state. This supports the well-accepted mechanistic concept.[2] The enthalpies of activation for VII and VIII were found to be 45.0 and 42.5 kcal/mol, respectively. Wigfield and Phelps reported recently[17] that the major component of the free energy barrier in the sodium borohydride reduction of hindered ketones, which alters reactivity, is entropy.

Although ester pyrolysis and ester formation are very different processes, it is interested to compare the two reactions sterically. Newman[18] proposed that steric effects at the β carbon in acid esterification was greater than at the α carbon. However, Sniegoski[19] has challenged Newman's interpretation of the data.

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Electrocyclic Synthesis of 5,6- and 7,8-Dihydroquinolines and 5,6- and 7,8-Dihydroisoquinolines

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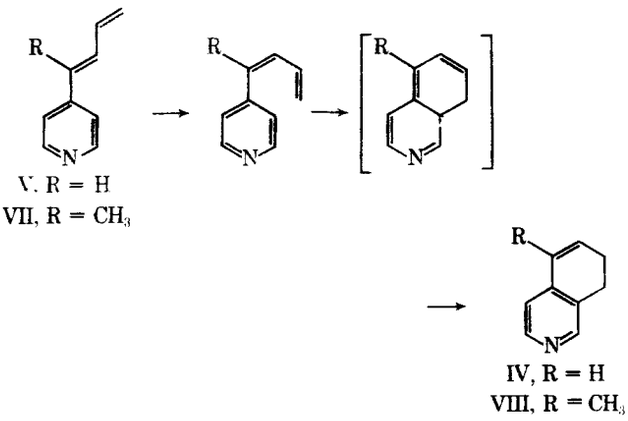
The gas-phase pyrolysis of a number of 1-(ω-pyridinyl)-1,3-butadienes (650 °C, 1 mm, and a contact time ~0.1 s) has been studied. The following results were obtained: 1-(α-pyridinyl)-1,3-butadiene yields 5,6-dihydroquinoline, 1-(β-pyridinyl)-1,3-butadiene yields 5,6-dihydroisoquinoline (35%) and 7,8-dihydroquinoline (65%), and 1-(γ-pyridinyl)-1,3-butadiene yields 7,8-dihydroisoquinoline. Analogous results were obtained on pyrolysis of 1-methyl-1-(ω-pyridinyl)-1,3-butadienes and 1-(6'-methyl-2'-pyridinyl)-1,3-butadiene. The structures of these 5,6- and 7,8-dihydroquinoline and 5,6- and 7,8-dihydroisoquinoline isomers were determined by spectral methods, dehydrogenation to the parent aromatic heterocycle, and in the case of 5,6- and 7,8-dihydroquinoline by use of Eu(fod)$_3$ NMR shift reagent. The mechanism of this reaction is discussed.

We should like to report a general synthesis of 5,6- and 7,8-dihydroquinolines (I, II) and 5,6- and 7,8-dihydroisoquinolines (III, IV) based on joining onto a pyridine ring a specific partially reduced aromatic ring. The critical ring closure reaction onto the pyridine nucleus is an electrocyclic reaction.[1] A communication reporting this reaction appeared 5 years ago.[2] The inaccessibility of I, II, III, and IV isomers convinced us that a detailed study to improve regioselectivity and yields and to determine the scope of this reaction was warranted.

The synthesis is based on the gas-phase pyrolysis of the appropriate 1-(ω-pyridinyl)-1,3-butadiene. Pyrolysis of 1-(γ-pyridinyl)-1,3-butadiene (V)[3] in the gas phase at 650 °C

and 1 mm pressure in a flow system with a contact time of about 0.1 s yields IV. No isoquinoline or quinoline as previously reported[2] were observed. This difference probably results from the lower temperature used. This result can be rationalized by the following reaction sequence. *cis*-V undergoes a disrotatory electrocyclic reaction to yield 8,9-dihydroisoquinoline. This step is related to the thermally allowed disrotatory reaction converting a conjugated triene into a 1,3-cyclohexadiene.[1,4-6] In the case of *cis*-V, the triene undergoing reaction is composed of the two double bonds of the 1,3-butadiene and two π electrons from the pyridine ring. Analogous examples in which a benzene ring contributes two π electrons to a triene system in thermally allowed electrocyclic reactions have been reported.[7-9] Clearly, this involves disruption of the aromatic 6-π-electron system of the pyridine ring. The high temperature required for the reaction may reflect the loss of resonance energy in the transition state. This is followed rapidly by a symmetry allowed 1,5-suprafacial sigmatropic hydrogen rearrangement leading to restoration of the aromatic pyridine nucleus.[10] Since only *cis*-V has the proper geometry to undergo electrocyclic reaction, the first step in the case of *trans*-V must be an isomerization of trans to cis.



