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Thermal Rearrangements of Cyclic Amine Ylides. II.[1] Ring-expansion of 4- and 6-Vinyl-1,2,5,6-tetrahydropyridine and 2-Vinylpiperidine N-Imides

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The thermolysis of the 4-vinyl-1,2,5,6-tetrahydropyridine N-imide (**13a**) resulted in both [1,2-]- and [2,3]-sigmatropic rearrangements to give the tetrahydro-1,2-diazepine (**18**) and the 3,3-divinyltetrahydropyrazole (**19**), respectively; this reaction mechanism was confirmed by a deuterium-labelling experiment. In contrast, the thermolysis of both 6-vinyl-1,2,5,6-tetrahydropyridine N-imide (**13b**) and 2-vinylpiperidine N-imide (**17**) resulted in only [2,3] rearrangement with the vinyl group to give nine-membered ring products, the tetrahydro- (**21**) and the hexahydro-1,2-diazonine (**25**), respectively. The starting vinyltetrahydropyridine N-imides (**13a, b**) were prepared from the corresponding vinylpyridines (**10a, b**), and 2-vinylpiperidine N-imide (**17**) was prepared from 1-ethoxycarbonyl-2-vinylpiperidine (**14**).

Keywords——thermolysis; sigmatropic rearrangement; ring-expansion; N-imides; tetrahydropyridines; piperidines; 1,2-diazonines; 1,2-diazepines; deuterium-labelling experiment

In recent years, ylides have been used increasingly as reactive intermediates in organic syntheses, particularly in reactions involving either thermal[2–4] or photochemical[5,6] intramolecular rearrangements and intermolecular cycloadditions. Thermal reactions of the open-chain amine N-ylides (**1**),[7,8] N-imides (**2**),[3,9,10] and N-oxides (**3**)[11] have been widely investigated, as have those of S-ylides (**4**)[12] and S-imides (**5**).[4] As regards aminimides, the allyl N-imides (**6**) are known to undergo competing [1,2]- and [2,3]-sigmatropic rearrangements in a ratio that depends on the imide structure and the reaction conditions, but the latter rearrangement usually predominates over the former,[10] whereas the pentadienylamine N-imides (**7**) undergo [1,2] and [2,5] rearrangements predominantly over the [2,3] rearrangement.[10] On the other hand, as for cyclic amine N-imides, the piperidine N-imides (**8**) and the similar pyrrolidine N-imides have been shown to undergo a Stevens-type [1,2] rearrangement to give the corresponding ring expansion products.[13]

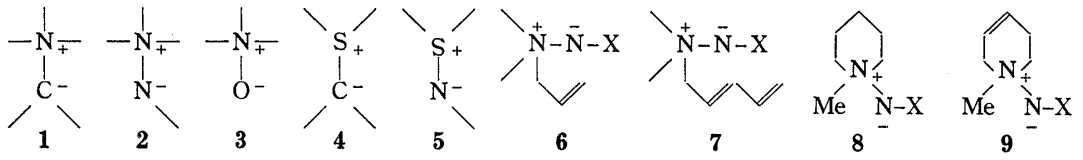

Chart 1

In connection with the above-mentioned studies and the thermal behavior of cyclic sulfonium ylides,[14,15] we were interested in examining such reactions of unsaturated cyclic amine N-imides and we have already reported that the thermolysis of the 1,2,5,6-tetrahydropyridine N-imides (**9**) resulted in [2,3] rearrangement to give the 3-vinyltetrahydropyrazoles.[1] We report here the syntheses and the results of thermolysis of the title cyclic amine N-imides (**13a, b** and **17**) having a vinyl group. These compounds were expected to undergo different types of rearrangements from that observed for the imides (**9**) because of the presence of another unsaturated moiety.[16]

Syntheses of the Starting N-Imides

The synthetic routes to the N-imides used in the present thermolysis are shown in Chart 2. The 4-vinyl- (**10a**) and 2-vinyl-pyridine (**10b**) were aminated with O-mesitylenesulfonylhydroxylamine (MSH: H_2NOMes)[17] and the resulting N-aminopyridinium mesitylenesulfonates were treated with sodium borohydride in the presence of ethyl chloroformate to give the corresponding 1-ethoxycarbonylamino-1,2,5,6-tetrahydropyridines (**11**). The tetrahydropyridines (**11**) were methylated with methyl iodide to give the salts (**12**), which were treated with sodium hydroxide solution to give the desired 4-vinyl- (**13a**) and 6-vinyl-1,2,5,6-tetrahydropyridine N-imide (**13b**), respectively.

