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Thermal Rearrangements of 1,2-Dihydropyridines

Iltifat Hasan and Frank W. Fowler*

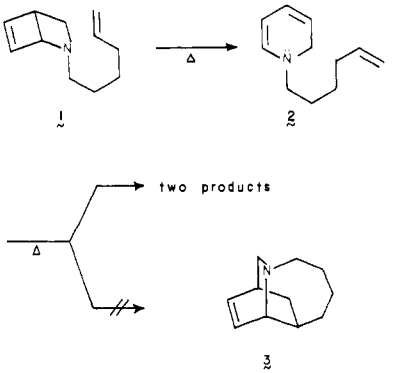
Contribution from the Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11794. *Received May 5, 1978*

Abstract: The *N*-(5-hexenyl)-1,2-dihydropyridine ring system (**2**) thermally rearranges to give two isomeric tricyclic imines to which the 10-methyl-9-azabicyclo[5.2.2.0^{1,5}]undec-8-ene structure (**5**) was assigned. The intermediacy of a 3-methyl-2-pentenyl-2,3-dihydropyridine (**8**) was detected. The thermal rearrangement of N-substituted 1,2-dihydropyridines to 3-methyl-2,3-dihydropyridines appears to be a general reaction. For example, *N*-ethyl-1,2-dihydropyridine gave the isomeric 2,3-dimethyl-2,3-dihydropyridine on heating to 200 °C. Mechanisms for these thermal rearrangements are discussed.

Authentic derivatives of the 1,2-dihydropyridine ring system without stabilizing electron-withdrawing groups on the ring are relatively rare.[1] As a consequence, little information is available concerning their chemistry. There has been recent interest[2] in these unstabilized 1,2-dihydropyridines because of their implication as pivotal intermediates in the biosynthesis of the indole alkaloids.[3]

We have recently developed a general synthesis to N-substituted 1,2-dihydropyridines[4] and now report some studies on their thermal rearrangements.

The *N*-(5-hexenyl)-1,2-dihydropyridine (**2**) is of interest because it possesses the necessary structural features to undergo an intermolecular Diels–Alder reaction[5] to give the tricyclic isoquinuclidine ring system analogous to that present in *Iboga* alkaloids. This type of synthetic methodology has been suggested from biosynthetic studies;[6] however, heating **1** in the gas phase at 250 °C for 1 h gave a 2:1 mixture of two products whose spectral data were clearly inconsistent with the tricyclic amine **3**.



1 **2** **3**

These products have similar properties and are very difficult to separate. The major component can be separated from the minor component by a tedious gas chromatographic process. The high-resolution mass spectra of these two compounds indicate that they are isomeric with the dihydropyridine **2** and each other. Although the data suggest that they are both tricyclic, the absence of vinyl hydrogens in the ^{1}H NMR spectrum suggests that neither product is the anticipated Diels–Alder adduct **3**. Two distinguishing features of the ^{1}H NMR spectrum of the major product are a one-proton doublet at δ 8.25 and a three-proton doublet at δ 0.85, Reasonable assignments for these absorptions are an aldimine hydrogen and a methyl group adjacent to one hydrogen. The presence of the aldimine function in these products is also supported by an absorption in the infrared spectrum at 1605 cm^{-1} and by the

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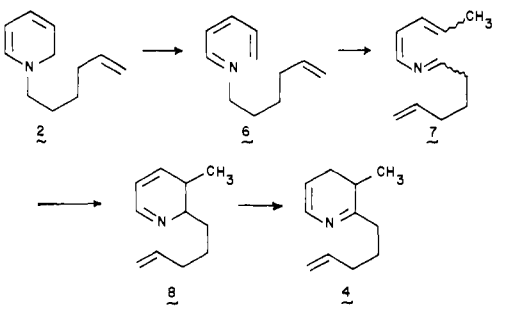
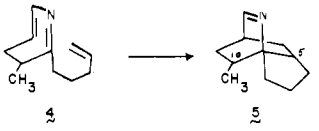
Scheme I



reaction with lithium aluminum hydride to give an amine.[7] The appearance of the infrared absorption at relatively low energy is consistent with the C=N function being part of a strained ring system.[8] The high-resolution mass spectrum shows the base peak to be the parent ion with the loss of C_3H_6. This favorable process is strongly suggestive of the loss of propylene in a retro-Diels–Alder reaction.[9]