V, R = H
VII, R = CH_3

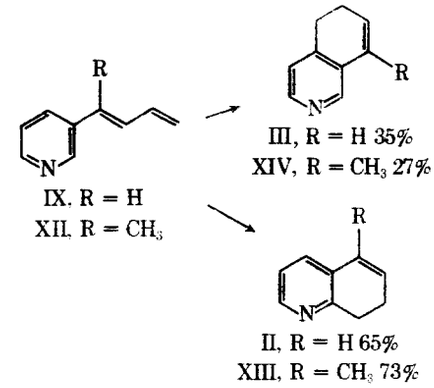
IV, R = H
VIII, R = CH_3

The starting 1-(ω-pyridinyl)-1,3-butadienes were prepared by a Wittig reaction of allylidenetriphenylphosphorane with ω-pyridinyl carboxaldehydes, albeit in low yield (~25%). 1-(α-, β-, and γ-pyridinyl)-1,3-butadienes are known but their spectral properties have not been reported.[3]

Cis and trans geometric isomers of both 1-(β-pyridinyl)-1,3-butadiene (IX) and V were obtained. In both, the cis was the predominant. Stereochemistry was assigned on the basis of uv spectra on the assumption that the *trans*-V or IX would absorb at longer wavelength and that ϵ would be greater than that of the corresponding cis isomer by analogy to the uv of *cis*- and *trans*-1-phenyl-1,3-butadiene.[11] Only a single geometric isomer of 1-(α-pyridinyl)-1,3-butadiene (X) was isolated. Its uv spectra was significantly different from those of either V or IX. It had considerable fine structure and the lowest energy absorption was shifted to longer wavelength.

1-Methyl-1-(ω-pyridinyl)-1,3-butadienes were prepared in three steps. Addition of allyl Grignard reagent to ω-acetylpyridine yields an alcohol which was converted to the corresponding chloride by treatment with $SOCl_2$. The chloride was dehydrohalogenated with KOH/CH_3OH to yield a mixture of the desired 1-methyl-1-(ω-pyridinyl)-1,3-butadiene and 2-(ω-pyridinyl)-1,4-pentadiene. The desired conjugated isomer was always predominant. Only a single geometric isomer of the three 1-methyl-1-(ω-pyridinyl)-1,3-butadienes was ever isolated. No attempt was made to determine if it was the *E* or *Z* isomer. Pyrolyses were carried out on mixtures of these isomers. Control experiments showed that 2-(ω-pyridinyl)-1,4-pentadienes were unchanged on pyrolysis. 1-(6′-Methyl-2′-pyridinyl)-1,3-butadiene (XI) was prepared in an analogous manner by addition of allyl Grignard reagent to 6-methyl-2-pyridinecarboxaldehyde in 59% overall yield.

Pyrolysis of IX[3] yields a mixture of III and II in a ratio of 1:2, in addition to small amounts of recovered IX. Neither quinoline nor isoquinoline were ever observed. Pyrolysis of 1-methyl-(β-pyridinyl)-1,3-butadiene (XII) yields a mixture of 5-methyl-7,8-dihydroquinoline (XIII) and 8-methyl-5,6-dihydroisoquinoline (XIV) (~3:1).

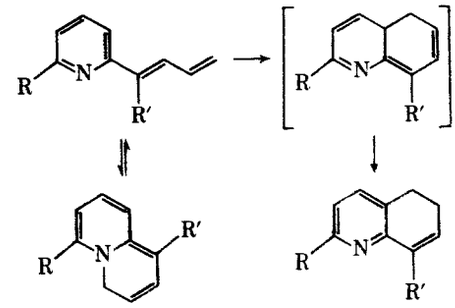


IX, R = H
XII, R = CH_3

III, R = H 35%
XIV, R = CH_3 27%

II, R = H 65%
XIII, R = CH_3 73%

Pyrolysis of X[3] yields I and small amounts of recovered X. Neither quinoline nor 4-quinolizine were ever observed. This selectivity may not reflect high regioselectivity in the electrocyclic reaction, but rather the instability of the 4-quinolizine ring system. 4-Quinolizine is expected to open to yield X on the basis of previous work.[12] Likewise, pyrolysis of XI yields 2-methyl-5,6-dihydroquinoline (XV) and small amounts of recovered XI. Neither 2-methylquinoline nor 6-methyl-4-quinolizine were observed. Pyrolysis of 1-methyl-1-(α-pyridinyl)-1,3-butadiene (XVI) yields 8-methyl-5,6-dihydroquinoline (XVII). Neither 8-methylquinoline nor 1-methyl-4-quinolizine were observed.



