of **17** to **13** are of course possible.

(10) E. Vedejs, W. R. Wilbur, and R. Tweig, *J. Org. Chem.*, **42**, 401 (1977); W. C. Agosta and S. Wolff, *ibid.*, **40**, 1027 (1975); E. Wenkert, B. L. Mylari, and L. L. Davis, *J. Am. Chem. Soc.*, **90**, 3870 (1968); G. Stork and J. Ficini, *ibid.*, **83**, 4678 (1961); W. Kirmse, "Carbene Chemistry", Academic Press, New York, N.Y., 1964, p 120; W. J. Baron, M. R. DeCamp, M. E. Hendrick, M. Jones, Jr., R. H. Levin, and M. B. Sohn, *Carbenes 1973*, **1**, 1–152 (1973).

(11) (a) The general capacity of phthalimides to undergo ring expansion to substituted isoquinolines has, however, long been known; see J. G. M. Hill, *J. Org. Chem.*, **30**, 620 (1965). (b) A different type of homologation of a phthalimide group was recently reported: P. H. Mazzocchi, M. W. Bowen, and N. K. Narain, *J. Am. Chem. Soc.*, **99**, 7063 (1977).

(12) Because of its simplicity this procedure represents an improvement over one recently published: A. K. Bose, "Organic Syntheses", Collect. Vol. 5, Wiley, New York, N.Y., 1973, p 975.

(13) S. Gabriel, *Chem. Ber.*, **38**, 633 (1905).

(14) S. Gabriel, *Chem. Ber.*, **41**, 243 (1908).

(15) On long standing **9** changes its crystalline form; the new polymorph, mp 121–123 °C, shows the ketone carbonyl stretch shifted to 1740 cm^{-1} and the appearance of the fingerprint region substantially altered.

(16) On some runs the same yields could be obtained within 24 h. On much longer standing the product begins to redissolve, eventually giving a clear colorless solution. The same phenomenon was observed in neutral H_2O.

(17) This compound crystallizes in several forms, whose apparent colors range from green through yellow to red-orange; however, when the macrocrystalline structure is destroyed, such as by fine grinding or solution, the same yellow-green material is obtained. Solutions of **13** show a bright blue fluorescence under 365-nm light.

Studies on the Intramolecular Addition of Vinyl Nitrenes to Olefins

Albert Padwa* and Per H. J. Carlsen

Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214

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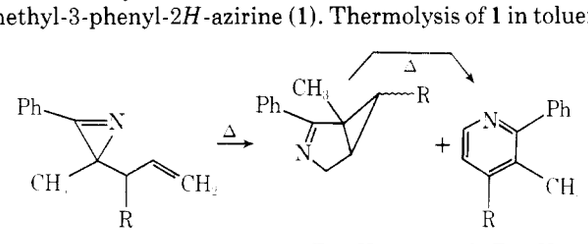
A series of 2-allyl-substituted 2*H*-azirines were found to undergo smooth rearrangement to afford 3-azabicyclo[3.1.0]hex-3-enes in high yield on thermolysis. The reactions can best be rationalized in terms of an equilibration of the 2*H*-azirine ring with a transient vinyl nitrene which subsequently adds to the adjacent π bond. The initially formed bicycloaziridine rearranges to the 3-azabicyclohexene ring system by means of a 1,3-sigmatropic shift. Evidence favoring this pathway is provided by the isolation of 2-phenyl-3-methyl-5-vinyl-Δ^1-pyrroline from the thermolysis of 2-(2-butenyl)-2-methyl-3-phenyl-2*H*-azirine. The formation of the Δ^1-pyrroline ring system can be rationalized as proceeding via a homo[1,5] hydrogen migration from a 6-endo methyl-substituted bicycloaziridine intermediate. Thermolysis of 3-methyl-2-phenyl-2-allyl-substituted 2*H*-azirines affords mixtures of 3-azabicyclohexenes and indoles. The distribution of products with this ring system is controlled by the rates of nitrene attack on the double bond vs. electrocyclization on the adjacent phenyl ring. Finally, the thermolysis of methyl 4-(3-methyl-2-phenyl-2*H*-azirin-2-yl)-2-butenoate results in a novel rearrangement and produces 2-methyl-3-phenyl-5-carbomethoxypyridine as the major product. A tentative but reasonable mechanistic rationale is advanced to rationalize this reaction.

The ready availability of 2*H*-azirines has spurred considerable activity in the chemistry of these strained heterocycles.[1,2] Photochemical and thermal cleavage preferences in 2*H*-azirines appear to be quite distinct.[1,2] Photolysis of 2*H*-azirines leads to irreversible ring opening and the formation of nitrile ylides as intermediates.[3,4] These species may be intercepted by a variety of dipolarophiles to form five-membered heterocyclic rings.[5,6] In certain cases the initially formed 1,3-dipole can be intramolecularly trapped to give novel azabicyclohexenes.[7-10] For example, irradiation of allyl-substituted 2*H*-azirines produces 2-azabicyclo[3.1.0]hex-2-enes via an unusual 1,1-cycloaddition reaction of the 1,3-dipole.[7] Products formed on thermal excitation of the 2*H*-azirine system, on the other hand, appear to involve vinyl nitrenes as intermediates.[11-23] Since examples of the direct addition of vinyl nitrenes to olefins to give aziridines have appeared infrequently in the literature,[24] we decided to investigate the thermal chemistry of a number of allyl-substituted 2*H*-azirines in order to determine whether the initially generated vinyl nitrene would undergo addition to the neighboring double bond. We report here the results of these studies.[25]

Results

The synthesis of the 2-allyl-substituted 2*H*-azirine system was straightforward and involved a modified Neber reaction in which variously substituted 2-methyl-1-phenyl-4-penten-1-ones were allowed to react with dimethylhydrazine. Treatment of the resulting dimethylhydrazone with methyl iodide followed by reaction with base gave the desired 2-allyl-substituted 2*H*-azirines in good yield.

We initially examined the thermal behavior of 2-allyl-2-methyl-3-phenyl-2*H*-azirine (**1**). Thermolysis of **1** in toluene



1, R = H **2**, R = H **3**, R = H
4, R = CH_3 **5**, R = CH_3 **6**, R = CH_3

at 195 °C for 180 h or in the absence of solvent at 250 °C for 1.5 h gave 1-methyl-2-phenyl-3-azabicyclo[3.1.0]hex-2-ene (**2**, 90%) and 3-methyl-2-phenylpyridine (**3**, 10%). The identity of **2** was determined by its straightforward spectral characteristics [NMR (100 MHz) τ 9.55 (t, 1 H, J = 4.0 Hz), 9.04 (dd, 1 H, J = 8.0, 4.0 Hz), 8.57 (s, 3 H), 8.36 (m, 1 H), 6.25 (dd, 1 H, J = 17.5, 2.0 Hz), 6.02 (dd, 1 H, J = 17.5, 5.0 Hz), 2.2–2.8 (m, 5 H)] as well as its facile conversion into **3** on further heating. Thermolysis of the closely related 2-(1-methylallyl)-substituted azirine **4** gave 1,6-dimethyl-2-phenyl-3-azabicyclo[3.1.0]hex-2-ene (**5**, 58%) as a 1:1 mixture of endo and exo isomers as well as 3,4-dimethyl-2-phenylpyridine (**6**, 25%). The mixture of exo and endo isomers of **5** was smoothly converted into pyridine **6** on further heating.

Subjection of azirine **7** to similar pyrolysis conditions gave 1,4-dimethyl-2-phenyl-3-azabicyclo[3.1.0]hex-2-ene (**8**, 71%), 2-phenyl-3-methyl-5-vinyl-Δ^1-pyrroline (**9**, 21%) as an inseparable cis–trans mixture, and a trace amount (<5%) of

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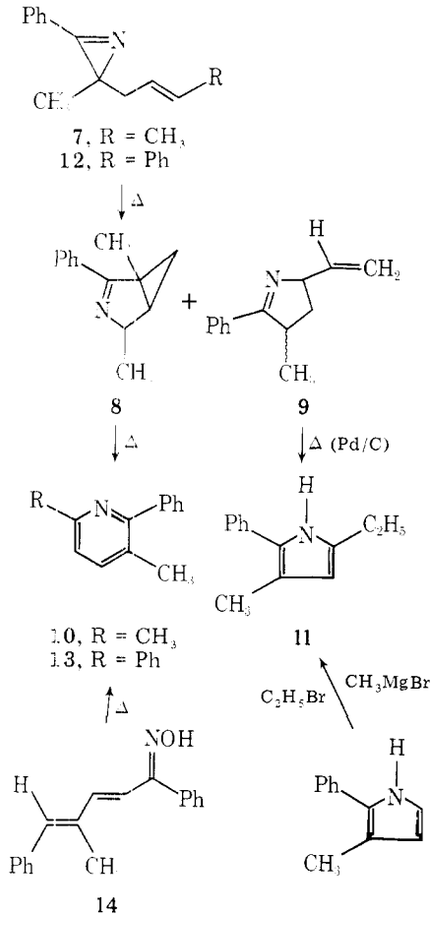
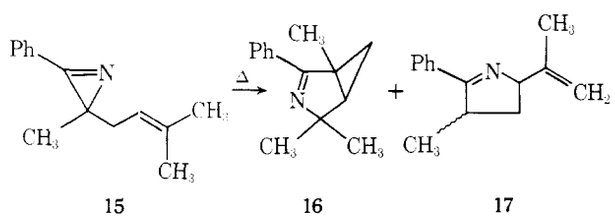


2,5-dimethyl-6-phenylpyridine (**10**). The structure of Δ^1-pyrroline **9** was confirmed by refluxing **9** in toluene in the presence of palladium on carbon (5%) for 48 h. This resulted in the quantitative formation of 2-phenyl-3-methyl-5-ethylpyrrole (**11**). The structure of pyrrole **11** was verified by comparison with an authentic sample prepared from the reaction of 2-phenyl-3-methylpyrrole anion with ethyl bromide. That Δ^1-pyrroline **9** did not arise from 3-azabicyclohexene **8** was shown by heating **8** under conditions similar to those used for the pyrolysis of azirine **7**. Under these conditions **8** was converted exclusively into pyridine **10**.

