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Thermal Rearrangements of Cyclic Amine Ylides. IV.[1] Rearrangement of β,γ-Unsaturated 1-Alkylpiperidine *N*-Oxides: Formation of 1,2-Oxazepine Derivatives

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The thermolysis of 1-methyl-2-vinylpiperidine *N*-oxide (**13**) resulted in Meisenheimer [1, 2] rearrangement to give the hexahydro-1,2-oxazepine (**23**) and no [2, 3]-sigmatropic rearrangement product (**24**). Similarly, the 1-methyl-1,2,5,6-tetrahydropyridine *N*-oxides (**15**), on heating, gave only the tetrahydro-1,2-oxazepines (**26**, **27**), together with the Hofmann-type elimination products (**28**). The thermolysis of 1-benzyl-2-phenyl-(**20a**) and 1-benzyl-2-vinyl-piperidine *N*-oxide (**20b**) afforded the corresponding 1-benzyloxypiperidines (**32**) as well as the 1,2-oxazepines (**31**). These results are different from those observed for open-chain allylamine *N*-oxides and 1-alkyl-2-vinylpiperidine *N*-imides and *N*-ylides, which are known to undergo only [2,3]-sigmatropic rearrangement.

Keywords——thermolysis; ring-expansion; rearrangement; Meisenheimer rearrangement; 1-alkylpiperidine *N*-oxide; 1-alkyltetrahydropyridine *N*-oxide; 1,2-oxazepine

Ylides have been used as reactive intermediates in organic syntheses, particularly in reactions involving either thermal[2,3] or photochemical[3,4] intramolecular rearrangements and intermolecular cycloadditions. The open-chain allylamine *N*-ylides (**1a**),[5] *N*-imides (**1b**),[6] and *N*-oxides (**1c**)[7] are known to undergo competing [1,2]- and [2,3]-sigmatropic rearrangements to give the corresponding products shown in Chart 1; usually the latter occurs predominantly in all cases. As regards cyclic amines, whereas the 2-phenylpiperidine *N*-imides (**2**) undergo the Stevens-type [1,2] rearrangement to give the ring-expansion products (**3**),[8] both β,γ-unsaturated six-membered cyclic amine *N*-imides (**4**[9] and **6**[10]) undergo [2,3]-sigmatropic rearrangement with the double bond to give the corresponding products **5** and **7**, and the [1,2] rearrangement products are not formed. We have also reported that the [2,3] rearrangement with the vinyl group predominates over that with the cyclic double bond to give the tetrahydrodiazonines (**9**) in the thermolysis of the *N*-imides (**8**).[10] On the other hand, it is known that the thermolysis of the 1-methyl-2-arylpiperidine *N*-oxides (**10**) resulted in Meisenheimer-type [1,2] rearrangement[11] to give the ring-expansion products (**11**),[12] analogously to the case of the *N*-imides (**2**).

In connection with the above results, we were interested in examining the thermal behavior of the title cyclic amine *N*-oxides and we found that the Meisenheimer rearrangement takes place preferentially in spite of the presence of the double bond in the β-position,[13] in contrast to the cases of the *N*-imides (**4**, **6**, and **8**) having analogous unsaturated structures.

Syntheses of the Starting *N*-Oxides

The synthetic routes to the β,γ-unsaturated 1-alkylpiperidine *N*-oxides used in the present thermolysis are shown in Chart 2. 1-Methyl-2-vinylpiperidine (**12**), prepared from piperidine-2-ethanol,[10] was treated with *m*-chloroperbenzoic acid (*m*-CPBA) to give its *N*-oxide (**13**) in 71% yield. Pyridine and 2-phenylpyridine were treated with methyl iodide followed by reduction with sodium borohydride to give 1-methyl-1,2,5,6-tetrahydropyridines (**14a**, **b**),[14]

