Preparation and Thermolysis of *cis*- and *trans*-1-Hydroxy-2-(2-pyridyl)cyclopentanes and *cis*- and *trans*-1-Hydroxy-2-(2-pyrazyl)cyclopentanes

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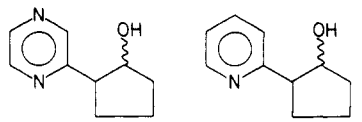
The syntheses of *cis*- and *trans*-1-hydroxy-2-(2-pyridyl)cyclopentanes as well as *cis*- and *trans*-1-hydroxy-2-(2-pyrazyl)cyclopentanes have been carried out, and their stereochemical assignments were done by using IR and NMR data. The thermolyses of these pyrazylethanols and pyridylethanols have been studied in diglyme solutions at 170 °C. While the pyrazylethanols mainly undergo dehydration, the pyridylethanols thermolyze via a much more complex reaction process.

We have recently reported that 2-(2-hydroxy-2-arylethyl)pyrazines[1] and a large variety of other 2-(2-pyrazyl)ethanols[2,3] undergo a thermal retro-ene type reaction to yield a mixture of the corresponding alkylpyrazine and aldehyde. A mechanistic study suggested that the reaction proceeds via a nonpolar concerted six-membered ring transition state[1] (Scheme I). Similar reactions have also been reported for a variety of 2-(2-pyridyl)ethanols[2-5] and are likewise suggested to proceed via a concerted mechanism (Scheme I).

The present investigation was aimed at extending this study to cyclic pyrazylethanols (A) and cyclic pyridylethanols (B), where, in each case, the stereochemical re-



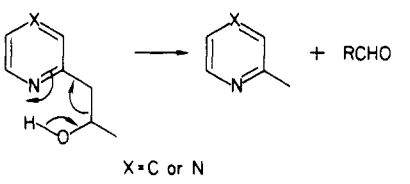
A B

lationship of the heteroaromtic ring and the hydroxyl group provides an additional mechanistic tool for studying these reactions.

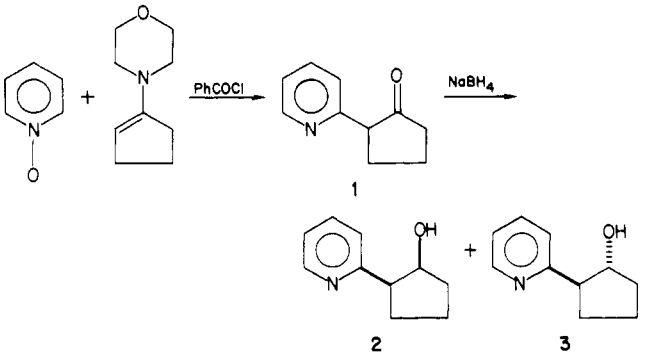
The synthesis of the pyridine derivatives was carried out as described in Scheme II. The condensation[6] of the morpholine enamine with pyridine *N*-oxide in the presence of benzoyl chloride gave the ketone **1** in 46% yield, and the product was purified by distillation. It is quite interesting to note that in an attempt to purify the ketone **1** by TLC on silica gel (SG), an air oxidation took place resulting in the formation of a mixture of **4** and **5** (Scheme III). It was established that this oxidation is catalyzed by the silica gel and probably proceeds via the hydroperoxide, which can lead to **4** or undergo further oxidation to give **5**.

Reduction of **1** with $NaBH_4$ gave a nearly quantitative yield of a 1:1 mixture of the cis and trans alcohols **2** and **3**, respectively. The stereochemistry of the two isomers was established from their NMR and IR spectra. The IR spectrum of **2** in CCl_4 shows a broad OH stretching band centered at 3350 cm^{-1}. The position of this band and its intensity relative to the CH stretching bands do not change with dilution. Also, no band consistent with the presence of a free OH appears with dilution. These results indicate the presence of an intramolecular hydrogen bonding in **2**. The spectrum of **3** shows a broad OH stretching band at