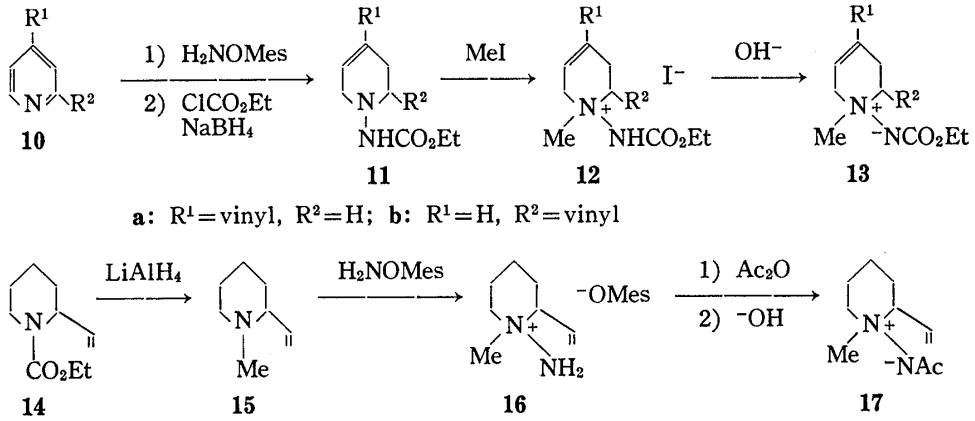

Chart 2

The 2-vinylpiperidine N-imide (**17**) was prepared from 1-ethoxycarbonyl-2-vinylpiperidine (**14**), which was derived from piperidine-2-ethanol according to the procedure described for the preparation of 1-benzoyl-2-vinylpiperidine by Vedejs.[15] Lithium aluminum hydride reduction of **14** in tetrahydrofuran gave the N-methylpiperidine (**15**), which was then treated with MSH to give the N-aminopiperidinium salt (**16**). Treatment of the salt (**16**) with ethyl chloroformate in the presence of an alkali resulted in decomposition and gave no N-ethoxycarbonylimide. Therefore, the salt (**16**) was acetylated with acetic anhydride and then treated with sodium hydroxide solution to give the N-acetylimide (**17**). All the new N-imides thus obtained were characterized by elemental and spectral analyses.

Thermolysis of the N-Imides

Thermolysis of the 4-vinyl-1,2,5,6-tetrahydropyridine N-imide (**13a**) in refluxing xylene for 6 h followed by chromatography on silica gel gave the 5-vinyl-2,3,6,7-tetrahydro-1,2-diazepine (**18**) and the 3,3-divinyltetrahydropyrazole (**19**) in yields of 24% and 27%, respectively. The formation of the ring-contraction product (**19**) may involve a [2,3]-sigmatropic rearrangement with the double bond in the ring, analogous to that observed for the N-imides (**9**), which gave 3-vinyltetrahydropyrazole derivatives.[1] However, two possible mechanisms; *i.e.*, [1,2] and [2,5] rearrangements, have been considered for the formation of the ring-expansion product (**18**). Therefore, the following deuterium-labelling experiment was carried out in order to clarify the mechanism.

Thermolysis of the 2,6-dideuterio-4-vinyl-1,2,5,6-tetrahydropyridine N-imide (**13a-D**), prepared from 4-vinylpyridine by using $NaBD_4$ instead of $NaBH_4$ in the manner described for the preparation of **13a**, resulted in the formation of the labelled compounds (**18-D**) and (**19-D**) in yields similar to those of **18** and **19**, respectively. and the [2,5] rearrangement product (**20**) could not be isolated. These labelled compounds were characterized by mass and proton nuclear magnetic resonance spectral comparison with the corresponding unlabelled compounds, (**13a**), (**18**), and (**19**), respectively.

