analysis of the distillate showed two peaks having an area ratio of 27:73. The two peaks were separated by preparative VPC. For **14**: mp 146–147 °C; mass spectrum, *m/e* 550; UV 241 nm (ϵ 18000); ^{1}H NMR δ (ppm) 0.25 (18 H, s, Me_3Si), 0.29 (36 H, s, Me_2Si). Anal. Calcd for $C_{18}H_{54}Si_{10}$: C, 39.20; H, 9.87. Found: C, 38.99; H, 9.93. For **15** (mixture of isomers): mp 150–151 °C; mass spectrum, *m/e* 550. Anal. Calcd for $C_{18}H_{54}Si_{10}$: C, 39.20; H, 9.87. Found: C, 39.41; H, 10.01.

Isomerization of 12. A mixture of 3 g (5.5 mmol) of **12** and 0.4 g (3.0 mmol) of aluminum chloride in 50 mL of benzene was stirred at room temperature for 10 h. Acetone (5 mL) was added to the mixture, and the solvent was distilled off. The residue of the flask was distilled under reduced pressure to give 2.8 g of white crystals. Methylation of the product using methylmagnesium bromide followed by distillation under reduced pressure afforded 2.6 g of crystals. VPC analysis of the distillate showed two peaks having an area ratio of 27:73. All spectral data for **14** and a mixture of isomers separated by preparative VPC were identical with those obtained from isomerization of **10**.

Acknowledgment. The cost of this research was defrayed partly by a Grant-in-Aid for Scientific Research by the Ministry of Education to which our thanks are due. We also express our appreciation to Toshiba Silicon Co., Ltd., and Shin-etsu Chemical Co., Ltd., for a gift of organochlorosilanes.

Registry No. 1, 4098-30-0; 2, 23118-85-6; 3, 23118-87-8; 4, 23118-86-7; 5, 57171-38-7; 6, 79769-57-6; 7, 79769-58-7; 9, 30314-60-4; 10, 37249-28-8; 11, 23118-89-0; 12, 79769-59-8; 13, 79769-60-1; 14, 79769-61-2; 15, 79769-62-3; $AlCl_3$, 7446-70-0; Me_3SiCl, 75-77-4; $PhMe_2SiCl$, 768-33-2; Me_2SiCl_2, 75-78-5; $MeSiCl_3$, 75-79-6.

Metal-Catalyzed Reactions of Allylazirines

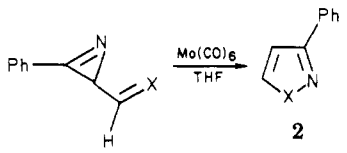
Taeko Izumi and Howard Alper*[1]

Department of Chemistry, University of Ottawa Ottawa, Ontario, Canada K1N 9B4

Received September 14, 1981

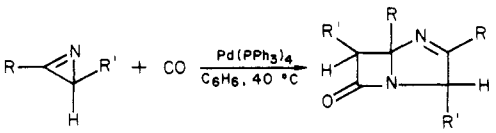
Tetrakis(triphenylphosphine)palladium(0) and certain other palladium(0) compounds catalyze the conversion of 2-allylazirines to pyridines and pyrroles. The reaction is sensitive to the atmosphere in which it is conducted, as well as to the pressure. The use of other catalysts (e.g., molybdenum and rhodium carbonyls) for the ring opening of 2-allylazirines is also described. A mechanism, involving a key common intermediate, is proposed for the formation of pyridines and pyrroles.