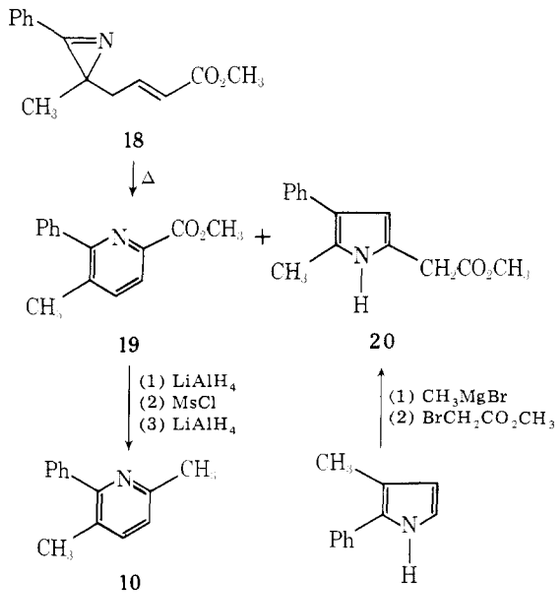
The thermal rearrangement of (*E*)-2-cinnamyl-2-methyl-3-phenyl-2*H*-azirine (**12**) was also studied. Thermolysis of **12** gave 2,6-diphenyl-3-methylpyridine (**13**, 49%) as the only characterizable material. The structure of **13** was verified by comparison with an authentic sample prepared from the thermolysis of oxime **14**. In this case there was no detectable quantities of a 3-aza-substituted bicyclohexene. It would appear as though the initially formed azabicyclohexene is converted into pyridine **13** at a faster specific rate than it is formed.

We also studied the thermal behavior of azirine **15** and found that it was converted to 1,4,4-trimethyl-2-phenyl-3-azabicyclo[3.1.0]hex-2-ene (**16**, 60%) [NMR (100 MHz) τ 9.44 (t, 1 H, J = 4.0 Hz), 9.20 (dd, 1 H, J = 8.0, 4.0 Hz), 8.77 (s, 3 H), 8.67 (s, 3 H), 8.57 (s, 3 H), 8.53 (dd, 1 H, J = 8.0, 4.0 Hz),



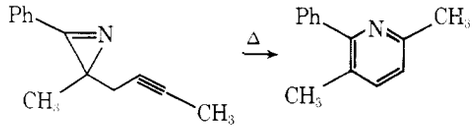
2.2–2.9 (m, 5 H)] and a 1:1 cis–trans mixture of isomeric 2-phenyl-3-methyl-5-(2-propenyl)-Δ^1-pyrrolines (**17**, 30%).

We also decided to investigate the thermal behavior of a 2*H*-azirine which possessed an electron-withdrawing substituent on the double bond. To this end we synthesized methyl 4-(2-methyl-3-phenyl-2*H*-azirin-2-yl)-2-butenoate (**18**). Heating a sample of **18** in toluene at 180 °C gave rise to



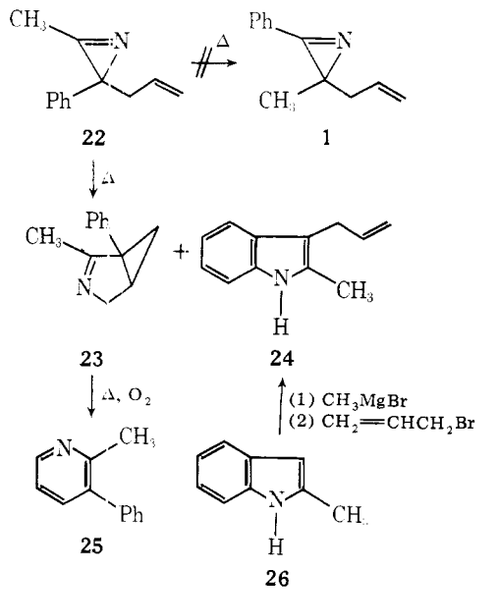
pyridine **19** (47%) and pyrrole **20** (37%). The structure of **19** was confirmed by its straightforward conversion ($LiAlH_4$, MsCl, $LiAlH_4$) to 2,5-dimethyl-6-phenylpyridine (**10**),[26] while the identity of **20** was established by comparison with an independently synthesized sample prepared from the reaction of 2-phenyl-3-methylpyrrole anion with methyl α-bromoacetate.

Further examples which would support the generality of these rearrangements were sought. With this in mind, we decided to prepare an acetylenic 2*H*-azirine with the expectation that this system might undergo some interesting thermal chemistry. Flash vacuum pyrolysis (500 °C at 0.005 mm) of a sample of 2-(2-butynyl)-2-methyl-3-phenyl-2*H*-azirine (**21**) through a quartz tube gave 2,5-dimethyl-6-



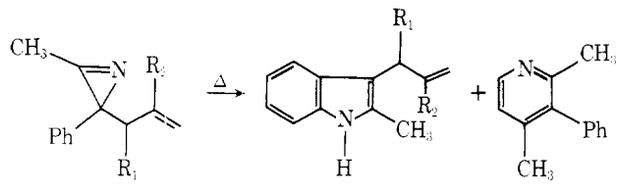
phenylpyridine (**10**) as the only characterizable product in 34% isolated yield.

Attention was next turned to the thermal behavior of the closely related 2-allyl-3-methyl-2-phenyl-2*H*-azirine system. Thermolysis of azirine **22** in toluene at 180 °C for 28 h gave rise to a mixture of 2-methyl-1-phenyl-3-azabicyclo[3.1.0]hex-2-ene (**23**, 31%), 3-allyl-2-methylindole (**24**, 58%), and a trace amount (5%) of 2-methyl-3-phenylpyridine (**25**). The identity of azabicyclohexene **23** was determined by its straightforward spectral characteristics [NMR ($CDCl_3$, 60 MHz) τ 9.48 (t, 1 H, J = 4.0 Hz), 8.56 (dd, 1 H, J = 8.0, 4.0 Hz), 8.13 (t, 3 H, J = 2.0 Hz), 7.98 (m, 1 H), 6.30 (dq, 1 H, J = 17.5, 2.0 Hz), 5.92 (ddq, 1 H, J = 17.5, 5.0, 2.0 Hz), 2.80 (s, 5 H)] as well as its facile conversion into 2-methyl-3-phenylpyridine (**25**) on further heating. The structure of indole **24** was verified by comparison with an authentic sample prepared from the rection of 2-methylindole (**26**) with allyl bromide. Careful monitoring of the reaction showed that **22** was not converted



to **1** by a Cope rearrangement, as had been encountered with the closely related cyclopropene system.[27]

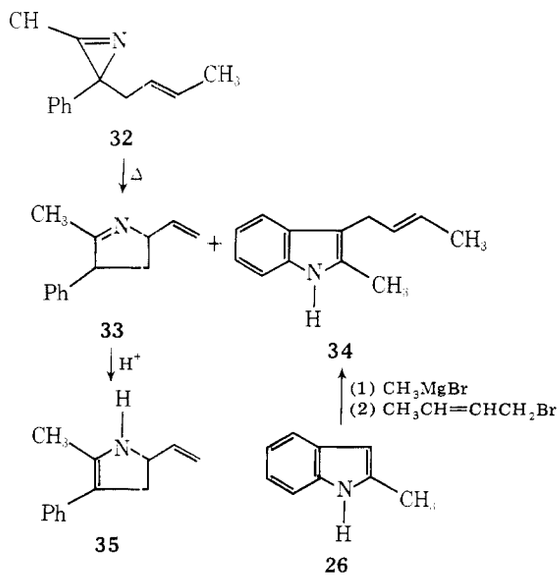
Subjection of azirine **27** to similar pyrolysis conditions gave 2-methyl-3-(1-methylallyl)indole (**28**) and 2,4-dimethyl-3-phenylpyridine (**29**) as the major thermal products. The



27, $R_1 = CH_3$; $R_2 = H$ **28**, $R_1 = CH_3$; $R_2 = H$ **29**
30, $R_1 = H$; $R_2 = CH_3$ **31**, $R_1 = H$; $R_2 = CH_3$

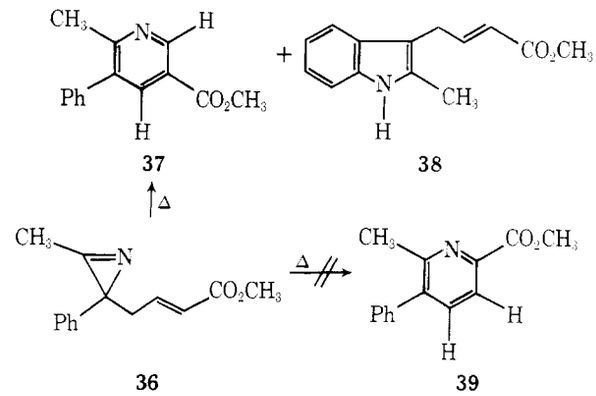
structure of indole **28** was verified by comparison with an authentic sample prepared from the reaction of 2-methylindole (**26**) with 3-chloro-1-butene. In this case there were no detectable quantities of a 3-aza-substituted bicyclohexene. Thermolysis of the closely related 2-(2-methylallyl)-3-methyl-2-phenyl-2*H*-azirine (**30**) gave indole **31** (89%) as the only characterizable material. The structure of this material was verified by comparison with an authentic sample.

When the thermolysis of azirine **32** was carried out in toluene at 180 °C, a mixture of the cis and trans isomers of Δ^1-pyrroline **33** as well as indole **34** were isolated in good yield.



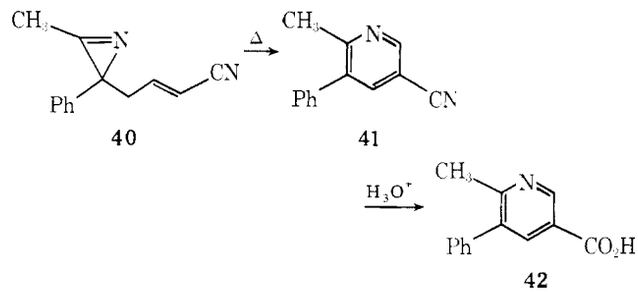
Further evidence supporting the structure of Δ^1-pyrroline was obtained by its ready conversion to **35** on treatment with catalytic quantities of *p*-toluenesulfonic acid. Confirmation of the structure of indole **34** was obtained by comparison with an authentic sample prepared by treating 2-methylindole with 1-bromo-2-butene.