The above information plus the fact that an intramolecular cycloaddition reaction is the simplest route to a tricyclic product from a monocyclic reactant led us to postulate that the products of the thermal rearrangement of **2** are two isomers of structure **5.**

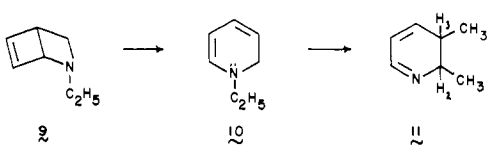


A likely precursor to this ring system would be dihydropyridine **4.** This 3,4-dihydropyridine is isomeric with the 1,2-dihydropyridine **2.** Although the Diels–Alder reactions of 2-azadienes are rare, there are precedents for this transformation.[11]

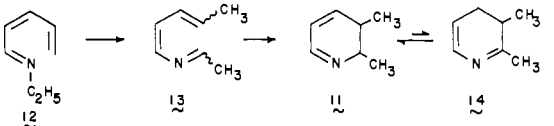
Isomerism in **5** is possible at either C-5 or C-10. We believe that the two products observed are a result of isomerism at C-5 and both products have the methyl group at C-10 endo to the C=N bridge. The endo methyl group would be the stereochemical consequence if the diene approach the dienophile from the sterically less hindered face opposite to the methyl group on the six-membered ring of **4.**[10a] The major isomer most likely has the hydrogen at C-5 exo to the C=N bridge. This speculation is supported by the observation that the analogous carbocycle, 1-(5-pentenyl)-1,3-cyclohexadiene, undergoes an intramolecular Diels–Alder reaction to give two products epimeric at C-5 in almost the same ratio that we observe for the heterocycle **4** with the major isomer having the hydrogen at C-5 exo to the C=C bridge.[10b]

The formation of the prerequisite 3,4-dihydropyridine **4** from the 1,2-dihydropyridine **2** can be envisioned according to Scheme **I.** The electrocyclic transformations of the cyclic dienes to acyclic trienes have precedence in carbocyclic as well as heterocyclic chemistry.[12] The 1,7 hydrogen shift and the 1,5 hydrogen shift both have precedence,[13] and would be expected to occur readily under the reaction conditions.

The thermal rearrangement of the *N*-ethyl-1,2-dihydropyridine (**10**) supports the above scheme. This dihydropyridine does not contain an alkenyl chain and cannot undergo the intramolecular Diels–Alder reaction. Heating **9** in the gas phase

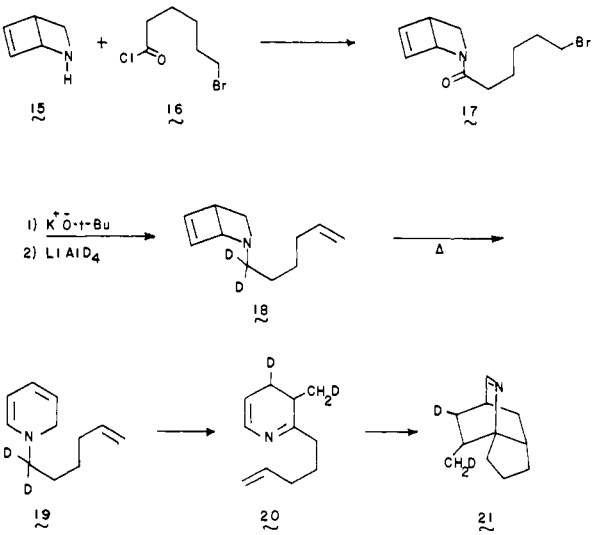


at 200 °C for 1 h produced the 2,3-dimethyl-2,3-dihydropyridine (**11**). It is apparent from the ^1H NMR data that only one of the two possible stereoisomers (cis and trans) was observed for **11.** The large coupling constant of the hydrogen at C-2 with the hydrogen at C-3 (J = 11 Hz) suggests that the hydrogens H_2 and H_3 are trans with respect to each other. Oxidation of this compound to the known 2,3-lutidine provided additional evidence for the proposed structure. The mechanism for this reaction would be analogous to that previously described for *N*-hexenyl-1,2-dihydropyridine (**2**). Since the 1,5 hydrogen shift should be favorable, the failure to observe the 3,4-dihydropyridine **14** is strongly suggestive that it is *less* stable than the isomeric 2,3-dihydropyridine **11.**