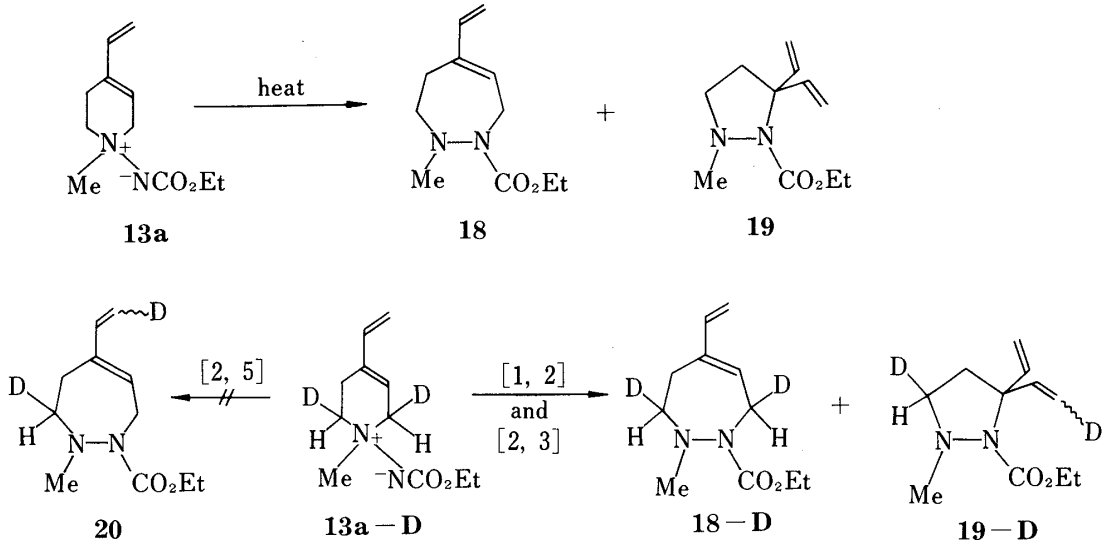

Chart 3

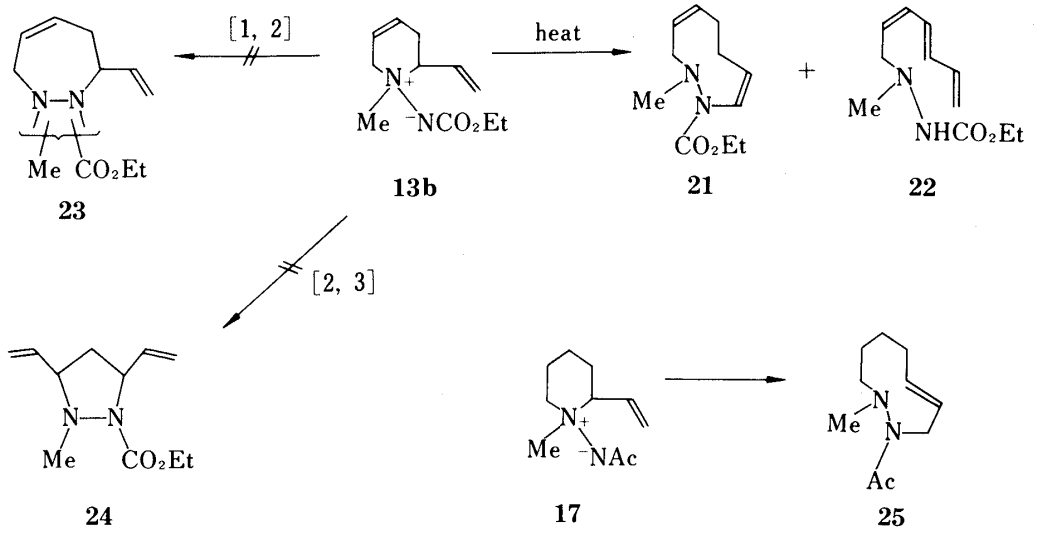

Chart 4

This result clearly indicates that the formation of the 1,2-diazepine (**18**) from **13a** proceeds through a Stevens-type [1,2] rearrangement and that [2,5] rearrangement with the vinyl group does not occur. In addition, [1,2] rearrangement does not occur to the 6-position. As compared with the case of the open-chain pentadienylamine N-imides (**7**),[10] the imide anion in **13a** is too distant from the vinyl group to attack it, and thus may react predominantly either at the double bond in the ring or at the allylic 2-position.