We have also examined the thermolysis of methyl (*E*)-4-(3-methyl-2-phenyl-2*H*-azirin-2-yl)-2-butenoate (**36**) and find



that this compound exhibits substantially different chemical behavior from that encountered with the closely related structural isomer **18**. Heating a sample of azirine **36** in toluene at 185 °C gave 2-methyl-3-phenyl-5-carbomethoxypyridine (**37**, 70%) and methyl (*E*)-4-(2-methylindol-3-yl)-2-butenoate (**38**, 30%) as the only characterizable products. The structure of indole **38** was established by an independent synthesis. Structure **37** could be distinguished from the isomeric 2-methyl-3-phenyl-6-carbomethoxypyridine (**39**) by examination of its unique NMR spectrum, which showed methyl singlets at τ 7.40 (3 H) and 6.04 (3 H), the aromatic protons as a multiplet at τ 2.48–2.72 (5 H), and the pyridine ring protons as doublets at τ 1.86 and 0.90 (J = 2.0 Hz). The magnitude of the coupling constant (J = 2.0 Hz) is consistent with the assigned meta disposition of the ring protons. Pyridine **39** would be expected to exhibit a coupling constant of ca. 8.0 Hz for the ring protons, as was observed with pyridine **19** (see Experimental Section). Unequivocal proof for the structure of pyridine **37** was obtained by comparison with an authentic sample provided by Professor Julia.[28]

A related rearrangement was also encountered when azirine **40** was subjected to thermolysis. The major component iso-

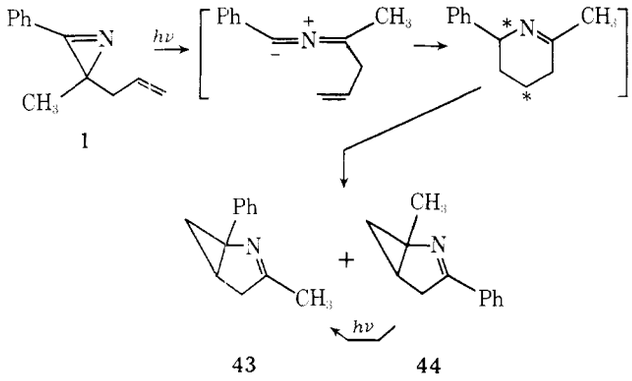


lated (77%) was identified as 2-methyl-3-phenyl-5-cyanopyridine (**41**) on the basis of its spectral properties [NMR (100 MHz) τ 7.48 (s, 3 H), 2.58–2.92 (m, 5 H), 2.35 (d, 1 H, J = 2.0 Hz), 1.38 (d, 1 H, J = 2.0 Hz)] and by hydrolysis to the known 6-methyl-5-phenylnicotinic acid (**42**).[28]

Discussion

Previous papers from this laboratory have established that the irradiation of allyl-substituted 2*H*-azirines produces 2-azabicyclo[3.1.0]hex-2-enes as primary photoproducts.[7] The photoreaction has been proposed to proceed via C–C bond cleavage and generation of a bent nitrile ylide intermediate

(carbene-like). Attack of the carbene carbon of the dipole onto the terminal position of the neighboring double bond generates a six-membered ring trimethylene intermediate which subsequently collapses to the observed 2-azabicyclohexene ring system.



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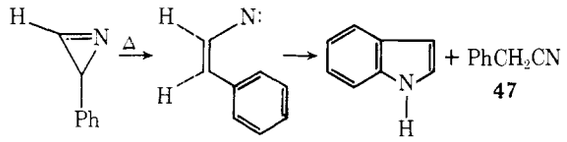
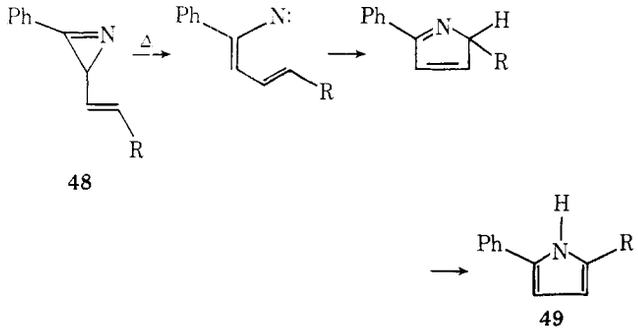
43 44

In contrast to the photochemical results, the thermal transformations observed with these systems can best be rationalized in terms of an equilibration of the 2*H*-azirine with a transient vinyl nitrene which subsequently rearranges to the final 3-azabicyclohexene ring system. The products formed on thermal decomposition of 2*H*-azirines generally appear to involve C–N rather than C–C bond cleavage.[11-23] In some cases C–N bond cleavage ultimately leads to fragmentation of the three-membered ring with the subsequent formation of a nitrile and carbene,[11] and in other cases it results in the formation of indoles[14] and pyrroles.[22,29] Thus, Isomura and co-workers report that the thermolysis of 2-phenyl-2*H*-azirine (**45**) produces a 1:1 mixture of indole (**46**) and phenyl aceto-



45 46 47

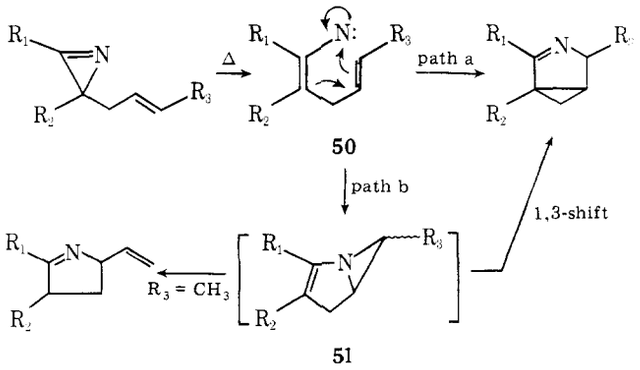
nitrile (**47**) in 86% isolated yield.[13] The most obvious mechanism for the formation of **46** involves the generation of a vinyl nitrene intermediate followed by electrocyclic closure. Similarly, the thermal rearrangements of a series of vinyl-substituted 2*H*-azirines are best accounted for by C–N bond cleavage, leading to a vinyl nitrene intermediate.[22,29] In fact,



48 49

Nishiwaki and co-workers[17,21,30] have shown that the vinyl nitrene intermediate generated from the thermolysis of the 2*H*-azirine ring can actually be trapped with phosphines.

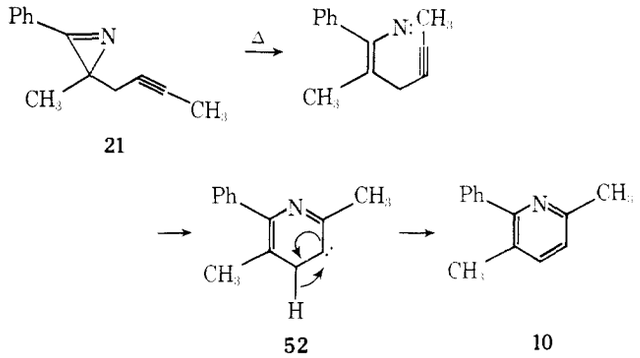
The formation of 3-azabicyclo[3.1.0]hex-2-enes as reaction products with the above systems suggests that the route by which the initially generated vinyl nitrene intermediate rearranges to the final product (path a) involves attack of the neighboring π system on the electrophilic singlet nitrene followed by bond reorganization. An equally plausible mecha-



50 51

nism (path b) involves intramolecular addition of the nitrene onto the adjacent π bond to give a bicycloaziridine (**51**) as a transient intermediate. This species can subsequently rearrange to the observed product by a 1,3-sigmatropic shift. The allowed concerted thermal 1,3-shift requires an inversion of the migration center, and this seems sterically prohibited in this system. Although a "forbidden" 1,3-suprafacial concerted process cannot be excluded,[31] the rearrangement of **51** to the observed azabicyclohexene probably involves a diradical intermediate by analogy with the results obtained with the parent carbocycle.[32,33] Several examples of intramolecular addition to nitrenes onto adjacent double bonds are available in the literature[34-36] and provide reasonable chemical analogy for path b. Additional evidence favoring this pathway is provided by the isolation of Δ^1-pyrrolines **9**, **17**, and **33** from the thermolysis of azirines **7**, **15**, and **32**. The formation of the Δ^1-pyrroline ring system can be rationalized as proceeding via a homo[1,5] hydrogen migration from the endo isomer of bicycloaziridine **51**. This transformation is related to the homo[1,5] sigmatropic reaction which occurs on thermolysis of bicyclo[3.1.0]hex-2-ene-*endo*-6-carboxaldehydes.[37,38]

The formation of pyridine **10** from azirine **21** is also com-

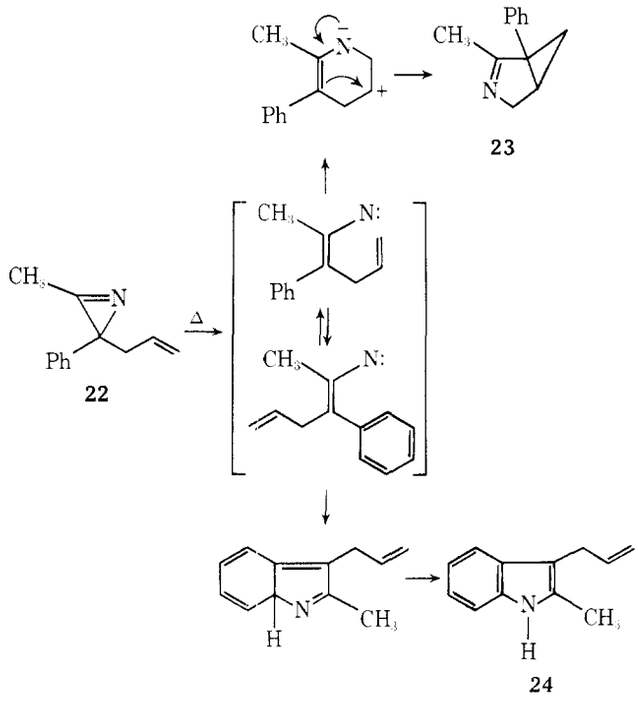


21 52 10

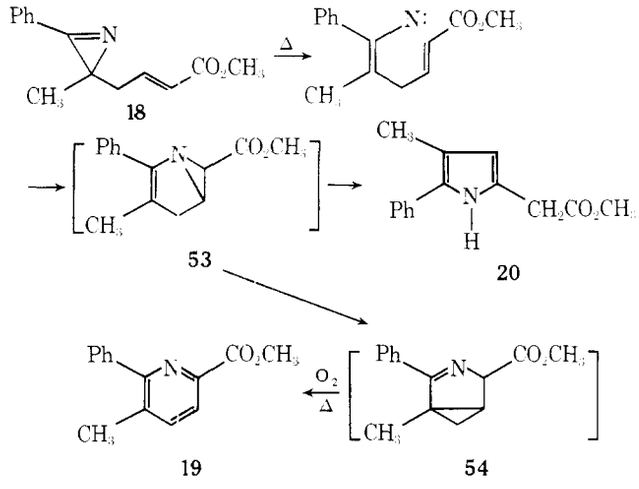
patible with a vinyl nitrene intermediate. In this case, attack by the neighboring acetylenic functionality on the nitrene will lead to carbene **52**, which would be expected to undergo a facile hydrogen migration to produce **10**.