X, R = H; R′ = H
XVI, R = H; R′ = CH_3
XI, R = CH_3; R′ = H

I, R = H; R′ = H
XVII, R = H; R′ = CH_3
XV, R = CH_3; R′ = H

The I, II, III, and IV isomers are new compounds. Their structures were determined by spectral methods (ir, NMR, uv). In addition, a pure sample of each dihydro isomer was dehydrogenated by oxidation with 2,3-dichloro-5,6-dicyanoquinone (DDQ) in dimethoxyethane at 50 °C.[13] The identity of the parent aromatic heterocycle obtained was determined by GLC and NMR spectra. These results were consistent. Finally, the structures of I and II obtained respectively from the pyrolysis of X and IX were confirmed by use of $Eu(fod)_3$ NMR shift reagent. $Eu(fod)_3$ behaves as a Lewis acid and thus is expected to coordinate to the nitrogen of these dihydroquinoline isomers.[14,15] The effect of $Eu(fod)_3$ on the chemical shift of a particular proton in the substrate is related to the concentration of $Eu(fod)_3$ as well as to the distance and geometry of the proton from the Eu^{3+} ion.[15] Those protons which are closest to the Eu^{3+} ion shift the most.[15] On this basis, we expect major downfield shifts for the aromatic proton

at C-2 and for the vinylic proton at C-8 in I. On the other hand, we expect major downfield shifts of the aromatic proton at C-2 and the benzylic protons at C-8 in II. Results consistent with these expectations were obtained. For supporting data—spectra, as well as plots of the chemical shifts of each proton vs. the sum of all the chemical shifts of these protons observed at various concentrations of $Eu(fod)_3$[16]—see supplementary material in the microfilm edition.

Experimental Section

All reactions were carried out under an atmosphere of prepurified nitrogen. Ir spectra were determined as neat liquids on a Perkin-Elmer 337 spectrometer. They were calibrated against known peaks in a polystyrene film. NMR spectra were recorded on a Varian XL-100 spectrometer. Spectra were taken using 10% solutions in $CDCl_3$ with an internal standard of Me_4Si. Samples of all compounds for spectral and elemental analysis were purified by preparative vapor phase chromatography on a Hewlett-Packard F & M 700 using a 20% FFAP (Varian) on 60/80 mesh Chromosorb P, which had been modified by addition of 10% powdered KOH, 10 ft × 0.25 in. column at a temperature of 165 °C. Ultraviolet spectra were obtained in spectrograde cyclohexane on a Beckman Acta M spectrometer. Melting points were taken on a Hoover-Thomas apparatus and are uncorrected. Picrate derivatives were prepared by standard procedures and were recrystallized from 95% ethanol. Microanalysis was performed by Elek Microanalytical Laboratories, Torrance, Calif.

1-(α-Pyridinyl)-1,3-butadiene (X). In a 500-ml three-necked round-bottom flask equipped with a pressure-equalizing addition funnel, a reflux condenser, and a rubber septum were placed 39.1 g (103 mmol) of allyltriphenylphosphonium bromide (Aldrich), 200 ml of anhydrous ether, and a Teflon-covered magnetic stirring bar. *n*-Butyllithium (Alfa) in hexane (1.9 M, 52 ml) was added by syringe. The solution was refluxed for 1 h. α-Pyridinecarboxaldehyde (Aldrich), 9.5 g (89 mmol), was added dropwise to the stirred solution of ylide. After 3 h, the mixture was filtered to remove triphenylphosphine oxide. Volatile solvents were removed from the filtrate by evaporation under reduced pressure. The volatile product was separated from the nonvolatile residue by bulb to bulb distillation at 60 °C (0.1 mm) to yield 4.5 g (34 mmol, 39%) of X. Only a single isomer of X was ever isolated: ^1H NMR δ 8.6 (d, 1 H, J = 6 Hz), 7.6 (m, 2 H), 7.2 (m, 2 H), 6.5 (m, 2 H), 5.4 (dd, 2 H, J = 14 and 8 Hz); ir C=C 1626 cm^{-1}; uv λ 2620 Å, ε 3.05 × 10^4, λ 2740 Å, ε 2.77 × 10^4, λ 2930 Å, ε 2.26 × 10^4, λ 3020 Å, ε 2.26 × 10^4, λ 3150 Å, ε 1.24 × 10^4; mp (picrate) 145.5 °C (lit. mp 146.5–147 °C).[12]

1-(β-Pyridinyl)-1,3-butadiene (IX) was prepared as above from β-pyridinecarboxaldehyde (Aldrich) in 29% yield. It was separated into cis and trans geometric isomers in a ratio of 64/36 by preparative GLC. The cis isomer had the shorter retention time.