Next, thermolysis of the 6-vinyl-1,2,5,6-tetrahydropyridine N-imide (**13b**) in refluxing xylene for 3 h resulted in [2,3] rearrangement with the 2-vinyl group and cyclic elimination[18] to give the nine-membered tetrahydro-1,2-diazonine (**21**) and the heptatrienylhydrazine derivative (**22**) in yields of 20% and 38%, respectively. In this case, other compounds such as the [1,2] rearrangement products (**23**) and another [2,3] rearrangement product (**24**) could not be isolated, in contrast to the case of the 4-vinyl analogs (**13a**). Similarly, thermolysis of the 2-vinylpiperidine N-imide (**17**) gave the [2,3] rearrangement product (**25**)[19] in 82% yield as the sole product, and no [1,2] rearrangement product was obtained as in the cases of 2-vinylpiperidine C-ylides and thiepane C-ylides.[15] These results show that the [2,3] rearrangement

with the 2-vinyl group predominates over that with the cyclic double bond and the [1,2] rearrangement. Studies on the stereochemistry of the present reactions and on synthetic applications of the results to other systems are in progress.

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 (MS) spectra were obtained on a JEOL JMS-D100 instrument. ^{1}H-NMR spectra were recorded on a JEOL JNM-MH-100 spectrometer in $CDCl_3$ solution using tetramethylsilane as an internal standard unless otherwise stated, and spectral assignments were confirmed by spin-decoupling experiments and, in the case of NH protons, by exchange with D_2O. ^{13}C-NMR spectra were recorded on a JEOL FX-100 spectrometer. Microanalyses were performed in the Microanalytical Laboratory of this School by Mrs R. Igarashi.

1-Ethoxycarbonylamino-4-vinyl-1,2,5,6-tetrahydropyridine (11a)——A solution of O-mesitylenesulfonylhydroxylamine (1.05 mol eq) in ether (50—100 ml) was added dropwise to a solution of 4-vinylpyridine (**10a**: 10.5 g, 0.1 mol) in ethanol (200 ml) containing paraformaldehyde as a stabilizer, with stirring in an ice bath. After stirring for an additional 0.5 h, a solution of ethyl chloroformate (16.4 g, 0.15 mol) in ethanol (50 ml) was added dropwise to the mixture in the ice bath and then solid $NaBH_4$ (7.6 g, 0.2 mol) was added in small portions to the reaction mixture. The mixture was stirred for 5—6 h at room temperature. After removal of the solvent *in vacuo*, the residue was extracted with CH_2Cl_2 and the extract was washed with satd. NaCl, dried over K_2CO_3, and evaporated to dryness *in vacuo*. The residue was chromatographed on silica gel using CH_2Cl_2–acetone (50: 1) as an eluent to give **11a**: 1.23 g, 6.3% yield, mp 69—70°C, colorless prisms (from *n*-hexane–benzene). MS *m/e*: 196 (M^+). IR ν_{max}^{KBr} cm^{-1}: 1700 (C=O), 3250 (NH). NMR δ: 2.40 (2H, m, 5-H_2), 3.08 (2H, m, 6-H_2), 3.50 (2H, m, 2-H_2), 5.68 (1H, m, 3-H), 5.08 (1H, d, J=11 Hz, 2′-*cis*-H), 5.17 (1H, d, J=18 Hz, 2′-*trans*-H), 6.41 (1H, dd, J=11 and 18 Hz, 1′-H), 6.32 (1H, br, NH), 1.28 and 4.23 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{10}H_{16}N_2O_2$: C, 61.22; H, 8.16; N, 14.29. Found: C, 60.94; H, 8.09; N, 14.22.