Whereas 3-phenyl-2-methyl-2-allyl-substituted 2*H*-azirines (e.g., **1**) give only 3-azabicyclohexenes on thermolysis, the isomeric 3-methyl-2-phenyl-2-allyl-substituted azirines (e.g., **22**) also produce significant quantities of indoles. The distribution of products with the latter system will be controlled by the rates of nitrene attack on the double bond vs. electrocyclization on the adjacent phenyl ring. It should be noted that there are several examples in the literature which provide good analogy for the cyclization of a butadienyl nitrene to a five-membered ring.[22,29,39]

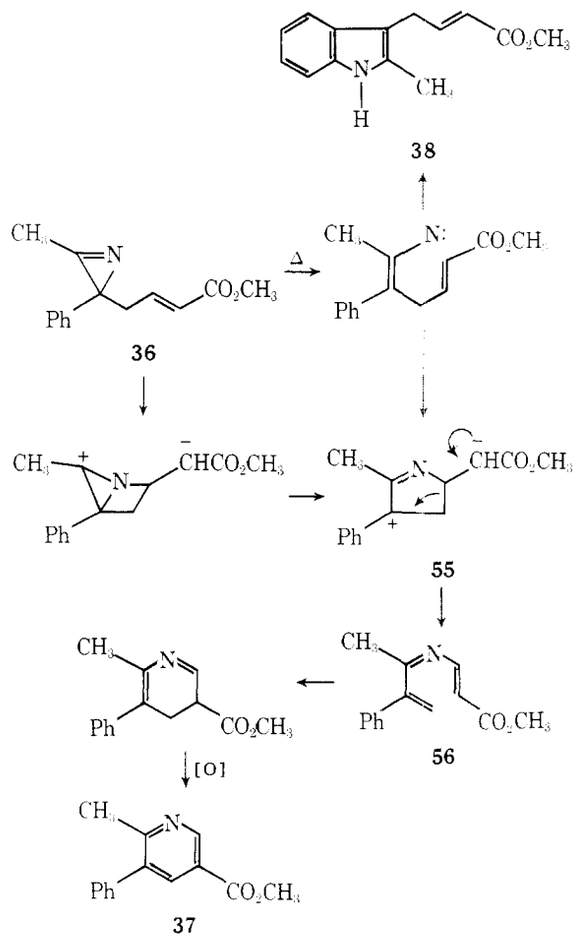
The thermolysis of the carbomethoxy-substituted allyl 2*H*-azirine **18** represents a novel reaction and merits some comment. In simplest valence bond terms, this transformation is explicable in terms of an attack by the vinyl nitrene onto the neighboring double bond to give a short-lived bicycloaziridine



53. Heterolytic cleavage of the C–N bond followed by proton reorganization would furnish pyrrole **20.** The initially produced six-ring zwitterion (or structure **53**) would also be expected to afford the azabicyclohexene ring system **54,** which could in turn give rise to pyridine **19** on further heating.



The conversion of the isomeric carbomethoxy-substituted 2*H*-azirine **36** to pyridine **37,** on the other hand, proceeds by an entirely different pathway. Although information on the mechanistic details of this reaction is minimal, a tentative yet reasonable rationale can be advanced. Thus, the formation of pyridine **37** may be attributed to conjugate addition of the vinyl nitrene onto the electron-deficient double bond. The initially produced five-ring zwitterion **55** can then undergo a subsequent fragmentation to give azatriene **56.** This species would be expected to undergo a ready electrocyclic closure followed by oxidation to ultimately afford pyridine **37.** An alternative path involving nucleophilic attack by the available lone pair of electrons in starting material onto the conjugated double bond also seems possible. A similar mechanism would account for the conversion of azirine **40** to pyridine **41.** The difference in behavior of the isomeric carbomethoxy-substituted azirines (i.e., **18** vs. **37**) can be attributed to the difference in nucleophilicity of the nitrogen atom present in starting material or in the vinyl nitrene intermediate.



Experimental Section

All melting and boiling points are uncorrected. Elemental analyses were performed by Atlantic Microlabs, Atlanta, Ga. The infrared absorption spectra were determined on a Perkin-Elmer Model 137 Infracord spectrophotometer. The ultraviolet absorption spectra were measured with a Cary Model 14 recording spectrophotometer using 1-cm matched cells. The proton magnetic resonance spectra were determined at 100 MHz using a Jeolco ML-100 and a Varian XL-100 spectrometer. Mass spectra were determined with a Perkin-Elmer RMU6 mass spectrometer at an ionizing voltage of 70 eV.

Thermolysis of 2-Allyl-2-methyl-3-phenyl-2*H*-azirine (1). A solution containing 700 mg of azirine **1** in 15 mL of toluene was heated at 195 °C in a sealed tube for 180 h. Removal of the solvent under reduced pressure left a yellow oil which contained two components. Liquid–liquid partition chromatography of the mixture gave 1-methyl-2-phenyl-3-azabicyclo[3.1.0]hex-2-ene (**2**; 637 mg, 92%) as a clear oil: NMR (CCl_4, 100 MHz) τ 9.55 (t, 1 H, J = 4.0 Hz), 9.04 (dd, 1 H, J = 8.0, 4.0 Hz), 8.57 (s, 3 H), 8.36 (m, 1 H), 6.25 (dd, 1 H, J = 17.5, 2.0 Hz), 6.02 (dd, 1 H, J = 17.5, 5.0 Hz), 2.2–2.8 (m, 5 H). When the signals at τ 6.25 and 6.02 were irradiated with an external field, the multiplet at τ 8.36 collapsed to a doublet of doublets with J = 8.0 and 4.0 Hz. IR (neat) 3055, 2950, 2910, 2840, 1593, 1570, 1492, 1445, 1385, 1340, 1000, 775, 698 cm^{-1}; UV (cyclohexane) 239 nm (ϵ 11 000); *m/e* 171 (M^+ and base), 156, 143, 115, 77.

Anal. Calcd for $C_{12}H_{13}N$: C, 84.17; H, 7.65; N, 8.18. Found: C, 84.08; H, 7.62; N, 8.04.

The minor component isolated from the column (70 mg, 10%) was identified as 3-methyl-2-phenylpyridine (**3**) by comparison with an authentic sample:[40] picrate mp 164–165 °C (lit.[40] mp 163–164 °C); NMR (CCl_4, 100 MHz) τ 7.68 (s, 3 H), 3.00 (dd, 1 H, J = 8.0, 4.5 Hz); IR (neat) 3030, 2941, 1582, 1570, 1430, 803, 787, 746, 701 cm^{-1}.

Subjection of azabicyclohexene **2** to 195 °C for 85 h resulted in its partial conversion to 3-methyl-2-phenylpyridine (**3**).

Thermolysis of 2-Methyl-2-(1-methylallyl)-3-phenyl-2*H*-azirine (4). A solution containing 200 mg of azirine **4**[7] in 15 mL of toluene was heated at 195 °C in a sealed tube for 182 h. Removal of the solvent under reduced pressure left a yellow oil which was subjected to thick-layer chromatography using a 1:5 ether–cyclohexane mixture as the eluent. The first band consisted of a 1:1 mixture of the endo and exo isomers of 1,6-dimethyl-2-phenyl-3-

azabicyclo[3.1.0]hex-2-ene (**5**, 58%). The two isomers were eventually separated by extensive multielutions on a thick-layer plate. The endo isomer showed the following spectral properties: NMR (CCl_4, 100 MHz) τ 9.25 (d, 3 H, J = 6.0 Hz), 8.78 (dq, 1 H, J = 8.0, 6.0 Hz), 8.58 (s, 3 H), 8.38 (ddd, 1 H, J = 8.0, 7.0, 2.0 Hz), 6.44 (dd, 1 H, J = 18.0, 2.0 Hz), 6.07 (dd, 1 H, J = 18.0, 7.0 Hz), 2.2–2.8 (m, 5 H); IR (neat) 3030, 2955, 2910, 1595, 1570, 1490, 1445, 1380, 1340, 1320, 1000, 781, 758, 697 cm^{-1}; UV (cyclohexane) 237 nm (ϵ 12 000); m/e 185 (M^+), 184 (base), 170, 155, 143, 129, 115.

The exo isomer exhibited the following spectral properties: NMR (CCl_4, 100 MHz) τ 9.30 (p, 1 H, J = 6.0 Hz), 8.81 (d, 3 H, J = 6.0 Hz), 8.75 (ddd, 1 H, J = 6.0, 5.0, 2.0 Hz), 8.62 (s, 3 H), 6.22 (dd, 1 H, J = 17.0, 2.0 Hz), 6.06 (dd, 1 H, J = 17.0, 5.0 Hz), 2.20–2.80 (m, 5 H); IR (neat) 3025, 2950, 2915, 1592, 1565, 1490, 1445, 1388, 1340, 1307, 1000, 780, 740, 695 cm^{-1}; UV (cyclohexane) 236 nm (ϵ 12 000); MS m/e 185 (M^+), 184 (base), 170, 155, 143, 129, 115.

The second band isolated from the thick-layer plate (25%) was identified as 3,4-dimethyl-2-phenylpyridine (**6**) by comparison with an authentic sample:[26] picrate mp 171–172 °C (lit.[26] mp 174–175 °C); NMR (CCl_4, 100 MHz) τ 7.76 (s, 3 H), 7.68 (s, 3 H), 3.04 (d, 1 H, J = 5.0 Hz), 2.62 (m, 5 H), 1.70 (d, 1 H, J = 5.0 Hz); IR (neat) 3050, 2950, 1580, 1444, 1400, 1382, 1183, 1060, 1010, 824, 783, 747, 700 cm^{-1}.

Thermolysis of a sample of either the *exo*- or *endo*-azabicyclohexene **5** in toluene at 195 °C for 72 h gave pyridine **6** as the exclusive product.