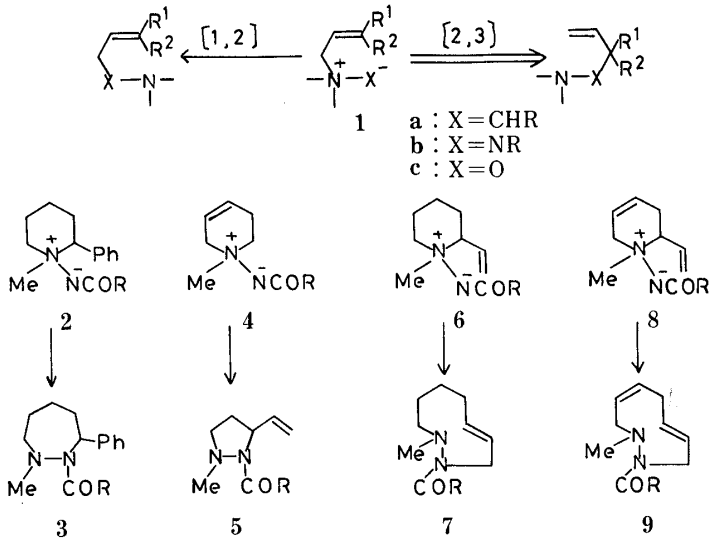


Chart 1

which gave the *N*-oxides (**15a, b**) on treatment with *m*-CPBA in *ca.* 85% yields. In order to prepare 2-vinyltetrahydropyridines, 1-methyl-2-vinylpyridinium iodides were reduced with sodium borohydride, but the desired products were not obtained. However, 2-ethynylpyridine (**16**)[15] was successively treated with methyl iodide and sodium borohydride to give the 6-styryl-1,2,5,6-tetrahydropyridine (**17**) in 28% yield, which was then oxidized with *m*-CPBA to give the *N*-oxide (**15c**) in 97% yield. Treatment of 2-phenylpiperidine[16] with benzoyl chloride gave 1-benzoyl-2-phenylpiperidine, which was then reduced with lithium aluminum hydride to give the 1-benzylpiperidine (**19**) in 95% yield. The oxidation of **19** with *m*-CPBA afforded the *N*-oxide (**20a**) in 86% yield. 1-Benzyl-2-vinylpiperidine *N*-oxide (**20b**) was obtained by the oxidation of 1-benzyl-2-vinylpiperidine (**21**) in 93% yield, which was prepared from piperidine-2-ethanol by the reported method.[17]