1-Ethoxycarbonylamino-1-methyl-4-vinyl-1,2,5,6-tetrahydropyridinium Iodide (12a)——A mixture of **11a** (600 mg) and methyl iodide (30 ml) was refluxed for 20 h. After removal of the excess reagent *in vacuo*, the resulting residue was recrystallized from methanol–ether to give **12a**: 980 mg, 95% yield, mp 124—127°C (dec.). IR ν_{max}^{KBr} cm^{-1}: 1735 (C=O), 3100 (NH). NMR (CD_3OD) δ: 2.7 (2H, m, 5-H_2), 3.84 (3H, s, N–Me), 4.0—4.6 (2H, m, 6-H_2), 4.6—5.0 (2H, m, 2-H_2), 4.7 (1H, br, NH), 5.82 (1H, m, 3-H), 5.29 and 5.42 (1H, d, J=11 Hz, and 1H, d, J=18 Hz, 2′-H_2), 6.78 (1H, dd, J=11 and 18 Hz, 1′-H), 1.33 and 4.32 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{11}H_{19}IN_2O_2$: C, 39.05; H, 5.62; N, 8.28. Found: C, 38.93; H, 5.80; N, 8.24.

1-Methyl-4-vinyl-1-ethoxycarbonylimino-1,2,5,6-tetrahydropyridinium Ylide (13a)——A solution of the salt (**12a**: 625 mg) in water (20 ml) was titrated with 5% NaOH using phenolphthalein as an indicator and then concentrated *in vacuo* below 50°C. The residue was extracted with CH_2Cl_2 and the extract was passed through a short alumina column. The eluate was concentrated to give **13a**: 370 mg, quantitative yield, oil. MS *m/e*: 210 (M^+). IR ν_{max}^{film} cm^{-1}: 1620 (C=O). NMR δ: 2.6 (2H, m, 5-H_2), 3.44 (3H, s, N–Me), 3.6—3.9 (2H, m, 6-H_2), 4.3 (2H, m, 2-H_2), 5.70 (1H, m, 3-H), 5.21 and 5.28 (1H, d, J=11 Hz, and 1H, d, J=18 Hz, 2′-H_2), 6.47 (1H, dd, J=11 and 18 Hz, 1′-H), 1.22 and 3.99 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{11}H_{18}N_2O_2$: C, 62.83; H, 8.63; N, 13.32. Found: C, 62.78; H, 8.85; N, 13.08.

2,6-Dideuterio Compound (13a-D)——Compound **13a-D** was prepared from 4-vinylpyridine (**10a**: 2.63 g) by using $NaBD_4$ instead of $NaBH_4$ in the manner described for the preparation of **13a** *via* **11a** and **12a**. MS *m/e*: 212 (M^+ for $C_{11}H_{16}D_2N_2O_2$). NMR δ: 2.6 (2H, m, 5-H_2), 3.42 (3H, s, N–Me), 3.7—3.9 (1H, m, 6-H), 4.3 (1H, m, 2-H), 5.70 (1H, m, 3-H), 5.21 and 5.28 (1H, d, J=11 Hz, and 1H, d, J=18 Hz, 2′-H_2), 6.47 (1H, dd, J=11 and 18 Hz, 1′-H), 1.22 and 4.00 (3H, t, and 2H, q, CO_2Et).

1-Ethoxycarbonylamino-6-vinyl-1,2,5,6-tetrahydropyridine (11b)——Compound **11b** was prepared from 2-vinylpyridine (**10b**: 21 g) in the manner described for **11a**, 2.86 g, 7.2% yield, mp 61—62°C, colorless prisms (from *n*-hexane–benzene). MS *m/e*: 196 (M^+). IR ν_{max}^{KBr} cm^{-1}: 1690 (C=O), 3100 (NH). NMR δ: 2.3 (2H, m, 5-H_2), 3.1 (1H, m, 6-H), 3.4 (2H, m, 2-H_2), 5.4—5.9 (2H, m, 3- and 4-H), 5.14 and 5.17 (1H, dd, J=1 and 10 Hz, and 1H, dd, J=1 and 15 Hz, 2′-H_2), 5.8 (1H, m, 1′-H), 5.9 (1H, br, NH), 1.24 and 4.13 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{10}H_{16}N_2O_2$: C, 61.22; H, 8.16; N, 14.29. Found: C, 61.19; H, 8.40; N, 14.28.