Photochemical and thermal reactions of the three-membered ring heterocycles, azirines, have been investigated in considerable detail.[2] Metal complexes can induce some synthetically useful transformations of azirines under exceedingly mild conditions.[3] One example is the molybdenum hexacarbonyl induced intramolecular cycloaddition of 3-phenyl-2-substituted-2*H*-azirines (**1**) to

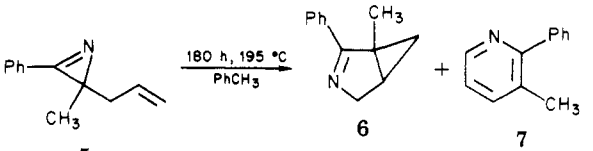


1, X = O, NR

five-membered ring heterocycles. This reaction occurs at room temperature, affording **2** in fine yields.[4] The synthesis of β-lactams (**4**) by the tetrakis(triphenylphosphine)palladium(0)-catalyzed carbonylation of azirines (**3**) is another noteworthy reaction.[3] 2-Allyl-substituted 2*H*-azirines undergo interesting thermal and photochemical reactions. For instance, when 2-allyl-2-methyl-3-phenyl-2*H*-azirine (**5**) was heated in a sealed tube for 180

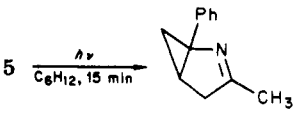


3 4



5 6 7

h at 195 °C, the 3-azabicyclo[3.1.0]hex-3-ene **6** was obtained in 90% yield and 3-methyl-2-phenylpyridine (**7**) was formed in 10% yield. *Partial* conversion of **6** to **7** occurred on extended heating (195 °C, 85 h).[5] In contrast, irradiation of **5** proved to be very facile (15 min, $\lambda > 250$ nm) leading to the quantitive formation of **8**.[6] The irradiation process likely occurs by carbon–carbon bond cleavage of **5**, while there is good evidence for carbon–nitrogen bond cleavage in the thermolysis of allylazirines.



8

This paper describes the interesting metal-catalyzed chemistry of allylazirines. Since it is probable that the molybdenum- and palladium-catalyzed reactions of simple

(1) E.W.R. Steacie Fellow, 1980–1982.
(2) For a review see: Nair, V.; Kim, K. H. *Heterocycles* **1977**, *7*, 353.
(3) Alper, H.; Perera, C. P.; Ahmed, F. R. *J. Am. Chem. Soc.* **1981**, *103*, 1289 and references cited therein.
(4) Alper, H.; Prickett, J. E.; Wollowitz, S. *J. Am. Chem. Soc.* **1977**, *99*, 4330.
(5) Padwa, A.; Carlsen, P. H. J. *J. Org. Chem.* **1978**, *43*, 2029. Padwa, A.; Carlsen, P. H. J. *Tetrahedron Lett.* **1978**, 433.
(6) Padwa, A.; Carlsen, P. H. J., *J. Am. Chem. Soc.* **1977**, *99*, 1514.

0276-7333/82/2301-0322$01.25/0 © 1982 American Chemical Society

Table I. Products Obtained from the Cleavage of Allylazirines

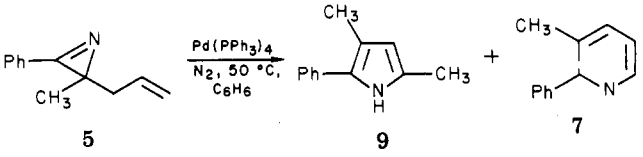
azirine	reaction atmosphere	catalyst	product	yield, %
5	N_2	$Pd(PPh_3)_4$	7	18
			9	20
	CO_2	$Pd(PPh_3)_4$	7	70
			9	trace
	CO_2	$Pd(dba)_2$	7	12
	CO_2	$Pd(dba)_2$, diphos	9	14
	CO_2	$Pd(diphos)_2$	...	...
	CO_2	$Mo(CO)_6$	...	...
10	CO_2	$Pd(PPh_3)_4$	11	18
			12	10
13	N_2	$Pd(PPh_3)_4$	14	30[a]
			15	33[b]
	CO_2	$Pd(PPh_3)_4$	14	19
			15	24
	CO_2	$Pd(dba)_2$	14	12
			15	30
	CO_2	$Rh_6(CO)_{16}$	14	6
			15	8
16	CO_2	$Pd(PPh_3)_4$	17	45
			18	14
			19	12
	CO_2	$Mo(CO)_6$	19	30