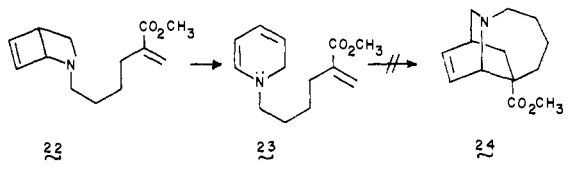
Heating the *N*-(5-hexenyl)-1,2-dihydropyridine using a flash thermolysis system[14] (see Experimental Section) instead of a sealed tube revealed a similar rearrangement to the 2,3-dihydropyridine to be occurring. Evaporation of **1** through a hot tube gave a mixture of the isomeric tricyclic imines **5a** and **5b** in addition to the 2,3-dihydropyridine **8.** Again the 3,4-dihydropyridine was not observed.

We have also prepared and studied the thermal rearrangement of the dideuterio derivative **19.** The data on the product indicate that the deuterium labeling is as depicted in structure **21** and are consistent with the pathway discussed above. The



deuterium substitution on the methyl group is apparent from the spectrum. The peak in the mass spectrum that showed loss of propylene from the parent ion of the unlabeled product still occurs at the same position, indicating the loss of propylene-d_2 from **21.**

In summary, we have studied the thermal rearrangements of 1,2-dihydropyridines. The primary products of these thermal rearrangements were the 2,3-dihydropyridines. This result strongly suggests that the more extensively conjugated 1,2-dihydropyridines are less stable than the 2,3-dihydropyridines. This would be contrary to previous speculation regarding the relative stability of these ring systems.[15] When a *N*-hex-5-enyl substituent was present on the 1,2-dihydropyridine the resulting 2,3-dihydropyridine isomerized to the presumably less stable 3,4-dihydropyridine which further reacted to give the tricyclic imine **5.** The failure of **2** to undergo an intramolecular Diels–Alder reaction is consistent with other observations by us that 1,2-dihydropyridines are relatively poor dienes in Diels–Alder reactions.[16] We attribute this lack of reactivity to a high degree of nonplanarity of the π system. In fact, when the more reactive acrylate **22** was heated in the gas phase ring opening to the dihydropyridine **23** occurs. Upon further heating no evidence for the Diels–Alder adduct **24** was observed.[17]



22 23 24

Experimental Section

The proton magnetic resonance spectra (^{1}H NMR) was recorded using a Varian EM-360 or HFT-80 spectrometer. Apparent coupling constants are reported and the multiplicities are indicated using s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. The carbon-13 magnetic resonance spectra (^{13}C NMR) were recorded using a Varian CFT-20 spectrometer. Chemical shifts for both the ^{13}C and ^{1}H NMR spectra are reported as δ values in parts per million from tetramethylsilane as an internal standard. The high-resolution mass spectra were recorded with an AEI-MS30, and the low-resolution mass spectra were recorded with a Hewlett-Packard 5983. Both spectrometers were operated at an ionization voltage of 70 eV. The preparative scale gas–liquid chromatography was carried out on a Hewlett-Packard 5830A instrument equipped with a thermal conductivity detector. The infrared spectra were recorded with a Perkin-Elmer 727 or 567 spectrometer. The relative intensities are indicated using s = strong, m = medium, and w = weak.