1-Ethoxycarbonylamino-1-methyl-6-vinyl-1,2,5,6-tetrahydropyridinium Iodide (12b)——A mixture of **11b** (1 g) and methyl iodide (30 ml) was refluxed for *ca.* 20 h and then evaporated to dryness *in vacuo* to give **12b** as a red solid, NMR δ: 2.70 (2H, m, 5-H_2), 3.48 (3H, s, N–Me), 4.4 (2H, m, 2-H_2), 4.6 (1H, m, 6-H), 5.1—5.3 (2H, m, 2′-H_2), 5.6—6.3 (3H, m, 3-, 4-, and 1′-H), 5.8 (1H, br, NH), 1.31 and 4.24 (3H, t, and 2H, q, CO_2Et). However, the product (**12b**: *ca.* 800 mg) was unstable and gradually decomposed during purification. Thus, the solid was used in the following reaction without purification.

1-Ethoxycarbonylimino-1-methyl-6-vinyl-1,2,5,6-tetrahydropyridinium Ylide (13b)——A solution of the salt (**12b**: *ca.* 500 mg, crude) in water was titrated with 5% NaOH and worked up as described for **13a** to

give the ylide (**13b**): 290 mg, oil. MS *m/e*: 210 (M^+). IR ν_{max}^{film} cm^{-1}: 1630 (C=O). NMR δ: 2.5 (2H, m, 5-H_2), 3.16 (3H, s, N–Me), 4.1—4.6 (3H, m, 2-H_2 and 6-H), 5.1—6.3 (5H, m, 3-, 4-, and 1′-H and 2′-H_2), 1.21 and 3.93 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{11}H_{18}N_2O_2$: C, 62.83; H, 8.63; N, 13.32. Found: C, 62.64; H, 8.79; N, 13.19.

1-Methyl-2-vinylpiperidine (**15**)——A solution of 1-ethoxycarbonyl-2-vinylpiperidine (**14**: 5.94 g), prepared from piperidine-2-ethanol by procedures similar to those described for 1-benzoyl-2-vinylpiperidine,[15] in anhydrous tetrahydrofuran (50 ml) was added dropwise with stirring to a suspension of $LiAlH_4$ (1.9 g) in tetrahydrofuran at room temperature. The reaction mixture was refluxed for 4 h with stirring, then cooled. Excess reagent was decomposed with water and the resulting precipitate was filtered off. The filtrate was dried over $MgSO_4$ and evaporated to dryness *in vacuo*. The residue was chromatographed on silica gel using *n*-hexane–ether (3: 1) as an eluent to give **15**: 3.03 g, 75% yield, oil. MS *m/e*: 125 (M^+). NMR δ: 1.0—2.1 (6H, m, 3-, 4-, and 5-H_2), 2.11 (3H, s, N–Me), 2.3 and 2.8 (each 1H, m, 6-H_2), 3.6 (1H, m, 2-H), 4.98 and 5.10 (1H, dd, J=2 and 10 Hz, and 1H, dd, J=2 and 18 Hz, 2′-H_2), 5.74 (1H, ddd, J=8, 10, 18 Hz, 1′-H). *Anal.* Calcd for $C_8H_{15}N$: C, 76.74; H, 12.08; N, 11.19. Found: C, 76.51; H, 12.11; N, 11.42.

1-Amino-1-methyl-2-vinylpoperidinium Mesitylenesulfonate (**16**)——A solution of O-mesitylenesulfonylhydroxylamine (*ca.* 9 g) in CH_2Cl_2 (50 ml) was added dropwise to a solution of **15** (3.03 g) in CH_2Cl_2 (20 ml) with stirring in an ice bath. The reaction mixture was stirred further for 1 h. After addition of ether (100 ml) to the reaction mixture, the resulting precipitates were collected and recrystallized from MeOH–AcOEt to give **16**: 6.08 g, 75% yield, mp 167—168°C, colorless prisms. *Anal.* Calcd for $C_{17}H_{28}N_2O_3S$: C, 59.98; H, 8.29; N, 8.23. Found: C, 60.00; H, 8.24; N, 8.13.