[a] New compound. Anal. Calcd for $C_{14}H_{15}N$: C, 85.24; H, 7.66; N, 7.10. Found: C, 85.04; H, 8.02; N, 6.83. [b] New compound. Anal. Calcd for $C_{14}H_{13}N$: C, 86.12; H, 6.63; N, 7.17. Found: C, 86.05; H, 6.27; N, 6.81.

azirines (see above) proceed via carbon–nitrogen bond cleavage of the azirine, such cleavage in the case of allylazirines would generate metal-complexed allyl-substituted vinylnitrenes. As reported herein, not only does the metal complex have an influence on the reaction course, as compared with the thermal process, but also the atmosphere used for the reaction is important as well.

Results and Discussion

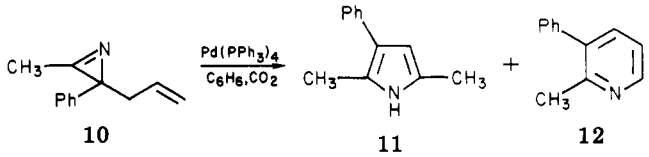
Exposure of **5** to a catalytic amount of tetrakis(tri-



phenylphosphine)palladium(0) [10:1 ratio of **5**:$Pd(PPh_3)_4$] in benzene at 50 °C gave 3,5-dimethyl-2-phenylpyrrole (**9**) in 20% yield and 3-methyl-2-phenylpyridine (**7**) in 18% yield, with the remainder being recovered starting material. Use of acetone as the reaction solvent gave **7** in the same yield but only a small amount (3.5%) of **9**.

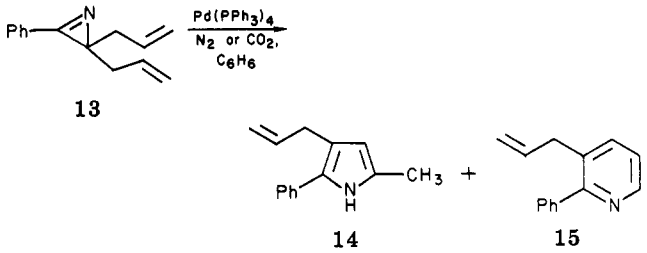
Although a variety of azirines can be carbonylated to β-lactams by using $Pd(PPh_3)_4$, allylazirines such as **5** were unreactive in the presence of carbon monoxide and the palladium catalyst. Use of carbon dioxide as the reaction atmosphere proved more fruitful, as **5** was converted to 3-methyl-2-phenylpyridine (**7**) in 70% yield, with only a trace of the pyrrole formed. Other palladium catalysts such as bis(dibenzylideneacetone)palladium(0) and (1,2-bis(diphenylphosphino)ethane)palladium(0) were of little use as catalysts for these reactions (Table I). Compounds **7** and **9**, as well as the products of the reactions of other allyl azirines, were identified by comparison of spectral data (Table II) with those for authentic materials (when available).

Reaction of 2-allyl-3-methyl-2-phenyl-2*H*-azirine (**10**), an isomer of **5**, with $Pd(PPh_3)_4$ under carbon dioxide af-



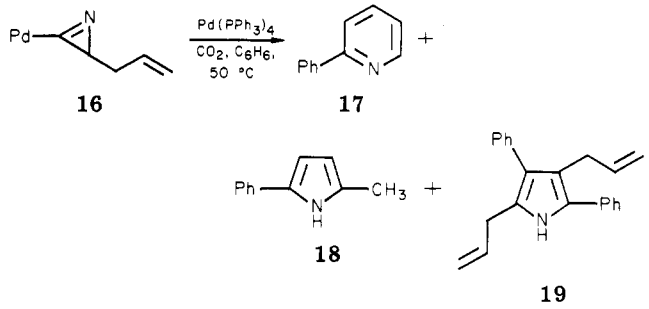
forded 2,5-dimethyl-3-phenylpyrrole (**11**) and 2-methyl-3-phenylpyridine (**12**). However, the product yields obtained in this reaction were in the same range as those realized for **7** and **9** in the reaction of **5** under nitrogen.