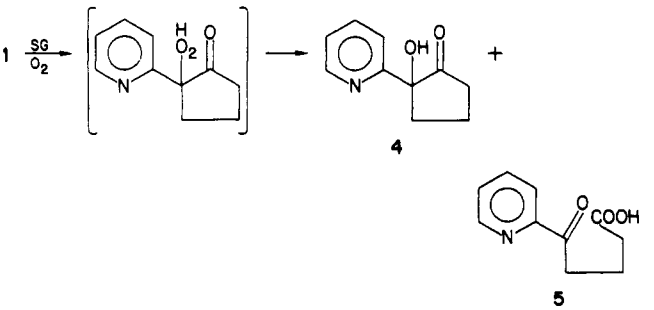
Scheme I



Scheme II



Scheme III



3450 cm^{-1} and a sharp band at 3630 cm^{-1}. The latter intensifies relative to the broad OH band with dilution, which indicates the presence of an intermolecular hydrogen bonding in **3**. These results establish that **2** and **3** have the cis and trans configuration, respectively. The NMR data for both **2** and **3** also support the above stereochemical assignments.

The synthesis of the pyrazine derivatives was first approached by a reaction analogous to that shown in Scheme II. The reaction of pyrazine *N*-oxide with the morpholine enamine and benzoyl chloride did not yield the desired ketone, and the pyrazine *N*-oxide was recovered unchanged. Similar results were obtained when other acyl halides were used to activate the system. Therefore, an alternative synthetic method was explored, and the desired 2-(2-pyrazyl)cyclopentanone (**6**) was obtained by reacting

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(2) Houminer, Y.; Sanders, E. B., U.S. Patent 4 259 969.
(3) Kornfeld, R. A.; Houminer, Y., unpublished results.
(4) Goldman, I. M. *J. Org. Chem.* **1963**, *28*, 1921.
(5) Hansen, D. W., Jr.; Sinsheimer, J. E.; Burckhalter, J. H. *J. Org. Chem.* **1976**, *41*, 3556.
(6) Crabb, T. A.; Jones, E. R. *Tetrahedron* **1970**, *26*, 1217.

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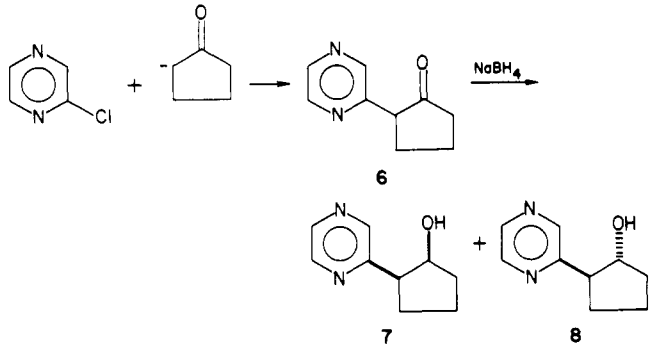
Scheme IV



Scheme V

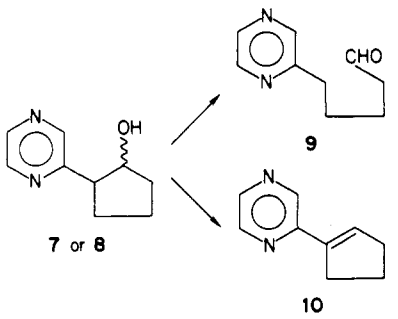


Table I. Percentage Composition[a] and Product Ratios in the Thermolysis of 2 in Diglyme at 170 °C (0.2 M)

time, h	2	3	2/3	11	12
10	61.0	28.2	2.158	5.8	4.2
13.5	57.0	36.5	1.400	6.5	7.6
16	47.3	37.5	1.263	8.4	9.6
17.5	45.3	37.0	1.224	7.9	9.1
19	43.2	37.8	1.143	8.5	10.2
21	38.5	38.0	1.014	9.1	11.9
23	37.1	37.1	1.000	9.4	14.3
25	37.4	38.9	0.962	9.4	14.9
29	32.4	38.7	0.839	10.4	17.9
32	29.1	37.1	0.784	10.2	20.5
35	28.2	36.7	0.769	10.3	23.0
41	26.8	35.9	0.747	11.2	26.7
57	21.9	28.1	0.779	10.4	42.1

[a] The accuracy of these determinations is ±3%.

the enolate anion of cyclopentanone with 2-chloropyrazine as shown in Scheme IV. A reasonable yield (34%) of the ketone was obtained only when the enolate anion of cyclopentanone was prepared in DMF using KH as the base. Reduction of the ketone **6** with $NaBH_4$ proceeded smoothly and gave a 1:1 mixture of the cis and trans alcohols **7** and **8**, respectively. The stereochemical assignments were carried out as in the case of **2** and **3**, using both IR and NMR data.