Thermolysis of (*E*)-2-(2-Butenyl)-2-methyl-3-phenyl-2*H*-azirine (7). A solution containing 100 mg of azirine **7**[7] in 10 mL of toluene was heated at 195 °C in a sealed tube for 166 h. Removal of the solvent left a yellow oil which was subjected to thick-layer chromatography using a 1:2 mixture of ether–cyclohexane as the eluent. The first fraction (21%) contained an inseparable mixture (1:1) of the cis and trans isomers of 2-phenyl-3-methyl-5-vinyl-Δ^1-pyrroline (**9**): NMR (CCl_4, 100 MHz) τ 8.82 and 8.84 (two doublets, 3 H, J = 7.0 Hz), 8.4–8.7 (m, 1 H), 8.10 (m, 1 H), 6.64 (m, 1 H), 5.40 (m, 1 H), 4.7–5.1 (m, 2 H), 3.8–4.2 (m, 1 H), 2.1–3.0 (m, 5 H); IR (neat) 3080, 3020, 2960, 2925, 2865, 1639, 1605, 1570, 1492, 1445, 1373, 1330, 1267, 1019, 990, 920, 775, 695 cm^{-1}; MS m/e 185 (M^+), 170, 143, 115, 77; UV (methanol) 243 nm (ϵ 13 200).

A 100-mg sample of Δ^1-pyrroline **9** in 50 mL of toluene containing 100 mg of 5% palladium on carbon was heated at reflux for 48 h. Removal of the catalyst followed by evaporation of the solvent left 93 mg of 2-phenyl-3-methyl-5-ethylpyrrole (**11**): NMR (CCl_4, 100 MHz) τ 8.79 (t, 3 H, J = 8.0 Hz), 7.81, (s, 3 H), 7.44 (q, 2 H, J = 8.0 Hz), 4.32 (d, 1 H, J = 3.0 Hz, collapsed to a singlet with D_2O wash), 2.6–3.0 (m, 5 H), 2.0–2.6 (1 H, broad s, exchanged with D_2O); IR (neat) 3420, 3050, 2960, 2920, 2860, 1600, 1510, 1485, 1440, 1375, 1335, 1140, 800, 760, 695, 640 cm^{-1}; MS m/e 185 (M^+), 170, 147, 105, 77.

Anal. Calcd for $C_{13}H_{15}N$: C, 84.28; H, 8.16; N, 7.56. Found: C, 84.10; H, 8.05; N, 7.82.

The second band isolated from the thick-layer plate of the crude thermolysis mixture (71%) contained a clear oil whose structure was assigned as *exo*-1, 4-dimethyl-2-phenyl-3-azabicyclo[3.1.0]hex-2-ene (**8**): NMR (CCl_4, 100 MHz) τ 9.52 (t, 1 H, J = 4.0 Hz), 9.04 (dd, 1 H, J = 8.0, 4.0 Hz), 8.75 (d, 3 H, J = 7.0 Hz), 8.54 (dd, 1 H, J = 8.0, 4.0 Hz), 8.04 (s, 3 H), 6.13 (q, 1 H, J = 7.0 Hz), 2.1–2.8 (m, 5 H); IR (neat) 3060, 3025, 2960, 2920, 2855, 1592, 1568, 1490, 1442, 1385, 1340, 1290, 1210, 1170, 1064, 1020, 1000, 990, 775, 700 cm^{-1}; UV (cyclohexane) 238 nm (ϵ 10 200); MS m/e 185 (M^+), 184 (base), 170, 155, 141, 129, 115, 77.

Anal. Calcd for $C_{13}H_{15}N$: C, 84.28; H, 8.16; N, 7.56. Found: C, 84.06; H, 8.20; N, 7.40.

The NMR spectrum of the crude reaction mixture showed the presence of small quantities (ca. 5%) of 2,5-dimethyl-6-phenylpyridine (**10**) (singlets at τ 7.72 and 7.52). Thermolysis of a sample of azabicyclohexene **8** at 195 °C for 96 h gave pyridine **10** as the exclusive product,[26] picrate mp 139–140 °C (lit.[26] mp 134–135 °C).

Independent Synthesis of 2-Phenyl-3-methyl-5-ethylpyrrole (11). The structure of the pyrrole obtained from the palladium-induced isomerization of Δ^1-pyrroline **9** was established by comparison with an independently synthesized sample. A solution containing 17.3 g of 2-methyl-1-phenyl-4-penten-1-one in 500 mL of methanol was ozonized at −78 °C. Standard workup conditions afforded 3-methyl-4-phenyl-4-oxybutanal in 92% yield: bp 94–95 °C (0.1 mm); NMR ($CDCl_3$, 60 MHz) τ 8.88 (d, 3 H, J = 7.5 Hz), 7.58 (dd, 1 H, J = 18.0, 6.0 Hz), 6.94 (dd, 1 H, J = 18.0, 8.0 Hz), 6.10 (dp, 1 H, J = 7.5, 6.0 Hz), 2.46–2.80 (m, 3 H), 2.0–2.4 (m, 2 H), 0.3 (s, 1 H); IR (neat) 3010, 2940, 2820, 2700, 1725, 1675 cm^{-1}; MS m/e 176 (M^+), 158, 148, 134, 105 (base), 77.

To a solution containing 3.5 g of the above aldehyde in 40 mL of methanol was added 15 mL of concentrated ammonium chloride and 10 mL of concentrated ammonia. The mixture was heated at reflux for 1 h, cooled, and extracted with ether. The ether layer was washed with water, dried over magnesium sulfate, and concentrated under reduced pressure to give 2-phenyl-3-methylpyrrole in quantitative yield: NMR (CCl_4, 60 MHz) τ 7.80 (s, 3 H), 4.10 (t, 1 H, J = 3.0 Hz), 3.62 (t, 1 H, J = 3.0 Hz), 2.85 (s, 5 H), 2.4 (broad s, 1 H); IR (neat) 3380, 3030, 2910, 1595, 1495, 1470, 1440, 1400, 1255, 1190, 1110, 1075, 1060, 1010, 897, 842, 765, 725, 699 cm^{-1}; MS m/e 157 (M^+), 156 (base), 129, 128, 105, 77.

To a solution containing 1.57 g of 2-phenyl-3-methylpyrrole in 20 mL of ether at 0 °C was added 3.6 mL of a 2.9 M methylmagnesium bromide solution. After stirring for 30 min, a 2.0-g sample of ethyl bromide was added and the resulting mixture was allowed to stir for 12 h at room temperature. Removal of the solvent followed by thick-layer chromatography gave a pure sample of 2-phenyl-3-methyl-5-ethylpyrrole (31%) which was identical with that obtained from the palladium-induced isomerization of Δ^1-pyrroline **9**.

Preparation and Thermolysis of (*E*)-2-Cinnamyl-2-methyl-3-phenyl-2*H*-azirine. A sample of azirine **12** was prepared by the method previously outlined:[7] bp 132–136 °C (0.2 mm); NMR (CCl_4, 100 MHz) τ 8.58 (s, 3 H), 7.56 (dd, 1 H, J = 14.0, 7.0 Hz), 7.34 (dd, 1 H, J = 14.0, 7.0 Hz), 3.76 (dt, 1 H, J = 16.0, 7.0 Hz), 3.54 (d, 1 H, J = 16.0 Hz), 2.0–3.0 (m, 10 H); IR (neat) 3080, 3060, 3020, 2920, 1724, 1594, 1485, 1450, 1374, 1192, 961, 761, 748, 688 cm^{-1}; UV (cyclohexane) 247 nm; MS m/e 247 (M^+), 246, 245, 121, 119, 117, 105, 91, 77.

Anal. Calcd for $C_{18}H_{17}N$: C, 87.41; H, 6.93; N, 5.66. Found: C, 87.20; H, 6.85; N, 5.62.

Distillation of the above azirine through a 9 in Vigreux column at 200 °C gave a 49% yield of 2,6-diphenyl-3-methylpyridine (**13**): bp 165–168 °C (0.03 mm); picrate mp 172–173 °C; NMR (CCl_4, 100 MHz) τ 7.72 (s, 3 H), 2.4–2.9 (m, 10 H), 1.98 (m, 2 H); IR (neat) 3055, 3025, 2920, 1582, 1560, 1490, 1455, 1430, 1372, 1309, 1264, 1302, 1065, 1015, 830, 784, 760, 749, 692, 633 cm^{-1}; MS m/e 245 (M^+), 244 (base), 77.

An authentic sample of pyridine **13** was independently synthesized according to the procedure of Scholtz[41] and was identical to that obtained from the thermolysis of azirine **12**.

Thermolysis of 2-Methyl-2-(3-methyl-2-butenyl)-3-phenyl-2*H*-azirine (15). A solution containing 400 mg of azirine **15**[7] in 12 mL of toluene was heated at 195 °C in a sealed tube for 58 h. Removal of the solvent left a yellow oil which was subjected to thick-layer chromatography using a 2:5 mixture of ether–cyclohexane as the eluent. The material isolated in the first band contained a 1:1 mixture of isomeric 2-phenyl-3-methyl-5-(2-propenyl)-Δ^1-pyrrolines (**17**). Isomer A: NMR (CCl_4, 100 MHz) τ 8.82 (d, 3 H, J = 7.5 Hz), 8.26 (s, 3 H), 8.12 (t, 1 H, J = 8.0 Hz), 8.08 (t, 1 H, J = 8.0 Hz), 6.55 (m, 1 H), 5.42 (broad t, 1 H, J = 8.0 Hz), 5.22 (broad s, 1 H), 5.05 (broad s, 1 H), 2.0–2.8 (m, 5 H); IR (neat) 3020, 2940, 1650, 1640, 1575, 1515, 1450, 1340, 1240, 1160, 1125, 1075, 1030, 900, 780, 694 cm^{-1}; MS m/e 199 (M^+), 184, 157, 115, 77.

The other isomer (B) showed the following spectral properties: NMR (CCl_4, 100 MHz) τ 8.81 (d, 3 H, J = 7.0 Hz), 8.19 (s, 3 H), 8.07 (m, 1 H), 7.50 (dt, 1 H, J = 12.0, 8.0 Hz), 6.58 (m, 1 H), 5.44 (dd, 1 H, J = 8.0, 7.0 Hz), 5.20 (broad s, 1 H), 5.11 (broad s, 1 H), 2.0–2.8 (m, 5 H); IR (neat) 3020, 2940, 1645, 1630, 1570, 1500, 1450, 1335, 1270, 1130, 1075, 1030, 1000, 901, 775, 697 cm^{-1}; MS m/e 199 (M^+), 184, 157, 104, 77.

The second band from the thick-layer plate contained a clear oil (60%) whose structure was assigned as 1,4,4-trimethyl-2-phenyl-3-azabicyclo[3.1.0]hex-2-ene (**16**) on the basis of its spectral data: NMR (CCl_4, 100 MHz) τ 9.44 (t, 1 H, J = 4.0 Hz), 9.20 (dd, 1 H, J = 8.0, 4.0 Hz), 8.77 (s, 3 H), 8.67 (s, 3 H), 8.57 (s, 3 H), 8.53 (dd, 1 H, J = 8.0, 4.0 Hz), 2.2–2.9 (m, 5 H); IR (neat) 3020, 2940, 1600, 1570, 1493, 1443, 1385, 1355, 1340, 1265, 1235, 1190, 1075, 1030, 1010, 1000, 975, 833, 780, 700 cm^{-1}; MS m/e 199 (M^+), 184, 157, 143, 128, 115, 77.