N-(5-Hexenyl)-1,2-dihydropyridine (2). To 25 mL of 1.5 M methyllithium in ether and 20 mL of dry tetrahydrofuran under N_2 cooled in an acetone–ice bath (ca. −15 °C) was added 2.00 g of *N*-methoxycarbonyl-2-azabicyclo[2.2.0]hex-5-ene. The reaction mixture was allowed to stir for 5 min and the excess methyllithium was destroyed by slowly adding cold water. To this mixture, 2.35 g of 6-bromo-1-hexene was added. The reaction mixture was refluxed for 48 h and was then added to cold water. The organic layer was separated and washed with water. The amine **1** was separated from the nonbasic impurities by extraction with 5% HCl. These acidic extracts were combined, neutralized with a saturated Na_2CO_3 solution, and extracted with ether. The ether extracts were combined, dried with anhydrous Na_2CO_3, and concentrated in vacuo to give 1.58 g (68%) of amine **2.** This could be further purified by passing it through basic alumina with hexane–ether (3:1): ^{1}H NMR (benzene-d_6, HFT-80) δ 1.23–2.58 (m, 9 H), 2.85–3.08 (m, 1 H), 3.63 (d of d, 1 H, J = 8, 7 Hz), 4.38–4.53 (m, 1 H), 4.78–6.03 (m, 3 H), 6.10 (t, 1 H, J = 3.0 Hz), and 6.32 (t, 1 H, J = 3.0 Hz); IR (film) 2940 (s), 1640 (m), 990 (m), 910 (m), and 750 cm^{-1} (m).

Amine **1** (20 mg) was added to a 23 × 3.0 cm Pyrex tube closed at one end with a smaller attached tube (10 × 150 mm) at the other end. The smaller tube was connected to an apparatus that allowed the reaction vessel to be alternately evacuated and flushed with N_2. The amine **1** was cooled to −78 °C and the reaction vessel was evacuated and flushed with N_2 five times. The reaction vessel was then evacuated to ca. 0.1 Torr and the smaller tube was sealed. The reaction vessel was then heated to 150 °C for 1 h. Cooling the smaller tube to −78 °C resulted in condensation of the product. The dihydropyridine **2**, obtained by removal of the 10-mm tube, showed ^{1}H NMR (benzene-d_6, HFT-80) δ 1.00–2.50 (m, 8 H), 3.68 (d of d, 2 H, J = 4, 2 Hz), and 4.00–6.05 (m, 7 H); IR (film) 2945 (s), 1640 (s), 1570 (s), and 910 cm^{-1} (s).

9-Methyl-10-azatricyclo[5.2.2.0^{1,5}]undec-2-enes (5a,b). This reaction was most conveniently carried out by heating *N*-(5-hexenyl)-2-azabicyclo[2.2.0]hex-5-ene (**1**) in the gas phase at 250 °C for 1 h. The experimental procedure is the same as previously described for the synthesis of *N*-(5-hexenyl)-1,2-dihydropyridine (**2**). At this temperature, we have observed that the dihydropyridine **2** was rapidly produced. The dihydropyridine **2** slowly rearranged to give a 2:1 mixture of two products. The ^{1}H NMR spectrum (benzene-d_6, HFT-80) of this mixture showed two one-proton doublets (J = 4.8 Hz) centered at δ 8.25 and 8.15 plus two three-proton doublets (J = 6 Hz) centered at δ 0.85 and 0.80. The ^{13}C NMR spectrum (benzene-d_6, CFT-20) showed a total of 19 lines (δ 171.48, 170.54, 43.12, 37.88, 34.85, 33.69, 32.51, 32.23, 31.91, 31.03, 23.52, 23.15, 19.01, 15.88). These compounds could be separated by analytical gas chromatography (6 ft × 1/8 in. OV-225, oven temperature 95 °C). A high-resolution mass spectrum of the two isomers gave *m/e* of 163.1344 (major isomer) and 163.1334 (minor isomer). Calcd for $C_{11}H_{17}N$: 163.1361.