Thermolyses were carried out in diglyme-d_{14} at concentrations of 0.2 M and were followed by NMR as described previously.[1] We shall first discuss the results obtained for the pyrazine derivatives **7** and **8**. Reaction at 170 °C gave only a trace amount of the expected aldehyde **9** (Scheme V). Instead, the major product from both **7** and **8** was the dehydration product **10**. After 115 h at 170 °C, **7** gave <3% of **10** whereas **8** gave 25% of the same product, indicating faster dehydration of the trans isomer. It appears from these results that both **7** and **8** lack the regular retro-ene type reactivity characteristic of a large variety of 2-(2-pyrazyl)ethanols.[1] Additional evidence for this behavior was obtained from the following experiment: when **7** and **8** were pyrolyzed neat at 450 °C for 2 min under a flow of N_2, both were essentially unchanged.[7]

Scheme VI

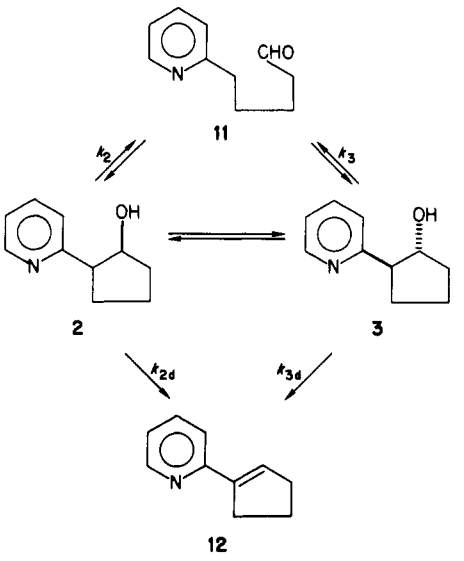


Table II. Percentage Compositions[a] and Product Ratios in the Thermolysis of 3 in Diglyme at 170 °C (0.2 M)

time, h	2	3	2/3	11	12
10	20.4	70.5	0.289	2.6	7.6
13.5	21.2	65.3	0.330	2.9	9.6
16	24.2	61.8	0.391	3.6	11.2
17.5	26.2	57.1	0.459	3.9	11.3
19	26.7	57.4	0.464	4.4	13.6
21	26.5	54.3	0.481	5.0	14.3
23	27.0	54.1	0.500	5.4	15.6
25	27.3	48.4	0.563	5.8	16.8
29	28.0	44.7	0.627	6.3	21.1
32	25.5	40.7	0.625	6.5	24.2
35	25.4	40.3	0.644	7.3	25.8
41	24.7	37.1	0.667	7.5	32.7
57	21.6	28.4	0.758	8.1	47.9

[a] The accuracy of these determinations is ±3%.

Table III. Percentage Compositions[a] in the Thermolysis of 11 in Diglyme at 170 °C (0.12 M)

time, h	11	(2 + 3)	12
1	91.5		
5	77.6		
10	62.0	29.9	3.0
15	46.6	41.2	3.8
18	42.1	50.0	5.9
22	38.6	48.4	7.3
26	32.6	53.8	9.9
31	28.3	52.9	13.9
36	26.4	55.5	17.3
41	22.4	54.2	18.3
47	17.9	52.0	21.0
53	16.5	50.9	25.0
60	14.9	49.1	27.5
70	11.8	46.6	34.5
82	12.3	45.5	40.3

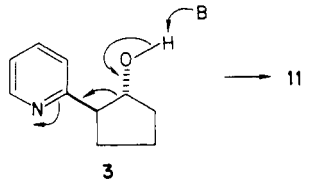
[a] The accuracy of these determinations is ±3%.

Under these conditions, 2-(2-hydroxy-4-methylpentyl)-3,5,6-trimethylpyrazine,[3] for example, is converted almost quantitatively to tetramethylpyrazine and isovaleraldehyde.

The thermolysis of each of the pyridine derivatives **2** and **3**, in diglyme-d_{14} at 170 °C, was found to proceed much faster than that of the pyrazine analogues. The overall process taking place appears to be kinetically very complex and can be summarized in Scheme VI. The results ob-

(7) Some dehydration (~5%) is observed under these conditions.