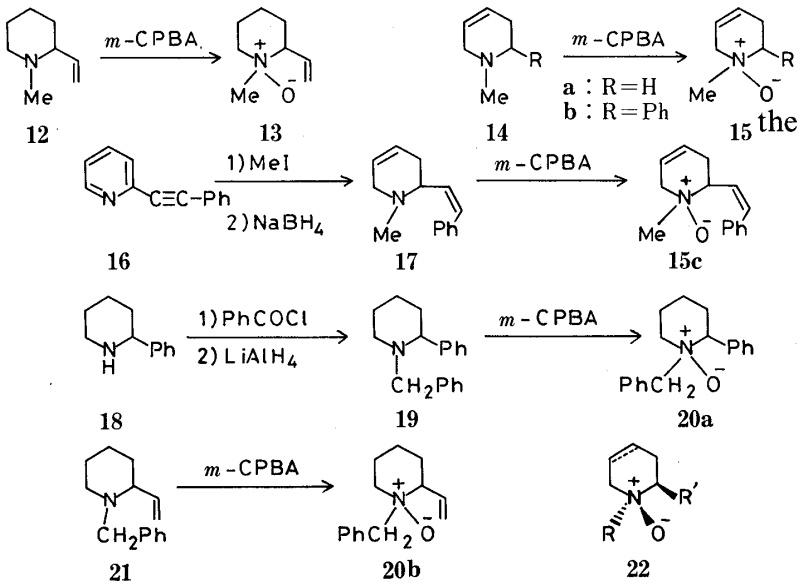


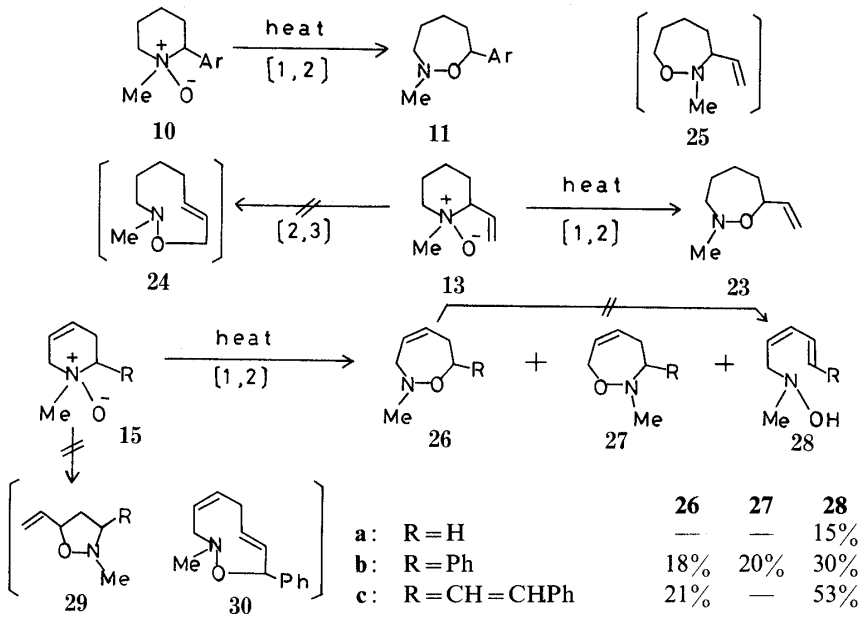
Chart 2

All the new *N*-oxides thus obtained were characterized by elemental and spectral analyses. The *N*-oxidation[18] of 1-alkylpiperidines is known to proceed preferentially at the axial position, as does *N*-alkylation.[19] Thus, the axial approach of the peracid on the

diequatorial conformers of the 1,2-disubstituted cyclic amines used may predominate, giving the corresponding diastereomers in which the *N*-oxide group and the α-substituent are *cis*, as shown in the structure **22**, as the sole products. However, the stereochemistry was not examined in detail. The geometry of the styryl group in **15c** and **17** was concluded to be *cis* from the ^{1}H-NMR spectra.

Thermolysis of the *N*-Oxides

Heating 1-methyl-2-vinylpiperidine *N*-oxide (**13**) in mesitylene at 155 °C resulted in Meisenheimer-type [1,2] rearrangement to give the ring-expansion product, 2-methyl-7-vinylhexahydro-1,2-oxazepine (**23**), in 48% yield, but another possible [1,2] rearrangement product (**25**) was not obtained. This result is analogous to those observed for 2-arylpiperidine *N*-imides (**2**)[8] and *N*-oxides (**10**).[12] It should be noted that the formation of the expected [2,3] rearrangement product, the oxazonine derivative (**24**), was not observed, in contrast to the case of the 2-vinylpiperidine *N*-imides (**6**).[10] In addition, the thermolysis of the fully saturated compound, 1-methylpiperidine *N*-oxide, resulted in decomposition to give no characterizable products.



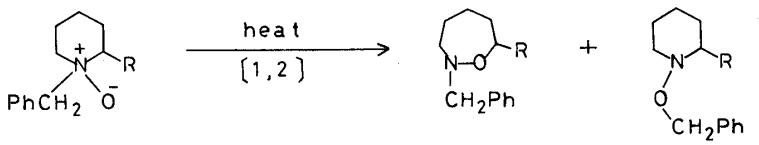
		26	27	28
a:	R=H	—	—	15%
b:	R=Ph	18%	20%	30%
c:	R=CH=CHPh	21%	—	53%

Chart 3

Next, the thermal behavior of cyclic amine *N*-oxides having a double bond in the ring was examined. The thermolysis of the 6-unsubstituted 1-methyl-1,2,5,6-tetrahydropyridine *N*-oxide (**15a**) afforded only the Hofmann-type elimination product (**28a**) in 15% yield and no rearrangement products. On the other hand, heating the 6-phenyltetrahydropyridine *N*-oxide (**15b**) in xylene at 140 °C gave two kinds of 1,2-oxazepines (**26b**) and (**27b**) in yields of 18 and 20%, respectively, together with the elimination product (**28b**) in 30% yield. The 1,2-oxazepine (**26b**), upon further heating, did not give the ring-opened compound (**28b**), which thus might be formed from the *N*-oxide (**15**) directly. Similarly, the thermolysis of the styryl compound (**15c**) having another double bond on the 6-position resulted in the formation of the oxazepine (**26**) and the elimination product (**28c**) in yields of 21 and 53%, respectively, but the oxazepine (**27**) could not be isolated.