^{1}H NMR of major isomer (benzene-d_6, HFT-80) δ 0.85 (d, 3 H, J = 6 Hz), 1.3–3.2 (m, 13 H), and 8.25 (d, 1 H, J = 4 Hz); minor isomer δ 0.80 (d, 3 H, J = 6 Hz), 1.15–2.90 (m, 13 H), and 8.15 (d, 1 H, J = 4 Hz); ^{13}CNMR major isomer (benzene-d_6, CFT-20) δ 171.5, 43.2, 38.4, 35.4, 34.3, 32.9, 32.7, 32.4, 31.6, 23.6, 18.3; IR (film) 2950 (s), 1605 (m), 1450 (m), 1370 (s), and 930 cm^{-1} (s); MS (70 eV) *m/e* (rel intensity) major isomer 163 (47.8), 148 (14.5), 121 (100), 109 (44.3), 107 (64), 95 (9); minor isomer 163 (14.40), 148 (58), 133 (19.0), 131 (94), 118 (47), 93 (38), 79 (37.8), 67 (49.4), 43 (100), and 39 (61.7).

N-Ethyl-1,2-dihydropyridine (10). A 100-mL three-neck round-bottom flask was equipped with a magnetic stirrer and rubber septa and was connected to a mercury bubbler so that the system could be alternatively evacuated and flushed with nitrogen. The flask was charged with a slight positive pressure of nitrogen and 25 mL of 2.06 M methyllithium in ether (Alfa Inorganics) was added. This was followed by 20 mL of dry tetrahydrofuran and the reaction mixture was cooled to ca. −15 °C (ice–acetone). To this was added slowly 2.00 g of *N*-methoxycarbonyl-2-azabicyclo[2.2.0]hex-5-ene. The reaction mixture was allowed to stir for 15 min and the excess methyllithium was quenched with 15 mL of water. The organic layer was separated and the aqueous layer was extracted with ether. The organic fractions were combined and dried with anhydrous sodium carbonate and the amine was concentrated by removal of the solvent using an efficient distillation apparatus.

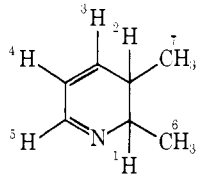
To 2-azabicyclo[2.2.0]hex-5-ene, slightly contaminated with solvent, were added 0.80 g of triethylamine and 0.6 g of acetyl chloride. After 10 min, the reactants were filtered and solvent removed in vacuo to yield 0.66 g (36% yield) of *N*-acetyl-2-azabicyclo[2.2.0]hex-5-ene. The product could be further purified by chromatography (on alumina using an ether–ethyl acetate gradient): ^{1}H NMR ($CDCl_3$, EM-360) δ 1.90 (d, 3 H, J = 2.5 Hz), 3.30–4.22 (m, 3 H), 4.80–5.03 (m, 1 H), 6.39–6.64 (m, 2 H); IR (film) 1650 (s), 1545 (w), and 1411 cm^{-1} (s, broad).

To a stirring mixture of 0.5 g of $LiAlH_4$ in 25 mL of dry ether under nitrogen cooled in an ice bath was added 1.0 g of *N*-acetyl-2-azabicyclo[2.2.0]hex-5-ene. The reaction mixture was allowed to warm to room temperature and stir for 4 h. The excess $LiAlH_4$ was decomposed by adding 0.5 mL of H_2O and 1 mL of 10% NaOH followed by 0.5 mL of H_2O. The precipitate was filtered and the solvent was removed by distillation to give 0.775 g (87.5%) of *N*-ethyl-2-azabicyclo[2.2.0]hex-5-ene (**9**): ^{1}H NMR (HFT-80, benzene-d_6) δ 0.9 (t, 1 H, J = 8 Hz), 2.25–2.265 (m, 3 H), 3.85–3.15 (m, 1 H), 3.60 (d of d, 1 H, J = 8, 7 Hz), 4.38–4.53 (m, 1 H), 6.10 (t, 1 H, J = 3.0 Hz), and 6.45 (t, 1 H, J = 3 Hz); IR (film 2940 (s), 1640 (m), 1370 (m), 1100 (s), 1050 (s), 890 (m), and 750 cm^{-1} (s).