Scheme VII



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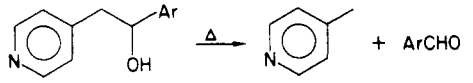
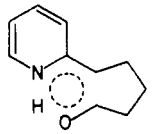
Scheme VIII



tained from the thermolysis of **2**, **3**, and **11** are presented in Tables I, II, and III, respectively. Several very interesting conclusions can be drawn from these results. We were able to establish that both **2** and **3** undergo isomerization to each other either directly or via the aldehyde **11**, since the latter was found to undergo ring closure to give both **2** and **3**. Starting from either **2**, **11**, or **3**, an equilibrium is reached between **2** and **3** where the ratio **2**/**3** is 0.75. This result suggests that the trans isomer is more stable in diglyme solution.

Both **2** and **3** also undergo a slow dehydration to form **12**. It was found that the trans isomer dehydrates slightly faster than the cis isomer ($k_{3d} > k_{2d}$). The formation of water during the process further complicates the kinetics, since water has a slight catalytic effect on aldehyde formation and possibly on the other reactions as well. The yield of **12** after 57 h at 170 °C is 42% and 48% from **2** and **3**, respectively. This is also approximately the time needed for **2** and **3** to equilibrate, and at this point the yield of **11** is 10% and 8% from **2** and **3**, respectively.

The formation of the aldehyde **11** from the cis isomer **2** is faster than from the trans isomer **3** ($k_2 > k_3$). We estimate, on the basis of initial rates, that $k_2/k_3 = 2$. This order of reactivity is indeed expected on the basis of our previous studies on the mechanism of this reaction. The proximity of the reacting functional groups in **2** enables the reaction to proceed via the concerted transition state **13**. Such a mechanism is stereochemically impossible in



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the trans isomer **3**. Hence, the formation of **11** from **3** proceeds at least in part through its isomerizations to **2**, which in turn forms **11**. Nevertheless, our results suggest that **11** is also formed directly from **3**, most likely by a base-catalyzed retro-aldol type cleavage (Scheme VII). This is supported by our previous finding[3,8] that 2-(4-pyridyl)ethanols, even though less reactive than their isomeric 2-(2-pyridyl)ethanols, undergo thermolysis to form 4-picoline and the corresponding aldehyde (Scheme VIII).

Perhaps the most interesting observation made in this study is the thermal ring closure of the aldehyde **11** to form a mixture of **2** and **3**. Such a reversible reaction has never been detected in any of our previous studies.[1,3] Moreover, when a 1:1 mixture of 2-picoline and butyraldehyde in diglyme (0.2 M of each) was heated at 170 °C, no formation of 1-(2-pyridyl)-2-hydroxypentane could be detected even after 24 h. Instead, the butyraldehyde underwent self-condensation by either aldol-type or polymerization reactions as was evident by the disappearance of the aldehydic proton from the NMR spectrum of the mixture. However, the 2-picoline remained unchanged. Therefore, it appears that the ring closure reaction in **11** is unique to this system. It is very likely that the intramolecular nature of this reaction makes it proceed much more rapidly than a similar bimolecular reaction.

(8) Houminer, Y.; Williams, D. L. *J. Org. Chem.* **1983**, *48*, 2622.

Experimental Section

All reactions involving organometallic reagents were carried out under a N_2 atmosphere. Melting points were determined with a Thomas-Hoover capillary melting point appratus and are uncorrected. IR spectra were recorded with a Perkin-Elmer Model 621 spectrophotometer. NMR spectra were recorded with a Brucker Model WP80 spectrometer, and the chemical shifts are given in δ units downfield from internal Me_4Si. MS spectra were recorded with a Finnigan Model 3300 mass spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Both qualitative and preparative TLC were carried out on silica gel GF plates with hexane containing 15–40% acetone as the eluent.