Anal. Calcd for $C_{14}H_{17}N$: C, 84.37; H, 8.60; N, 7.03. Found: C, 84.17; H, 8.45; N, 7.08.

Thermolysis of Methyl 4-(2-Methyl-3-phenyl-2*H*-azirin-2-yl)-2-butenoate (18). A solution containing 75 mg of (*E*)- or (*Z*)-azirinyl-2-butenoate **18**[42] in 10 mL of toluene was heated in a sealed tube at 180 °C for 124 h. Removal of the solvent under reduced pressure left a yellow oil which was subjected to thick-layer chromatography. The minor component (37%) isolated from the thick-layer plate was a colorless oil whose structure was assigned as methyl 4-methyl-5-phenylpyrrol-2-ylacetate (**20**) on the basis of its spectral data: NMR ($CDCl_3$, 100 MHz) τ 7.76 (s, 3 H), 6.34 (s, 2 H), 6.28 (s, 3 H), 4.07 (d, 1 H, J = 1.5 Hz), 2.54–2.90 (m, 5 H), 2.16 (broad s, 1 H, exchanged with D_2O); IR (neat) 3300, 2900, 1720, 1600, 1510, 1430, 1242, 1205, 1156, 1012, 792, 767, 697 cm^{-1}; UV (cyclohexane) 350 nm (ϵ 830), 278 (9700), 236 (7700); MS m/e 229 (M^+), 170, 158, 127, 105, 77.

Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.30; H, 6.50; N, 6.30.

The structure of this material was verified by comparison with an independently synthesized sample. To a solution containing 15.7 g of 2-phenyl-3-methylpyrrole in 15 mL of benzene at 10 °C was added 3.6 mL of a 2.9 M methylmagnesium bromide solution. After stirring for 30 min, a 2.5-g sample of methyl bromoacetate was added and the resulting mixture was allowed to stir at room temperature for 12 h. After careful hydrolysis, the solution was dried and concentrated under reduced pressure. The crude oil was purified by thick-layer chromatography using a 5% acetone–hexane mixture as the eluent to give a pure sample of methyl 4-methyl-5-phenylpyrrol-2-ylacetate (**20**) which was identical in every detail with the minor component obtained from the thermolysis of azirine **18**.

The major product obtained from the thermolysis of azirine **18** (47%) was identified as 2-phenyl-3-methyl-6-carbomethoxypyridine (**19**): NMR ($CDCl_3$, 100 MHz) τ 7.60 (s, 3 H), 6.01 (s, 3 H), 2.40–2.70 (m, 5 H), 2.0 and 2.32 (AB pattern, 2 H, J = 8.0 Hz); IR (neat) 2900, 1710, 1595, 1430, 1390, 1300, 1235, 1205, 1136, 1110, 1020, 922, 855, 787, 766, 743, 699 cm^{-1}; UV (cyclohexane) 342 nm (ϵ 630), 278 (6400), 238 (10 400); MS m/e 227 (M^+), 226 (base), 212, 170, 169, 168, 167, 166, 115, 105, 77.

Anal. Calcd for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77; N, 6.16. Found: C, 73.87; H, 5.68; N, 6.06.

The structure of this material was assigned on the basis of its conversion to 2,5-dimethyl-6-phenylpyridine (**10**).[26] To a slurry containing 25 mg of lithium aluminum hydride in 5 mL of ether was added 8.5 mg of the above pyridine in 1 mL of ether. The reaction mixture was stirred at room temperature for 12 h followed by a basic workup. The resulting oil was identified as 2-phenyl-3-methyl-6-hydroxymethylpyridine on the basis of its spectral properties: NMR ($CDCl_3$, 100 MHz) τ 9.7 (broad s, 1 H), 7.66 (s, 3 H), 5.29 (s, 2 H), 2.96 (d, 1 H, J = 8.0 Hz), 2.58 (m, 5 H), 2.48 (d, 1 H, J = 8.0 Hz); IR (KBr) 3175 (broad), 1590, 1575, 1450, 1430, 1220, 1185, 1073, 1006, 990, 830, 784, 764, 699 cm^{-1}; MS m/e 197, 196, 182, 180, 152, 105 (base), 77.

The above alcohol was dissolved in 1 mL of methylene chloride which contained 4 drops of triethylamine. This mixture was cooled to −15 °C, and then 3 drops of methanesulfonyl chloride was added. The mixture was allowed to stir for 15 min and then was taken up in methylene chloride and washed with a 10% hydrochloric acid solution followed by a saturated sodium bicarbonate solution. The organic layer was dried over magnesium sulfate and concentrated under reduced pressure. The resulting mesylate was taken up in 1 mL of ether to which 25 mg of lithium aluminum hydride was added. The resulting mixture was stirred at room temperature for 12 h. The normal basic workup afforded 6.2 mg of 2,5-dimethyl-6-phenylpyridine (**10**), which was identical in every detail with an authentic sample.[26]

Preparation and Thermolysis of 2-(2-Butynyl)-2-methyl-3-phenyl-2*H*-azirine (21). The azirine was prepared in the normal manner[7] from the corresponding trimethylhydrazonium iodide salt: bp 80–81 °C (0.03 mm); NMR ($CDCl_3$, 100 MHz) τ 8.52 (s, 3 H), 8.26 (t, 3 H, J = 2.7 Hz), 7.64 (dq, 1 H, J = 16.5, 2.7 Hz), 7.32 (dq, 1 H, J = 16.5, 2.7 Hz), 2.48–2.68 (m, 3 H), 2.16–2.36 (m, 2 H); IR (neat) 3050, 2940, 2230, 1735, 1600, 1580, 1495, 1450, 1370, 1235, 1195, 1155, 1072, 1010, 976, 926, 875, 763, 687 cm^{-1}; UV (cyclohexane) 242 nm (ϵ 14 000); MS m/e 183 (M^+), 182 (base), 168, 142, 131, 115, 105, 77.

Anal. Calcd for $C_{13}H_{13}N$: C, 85.20; H, 7.15; N, 7.64. Found: C, 85.14; H, 7.03; N, 7.68.

A 100-mg sample of the above azirine was sublimed (0.005 mm) through a 40-cm quartz tube which was held at 500 °C. The products formed were collected on a liquid nitrogen cold finger. The resulting residue was subjected to thick-layer chromatography using a 20% ether–hexane mixture as the eluent. The major component (34%) isolated from the thick-layer plate was identified as 2,5-dimethyl-6-phenylpyridine (**10**) by comparison with an authentic sample:[26] picrate mp 138–139 °C (lit.[26] mp 134–135 °C); NMR (benzene-d_6, 100 MHz) τ 7.97 (s, 3 H), 7.54 (s, 3 H), 3.55 and 2.98 (AB pattern, 2 H, J = 8.0 Hz), 2.70–2.90 (m, 3 H), 2.32–2.44 (m, 2 H); IR (neat) 3030, 2875, 1587, 1563, 1455, 1429, 1370, 1250, 1125, 1062, 1028, 818, 786, 735, 698 cm^{-1}; UV (cyclohexane) 281 nm (ϵ 5000), 238 (7200); MS m/e 183 (M^+), 182 (base), 168.

Thermolysis of 2-Allyl-3-methyl-2-phenyl-2*H*-azirine (22). A solution containing 100 mg of azirine **22**[7] in 20 mL of toluene was heated in a sealed tube at 180 °C for 28 h. Removal of the solvent left a yellow oil which was subjected to thick-layer chromatography using a 15% acetone–hexane mixture as the eluent. The first component isolated from the column (58%) was identified as 3-allyl-2-methylindole (**24**) on the basis of its spectroscopic properties and by comparison with an independently synthesized sample: NMR (CCl_4, 60 MHz) τ 7.87 (s, 3 H), 6.68 (d, 2 H), 4.85–5.30 (m, 2 H), 3.70–4.45 (m, 1 H), 2.5–3.2 (m, 5 H); IR (neat) 3400, 3030, 3020, 2965, 2910, 1630, 1600, 1475, 1455, 1425, 1385, 1292, 1215, 1150, 1070, 985, 910, 740 cm^{-1}; UV (cyclohexane) 290 nm (ϵ 4700), 283 (5950), 274 (6200), 268 (5500), 222 (28 000); MS m/e 171 (M^+), 170, 156, 144, 131 (base), 119, 117, 91, 77.

An authentic sample of 3-allyl-2-methylindole (**24**) was prepared by treating 2-methylindole (**26**) with allyl bromide. To a solution containing 325 mg of 2-methylindole in 5 mL of benzene was added 0.9 mL of a 2.9 M solution of methylmagnesium bromide in ether. The mixture was stirred at 25 ° C for 30 min, and then 300 mg of allyl bromide was added. The mixture was allowed to stir at 25 °C for 12 h and was then poured into 100 mL of a 1.0 M hydrochloric acid solution and extracted with ether. The ether layer was washed with water, dried over magnesium sulfate, and concentrated under reduced pressure. Chromatography of the residue on a thick-layer plate gave a 51% yield of 3-allyl-2-methylindole (**24**), which was identical with the major component isolated from the thermolysis of azirine **22**.

The second band obtained from the crude reaction mixture derived from the thermolysis of **22** contained a 5% yield of 2-methyl-3-phenylpyridine (**25**): picrate mp 132–133 °C (lit.[43] mp 135–136 °C); NMR ($CDCl_3$, 60 MHz) τ 7.50 (s, 3 H), 2.40–2.95 (m, 7 H), 1.60 (dd, 1 H, J = 5.0, 2.0 Hz); IR (neat) 3010, 2875, 1695, 1615, 1575, 1490, 1450, 1430, 1370, 1190, 1075, 1010, 810, 763, 738, 702 cm^{-1}; MS m/e 169 (M^+ and base), 168, 154.

The slowest moving band contained a pale oil (31%) whose structure was assigned as 2-methyl-1-phenyl-3-azabicyclo[3.1.0]hex-2-ene (**23**): NMR ($CDCl_3$, 60 MHz) τ 9.48 (t, 1 h, J = 4.0 Hz), 8.56 (dd, 1 H, J = 8.0, 4.0 Hz), 8.13 (t, 3 H, J = 2.0 Hz), 7.98 (m, 1 H), 6.30 (dq, 1 H, J = 17.5, 2.0 Hz), 5.92 (ddq, 1 H, J = 17.5, 5.0, 2.0 Hz), 2.80 (s, 5 H); IR (neat) 3030, 3000, 2920, 2860, 1695, 1630, 1610, 1502, 1460, 1442, 1385, 1310, 1270, 1195, 1160, 1095, 1070, 1026, 935, 830, 757, 700 cm^{-1}; UV (cyclohexane) 250 nm (ϵ 930); MS m/e 171 (M^+ and base), 170, 156, 130, 129, 128, 115, 102, 91, 77.