In the case of a diallylazirine, 2,2-diallyl-3-phenyl-2*H*-azirine (**13**), the expected pyrrole (**14**) and pyridine (**15**)



derivatives were obtained in somewhat higher yields by using CO_2 rather than a nitrogen atmosphere for the $Pd(PPh_3)_4$-catalyzed reaction. Both products were also obtained using $Pd(dba)_2$ as the catalyst.

The behavior of a monoallylazirine, lacking any other substituent at the 2-position, toward $Pd(PPh_3)_4$ was also examined. 2-Allyl-3-phenyl-2*H*-azirine (**16**) was prepared



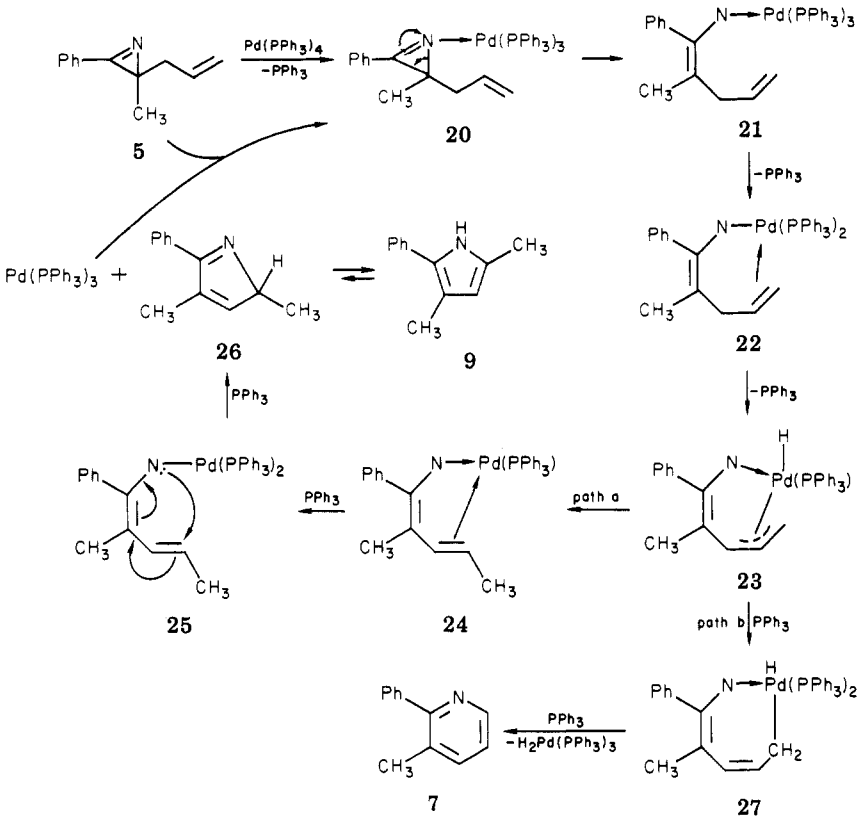
from 1-phenyl-4-penten-1-one by a modified Neber reaction. The $Pd(PPh_3)_4$-catalyzed reaction of **16** afforded 2-phenylpyridine in 45% yield, together with small amounts of the expected 2-methyl-5-phenylpyrrole (**18**) and a compound assigned structure **19** on the basis of spectral data (e.g., ^{13}C shows two different allyl groups).

Pressure does have an effect on the reaction, since it results in the formation of pyridines in fine yields. For example, the yield of 2-phenylpyridine (**17**) increased from 45 to 75% when the reaction of **16** was repeated at 24.5 atm for 20 h at 50 °C. Raising the temperature to 80 °C resulted in the formation of **17** in essentially the same yield (77%). Pyrroles (**18**, **19**) were not isolated from any of the reactions effected at elevated pressures. They were also small amounts of products possibly resulting from reaction of the azirine with carbon dioxide,[7] since they exhibited carbonyl absorption in the infrared region at 1740–1750 cm^{-1}. However, all attempts to isolate these byproducts in analytically pure form failed.