***cis*-IX:** ^1H NMR δ 8.6 (s, 1 H), 8.5 (d, 1 H, J = 6 Hz), 7.65 (d, 1 H, J = 8 Hz), 7.3 (dd, 1 H, J = 8 and 6 Hz), 6.8 (m, 1 H), 6.4 (m, 2 H), 5.4 (dd, 2 H, J = 16 and 10 Hz); ir C=C 1600 cm^{-1}; uv λ 2600 Å, ε 3.19 × 10^4; mp (picrate) 134 °C (lit. mp 138 °C).[3]

***trans*-IX:** ^1H NMR δ 8.65 (s, 1 H), 8.5 (d, 1 H, J = 5 Hz), 7.77 (d, 1 H, J = 9 Hz), 7.3 (dd, 1 H, J = 9 and 5 Hz), 7.0–6.3 (m, 3 H), 5.3 (dd, 2 H, J = 18 and 10 Hz); ir C=C 1600 cm^{-1}; uv λ 2675 Å, ε 4.17 × 10^4; mp (picrate) 115 °C.

1-(γ-Pyridinyl)-1,3-butadiene (V)[3] was prepared as above from γ-pyridinecarboxaldehyde (Aldrich) in 21% yield. It was separated into cis and trans geometric isomers in a ratio of 60:40 by GLC.

***cis*-V:** ^1H NMR δ 8.6 (d, 2 H, J = 8 Hz), 7.2 (d, 2 H, J = 9 Hz), 6.9 (m, 1 H), 6.5 (m, 2 H), 5.4 (dd, 2 H, J = 16 and 8 Hz); ir C=C 1600 cm^{-1}; uv λ 2650 Å, ε 2.29 × 10^4.

***trans*-V:** ^1H NMR δ 8.5 (d, 2 H, J = 5 Hz), 7.3 (d, 2 H, J = 5 Hz), 7.1–6.3 (m, 3 H), 5.5 (dd, 2 H, J = 16 and 10 Hz); ir C=C 1610 cm^{-1}; uv λ 2700 Å, ε 3.61 × 10^4; mp (picrate) 131 °C.

1-Methyl-1-(α-pyridinyl)-1,3-butadiene (XVI) was prepared in three steps from 2-acetylpyridine. Intermediate products were neither purified nor characterized. The following apparatus was used for each step: a 250-ml three-necked round-bottom flask equipped with a reflux condenser, a pressure-equalizing addition funnel, a rubber septum, and a Teflon-coated magnetic stirring bar. 2-Acetylpyridine (Reilly), 4.2 g (35 mmol), and 50 ml of anhydrous ether were placed in the flask. Allylmagnesium chloride (Alfa), 1.9 M in THF, 28 ml (70 mmol), was added dropwise to the stirred, cooled (0 °C) solution of 2-acetylpyridine. After 3 h 50 ml of a saturated NH_4Cl solution was added. The organic and aqueous layers were separated. The aqueous layer was extracted with 2 × 50 ml of ether. The combined ether extracts were dried over anhydrous $MgSO_4$ and filtered, and the volatile solvents removed by evaporation under reduced pressure to yield 2-(α-pyridinyl)-2-hydroxy-4-pentene. Thionyl chloride, 5 ml (70 mmol), was placed in the flask. The above alcohol, 5.2 g (35 mmol), dissolved in 20 ml of $CHCl_3$ was added dropwise to the cooled (0 °C) solution of $SOCl_2$. After the addition was complete, the flask was heated at 80 °C for 15 min until the evolution of SO_2 had subsided. The solution was cooled and made basic by addition of concentrated K_2CO_3. The layers were separated and the aqueous phase extracted with 3 × 50 ml of ether. The ether extracts were combined, dried over anhydrous $MgSO_4$, and filtered, and the volatile solvents removed by evaporation under reduced pressure to yield 2-(α-pyridinyl)-2-chloro-4-pentene. Ten grams of KOH and 50 ml of CH_3OH were placed in the flask. The above chloride, 5.8 g (35 mmol), dissolved in 10 ml of CH_3OH was added to the refluxing solution of KOH/CH_3OH. After 4 h, the reaction mixture was cooled and extracted with 3 × 100 ml of CH_2Cl_2. The combined CH_2Cl_2 extracts were dried over anhydrous $MgSO_4$ and filtered, and the volatile solvents removed by evaporation under reduced pressure. The volatile products were separated from nonvolatiles by bulb to bulb distillation at 75 °C (0.1 mm) to yield 2.6 g (51%) of a mixture of XVI and 2-(α-pyridinyl)-1,4-pentadiene in a ratio of 66:34. The XVI had the longer retention time.