1-Acetylimino-1-methyl-2-vinylpiperidinium Ylide (**17**)——A mixture of the salt (**16**: 800 mg) and acetic anhydride (8 ml) was refluxed for 12 h and then evaporated to dryness *in vacuo*. The residue was dissolved in water (10 ml). The solution was titrated with 5% NaOH using phenolphthalein as an indicator and evaporated to dryness *in vacuo* below 50°C. The residue was extracted with CH_2Cl_2 and the extract was dried over K_2CO_3 and concentrated *in vacuo*. The residue was chromatographed on alumina using CH_2Cl_2–MeOH (50: 1) as an eluent to give the ylide (**17**): 200 mg, 46% yield, oil. MS *m/e*: 182 (M^+). IR ν_{max}^{film} cm^{-1}: 1580 (C=O). NMR δ: 1.3—2.2 (6H, m, 3-, 4-, and 5-H_2), 1.82 (3H, s, Ac), 3.1—3.6 (2H, m, 6-H_2), 3.34 (3H, s, N–Me), 5.4 (1H, m, 2-H), 5.31 and 5.34 (1H, d, J=17 Hz, and 1H, d, J=10 Hz, 2′-H_2), 6.31 (1H, ddd, J=8, 10, and 17 Hz, 1′-H). *Anal.* Calcd for $C_{10}H_{18}N_2O$: C, 65.89; H, 9.96; N, 15.37. Found: C, 65.79; H, 10.15; N, 15.23.

Thermolysis of the Imide (**13a**)——A mixture of **13a** (220 mg) and xylene (5 ml) was refluxed for 6 h. After cooling, the reaction solution was chromatographed on silica gel using CH_2Cl_2–acetone (50: 1) as an eluent to give **18** and **19** successively. These products were further purified by rechromatography on silica gel with *n*-hexane–ether (3: 1).

2-Ethoxycarbonyl-1-methyl-5-vinyl-2,3,6,7-tetrahydrodiazepine (**18**): 51 mg, 24% yield, pale yellow oil. MS *m/e*: 210 (M^+). IR ν_{max}^{film} cm^{-1}: 1690 (C=O). ^{1}H-NMR δ: 2.5 (2H, m, 6-H_2), 2.60 (3H, s, 1-Me), 3.1 (2H, m, 7-H_2), 4.1 (2H, m, 3-H_2), 5.74 (1H, m, 4-H), 4.99 and 5.14 (1H, d, J=8 Hz, and 1H, d, J=15 Hz, 2′-H_2), 6.37 (1H, dd, J=8 and 15 Hz, 1′-H), 1.30 and 4.20 (3H, t, and 2H, q, CO_2Et). ^{13}C-NMR δ: 14.862 (q), 24.754 (t), 42.736 (q), 55.699 (t), 61.351 (t), 61.643 (t), 111.300 (t), 129.085 (d), 139.564 (s), 139.564 (d), 156.522 (s). *Anal.* Calcd for $C_{11}H_{18}N_2O_2$: C, 62.83; H, 8.63; N, 13.32. Found: C, 62.82; H, 8.85; N, 13.11.

2-Ethoxycarbonyl-1-methyl-3,3-divinyltetrahydropyrazole (**19**): 60 mg, 27% yield, oil. MS *m/e*: 210 (M^+). IR ν_{max}^{film} cm^{-1}: 1700 (C=O). NMR δ: 2.30 (2H, t, J=7 Hz, 4-H_2), 2.61 (3H, s, 1-Me), 3.09 (2H, t, J=7 Hz, 5-H_2), 5.16 and 5.19 (2H, d, J=16 Hz, and 2H, d, J=10 Hz, =CH_2 × 2), 6.16 (2H, dd, J=10 and 16 Hz, –CH= × 2), 1.28 and 4.20 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{11}H_{18}N_2O_2$: C, 62.83; H, 8.63; N, 13.32. Found: C, 62.69; H, 8.60; N, 13.22.

Thermolysis of the Deuterio Compound (**13a-D**)——A mixture of **13a-D** (150 mg) and xylene (40 ml) was refluxed for 5 h and worked up as described for **13a** to give the 3,7-di-D-diazepine (**18-D**) and the 5,2′-di-D-pyrazole (**19-D**).

18-D: 34 mg, 23% yield, MS *m/e*: 212 (M^+ for $C_{11}H_{16}D_2N_2O_2$). NMR δ: 2.5 (2H, m, 6-H_2), 3.1 (1H, m, 7-H), 4.1 (1H, m, 3-H), 5.82 (1H, m, 4-H); other signals are quite similar to those for **13a**.