A number of other metal complexes were used as catalysts for the cleavage of allylazirines. While **14** and **15** were obtained in poor yields by exposure of the diallylazirine **13** to hexarhodium hexadecacarbonyl (50 °C, 1 atm of

(7) For an example of the reaction of small ring compounds with CO_2, see: Inoue, Y.; Hibi, T.; Satake, M.; Hashimoto, H. *J. Chem. Soc., Chem. Commun.* **1979**, 982.

Scheme I

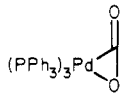


CO_2), no reaction occurred by using chlorodicarbonylrhodium(I) dimer, tetrakis(triphenylphosphine)platinum, or molybdenum hexacarbonyl as the catalyst. While the molybdenum complex was also ineffective for other 2-allyl-2-substituted-azirines (e.g., **5**), it did effect the conversion of **16** to the pyrrole **19** in 30% yield.

The formation of pyridines and pyrroles from allylazirines can be rationalized by the pathways outlined in Scheme I (illustrated for **5**). Coordination of the azirine nitrogen to palladium (**20**) would weaken the carbon–nitrogen single bond, the cleavage of which would generate **21**. Unlike simple nitrene–metal complexes, compound **21** has an allylic group and binding of the double bond of the allyl unit to palladium is conceivable (**22**). The palladium hydride **23**, formed on allylic hydrogen abstraction, can react by two (or more) pathways. Delivery of the hydride to the least substituted terminal carbon of the allyl unit would give **24** and then **25** (with PPh_3—path a). Cyclization and decomplexation would afford **26** and $Pd(PPh_3)_3$. The latter can then react with additional azirine **5** to regenerate **20**, completing the catalytic cycle, while **26** would readily isomerize to the pyrrole **9**. Complex **25** is of the same structural type as the intermediate formed on metal-induced cleavage of a vinylazirine such as (*E*)-3-phenyl-2*H*-azirine-2-acrylate.[4]

Instead of hydrogen transfer from palladium to the organic ligand, **23** can experience $\pi \rightarrow \sigma$ allyl conversion giving **27** (path b). Dehydrogenation and elimination from **27** would result in the formation of the pyridine **7** and $Pd(PPh_3)_2H_2$ which, with readdition of PPh_3 (previously disassociated), would give $Pd(PPh_3)_3$ and hydrogen. It is also possible that, in the presence of PPh_3, **27** eliminates $Pd(PPh_3)_3$ and hydrogen directly.

What is the function of carbon dioxide in these reactions? Carbon dioxide may react with the azirine complex **20** formed initially (or **21**), the resultant bound CO_2 affecting the ease of cleavage of the three-membered ring or the complexation of the allylic double bond to palladium. Alternatively, CO_2 may react with $Pd(PPh_3)_3$ to form **28**, the latter exhibiting different reactivity than $Pd(PPh_3)_3$ toward the azirine. It is not clear why there is greater selectivity for pyridine formation (i.e., path b) at elevated pressures of carbon dioxide.



28

In conclusion, $Pd(PPh_3)_4$ can catalyze the conversion of allylazirines to pyridines and pyrroles under gentle conditions, with the reaction atmosphere and pressure used being of importance.

Experimental Section

General Remarks. Infrared determinations were made by using a Unicam SP-1100 spectrometer, equipped with a calibration standard. Proton magnetic resonance spectra were recorded on a Varian T-60 or HA-100 spectrometer, and a Varian FT-80 spectrometer, operating in the fully and partially decoupled modes, was used for carbon magnetic resonance spectra. Mass spectra were run on a Varian MS902 spectrometer. Melting point determinations were made by using a Fisher-Johns apparatus. Elemental analyses were carried out by Canadian Microanalytical Service, Vancouver, Canada.