In the cases of all the *N*-oxides (**15**), the [2,3] rearrangement products such as the tetrahydroisoxazoles (**29**) and the oxazonine derivative (**30**) were not observed. These results for **15** show that the [1,2] rearrangement occurs to either the allylic or the benzylic carbon,

whereas the [2,3]-sigmatropic rearrangement does not occur with the double bond or with the vinyl group, in contrast to the *N*-imides (**4**, **6**, and **8**).



	20	31	32
a: R=Ph		15%	50—60%
b: R=CH=CH$_2$		20%	55%

Chart 4

Heating the 1-benzylpiperidine *N*-oxides (**20b**, **b**) resulted in the formation of the 1,2-oxazepines (**31**) and the *N*-benzyloxypiperidines (**32**) in yields of 20—25 and 50—60%, respectively. This result indicates that the Meisenheimer rearrangement to the *N*-benzylic carbon predominates over that to the ring carbon. In the case of the 2-vinyl compound (**20b**), the [2,3] rearrangement product was also not obtained.

In conclusion, whereas open-chain allylamine *N*-oxides preferentially undergo thermal [2,3]-sigmatropic rearrangement by analogy with allylamine *N*-imides, the unsaturated cyclic amine *N*-oxides undergo only the Meisenheimer [1,2] rearrangement, in contrast to the analogous cyclic amine *N*-imides and cyclic sulfonium ylides,[20] which give only [2,3] rearrangement products and no [1,2] rearrangement products. At present, however, no plausible explanation can be offered to account for the differences. In the cases of the 1-alkyl-2-vinylpiperidine *N*-imides[21] and *N*-ylides,[22] either diastereomer readily undergoes thermal [2,3] rearrangement. Therefore, it seems unlikely that [2,3] rearrangement of the *cis* diastereomers of the *N*-oxides used in the present thermolysis is sterically unfavorable.

Experimental

Melting points were measured on a Yamato MP-21 apparatus and are uncorrected. Infrared (IR) spectra were determined with a JASCO IRA-2 spectrometer and mass spectra (MS) were recorded on a JEOL D-100 instrument. Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-MH100 spectrometer in $CDCl_3$ using tetramethylsilane as an internal standard; spectral assignments were confirmed by spin-decoupling experiments. Microanalyses were performed in the Microanalytical Laboratory of this school by Mrs. R. Igarashi.

1-Methyl-2-vinylpiperidine *N*-Oxide (13)——Solid *m*-chloroperbenzoic acid (*m*-CPBA: 2.3 g, 1.1 mol eq) was added in small portions to a solution of 1-methyl-2-vinylpiperidine (**12**: 1.5 g)[10] in CH_2Cl_2 (20 ml) with stirring in an ice bath. The reaction mixture was stirred for an additional 1 h and then evaporated to dryness *in vacuo*. The residue was chromatographed on alumina using CH_2Cl_2–MeOH (100:1) as an eluent to give the *N*-oxide (**13**): 71% yield, mp 151—152 °C, colorless prisms (from CH_2Cl_2–*n*-hexane). MS *m/z*: 141 (M^+). NMR δ: 1.20—2.45 (6H, m, 3-, 4-, and 5-H_2), 3.04 (3H, s, NMe), 3.11—3.50 (3H, m, 2-H and 6-H_2), 5.26 (1H, dd, J=16 and 1 Hz, *trans*-2′-H), 5.29 (1H, dd, J=11 and 1 Hz, *cis*-2′-H), 6.18 (1H, m, 1′-H). *Anal.* Calcd for $C_8H_{15}NO$: C, 68.09; H, 10.64; N, 9.93. Found: C, 68.02; H, 10.39; N, 9.71.