The *N*-ethyl-1,2-dihydropyridine (**10**) could be prepared as previously described for *N*-(5-hexenyl)-1,2-dihydropyridine (**2**): ^{1}H NMR (HFT-80, benzene-d_6) δ 0.75 (t, 3 H, J = 8 Hz), 2.45 (q, 2 H, J = 8 Hz), 3.65 (d of d, 2 H, J = 4, 2 Hz), 4.65–6.05 (m, 3 H), and 7.63 (m, 1 H); IR (film) 2950 (m), 2920 (w), 1660 (w), and 720 cm^{-1} (s).

2,3-Dimethyl-2,3-dihydropyridine (11). *N*-Ethyl-2-azabicyclo[2.2.0]hex-5-ene (**9**, 50 mg) was subjected to sealed tube pyrolysis (as described previously for the synthesis of *N*-(5-hexenyl)-1,2-dihydropyridine) for 1 h at 200 °C to give 2,3-dimethyl-2,3-dihydropyridine: ^{1}H NMR (HFT-80, benzene-d_6) δ 0.78 (d, J = 7 Hz, 3 H), 1.03 (d, J = 7 Hz, 3 H), 2.93–3.45 (m, 1 H), 5.50 (AB quartet, J = 9 Hz, 2 H, both lines of the downfield doublet appear as a doublet of doublets, J = 3 and 4 Hz, respectively, and both lines of the upfield doublet appear as triplets, J = 2 Hz), 7.53–7.73 (m, 1 H, the position of the hydrogen at C-3 is obscured by impurities at 0.8–2.0); IR (film) 3050 (s), 3025 (s), 2970 (s), 1635 (s), 1580 (m), 1450 (s), 1375 (s), 1270 (w), 1240 (m), 1140 (m), 1100 (w), 1040 (w), 720 cm^{-1} (m). Proton decoupling experiments on 2,3-dimethyl-2,3-dihydropyridine (**11**) confirmed the above assignments. Irradiation of the signal at δ 1.03 assigned to protons H_6 resulted in the simplification of the multiplet at δ 2.93–3.45 to a broad doublet with coupling constant of 11 Hz (the large coupling constant strongly suggests a trans relationship between H_1 and H_2). Irradiation of the absorption at δ 5.50 assigned to vinyl hydrogens, H_3 and H_4, caused the collapse of the multiplet located at δ 7.53–7.73 (H_5) into a doublet (J = 3 Hz), MS (70 eV) *m/e* (rel intensity) 109.2 (65.8), 108.2 (100), 94.1 (89.8), 67.2 (42.1).

2,3-Lutidine from 11. Dry O_2 was bubbled through a solution of 50 mg of 2,3-dimethyl-2,3-dihydropyridine and 0.1 g of Pd/C in 300 μL of benzene-d_6 for 3 h. Bulb to bulb distillation of reaction mixture



yielded a homogeneous solution of 2,3-dimethylpyridine. It was characterized by comparing its R_f value, retention time, IR, and ^{1}H NMR with those of the authentic sample.

***N*-(5-Hexenyl)-*1,1-d*$_2$-2-azabicyclo[2.2.0]hex-5-ene (18).** To 2-azabicyclo[2.2.0]hex-5-ene (**15**) prepared as previously described were added 1.1 g (0.011 mol) of triethylamine and 1.8 g of 6-bromohexanoyl chloride in 5 mL of ether. After 30 min, 15 mL of water was added and the aqueous solution was extracted with ether. The ethereal extracts were combined and filtration followed by removal of the solvent in vacuo gave 1.87 g (0.007 mol) of amide (52% yield based on carbamate). Further purification was obtained by passing the product through a basic alumina column, eluting with ether/ethyl acetate gradient: ^{1}H NMR ($CDCl_3$, HFT-80) δ 1.65–2.2 (m, 6 H), 3.3–4.15 (m, 5 H), 4.80–5.0 (m, 1 H), and 6.35–6.50 (m, 2 H); IR (film) 2960 (m), 1650 (s), 1430 (s), 1300 (s), 1180 (s), 930 (s), and 750 cm^{-1} (m).