Tetrakis(triphenylphosphine)palladium(0)[8] and bis(dibenzylideneacetone)palladium(0)[9] were synthesized following literature procedures. Molybdenum and rhodium carbonyls, as well as tetrakis(triphenylphosphine)platinum and chlorodicarbonylrhodium(I) dimer, were commercial products (Strem Chemicals, Inc.).

Solvents were purified and dried by standard methods. Reactions at elevated pressures of carbon dioxide were run in a Parr reactor.

(8) Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121.
(9) Takahashi, Y.; Ito, E.; Sakai, S.; Ishii, Y. *J. Chem. Soc. D* **1970**, 1065.

Table II. Pertinent Spectral Data for the Reaction Products

compd	IR ν, cm^{-1}	^1H NMR, δ [a]	MS, m/e
7	1592, 1577	2.30 (s, 3 H, CH_3), 7.05-7.60 (m, 7 H, H4, H5, Ph), 8.53 (dd, 1 H, H6, J_{H5-H6} = 5 Hz, J_{H4-H6} = 1 Hz)	169
9	3480, 1530	2.14 (s, 3 H, CH_3), 2.20 (s, 3 H, CH_3), 5.75 (d, 1 H, CH, J = 3 H), 7.10-7.40 (m, 6 H, Ph and NH)	171
11	3460, 1515	2.13 (s, 3 H, CH_3), 2.25 (s, 3 H, CH_3), 5.99 (d, 1 H, CH_2, J = 3 Hz), 7.10-7.40 (m, 6 H, Ph and NH)	171
12	1578, 1561	2.48 (s, 3 H, CH_3), 7.00-7.50 (m, 7 H, H4, H5, Ph), 8.45 (dd, 1 H, H6, J_{H6-H5} = 5 Hz, J_{H6-H4} = 1.5 Hz)	169
14	3380, 1515	2.30 (s, 3 H, CH_3), 3.33 (d, 2 H, CH_2, J = 6 Hz), 5.10 (m, 2 H, CH_2=), 5.83 (m, 1 H, CH=), 5.93 (d, 1 H, J = 3 Hz, CH), 7.17-7.65 (m, 6 H, Ph and NH)	197
15	1650, 1590, 1575	3.35 (d, 2 H, CH_2, J = 6 Hz), 4.92 (m, 2 H, CH_2=), 6.00 (m, 1 H, CH=), 7.00-7.65 (m, 7 H, Ph, H4, H5), 8.55 (dd, 1 H, H6, J_{H5-H6} = 5 Hz, J_{H4-H6} = 1.5 Hz)	195
17	1578, 1570, 1562	7.00-8.00 (m, 8 H, Ph, H3-H5), 8.61 (m, 1 H, H6)	155
18	3380, 1515	2.27 (s, 3 H, CH_3), 5.88 (t, 1 H, H3), 6.35 (t, 1 H, H4), 7.1-7.5 (m, 8 H, Ph), 7.80 (s (br), 1 H, NH)	157
19 [b]	3380, 1523	3.20 (m, 4 H, CH_2), 4.95 (m, 4 H, CH_2=), 5.80 (m, 2 H, CH=), 7.22 (m, 10 H, Ph), 7.80 (s (br), 1 H, NH)	299

[a] $CDCl_3$ with Me_4Si as internal standard. [b] ^{13}C NMR ($CDCl_3$) δ 29.28 (CH_2), 30.85 (CH_2), 115.03 (CH_2=), 125.98, 126.11, 126.41, 126.64, 127.87, 128.02, 128.30, 128.66, 129.28, 130.06, 133.48, 138.07 (aromatic and heterocyclic carbons), 135.92 (CH=), 138.70 (CH=).