1-Methyl-1,2,5,6-tetrahydropyridine *N*-Oxide (15a)——1-Methyl-1,2,5,6-tetrahydropyridine (**14a**: 1.3 g)[14] was oxidized with *m*-CPBA and worked up as described for **13** to give the *N*-oxide (**15a**): 86% yield, mp <30 °C, colorless prisms (from CH_2Cl_2–*n*-hexane). MS *m/z*: 113 (M^+). NMR δ: 2.10—2.82 (2H, m, 5-H_2), 3.11—3.62 (2H, m, 6-H_2), 3.16 (3H, s, NMe), 3.71—4.25 (2H, m, 2-H_2), 5.50—6.05 (2H, m, 3- and 4-H). *Anal.* Calcd for $C_6H_{11}NO$: C, 63.71; H, 9.73; N, 12.39. Found: C, 63.50; H, 9.71; N, 12.11.

1-Methyl-6-phenyl-1,2,5,6-tetrahydropyridine *N*-Oxide (15b)——1-Methyl-6-phenyl-1,2,5,6-tetrahydropyridine (**14b**: 2 g)[14] was oxidized with *m*-CPBA and worked up as described for **13** to give the *N*-oxide (**15b**): 87% yield, mp 130—131 °C, colorless prisms (from CH_2Cl_2–*n*-hexane). MS *m/z*: 189 (M^+). NMR δ: 2.35—3.15 (2H, m, 5-H_2), 2.88 (3H, s, NMe), 4.02—4.30 (3H, m, 2-H_2 and 6-H), 5.45—6.07 (2H, m, 3- and 4-H), 7.42 and 7.70 (3H, m, and 2H, m, Ph–H). *Anal.* Calcd for $C_{12}H_{15}NO$: C, 76.19; H, 7.94; N, 7.41. Found: C, 75.98; H, 7.95; N, 7.37.

1-Methyl-6-styryl-1,2,5,6-tetrahydropyridine *N*-Oxide (15c)——A mixture of the 2-ethynylpyridine (**16**: 5.4 g),[15] methyl iodide (5 ml), ethanol (50 ml) was refluxed for 2 h. After removal of the solvent *in vacuo*, the residue was

washed with ether and then recrystallized from methanol to give 1-methyl-2-phenylethynylpyridinium iodide: 97% yield, mp 186—188 °C (dec.), yellow prisms. Solid $NaBH_4$ (2 g) was added in small portions to a solution of the salt (5.48 g) in ethanol (100 ml) with stirring at room temperature. The reaction solution was stirred for an additional 1 h and then concentrated *in vacuo*. The residue was extracted with CH_2Cl_2 and the extract was washed with satd. NaCl, dried, and concentrated *in vacuo*. The residue was chromatographed on silica gel using ether as an eluent to give 1-methyl-6-styryl-1,2,5,6-tetrahydropyridine (**17**): 28% yield, yellow oil. MS *m/z*: 199 (M^+). NMR δ: 2.18 (3H, s, NMe), 2.20—2.25 (2H, m, 5-H_2), 2.80 (2H, m, 2-H_2), 3.45 (1H, m, 6-H), 5.55—5.70 (3H, m, 3-, 4-, and 1′-H), 6.48 (1H, d, J=12 Hz, 2′-H), 7.00—7.10 (5H, m, Ph–H). *Anal.* Calcd for $C_{14}H_{17}N$: C, 84.42; H, 8.54; N, 7.03. Found: C, 84.67; H, 8.44; N, 6.82.

The compound (**17**: 0.9 g) was oxidized with *m*-CPBA and worked up as described for **13** to give the *N*-oxide (**15c**): 97% yield, yellow oil. MS *m/z*: 215 (M^+). NMR δ: 2.2—2.8 (2H, m, 5-H_2), 2.92 (3H, s, NMe), 3.80—3.85 (2H, m, 2-H_2), 4.20 (1H, m, 6-H), 5.40—5.80 (2H, m, 3- and 4-H), 6.11 (1H, dd, J=12 and 10 Hz, 1′-H), 6.77 (1H, dd, J=12 and 4 Hz, 2′-H), 7.15—7.23 (5H, m, Ph–H). This compound readily decomposed at room temperature and thus was used in the following reaction without further purification.