XVI: ^1H NMR δ 8.6 (d, 1 H, J = 5 Hz), 7.6 (m, 2 H), 7.2–6.6 (m, 3 H), 5.4 (dd, 2 H, J = 16 and 10 Hz), 2.25 (d, 3 H, J = 1 Hz); ir C=C 1600 cm^{-1}; uv λ 2780 Å, ε 2.1 × 10^4, λ 2920 Å, ε 1.95 × 10^4, λ 3020 Å, ε 1.6 × 10^4, λ 3170 Å, ε 4.5 × 10^3; mp (picrate) 152.5 °C. Anal. Calcd for $C_{10}H_{11}N$: C, 82.72; H, 7.64. Found: C, 82.95; H, 7.55.

1-Methyl-1-(β-pyridinyl)-1,3-butadiene (XII) was prepared as above from 3-acetylpyridine, 4.1 g (34 mmol) (Aldrich), to yield 1.9 g (13 mmol, 39%) of a mixture of XII and 2-(β-pyridinyl)-1,4-pentadiene in a ratio of 73:27. They were separated by preparative GLC. XII had a longer retention time.

XII: ^1H NMR δ 8.6 (s, 1 H), 8.4 (d, 1 H, J = 5 Hz), 7.7 (d, 1 H, J = 5 Hz), 7.2 (dd, 1 H, J = 8 and 5 Hz), 6.5 (m, 2 H), 6.3 (dd, 2 H, J = 15 and 8 Hz), 2.2 (s, 3 H); ir C=C 1630 cm^{-1}; uv λ 2700 Å, ε 2.05 × 10^4; mp (picrate) 154 °C. Anal. Calcd for $C_{16}H_{14}N_4O_7$ (picrate): C, 51.34; H, 3.77. Found: C, 50.97; H, 4.07.

1-Methyl-1-(γ-pyridinyl)-1,3-butadiene (VII) was prepared as above from 4-acetylpyridine (Reilly), 4.0 g (33 mmol), to yield 2.5 g (18 mmol, 52%) of a mixture of VII and 2-(γ-pyridinyl)-1,4-pentadiene in a ratio of 61:39. They were separated by preparative GLC. VII had a longer retention time.

VII: ^1H NMR δ 8.55 (d, 2 H, J = 6 Hz), 7.30 (d, 2 H, J = 6 Hz), 6.7 (m, 2 H), 5.4 (dd, 2 H, J = 14 and 7 Hz), 2.2 (s, 3 H); ir C=C 1595 cm^{-1}; uv λ 2750 Å, ε 1.97 × 10^4; mp (picrate) 155 °C. Anal. Calcd for $C_{16}H_{14}N_4O_7$ (picrate): C, 51.34; H, 3.77. Found: C, 51.13; H, 3.91.

1-(6′-Methyl-2′-pyridinyl)-1,3-butadiene (XI) was prepared as above from 6-methyl-2-pyridinecarboxaldehyde (Aldrich), 5.5 g (44 mmol), to yield 3.9 g (27 mmol, 59%) of XI: ^1H NMR δ 7.6 (dd, 1 H, J = 14 and 8 Hz), 7.2 (m, 3 H), 6.6 (m, 2 H, upon irradiation at 5.4, the multiplet collapsed to a doublet with J = 17 Hz), 5.4 (dd, 2 H, J = 20 and 10 Hz), 2.6 (s, 3 H); ir C=C 1600 cm^{-1}; uv λ 2620 Å, ε 1.75 × 10^4, λ 2700 Å, ε 1.63 × 10^4, λ 2950 Å, ε 1.31 × 10^4, λ 3050 Å, ε 1.38 × 10^4, λ 3180 Å, ε 8.14 × 10^3; mp (picrate) 136 °C. Anal. Calcd for $C_{16}H_{14}N_4O_7$ (picrate): C, 51.34; H, 3.77. Found: C, 51.36; H, 3.91.