Azirines Literature procedures were used to prepare 2-allyl-2-methyl-3-phenyl-2*H*-azirine (**5**) and 2-allyl-3-methyl-2-phenyl-2*H*-azirine (**10**).[6]

2,2-Diallyl-3-phenyl-2*H*-azirine (**13**) was prepared by a modified Neber reaction in which 4-benzoyl-1,6-heptadiene was treated with dimethylhydrazine according to the general procedure of Padwa and Carlsen.[6] The required 4-benzoyl-1, 6-heptadiene was synthesized by the following procedure. To a slurry of sodium hydride (0.1 mol) in dimethyl sulfoxide (100 mL) was added acetophenone (0.1 mol) at 25–35 °C. Allyl bromide (1 mol) was then added dropwise at 35 °C. The reaction mixture, after stirring for 3 h, was poured into ice water (200 mL) and extracted with ether. Removal of the ether followed by distillation at 85–87 °C (0.2 mm) afforded 4-benzoyl-1,6-heptadiene in 69% yield.

13: bp 88–90 °C (0.3mm); IR (neat) 1745 (C=N), 1655 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.45 (d, 2 H, J = 6 Hz, CH_2), 2.50 (d, 2 H, J = 6 Hz, CH_2), 5.00 (m, 4 H, CH_2=), 5.80 (m, 2 H, CH=), 7.50 (m, 5 H, Ph); mass spectrum, m/e 197 (M^+).

Anal. Calcd for $C_{14}H_{15}N$: C, 85.24; H, 7.66; N, 7.10. Found: C, 84.97; H, 7.84; N, 7.16.

2-Allyl-3-phenyl-2*H*-azirine (**16**) was prepared from 1-phenyl-4-penten-1-one[10] by a modified Neber reaction.[6]

16: bp 42–46 °C (0.07 mm); IR (neat) 1732 (C=N), 1638 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.31 (m, 3 H, CH (ring) and CH_2), 5.08 (m, 2 H, CH_2=), 5.80 m, 1 H, CH=), 7.60 (m, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 31.38 (saturated carbon of azirine), 37.77 (CH_2), 116.58 (CH_2=), 125.71 (quaternary carbon of phenyl group), 129.06, 129.29, 132.80 (other phenyl carbons), 135.23 (CH=), 171.48 (C=N); mass spectrum, m/e 157 (M^+).

Anal. Calcd for $C_{11}H_{11}N$: C, 84.04; H, 7.05; N, 8.91. Found: C, 84.10; H, 6.94; N, 8.10.

General Procedure for the $Pd(PPh_3)_4$-Catalyzed Reaction of 2-Allylazirines. Carbon dioxide (or nitrogen) was bubbled, for 10–30 min, through a dry benzene (40 ml) solution containing $Pd(PPh_3)_4$ (1.0 mmol). The allylazirine (10.0 mmol) in benzene (10 ml) was added, and the reaction mixture was then stirred at 50 °C under CO_2 or N_2. After no further conversion occurred (followed by thin-layer and/or gas chromatography), the solvent was removed by rotary evaporation and the products were separated by column chromatography with silica gel. The pyrrole was eluted with hexane (any recovered azirine was eluted after the pyrrole), and the pyridine was eluted by using 10% hexane–ethylacetate.

This procedure, using a Parr reactor, was applied to reactions effected at elevated pressures of carbon dioxide.

The reactions using other palladium complexes as well as different metal catalysts were run in a manner identical with that described for $Pd(PPh_3)_4$.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council for support of this work.

Registry No. **5**, 56434-95-8; **7**, 10273-90-2; **9**, 3274-53-1; **10**, 59175-18-7; **11**, 3771-60-6; **12**, 3256-89-1; **13**, 79815-47-7; **14**, 79815-48-8; **15**, 79815-49-9; **16**, 79815-50-2; **17**, 1008-89-5; **18**, 3042-21-5; **19**, 79815-51-3; $Pd(PPh_3)_4$, 14221-01-3; $Pd(dba)_2$, 32005-36-0; $Pd(dba)_2$diphos, 79827-24-0; $Pd(diphos)_2$, 31277-98-2; $Mo(CO)_6$, 13939-06-5; $Rh_6(CO)_{16}$, 28407-51-4.

(10) Marvell, E. N.; Li, T. H. C. *J. Am. Chem. Soc.* **1978**, *100*, 883.