1-Benzyl-2-phenylpiperidine *N*-Oxide (20a)——A mixture of 2-phenylpiperidine (**18**: 1.61 g),[16] benzoyl chloride (1.54 g, 1.1 mol eq), CH_2Cl_2 (30 ml), and 40% aq. K_2CO_3 (10 ml) was stirred at room temperature overnight. The CH_2Cl_2 layer was separated and the water layer was extracted with CH_2Cl_2. The combined CH_2Cl_2 solution was washed with satd. NaCl, dried, and evaporated to dryness to give 1-benzoyl-2-phenylpiperidine: quantitative yield, mp 87—89 °C, colorless prisms (from benzene–*n*-hexane). MS *m/z*: 265 (M^+). IR ν_{max}^{KBr} cm^{-1}: 1635 (C=O). NMR δ: 1.1—1.8 (6H, m, 3-, 4-, and 5-H_2), 1.7—2.5 (2H, m, 6-H_2), 2.6—3.0 (1H, m, 2-H), 7.0—7.6 (10H, m, Ph–H). A suspension of $LiAlH_4$ (380 mg) in tetrahydrofuran (10 ml) was added dropwise to a solution of the *N*-benzoyl compound (1.85 g) in tetrahydrofuran (20 ml) with stirring in an ice bath. The reaction mixture was stirred for a further 4 h. Excess reagent was decomposed with water and the resulting precipitate was filtered off. The filtrate was dried over $MgSO_4$ and concentrated *in vacuo* to give the 1-benzyl-2-phenylpiperidine (**19**): 95% yield, colorless oil. NMR δ: 0.9—2.0 (6H, m, 3-, 4-, and 5-H_2), 2.3—3.1 (2H, m, 6-H_2), 3.2—3.4 (1H, m, 2-H), 4.45 (2H, s, N–CH_2–), 7.0—7.5 (10H, m, Ph–H).

The *N*-benzyl compound (**19**: 1.3 g) was oxidized with *m*-CPBA and worked up as described for **13** to give the *N*-oxide (**20a**): 86% yield, mp 155—157 °C, colorless prisms (from CH_2Cl_2–*n*-hexane). MS *m/z*: 267 (M^+). NMR δ: 1.2—2.4 (6H, m, 3-, 4-, and 5-H_2), 2.9—3.1 (2H, m, 6-H_2), 4.03 (1H, m, 2-H), 3.93 and 4.31 (each 1H, d, J=12 Hz, N–CH_2–), 7.1—7.6 (10H, m, Ph–H). *Anal.* Calcd for $C_{18}H_{21}NO$: C, 80.86; H, 7.92; N, 5.24. Found: C, 80.69; H, 7.90; N, 5.12.

1-Benzyl-2-vinylpiperidine *N*-Oxide (20b)——1-Benzyl-2-vinylpiperidine (**21**: 1.8 g)[17] was oxidized with *m*-CPBA and worked up as described for **13** to give the *N*-oxide (**20b**): 93% yield, mp 131—132 °C, colorless prisms (from CH_2Cl_2–*n*-hexane). MS *m/z*: 217 (M^+). NMR δ: 1.22—2.50 (6H, m, 3-, 4-, and 5-H_2), 3.05 (2H, m, 6-H_2), 3.50 (1H, m, 2-H), 4.31 (2H, s, N–CH_2–), 5.33 (1H, dd, J=17 and 2 Hz, *trans*-2′-H), 5.41 (1H, dd, J=10 and 2 Hz, *cis*-2′-H), 6.51 (1H, ddd, J=17, 10, and 9 Hz, 1′-H), 7.40—7.50 (5H, m, Ph–H). *Anal.* Calcd for $C_{14}H_{19}NO$: C, 77.42; H, 8.76; N, 6.45. Found: C, 77.53; H, 8.78; N, 6.21.

Thermolysis of the *N*-Oxides: General Procedure——A mixture of an *N*-oxide (10—15 mmol) and a solvent (10—20 ml) was heated; the reaction was followed in terms of the disappearance of the spot of the starting *N*-oxide on thin-layer chromatography, and was complete in 1—2 h. After cooling, the reaction solution was chromatographed on silica gel using CH_2Cl_2 or CH_2Cl_2–MeOH (100:1) as an eluent to give the products. Reaction conditions are indicated thus: solvent, reaction temperature.