Pyrolysis of 1-(ω-Pyridinyl)-1,3-butadiene. The pyrolysis was performed using a 30-cm vertical tube oven. The diameter of the heated zone was 3.5 cm. The pyrolysis tube was made from a quartz tube (9 mm o.d., 8 mm i.d.), 250 cm long. It was wrapped in the form of a helical spiral of 30 turns. The height of the spiral was 30 cm. A 10-ml round-bottom flask containing a Teflon-covered magnetic stirring bar and the 1-(ω-pyridinyl)-1,3-butadiene to be pyrolyzed was connected to the bottom of the pyrolysis tube. The top of the pyrolysis tube was attached to a cold finger condenser which was cooled with liquid nitrogen. The outlet of the condenser was connected to a vacuum pump. The pyrolysis tube was heated to around 650 °C. The temperature was determined by use of a Leeds and Northrup potentiometer and an iron–constantan thermocouple. The 1-(ω-pyridinyl)-1,3-butadiene was distilled under vacuum into the pyrolysis tube by heating the 10-ml round-bottom flask to 75–90 °C with an oil bath. Under these conditions, about 1 g of 1-(ω-pyridinyl)-1,3-butadiene passed through the pyrolysis tube in 20 min. Thus the contact time is approximately 0.1 s. After completion of the pyrolysis, the cold finger condenser, with the pyrolysate frozen onto it, was disconnected from the pyrolysis tube and connected to a 10-ml round-bottom flask flushed with nitrogen. The coolant was allowed to evaporate and the product dripped off the condenser into the round-bottom flask.

X, 1.3 g (10.0 mmol), was pyrolyzed at 650 °C over a period of 21 min at a pressure of 0.1 mm. The product, 1.24 g, was analyzed by

GLC. In addition to recovered starting material, 0.44 g (3.3 mmol), there was isolated I, 0.8 g (6.1 mmol, 88% yield based on recovery starting material).

5,6-Dihydroquinoline (I): ^{1}H NMR δ 8.3 (d, 1 H, J = 7 Hz), 7.3 (d, 1 H, J = 7 Hz), 6.9 (dd, 1 H, J = 8 and 5 Hz), 6.6 (d, 1 H, J = 10 Hz), 6.3 (td, 1 H, J = 10 and 5 Hz), 2.8 (t, 2 H, J = 8 Hz), 2.4 (br m, 2 H); ir C=C 1640 cm^{-1}; uv λ 2890 Å, ϵ 7.9 × 10^3, λ 2570 Å, ϵ 6.55 × 10^3; mp (picrate) 179 °C. Anal. Calcd for $C_{15}H_{12}N_4O_7$ (picrate): C, 50.01; H, 3.36. Found: C, 50.01; H, 3.55.

IX, 1.5 g (11.4 mmol), was pyrolyzed at 648 °C over a period of 30 min at a pressure of 1 mm. The products, 1.2 g (9.2 mmol), were analyzed by GLC. There was no recovered starting material. II, 0.78 g (6 mmol), 52% yield, and III, 0.42 g (3.2 mmol), in 28% yield were obtained. II had the shorter retention time.

7,8-Dihydroquinoline (II): ^{1}H NMR δ 8.3 (d, 1 H, J = 6 Hz), 7.3 (d, 1 H, J = 7 Hz), 7.1 (dd, 1 H, J = 8 and 5 Hz), 6.42 (d, 1 H, J = 10 Hz), 6.1 (td, 1 H, J = 10 and 4 Hz), 3.0 (t, 2 H, J = 9 Hz), 2.5 (br m, 2 H); ir C=C 1640 cm^{-1}; uv λ 2570 Å, ϵ 1.11 × 10^4; mp (picrate) 176 °C. Anal. Calcd for $C_{15}H_{12}N_4O_7$ (picrate): C, 50.01; H, 3.36. Found: C, 50.00; H, 3.56.

5,6-Dihydroisoquinoline (III): ^{1}H NMR δ 8.3 (br s, 2 H), 7.1 (d, 1 H, J = 6 Hz), 6.58 (d, 1 H, J = 10 Hz), 6.2 (td, 1 H, J = 10 and 4 Hz), 2.9 (t, 2 H, J = 10 Hz), 2.5 (br s, 2 H); ir C=C 1580 cm^{-1}; uv λ 2550 Å, ϵ 2.0 × 10^4; mp (picrate) 150 °C. Anal. Calcd for $C_{15}H_{12}N_4O_7$ (picrate): C, 50.01; H, 3.36. Found: C, 50.21; H, 3.39.

V, 1.3 g (9.2 mmol), was pyrolyzed at 649 °C at a pressure of 0.8 mm over 27 min. The products, 0.9 g (7.1 mmol), were analyzed by GLC. Recovered starting material, 0.2 g (1.7 mmol), was isolated in a trans to cis ratio 3:1. The ratio of starting material prior to pyrolysis was 2:3 trans to cis. Cis reacts faster than trans, but some trans has reacted. In addition, there was isolated IV, 0.7 g (5.4 mmol), 70% corrected yield.