19-D: 41 mg, 27% yield, MS *m/e*: 212 (M^+ for $C_{11}H_{16}D_2N_2O_2$). NMR δ: 2.34 (2H, br d, J=7 Hz, 4-H_2), 3.11 (1H, br t, J=7 Hz, 5-H), 5.21 and 5.24 (1.5H, d, J=16 Hz, and 1.5H, J=10 Hz, =CH_2 and =CHD), 6.22 (2H, dd, J=10 and 16 Hz, –CH= × 2).

Thermolysis of the Imide (**13b**)——A mixture of **13b** (278 mg) and xylene (10 ml) was refluxed for 3 h and worked up as described for **13a** to give **21** and **22**.

2-Ethoxycarbonyl-1-methyl-2,5,6,9-tetrahydro-1,2-diazonine (**21**): 56 mg, 20% yield, oil. MS *m/e*: 210 (M^+). IR ν_{max}^{film} cm^{-1}: 1700 (C=O). ^{1}H-NMR δ: 2.2—2.6 and 3.2—3.4 (each 1H, m, 6-H_2), 2.65 (3H, s, 1-Me), 3.6—3.8 (2H, m, 9-H_2), 3.9 (2H, m, 3-H_2), 5.4—6.0 (4H, m, 4-, 5-, 7-, and 8-H), 1.27 and 4.23 (3H, t, and 2H, q, CO_2Et). ^{13}C-NMR δ: 14.813 (q), 25.681 (t), 42.639 (q), 52.336 (t), 61.010 (t), 61.302 (t), 123.724 (d), 126.746 (d), 130.543 (d), 132.687 (d), 156.811 (s). *Anal.* Calcd for $C_{11}H_{18}N_2O_2$: C, 62.83; H, 8.63; N, 13.32. Found: C, 62.99; H, 8.64; N, 13.13.

1-Ethoxycarbonyl-2-methyl-2-[1′-(2′,4′,6′-heptatrienyl)]-hydrazine (**22**): 104 mg, 38% yield, mp 56—57°C, colorless prisms (from *n*-hexane). MS *m/e*: 210 (M^+). IR ν_{max}^{KBr} cm^{-1}: 1710 (C=O), 3200 (NH). NMR δ:

3.42 (2H, t, $J=7$ Hz, 1′-H_2), 2.62 (3H, s, 2-Me), 5.1—6.4 (7H, m, olefinic protons), 5.7 (1H, br, NH), 1.26 and 4.19 (3H, t, and 2H, q, CO_2Et), *Anal.* Calcd for $C_{11}H_{18}N_2O_2$: C, 62.83; H, 8.63; N, 13.32. Found: C, 62.71; H, 8.77; N, 13.26.

Thermolysis of the Imide (17)——A mixture of **17** (120 mg) and xylene (8 ml) was refluxed for 4 h and worked up as described for **13a** to give 2-acetyl-1-methyl-2,3,6,7,8,9-hexahydrodiazonine (**25**): 98 mg, 82% yield, oil. MS *m/e*: 182 (M^+). IR ν_{max}^{film} cm^{-1}: 1660 (C=O). NMR (toluene-d_8, room temp.) δ: 1.1—1.9 (6H, m, 6-, 7-, and 8-H_2), 2.03 and 2.07 (1.2H, s, and 1.8H, s, Ac–Me), 2.4—3.1 (2H, m, 9-H_2), 2.51 and 2.82 (1.8H, s, and 1.2H, s, 1-Me), 3.5—4.0 (2H, m, 3-H_2), 5.4—6.2 (2H, m, 4- and 5-H); (at 120°C) δ: 1.2—1.6 (6H, m, 6-, 7-, and 8-H_2), 1.86 (3H, s, Ac–Me), 2.50 (3H, s, 1-Me), 2.8 (2H, m, 9-H_2), 3.7 (2H, m, 3-H_2), 5.4—6.1 (2H, m, 4- and 5-H). *Anal.* Calcd for $C_{10}H_{18}N_2O$: C, 65.89; H, 9.96; N, 15.37. Found: C, 65.67; H, 10.02; N, 15.32.

References and Notes

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19) The ^{1}H-NMR spectrum of this compound (**25**) showed a temperature dependence consistent with the predictable temperature-dependent inversion of the ring, as described in the experimental section. In addition, the starting N-imides (**13**) and (**17**) were obtained as the sole diastereomers (confirmed by NMR spectral analyses).