Thermolysis of 13——Conditions: mesitylene, 155 °C. 2-Methyl-7-vinylhexahydro-1,2-oxazepine (**23**): 48% yield, colorless oil. MS *m/z*: 141 (M^+). NMR δ: 1.50—2.12 (6H, m, 4-, 5-, and 6-H_2), 2.56 (3H, s, NMe), 2.70 (2H, m, 3-H_2), 4.12 (1H, m, 7-H), 5.06 (1H, dd, J=10 and 1 Hz, *cis*-2′-H), 5.12 (1H, dd, J=17 and 1 Hz, *trans*-2′-H), 5.92 (1H, ddd, J=17, 10, and 6 Hz, 1′-H). *Anal.* Calcd for $C_8H_{15}NO$: C, 68.09; H, 10.64; N, 9.93. Found: C, 67.97; H, 10.51; N, 9.69.

Thermolysis of 15a——Conditions: toluene, 110 °C. *N*-Methyl-*N*-[2-(*z*),4(*E*)-pentadien-1-yl]hydroxylamine (**28a**): 15% yield, yellow oil. MS *m/z*: 113 (M^+). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3200 (OH). NMR δ: 2.60 (3H, s, NMe), 3.47 (2H, d, J=7 Hz, 1-H_2), 5.6—6.8 (5H, m, olefinic H), 7.65 (1H, br, OH). *Anal.* Calcd for $C_6H_{11}NO$: C, 63.71; H, 9.73; N, 12.39. Found: C, 63.57; H, 9.82; N, 12.18.

Thermolysis of 15b——Conditions: xylene, 140 °C. 2-Methyl-7-phenyl-2,3,6,7-tetrahydro-1,2-oxazepine (**26b**): 18% yield, yellow oil. MS *m/z*: 189 (M^+). NMR δ: 2.00—2.51 (2H, m, 6-H_2), 2.65—3.30 (2H, m, 3-H_2), 2.69 (3H, s, NMe), 4.70—4.75 (1H, m, 7-H), 6.12—6.50 (2H, m, 4- and 5-H), 7.30—7.35 (5H, m, Ph–H). *Anal.* Calcd for $C_{12}H_{15}NO$: C, 76.91; H, 7.94; N, 7.41. Found: C, 76.93; H, 7.67; N, 7.14.

2-Methyl-3-phenyl-2,3,4,7-tetrahydro-1,2-oxazepine (**27b**): 20% yield, yellow oil. MS *m/z*: 189 (M^+). NMR δ: 2.02 (3H, s, NMe), 2.30—2.33 (2H, m, 4-H_2), 2.75—3.48 (3H, m, 3-H and 7-H_2), 5.70—5.75 (2H, m, 5- and 6-H), 7.30—7.35 (5H, m, Ph–H). *Anal.* Calcd for $C_{12}H_{15}NO$: C, 76.91; H, 7.94; N, 7.41. Found: C, 77.05; H, 8.10; N, 7.40.

N-Methyl-*N*-[2(*z*),4(*E*)-pentadien-1-yl]hydroxylamine (**28b**): 30% yield, orange oil. MS *m/z*: 189 (M^+). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3200 (OH). NMR δ: 2.64 (3H, s, NMe), 3.56 (2H, d, J=7 Hz, 1-H_2), 5.55—7.10 (4H, m, olefinic H), 7.30—7.35 (5H, m, Ph–H), 8.00 (1H, br, OH). *Anal.* Calcd for $C_{12}H_{15}NO$: C, 76.91; H, 7.94; N, 7.41. Found: C, 77.21;

H, 7.68; N, 7.11.

Thermolysis of 15c——Conditions: toluene, 110 °C. 2-Methyl-7-[(*Z*)-styryl]-2,3,6,7-tetrahydro-1,2-oxazepine (**26c**): 18% yield, yellow oil. MS *m/z*: 215 (M^+). NMR δ: 2.55 (2H, m, 6-H_2), 2.63 (3H, s, NMe), 3.42—3.46 (2H, m, 3-H_2), 4.90 (1H, m, 7-H), 5.45—5.92 (3H, m, 4-, 5-, and 1′-H), 6.50 (1H, d, J=12 Hz, 2′-H), 7.30—7.35 (5H, m, Ph–H). *Anal.* Calcd for $C_{14}H_{17}NO$: C, 78.14; H, 7.91; N, 6.51. Found: C, 77.85; H, 7.78; N, 6.39.