7,8-Dihydroisoquinoline (IV): ^{1}H NMR δ 8.4 (d, 1 H, J = 6 Hz), 8.38 (s, 1 H), 6.90 (d, 1 H, J = 6 Hz), 6.47 (d, 1 H, J = 10 Hz), 6.37 (td, 1 H, J = 10 and 5 Hz), 2.8 (t, 2 H, J = 8 Hz), 2.4 (br m, 2 H); ir C=C 1650 cm^{-1}; uv λ 2590 Å, ϵ 7.1 × 10^3; mp (picrate) 184 °C (lit. mp 184–185 °C).[2] Anal. Calcd for $C_{15}H_{12}N_4O_7$ (picrate): C, 50.01; H, 3.36. Found: C, 50.09; H, 3.55.

XI, 1.0 g (6.9 mmol), was pyrolyzed at 648 °C and 0.12 mm over 25 min. The products, 0.9 g (5.5 mmol), were analyzed by GLC. In addition to recovered starting material, 0.26 g (1.8 mmol), there was isolated XV, 0.54 g (3.7 mmol), 73% corrected yield.

2-Methyl-5,6-dihydroquinoline (XV): ^{1}H NMR δ 7.3 (d, 1 H, J = 7 Hz), 6.9 (d, 1 H, J = 7 Hz), 6.6 (d, 1 H, J = 10 Hz), 6.3 (td, 1 H, J = 10 and 4 Hz), 2.8 (t, 2 H, J = 9 Hz), 2.5 (s, 3 H), 2.4 (br m, 2 H); ir C=C 1650 cm^{-1}; uv λ 2400 Å, ϵ 4.53 × 10^3, λ 2580 Å, ϵ 5.1 × 10^3, λ 2940 Å, ϵ 7.3 × 10^3, λ 3150 Å, ϵ 5.78 × 10^3; mp (picrate) 144 °C. Anal. Calcd for $C_{16}H_{14}N_4O_7$ (picrate): C, 51.34; H, 3.77. Found: C, 51.39; H, 3.94.

Pyrolyses of 1-methyl-1-(ω-pyridinyl)-1,3-butadienes were carried out as previously described on mixtures of 1-methyl-1-(ω-pyridinyl)-1,3-butadiene and the isomeric 2-(ω-pyridinyl)-1,4-pentadiene. It was shown by control experiments that the 2-(ω-pyridinyl)-1,4-pentadienes were stable under the pyrolysis conditions. The yields of products are based on the amount of reactive 1-methyl-1-(ω-pyridinyl)-1,3-butadiene consumed in the pyrolysis reaction.

XVI, 0.75 g (5.2 mmol), was pyrolyzed at 654 °C at a pressure of 0.1 mm over 19 min. The products were analyzed by GLC. No starting material was recovered. XVII, 0.55 g (3.9 mmol), 72% yield, was isolated.

8-Methyl-5,6-dihydroquinoline (XVII): ^{1}H NMR δ 8.39 (d, 1 H, J = 6 Hz), 7.3 (t, 1 H, J = 6 Hz), 7.0 (dd, 1 H, J = 8 and 5 Hz), 6.1 (br s, 1 H), 2.8 (t, 2 H, J = 8 Hz), 2.3 (br m, 2 H), 2.18 (d, 3 H, J = 1 Hz); ir C=C 1665 cm^{-1}; uv λ 2620 Å, ϵ 5.7 × 10^3, λ 2900 Å, ϵ 8.04 × 10^3, λ 3000 Å, ϵ 6.5 × 10^3; mp (picrate) 132 °C. Anal. Calcd for $C_{10}H_{11}N$: C, 82.72; H, 7.64. Found: C, 82.87; H, 7.50.

XII, 0.84 g (5.8 mmol), was pyrolyzed at 652 °C at a pressure of 0.1 mm over 19 min. The products were analyzed by GLC. No starting material was recovered. The products were isolated: XIII, 0.49 g (3.3 mmol), 57%, and XIV, 0.17 g (1.2 mmol), 21%.

5-Methyl-7,8-dihydroquinoline (XIII): ^{1}H NMR δ 8.25 (d, 1 H, J = 6 Hz), 7.4 (d, 1 H, J = 8 Hz), 7.05 (dd, 1 H, J = 8 and 6 Hz), 6.8 (br s, 1 H), 2.92 (t, 2 H, J = 8 Hz), 2.4 (br m, 2 H), 2.0 (d, 3 H, J = 1 Hz); ir C=C 1650 cm^{-1}; uv λ 2600 Å, ϵ 9.4 × 10^3, λ 2860 Å, ϵ 7.65 × 10^3, λ 2980 Å, ϵ 4.87 × 10^3; mp (picrate) 175.5 °C. Anal. Calcd for $C_{16}H_{14}N_4O_7$ (picrate): C, 51.34; H, 3.77. Found: C, 51.42; H, 3.99.