2-(2-Pyridyl)cyclopentanone (1). A slightly modified literature procedure has been used.[6] To a solution of pyridine *N*-oxide (9.5 g, 0.1 mol) in CH_2Cl_2 (60 mL) at 0 °C was added dropwise with stirring 14.0 g (0.1 mol) of benzoyl chloride. A white precipitate formed and the mixture was stirred at 0 °C for 30 min. A solution of *N*-(1-cyclopenten-1-yl)morpholine (18.4 g, 0.12 mol) in CH_2Cl_2 (30 mL) was added slowly with stirring. The mixture was allowed to warm to room temperature and then refluxed for 5 h. The solvent was removed under reduced pressure and to the remaining orange oil was added 20% HCl solution (120 mL). The mixture was washed several times with ether. The aqueous solution was adjusted to pH ~8 with dilute NaOH solution and the oil which separated was extracted with CH_2Cl_2. The solution was dried ($MgSO_4$) and evaporated under reduced pressure to give 14.5 g of a brown oil. Distillation gave 7.4 (46%) of pure **1** as a yellow liquid: bp 65–67 °C (0.05 mmHg); IR (neat) 1735, 1640, 1585, 1415, 1140, 1115 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.65–2.75 (1 H, m, 3 CH_2), 3.48 (1 H, t, J = 11 Hz, CH), 6.65–7.75 (3 H, m, H-3, H-4, and H-5 pyridine), 8.56 (1 H, m, H-6 pyridine); MS, *m/e* (relative intensity) 161 (M^+, 49), 160 (16), 133 (13), 132 (15), 130 (11), 106 (100), 105 (10), 104 (12), 79 (11).

Anal. Calcd for $C_{10}H_{11}NO$: C, 74.51; H, 6.88; N, 8.69. Found: C, 74.22; H, 6.83; N, 8.46.

Sodium Borohydride Reduction of 1. To a solution of the ketone **1** (5 g) in EtOH (100 mL) was added at room temperature a large excess of sodium borohydride, and the mixture was stirred for 30 min. A few drops of acetic acid were added followed by the addition of water. The EtOH was evaporated under reduced pressure, and the products were extracted with CH_2Cl_2. The solution was dried ($MgSO_4$) and evaporated under reduced pressure to give 4.8 g of a liquid. Preparative TLC (hexane–acetone, 3:1) of the crude mixture gave 1.9 g (38%) of pure *cis*-1-hydroxy-2-(2-pyridyl)cyclopentane (**2**) as a liquid: bp 64 °C (0.05 mmHg); IR (neat) 3330, 1605, 1580, 1480, 1448, 1155, 1015 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.47–2.32 (6 H, m, 3 CH_2), 2.99 (1 H, m, CH), 4.56 (1 H, m, $J_{CH-CHOH}$ = 3.6 Hz, CHOH), 7.00–7.85 (3 H, m, H-3, H-4, and H-5 pyridine), 8.47 (1 H, m, H-6 pyridine); MS, *m/e* (relative intensity) 163 (M^+, <1), 135 (19), 122 (11), 118 (13), 117 (11), 107 (33), 106 (100), 93 (11), 78 (13).

Anal. Calcd for $C_{10}H_{13}NO$: C, 73.59; H, 8.03; N, 8.85. Found: C, 73.58; H, 8.18; N, 8.40.

Also separated by TLC was 2.1 g (42%) of pure *trans*-1-hydroxy-2-(2-pyridyl)cyclopentane (**3**) as a liquid: bp 76 °C (0.05 mmHg); IR (neat) 3340, 1605, 1580, 1480, 1440 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.40–2.38 (6 H, m, 3 CH_2), 3.00 (1 H, m, CH), 4.33 (1 H, m, $J_{CH-CHOH}$ = 7.8 Hz, CHOH), 7.00–7.75 (3 H, m, H-3, H-4, and H-5 pyridine), 8.45 (1 H, m, H-6 pyridine); MS, *m/e* (rel intensity) 163 (M^+, <1), 146 (16), 145 (19), 144 (13), 135 (16), 122 (12), 120 (14), 118 (15), 117 (10), 107 (19), 106 (100), 93 (13), 78 (11).

Anal. Calcd for $C_{12}H_{13}NO$: C, 73.59; H, 8.03; N, 8.58. Found: C, 73.39; H, 8.19; N, 8.46.

Oxidation of 1 on Silica Gel. A solution of the ketone **1** (300

mg) in CH_2Cl_2 (5 mL) was mixed with silica gel (8 g). The solvent was evaporated and the solid was left at room temperature in an open beaker for 2 h, at which point the yellow color disappeared. The silica gel was extracted with Et_2O and acetone, and the solvent was evaporated under reduced pressure. Separation by preparative TLC gave 85 mg (26%) of pure 2-hydroxy-2-(2-pyridyl)-cyclopentanone (**4**): mp 130–132 °C (needles from ether–hexane 1:1); IR (Nujol) 3100, 1745, 1595, 1440, 1140, 1075, 985 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.88–2.72 (6 H, m, 3 CH_2), 4.50 (1 H, s, OH), 7.10–7.87 (3 H, m, H-3, H-4, and H-5 pyridine), 8.54 (1 H, m, H-6 pyridine).