N-Methyl-*N*-[7-phenyl-2(*Z*), 4(*E*), 6(*Z*)-heptatrien-1-yl]hydroxylamine (**28c**): 53% yield, yellow oil. MS *m/z*: 215 (M^+). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3200 (OH). NMR δ: 2.59 (3H, s, NMe), 3.45 (2H, d, J=7 Hz, 1-H_2), 5.50—6.75 (6H, m, olefinic H), 7.20—7.27 (5H, m, Ph–H), 8.50 (1H, br, OH). *Anal.* Calcd for $C_{14}H_{17}NO$: C, 78.14; H, 7.91; N, 6.51. Found: C, 78.37; H, 8.16; N, 6.44.

Thermolysis of 20a——Conditions: mesitylene, 165 °C. 2-Benzyl-7-phenylhexahydro-1,2-oxazepine (**31a**): 25% yield, mp 47—48 °C, colorless prisms (from *n*-hexane). MS *m/z*: 267 (M^+). NMR δ: 1.2—2.0 (6H, m, 4-, 5-, and 6-H_2), 2.4—2.8 and 3.4—3.6 (1H, m, and 2H, m, 3-H_2 and 7-H), 4.15 and 4.44 (each 1H, d, J=10 Hz, NCH_2–), 6.8—7.5 (10H, m, Ph–H). *Anal.* Calcd for $C_{18}H_{21}NO$: C, 80.86; H, 7.92; N, 5.24. Found: C, 80.87; H, 7.86; N, 5.15.

1-Benzyloxy-2-phenylpiperidine (**32a**): 48% yield, colorless oil. MS *m/z*: 267 (M^+). NMR δ: 1.0—2.0 (6H, m, 3-, 4-, and 5-H_2), 2.2—2.9 (2H, m, 6-H_2), 3.3—3.5 (1H, m, 2-H), 4.67 (2H, s, OCH_2–), 7.1—7.5 (10H, m, Ph–H). *Anal.* Calcd for $C_{18}H_{21}NO$: C, 80.86; H, 7.92; N, 5.24. Found: C, 80.63; H, 7.96; N, 5.01.

Thermolysis of 20b——Conditions: xylene, 140 °C. 2-Benzyl-7-vinylhexahydro-1,2-oxazepine (**31b**): 27% yield, colorless oil. MS *m/z*: 217 (M^+). NMR δ: 1.15—1.90 (6H, m, 4-, 5-, and 6-H_2), 2.78—2.82 (2H, m, 3-H_2), 3.82 (2H, s, NCH_2–), 4.12 (1H, m, 7-H), 4.91 (1H, dd, J=10 and 1 Hz, *cis*-2′-H), 4.95 (1H, dd, J=18 and 1 Hz, *trans*-2′-H), 5.65 (1H, ddd, J=18, 10, and 8 Hz, 1′-H), 7.30—7.35 (5H, m, Ph–H). *Anal.* Calcd for $C_{14}H_{19}NO$: C, 77.42; H, 8.76; N, 6.45. Found: C, 77.29; H, 8.59; N, 6.28.

1-Benzyloxy-2-vinylpiperidine (**32b**): 55% yield, colorless oil. MS *m/z*: 217 (M^+). NMR δ: 1.05—1.83 (6H, m, 3-, 4-, and 5-H_2), 2.35—3.03 (2H, m, 6-H_2), 3.30 (1H, m, 2-H), 4.67 (2H, s, OCH_2–), 5.11 (1H, dd, J=10 and 2 Hz, *cis*-2′-H), 5.21 (1H, dd, J=18 and 2 Hz, *trans*-2′-H), 5.8—6.0 (1H, m, 1′-H), 7.30—7.35 (5H, m, Ph–H). *Anal.* Calcd for $C_{14}H_{19}NO$: C, 77.42; H, 8.76; N, 6.45. Found: C, 77.33; H, 8.75; N, 6.24.

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