8-Methyl-5,6-dihydroisoquinoline (XIV): ^{1}H NMR δ 8.4 (s, 1 H), 8.36 (d, 1 H, J = 6 Hz), 7.01 (d, 1 H, J = 6 Hz), 6.9 (br s, 1 H), 2.78 (t, 2 H, J = 8 Hz), 2.3 (br m, 2 H), 2.1 (d, 3 H, J = 2 Hz); ir C=C 1650 cm^{-1}; uv λ 2570 Å, ϵ 6.05 × 10^3; mp (picrate) 161 °C. Anal. Calcd for $C_{16}H_{14}N_4O_7$ (picrate): C, 51.34; H, 3.77. Found: C, 51.17; H, 4.11.

VII, 0.74 g (5.1 mmol), was pyrolyzed at 643 °C at a pressure of 0.1 mm over 24 min. The products were analyzed by GLC. In addition to recovered starting material, 0.1 g (0.7 mmol), there was isolated VIII (0.4 g, 2.8 mmol), 59% corrected yield.

5-Methyl-7,8-dihydroisoquinoline (VIII): ^{1}H NMR δ 8.4 (d, 1 H, J = 6 Hz), 8.37 (s, 1 H), 7.0 (d, 1 H, J = 6 Hz), 6.02 (br s, 1 H), 2.75 (t, 2 H, J = 8 Hz), 2.3 (br m, 2 H), 2.1 (d, 3 H, J = 2 Hz); ir C=C 1640 cm^{-1}; uv λ 2610 Å, ϵ 9.12 × 10^3; mp (picrate) 184 °C. Anal. Calcd for $C_{10}H_{11}N$: C, 82.72; H, 7.64. Found: C, 82.59; H, 7.54.

Dehydrogenation of Dihydroquinolines and Dihydroisoquinolines. A solution of 50 mg of the dihydroquinoline or dihydroisoquinoline and 5 ml of dry dimethoxyethane was treated with 90 mg of DDQ (Eastman), and heated at 50 °C for 24 h.[13] After an acid–base workup, product analysis was carried out by GLC. Retention times were identical with those of known samples of quinolines or isoquinolines. NMR spectra were also consistent.

Eu(fod)$_3$ Shift Experiments. Eu(fod)$_3$ was obtained from Bio-Rad Laboratories and was dried in a vacuum desiccator over phosphorus pentoxide prior to use. In a typical experiment, 50 μl of a 0.59 M solution of Eu(fod)$_3$ in $CDCl_3$ was syringed into a 5-mm NMR tube containing 50 mg of the dihydroquinoline in 0.4 ml of $CDCl_3$/1% Me_4Si. A spectrum was then taken of this new solution. This procedure was repeated until 200 μl of shift reagent solution had been added.

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Registry No.—I, 24334-23-4; I picrate, 54087-12-6; II, 37624-11-6; II picrate, 54086-93-0; III, 60498-99-9; III picrate, 60499-00-5; IV, 24334-24-5; IV picrate, 54087-13-7; *cis*-V, 60499-01-6; *trans*-V, 60499-02-7; *trans*-V picrate, 60499-03-8; VII, 60499-04-9; VII picrate, 60499-05-0; VIII, 60499-06-1; VIII picrate, 60499-07-2; *cis*-IX, 60499-08-3; *trans*-IX, 60499-09-04; *trans*-IX picrate, 60499-10-7; X 3054-98-6; XI, 10497-82-2; XI picrate, 10530-42-4; XII, 60499-11-8; XII picrate, 60499-12-9; XIII, 60499-13-0; XIII picrate, 60499-14-1; XIV, 60499-15-2; XIV picrate, 60499-16-3; XV, 60499-17-4; XV picrate, 60499-18-5; XVI, 60499-19-6; XVI picrate, 60499-20-9; XVII, 60499-21-0; XVII picrate, 60499-22-1; allyltriphenylphosphonium bromide, 1560-54-9; α-pyridinecarboxaldehyde, 1121-60-4; β-pyridinecarboxaldehyde, 500-22-1; γ-pyridinecarboxaldehyde, 872-85-5; 2-acetylpyridine, 1122-62-9; allyl chloride, 107-05-1; 2-(α-pyridinyl)-2-hydroxy-4-pentene, 60499-23-2; 2-(α-pyridinyl)-2-chloro-4-pentene, 60499-24-3; 3-acetylpyridine, 350-03-8; 4-acetylpyridine, 1122-54-9; 6-methyl-2-pyridinecarboxaldehyde, 1122-72-1.

Supplementary Material Available. NMR spectra of dihydroquinolines and plots of δ_i vs. $\Sigma\delta$ with Eu(fod)$_3$ (4 pages). Ordering information is given on any current masthead page.

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