Anal. Calcd for $C_{10}H_{11}NO_2$: C, 67.78; H, 6.26; N, 7.91. Found: C, 67.92; H, 6.38; N, 7.85.

Also separated by TLC was 120 mg (33%) of pure 5-(2-pyridyl)-5-oxopentanoic acid (**5**): mp 81–85 °C (needles from ether–hexane 1:1); IR (Nujol) 1720, 1705, 1590, 1370, 1315, 1220, 1115 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.85–2.66 (4 H, m, 2 CH_2), 3.32 (2 H, t, J = 9 Hz, CH_2CO), 7.08–8.12 (3 H, m, H-3, H-4, and H-5 pyridine), 8.68 (1 H, m, H-6 pyridine), 10.02 (1 H, br s, COOH).

Anal. Calcd for $C_{10}H_{11}NO_3$: C, 62.16; H, 5.74; N, 7.25. Found: C, 62.36; H, 5.97, N, 7.29.

2-(2-Pyrazyl)cyclopentanone (6). To a stirring suspension of oil-free KH (4 g, 0.1 mol) in DMF (100 mL), at 0 °C, was added slowly (40 min) a solution of cyclopentanone (8.4 g, 0.1 mol) in DMF (40 mL). The mixture was stirred at 0 °C until no more hydrogen was evolved. Chloropyrazine (11.4 g, 0.1 mol) was added dropwise and the mixture was left stirring at 0 °C for 2 h. Water was added, followed by dilute HCl (pH ~7). The product was extracted with Et_2O (2 × 100 mL) and CH_2Cl_2 (2 × 100 mL), and the combined organic layers were dried ($MgSO_4$) and evaporated under reduced pressure to give an oil. The oil was dissolved in 10% HCl and the mixture extracted with Et_2O (three times). The aqueous layer was neutralized with dilute NaOH to pH ~7 and extracted with CH_2Cl_2. The solution was dried ($MgSO_4$) and evaporated under reduced pressure (at 60 °C) to give 5.5 g (34%) of almost pure **6** as a solid: mp 80–82 °C. Sublimation at 75 °C (0.05 mmHg) and recrystalliztion from ether gave 4.1 g of pure **6** as plates: mp 83–85 °C; IR (Nujol) 1730, 1420, 1275, 1065, 1015 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.70–2.70 (6 H, m, 3 CH_2), 3.55 (1 H, t, CH), 8.48 (3 H, m, pyrazine).

Anal. Calcd. for $C_9H_{10}N_2O$: C, 66.65; H, 6.22; N, 17.27. Found: C, 66.83; H, 6.22; N, 17.20.

Sodium Borohydride Reduction of 6. To a solution of the ketone **6** (3.5 g) in 95% EtOH (100 mL) was added a large excess of sodium borohydride. The mixture was stirred at room temperature for 5 h. Water was added, followed by the addition of acetic acid to destroy excess reducing agent. The mixture was extracted with CH_2Cl_2 and the organic layer dried ($MgSO_4$) and evaporated under reduced pressure to give an oil. Repeated preparative TLC afforded 1.2 g (34%) of pure *cis*-1-hydroxy-2-(2-pyrazyl)cyclopentane (**7**): bp 110–115 °C (oven temperature, at 0.025 mmHg); IR (neat) 3360, 1525, 1480, 1410, 1335, 1020, 845 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.60–2.20 (6 H, m, 3 CH_2), 3.10 (1 H, m, CH), 4.52 (1 H, m $W_{1/2}$ = 11 Hz, CHOH), 8.48 (2 H, s, pyrazine), 8.55 (1 H, s, pyrazine).

Anal. Calcd for $C_9H_{12}N_2O$: C, 65.83; H, 7.37; N, 17.06. Found: C, 65.71; H, 7.40; N, 17.16.