Anal. Calcd for $C_{12}H_{13}N$: C, 84.17; H, 7.65; N, 8.18. Found: C, 84.07; H, 7.62; N, 8.04.

Preparation and Thermolysis of 2-(1-Methylallyl)-2-phenyl-3-methyl-2*H*-azirine (27). The azirine was prepared in the normal manner[7] from the corresponding trimethylhydrazonium iodide salt: bp 54–55 °C (0.05 mm); NMR (CCl_4, 60 MHz) indicated a 7:10 mixture of diastereomers with signals at τ 9.19 and 9.08 (both doublets with J = 7.0 Hz), 7.70 (two singlets with ca. 1.0-Hz spacing), 6.83 and 6.69 (two pentuplets with J = 7.0 Hz), 4.8–5.2 (m, 2 H), 4.0–4.7 (m, 1 H), 2.90 (s, 5 H); IR (neat) 3050, 3020, 2960, 2920, 1755, 1680, 1592, 1489, 1440, 1365, 1265, 995, 910, 772, 730, 695 cm^{-1}; UV (cyclohexane) 272 nm (ϵ 800), 256 (2000), 225 (7000); MS m/e 185 (M^+), 184, 171, 170 (base), 130, 129, 115, 77.

Anal. Calcd for $C_{13}H_{15}N$: C, 84.28; H, 8.16; N, 7.56. Found: C, 84.27; H, 8.42; N, 7.39.

A solution containing 280 mg of the above azirine in 10 mL of toluene was heated in a sealed tube at 180 °C for 53 h. Removal of the solvent left a brown oil which was subjected to thick-layer chromatography using a 20% acetone–hexane mixture as the eluent. The fastest moving band contained 35 mg (13%) of 2-methyl-3-(1-methylallyl)indole (**28**). The structure of this material was assigned on the basis of its spectral data and by comparison with an independently synthesized sample: NMR (CCl_4, 100 MHz) τ 8.60 (d, 3 H, J = 7.5 Hz), 7.72 (s, 3 H), 6.14 (m, 1 H), 4.98–5.20 (m, 2 H), 3.80–4.18 (m, 1 H), 3.00–3.30 (m, 2 H), 2.80 (broad s, 1 H, exchanged with D_2O), 2.60–2.76 (m, 1 H); IR (neat) 3330, 3030, 2940, 1625, 1590, 1450, 1415, 1355, 1290, 1240, 1220, 1062, 1010, 995, 935, 787, 765, 743, 699 cm^{-1}; UV (acetonitrile) 290 nm (ϵ 3660), 282 (4200), 223 (23 500); MS m/e 185 (M^+), 170 (base), 158, 146, 130, 115, 77.

Anal. Calcd for $C_{13}H_{15}N$: C, 84.28; H, 8.16; N, 7.56. Found: C, 83.93; H, 8.31; N, 7.75.

An authentic sample of indole **28** was prepared by treating 2-methylindole (**26**) with 3-chloro-1-butene and was identical in every detail with **28** obtained from the thermolysis of **27**.

The slowest moving component (11%) isolated from the thick-layer plate was identified as 2,4-dimethyl-3-phenylpyridine (**29**) by comparison with the spectral properties reported in the literature:[26] NMR (CCl_4, 100 MHz) τ8.00 (s, 3 H), 7.82 (s, 3 H), 3.14 (d, 1 H, J = 4.5 Hz), 2.80–3.00 (m, 2 H), 2.56–2.80 (m, 3 H), 1.84 (d, 1 H, J = 4.5 Hz); IR (neat) 3020, 2865, 1618, 1590, 1488, 1445, 1405, 1370, 1237, 1074, 1010, 829, 763, 702 cm^{-1}; MS m/e 183 (M^+), 182 (base), 169, 168, 167, 115, 77.

Thermolysis of 2-(2-Methylallyl)-3-methyl-2-phenyl-2*H*-azirine (30). A solution containing 200 mg of azirine **30**[7] in 10 mL of toluene was heated in a sealed tube at 180 °C for 118 h. Removal of the solvent left a yellow oil which was chromatographed on a thick-layer plate to give 2-methyl-3-(2-methylallyl)indole (**31**) as the ex-

clusive product (89% yield): NMR (CCl_4, 60 MHz) τ 8.33 (s, 3 H), 7.76 (s, 3 H), 6.68 (s, 2 H), 5.35 (m, 1 H), 3.0–3.16 (m, 3 H), 2.5–2.9 (m, 2 H, 1 proton exchanged with D_2O); IR (neat) 3400, 3060, 2960, 2910, 1640, 1616, 1580, 1460, 1430, 1370, 1335, 1300, 1240, 1220, 1150, 1132, 885, 740 cm^{-1}; UV (cyclohexane) 290 nm (ϵ 3950), 282 (5100), 278 (5330), 273 (5400), 222 (25 000); MS *m/e* 185 (M^+), 170, 144 (base).

Anal. Calcd for $C_{13}H_{15}N$: C, 84.28; H, 8.16; N, 7.56. Found: C, 84.19; H, 8.45; N, 7.48.

An authentic sample of indole **31** was prepared by treating 2-methylindole (**26**) with 3-chloro-2-methylpropene and was identical with the product obtained from the thermolysis of **30.**

Thermolysis of (*E*)-2-(2-Butenyl)-3-methyl-2-phenyl-2*H*-azirine (32). A solution containing 320 mg of **32** in 10 mL of toluene was heated at 180 °C for 53 h in a sealed tube. The brown residue obtained after removing the solvent under reduced pressure was subjected to preparative thick-layer chromatography using chloroform as the eluent. The slowest moving band contained 43 mg (14%) of a clear oil whose structure was assigned as 2-methyl-3-phenyl-5-vinyl-Δ^2-pyrroline (**35**) on the basis of its spectroscopic properties: NMR (CCl_4, 100 MHz) τ 8.12 (s, 3 H), 6.88 (dd, 1 H, J = 17.6, 6.0 Hz), 6.56 (dd, 1 H, J = 17.6, 4.5 Hz), 5.24 (dd, 1 H, J = 6.0, 4.5 Hz), 4.72–5.00 (m, 2 H), 4.08 (ddd, 1 H, J = 17.6, 11.0, 6.0 Hz), 3.50 (broad s, 1 H, exchanged with D_2O), 2.48–2.80 (m, 3 H), 2.0–2.16 (m, 2 H); IR (neat) 3230, 3030, 2875, 1655, 1590, 1517, 1440, 1361, 1275, 995, 926, 787, 758, 690 cm^{-1}; MS *m/e* 185 (M^+), 158, 129, 115, 105 (base), 77; UV (acetonitrile) 236 nm (ϵ 1530).

Anal. Calcd for $C_{13}H_{15}N$: C, 84.28; H, 8.16; N, 7.56. Found: C, 84.44; H, 8.36; N, 7.94.

When the crude reaction mixture was subjected to preparative vapor-phase chromatography (15% SE-30 column at 170 °C), two additional components were isolated. The faster moving component (76%) consisted of a mixture of isomers of 2-methyl-3-phenyl-5-vinyl-Δ^1-pyrroline (**33**), of which the major component showed the following spectroscopic properties: NMR ($CDCl_3$, 100 MHz) τ 8.16 (d, 3 H, J = 2.0 Hz), 7.90 (dd, 1 H, J = 14.0, 6.5 Hz), 7.40 (dd, 1 H, J = 14.0, 7.0 Hz), 5.39 (m, 2 H), 4.72–5.00 (m, 2 H), 4.08 (ddd, 1 H, J = 16.5, 10.0, 6.0 Hz), 2.76 (s, 5 H); IR (neat) 3175, 1650, 1495, 1450, 1370, 1235, 1064, 985, 926, 766, 702 cm^{-1}; UV (cyclohexane) 245 nm (ϵ 785); MS *m/e* 185 (M^+), 184, 170, 105 (base), 77.

Treatment of the isomeric mixture of Δ^1-pyrrolines with *p*-toluenesulfonic acid in chloroform resulted in isomerization of the double bond and afforded 2-methyl-3-phenyl-5-vinyl-Δ^2-pyrroline (**35**). A similar isomerization also occurred on chromatography over silica gel.

The slower moving component in the gas chromatogram (24%) was identified as (*E*)-3-(2-butenyl)-2-methylindole (**34**) on the basis of its spectral properties and by comparison with an independently synthesized sample: NMR ($CDCl_3$, 100 MHz) τ 8.36 (d, 3 H, J = 4.0 Hz), 7.68 (s, 3 H), 6.64 (m, 2 H), 4.44 (m, 2 H), 2.40–3.0 (m, 4 H), 2.30 (broad s, 1 H); IR (neat) 3390, 3010, 2900, 1680, 1620, 1590, 1490, 1450, 1430, 1285, 1250, 1155, 1140, 1100, 997, 745 cm^{-1}; UV (cyclohexane) 291 nm (ϵ 3200), 283 (4250), 279 (4430), 273 (4560), 223 (21 000); MS *m/e* 185 (M^+), 170, 157, 156, 146 (base), 144, 105, 77.

The structure of this material was unambiguously established by comparison with an authentic sample prepared by treating 2-methylindole (**26**) with 1-bromo-2-butene using the procedure previously described.

Thermolysis of Methyl (*E*)-4-(3-Methyl-2-phenyl-2*H*-azirin-2-yl)-2-butenoate (36). A solution containing 200 mg of the azirine in 10 mL of toluene was heated at 185 °C for 60 h. Removal of the solvent under reduced pressure left a yellow oil which contained two components. Subjection of the crude material to thick-layer chromatography using chloroform as the eluent resulted in a clean separation of the two products. The faster moving band contained 46 mg (23%) of a clear oil whose structure was assigned as methyl (*E*)-4-(2-methylindol-3-yl)-2-butenoate (**38**): NMR ($CDCl_3$, 100 MHz) τ 7.68 (s, 3 H), 4.26 (d, 1 H, J = 16.0 Hz), 2.56–3.04 (m, 5 H); IR (neat) 3400, 3010, 2910, 1695, 1645, 1450, 1430, 1342, 1265, 1198, 1165, 1025, 738 cm^{-1}; MS *m/e* 229, 214, 198, 197, 185, 170, 168, 144 (base), 131, 130, 77.

Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.20; H, 6.48; N, 6.06.

The structure of this material was verified by comparison with an independently synthesized sample. To a solution containing 1.31 g of 2-methylindole in 20 mL of tetrahydrofuran at −10 °C was added 3.5 mL of a 2.9 M solution of methylmagnesium bromide. The mixture was stirred for 30 min at 25 °C and then cooled to −10 °C. To this solution was added 2.3 g of methyl 4-iodocrotonate[44] in 10 mL of tetrahydrofuran. After stirring for 12 h at 25 °C, the mixture was hydrolyzed and extracted with ether. The organic layer was dried, concentrated under reduced pressure, and purified by vapor-phase chromatography using a 10% SE-30 column at 200 °C. The major product obtained (45%) was identical in every detail with a sample of **38** isolated from the thermolysis of azirine **36.**

The major component (53%) isolated from the thermolysis of azirine **36** was identified as 2-methyl-3-phenyl-5-carbomethoxypyridine (**37**), mp 65–66 °C, on the basis of its spectral data and by comparison with an authentic sample:[28] NMR ($CDCl_3$, 100 MHz) τ 7.40 (s, 3 H), 6.04 (s, 3 H), 2.48–2.72 (m, 5 H), 1.86 (d, 1 H, J = 2.0 Hz), 0.90 (d, 1 H, J = 2.0 Hz); IR (KBr) 3010, 2920, 1710, 1590, 1420, 1400, 1305, 1240, 1117, 1053, 1025, 966, 862, 800, 763, 709 cm^{-1}; MS *m/e* 227 (M^+), 226 (base), 225, 212, 196, 169, 168, 167, 141, 139, 127, 115, 77.

Hydrolysis of the above methyl ester using concentrated hydrochloric acid afforded a quantitative yield of 6-methyl-5-phenylnicotinic acid hydrochloride, mp 205–207 °C (lit.[28] mp 200–203 °C).

Thermolysis of 2-(3-Cyanopropen-2-yl)-2-phenyl-3-methyl-2*H*-azirine (40). A solution containing 35 mg of **40** in 10 mL of toluene was heated at 180 °C for 70 h. Removal of the solvent under reduced pressure left a yellow oil which was purified by thick-layer chromatography. The major component obtained was a clear oil (77%) whose structure was assigned as 2-methyl-3-phenyl-5-cyanopyridine (**41**) on the basis of its spectral data: NMR ($CDCl_3$, 100 MHz) τ 7.48 (s, 3 H), 2.58–2.92 (m, 5 H), 2.35 (d, 1 H, J = 2.0 Hz), 1.38 (d, 1 H, J = 2.0 Hz); IR (neat) 3010, 2900, 2220, 1590, 1540, 1490, 1450, 1425, 1390, 1259, 1227, 1053, 1030, 917, 775, 741, 727, 699 cm^{-}; UV (cyclohexane) 340 nm (ϵ 570), 321 (890), 274 (6230).

The structure of this material was further verified by hydrolysis with a concentrated hydrochloric acid solution to 6-methyl-5-phenylnicotinic acid hydrochloride: mp 203–204 °C (lit.[28] mp 200–203 °C); NMR (Me_2SO-d_6, 100 MHz) τ 7.28 (s, 3 H), 3.60 (broad s, 1 H, exchanged with D_2O), 2.16 (s, 5 H), 1.28 (d, 1 H, J = 2.0 Hz), 0.56 (d, 1 H, J = 2.0 Hz); IR (KBr) 3500–2300 (broad band), 1725, 1625, 1420, 1380, 1350, 1220, 1135, 1053, 772, 758, 725, 702 cm^{-1}.

The structure of this material was unambiguously established by hydrolysis of an authentic sample of 2-methyl-3-phenyl-5-carbomethoxypyridine (**37**) to the same acid hydrochloride as was obtained from cyanopyridine **40.**

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Registry No.—**1,** 56434-95-8; **2,** 57827-53-9; **3,** 10273-90-2; **4,** 56434-96-9; *endo*-**5,** 57827-54-0; *exo*-**5,** 57885-05-9; **6,** 27063-80-5; **7,** 62736-98-5; **8,** 65530-01-0; *cis*-**9,** 65495-80-9; *trans*-**9,** 65495-81-0; **10,** 27068-69-5; **11,** 65495-82-1; **12,** 65495-83-2; **13,** 28489-52-3; **13** picrate, 65495-84-3; **15,** 62737-00-2; **16,** 65495-87-6; *cis*-**17,** 65495-85-4; *trans*-**17,** 65495-86-5; **18,** 65495-88-7; **19,** 65495-89-8; **20,** 65495-90-1; **21,** 65495-91-2; **22,** 59175-18-7; **23,** 65516-35-0; **24,** 65495-76-3; **25,** 3256-89-1; **26,** 95-20-5; **27** (isomer I), 65495-64-9; **27** (isomer II), 65495-63-8; **28,** 65495-65-0; **29,** 29396-61-0; **30,** 59175-25-6; **31,** 65495-66-1; **32,** 59175-26-7; *cis*-**33,** 65495-68-3; *trans*-**33,** 65495-69-4; **34,** 65495-70-7; **35,** 65495-67-2; **36,** 65495-71-8; **37,** 10176-84-8; **38,** 65504-89-4; **40,** 65495-72-9; **41,** 10176-93-9; **42** (HCl), 65495-75-2; 2-methyl-1-phenyl-4-penten-1-one, 17180-49-3; 3-methyl-4-phenyl-4-oxybutanol, 65495-77-4; 2-phenyl-3-methylpyrrole, 20814-35-1; 2-phenyl-3-methyl-6-hydroxymethylpyridine, 65495-79-6; 2-phenyl-3-methyl-6-hydroxymethylpyridine mesylate, 65495-73-0; 2-(4-hexyn-2-yl)benzaldehydetrimethylhydrazonium iodide, 65495-74-1; 3-phenyl-4-methyl-5-hexen-2-onetrimethylhydrazonium iodide, 62737-09-1; methyl 4-iodocrotonate, 65495-78-5.

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(44) A sample of methyl 4-iodocrotonate was prepared in the following fashion. To a solution containing 20.5 g of methyl crotonate in 110 mL of carbon tetrachloride was added 29.1 g of *N*-bromosuccinimide and 100 mg of dibenzoyl peroxide. The mixture was heated at reflux for 48 h, filtered, and concentrated under reduced pressure. The resulting liquid was distilled at 92–95 °C (10 mm) to give 23 g of methyl 4-bromocrotonate. To a solution containing 9.0 g of this material in 300 mL of dry acetone was added 12 g of sodium iodide. The mixture was stirred at room temperaure for 20 h. A normal workup procedure gave a 93% yield of methyl 4-iodocrotonate.

Intramolecular Cyclization of Nitrile Imines. Synthesis of Indazoles, Fluorenes, and Aza Analogues[1a]

Curt Wentrup,*[1b] Angelika Damerius, and Werner Reichen[1c]

Fachbereich Chemie der Universität, D-3550 Marburg, Federal Republic of Germany, and Institut de Chimie Organique de l'Université, CH-1005 Lausanne, Switzerland

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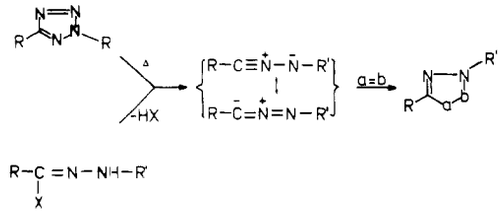
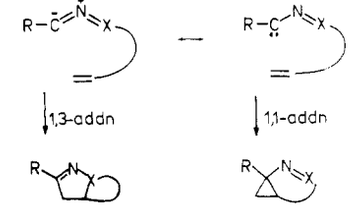
Flash thermolysis of 2,5-diaryltetrazoles **2** at 400–500 °C (10^{-3} mm) gives 3-arylindazoles **5** in yields of 96–100%. Thus, 2,5-diphenyl-, 2-(*p*-tolyl)-5-phenyl-, 2-phenyl-5-(*p*-tolyl)-, 2,5-di(*p*-tolyl)-, and 2-phenyl-5-(4-pyridyl)tetrazole furnish 3-phenyl-, 3-phenyl-5-methyl-, 3-(*p*-tolyl)-, 3-(*p*-tolyl)-5-methyl-, and 3-(4-pyridyl)indazole, respectively. Indazoles **5** are formed also by heating the tetrazoles **2** in tetralin at 207 °C for 15 min. Flash thermolysis of the same tetrazoles **2** at 800 °C (10^{-3} mm) gives 2,6-disubstituted fluorenes **7** (2,6 substituents = H or CH_3) or 3-azafluorene (**7e**) in yields of 90–100%. The thermolysis of 3-phenylpyrazolo[3,4-*b*]pyridine (**8**) at 770 °C resulted in a 49% conversion to 4-azafluorene (**9**). Thermolysis of 2,4-diphenyl-1,3,4-oxadiazolin-5-one (**16a**) at 500 °C (10^{-2} mm) gave 3-phenylindazole (94%); at 750 °C fluorene was obtained (84%). 2-Methyl-4-phenyl-1,3,4-oxadiazolin-5-one (**16b**) gave at 450 °C 3-methylindazole (89%) and at 650 °C styrene (94%). The results are interpreted in terms of the intermediate formation of nitrile imines by loss of N_2 from **2** and of CO_2 from **16**. The nitrile imines are regarded as a resonance hybrid of bent dipolar and carbene structures (**23**) which cyclize unto the remote aromatic ring.

The cycloaddition of 1,3 dipoles has become an important method for the synthesis of five-membered heterocyclic rings.[2] For example, nitrile imines generated by the thermal decomposition[3a] of 2,5-disubstituted tetrazoles[3c] or by base-induced elimination from hydrazonyl halides[3b] undergo in situ addition to acetylenes, olefins, and nitriles, yielding pyrazole



or triazole derivatives.[2] The cycloaddition of 1,3 dipoles can also take place intramolecularly to suitably oriented dipolarophiles.[4] Recently, it has been shown that intramolecular 1,1 addition of nitrile ylides[4,5] as well as nitrile imines[6] can compete with the normal 1,3 addition when certain geometric constraints are imposed. In these cases, the reactions can be formulated in terms of the carbene forms of the dipoles.[4,5]



Huisgen[2] recognized carbene forms as resonance structures of 1,3 dipoles; however, such species may exist in two distinct molecular geometries: a bent carbene-like structure and/or a linear dipolar structure.[7] The ab initio STO-3G and 4–31G

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