To 0.18 g (0.7 mmol) of *N*-(1-(6-bromohexanoyl)-2-azabicyclo[2.2.0]hex-5-ene) was added 6 mL of dry *tert*-butyl alcohol with 0.24 g (2.1 mmol) of potassium *tert*-butoxide. The reaction mixture was refluxed under nitrogen for 3.5 h and 15 mL of water was then added. The reaction mixture was extracted with ether. These extracts were combined and dried with Na_2CO_3 and the solvent was removed in vacuo to give 0.11 g (0.6 mmol) of product (84% yield). Further purification could be obtained by passing the product through a basic alumina column, eluting with an ether–ethyl acetate gradient: ^{1}H NMR (EM-360, $CDCl_3$) δ 1.31–2.33 (m, 8 H), 3.21–4.24 (m, 5 H), 4.79–5.02 (m, 1 H), and 6.33–6.61 (m, 2 H); IR (film) 1647 (s) and 1423 cm^{-1} (s). To a stirred solution of 0.25 g of $LiAlD_4$ in 15 mL of dry ether cooled to −20 °C and maintained under N_2 was slowly added 0.5 g of *N*-(1-(6-hexenoyl)-2-azabicyclo[2.2.0]hex-5-ene. After the addition was complete, the reaction mixture was allowed to warm up to room temperature and stirred for 4 h. The reaction was stopped by carefully adding 0.25 mL of H_2O, then 0.5 mL of 20% NaOH followed by 0.25 mL of H_2O. After the inorganic salts were filtered off, the organic portion was dried over anhydrous Na_2CO_3 and concentrated in vacuo to give 0.42 g of **18** (91% yield): ^{1}H NMR (benzene-d_6, HFT-80) δ 1.25–2.60 (m, 7 H), 2.85–3.06 (m, 1 H), 3.6 (d of d, 1 H, J = 8, 4 Hz), 4.35–4.47 (m, 1 H), 4.8–5.82 (m, 3 H), 6.08 (t, 1 H, J = 3 Hz), and 6.30 (t, 1 H, J = 3 Hz); IR (film) 2865 (s), 2825 (m), 1640 (s), 1460 (s), 900 (m), 740 cm^{-1} (m); MS (70 eV) *m/e* (rel intensity) 165 (26), 163 (33), 149 (40), 123 (68), 111 (82), 109 (78), 97 (98), and 96 (100).

9-Methyl-10-azatricyclo[5.2.2.0^{1,5}]undec-2-ene-*d*$_2$ (21). The dideuterio derivative (**18**) was subjected to sealed tube pyrolysis (as previously described for the preparation of **5**) at 250 °C for 1 h to give after GLC separation of the major isomer 9-methyl-10-azatricyclo[5.2.2.0^{1,5}]undec-2-ene-d_2: ^{1}H NMR (HFT-80, benzene-d_6) δ 0.78 (multiplet, 2 H), 1.00–2.3 (m, 12 H), 8.1 (d, J = 4 Hz, 1 H); MS (70 eV) *m/e* (rel intensity) 165 (65.3), 164 (18.7), 150 (27.5), 149 (27.8), 122 (31.7), 121 (100), 120 (62.8), 111 (48.9), 111 (26.9), 96 (82.8), 95 (44.7), 93 (49.8), 79 (30.3).

Controlled Thermal Reactions. These experiments were carried out using a quartz U-tube (30 cm overall length, 1.2 cm o.d.) with a male glass joint attached to one end. To the other end was attached a female glass joint with a vacuum take-off adaptor. The whole tube, including the female joint, was wrapped with Nichrome resistance wire. A thermocouple was attached to the center of the tube, and the tube was insulated with several layers of asbestos tape. The tube was heated to the desired temperature. The sample dissolved in benzene was placed in a flask and attached to the apparatus. A receiver flask was attached at the other end. The sample was cooled in dry ice–acetone (−78 °C) and the apparatus was evacuated and flushed several times with nitrogen. The apparatus was evacuated to 0.1–0.01 Torr and the receiver flask was cooled in dry ice–acetone. The sample was then passed through the hot tube and the product collected in the cold receiver flask.

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