Also separated by TLC was 1.4 g (40%) of pure *trans*-1-hydroxy-2-(2-pyrazyl)cyclopentane (**8**): bp 120–125 °C (oven temperature, at 0.025 mmHg); IR (neat) 3360, 1525, 1475, 1415, 1015, 845 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.52–2.41 (6 H, m, 3 CH_2), 3.09 (1 H, m, CH), 4.38 (1 H, m, $W_{1/2}$ = 17 Hz, CHOH), 8.35 (1 H, s, pyrazine), 8.46 (2 H, s, pyrazine).

Anal. Calcd for $C_9H_{12}N_2O$: C, 65.83; H, 7.37; N, 17.06. Found: C, 65.80; H, 7.50; N, 17.08.

The IR spectrum of **7** in CCl_4 shows a broad OH stretching band at 3430 cm^{-1}. This band intensity relative to the CH stretching region does not change with dilution. The spectrum does not show a free OH group. These results indicate the presence of intramolecular hydrogen bonding in **7**. The IR spectrum of **8** in CCl_4 shows a broad OH stretching band at 3500 cm^{-1} and a sharp band at 3630 cm^{-1} which intensifies relative to the broad band with dilution. These results establish the cis and trans configuration in **7** and **8**, respectively.

Thermolyses of 7 and 8 in Diglyme-d_{14}. Each of these substrates was thermolyzed in a NMR tube at a concentration of 0.2 M, for 115 h. The progress of the reaction was followed by NMR. The formation of 5-(2-pyrazyl)pentanal (**9**) was evident from the appearance of a triplet at δ 9.67 (CHO). The dehydration product, 1-(2-pyrazyl)cyclopentene (**10**), was easily detected by the appearance of a multiplet at δ 6.83 corresponding to the vinylic proton. Neither of these products was isolated.

5-(2-Pyridyl)pentanal (11). A 1:1 mixture of **2** and **3** (800 mg) was heated at 170 °C in a sealed tube for 40 h. NMR indicated the formation of 5–6% of **11**. Repeated TLC separation gave 55 mg of pure **11** as a liquid. An analytical sample was obtained by GC: IR (neat) 1720, 1585, 1560, 1470, 1430 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.82 (2 H, m, 2 CH_2), 3.43 (2 H, m, CH_2), 3.73 (2 H, m, CH_2), 7.16–7.85 (3 H, m, H-3, H-4, and H-5 pyridine), 8.50 (1 H, m, H-6 pyridine), 9.52 (1 H, t, CHO).

Anal. Calcd for $C_{10}H_{13}NO$: C, 73.59; H, 8.03; N, 8.58. Found: C, 73.44; H, 8.06; N, 8.52.

1-(2-Pyridyl)cyclopentene (12). A 1:1 mixture of **2** and **3** (200 mg) was heated at 170 °C in a sealed tube for 55 h. Preparative TLC afforded 90 mg of pure **12** as a liquid: IR (neat) 1620, 1580, 1555, 1465, 1430 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.78–2.99 (6 H, m, 3 CH_2), 6.60 (1 H, m, vinylic), 6.95–7.80 (3 H, m, H-3, H-4, and H-5 pyridine), 8.56 (1 H, m, H-6 pyridine); MS, m/e (relative intensity) 145 (M^+, 48), 144 (100), 143 (15), 130 (35), 117 (20), 77 (12).

Anal. Calcd for $C_{10}H_{11}N$: C, 82.72; H, 7.64; N, 9.65. Found: C, 82.44; H, 7.73; N, 9.65.

Kinetic Experiments. Reactions were carried out in diglyme-d_{14} (Merck Sharp & Dohme, Canada, Ltd.) that was dried over molecular sieves. A 0.1–0.2 M solution of each of the substrates (0.5 mL) was placed in a thick-walled NMR tube, and the tubes were sealed. Kinetic runs were carried out in a constant-temperature oil bath preheated to the desired temperature (170 ± 0.8 °C). The progress of each reaction was followed by NMR spectroscopy using a method similar to that described by us in an earlier study.[1] The protons in the 6-position of the pyridine rings in all reactants and products have very similar chemical shifts, and the integration of these protons remains constant during the thermolysis. Hence, percentage compositions were calculated from integration of peaks of both reactants and products in the aromatic region, CHOH, CHO, and vinylic regions. For example, in the thermolysis of **2** the percentage compositions of **11** and **12** were calculated from the measured integration ratios CHO/H-6 pyridine and CH vinylic/H-6 pyridine, respectively. The percentage compositions of **2** and **3** were calculated from the corresponding CHOH/H-6 pyridine integration ratios.

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