H, 6.02; N, 3.34. Found: C, 71.47; H, 6.03; N, 3.29.

Kinetic Measurements. All thermolysis experiments were carried out in a TAMSON TC-9 constant-temperature oil bath. All solvents used were purified and freshly distilled prior to use. A stock solution was prepared by dissolving 5.363 mg of 7 in 25 mL of the appropriate solvent. One milliliter of the above solution was diluted by a factor of 10. The resulting solution was distributed to six different sample tubes which were degassed and sealed. The tubes were inserted into a constant-temperature oil bath and were withdrawn at periodic intervals. Their UV spectra were determined by using a Hewlett-Packard 8451A diode array spectrophotometer. Absorbance data were acquired for at least four half-lives. First-order rate constants were calculated from a computer-assisted linear least-squares regression analysis of ln $[A - A_0]$ vs time. At least three runs were averaged for each data point. Agreement between runs was to within 10%. Correlation coefficients were generally >0.99. Erying and Arrhenius parameters were determined by least-squares analysis, by using rate constants for three different temperatures.

Acknowledgment. We gratefully acknowledge support of this work by the National Institutes of Health. Use of the high-field NMR spectrometer used in these studies was made possible through a NSF equipment grant.

The 1-Aza-Cope Rearrangement[1]

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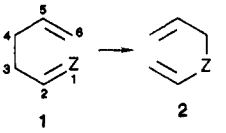
The 1-aza-Cope rearrangements of azavinylcyclohexene derivatives were investigated. It was observed that an *N*-acyl substituent on the 1-aza 1,5-diene provides a sufficient driving force for this normally contrathermodynamic process. Although simple derivatives have high activation energies proceeding in relative low overall yield, a methoxy substituent at C-4 of the aza diene as well as its incorporation into strained bicyclic ring systems facilitates the 1-aza-Cope rearrangement. Because the aza diene precursors are readily available by using the Diels–Alder reaction with acrolein derivatives, this process has synthetic potential for the preparation of nitrogen heterocycles. This scheme is illustrated with the preparation of a hydrolulolidine providing a formal total synthesis of (±)-aspidospermine.

It has been over 45 years since the 3,3-sigmatropic shift of 1,5-dienes (the Cope rearrangement) has been recognized as a general transformation in organic chemistry.[2,3] This reaction has continued to attract the attention of organic chemists, particularly with respect to studies directed to understanding the reaction pathway. At least two geometries,[4] chair and boat, and three mechanisms have often been proposed and are possibly operative among the various Cope rearrangements.[3a,b]

Uncertainties about the mechanism of the Cope rearrangement have not prevented this reaction from being exploited by synthetic chemists. It has been valuable for the alteration of the connectivity to produce new structures that would not be readily accessible with other methods.[5]

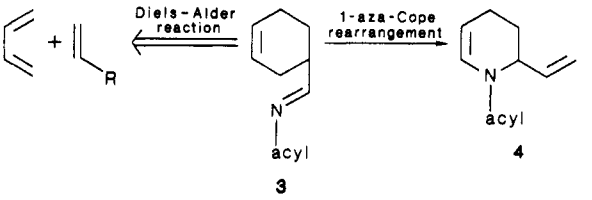
Heteroatomic versions of the Cope rearrangement, Z = O or NR, are known. Primarily because of the greater stability of carbon–heteroatom π-bonds[6] these reactions are usually driven from right to left (**2** → **1**) (Scheme I). When Z = O this reaction is the well-known Claisen rearrangement and has taken on considerable importance

Scheme I



1 2

Scheme II



3 4

as a synthetic transformation[7] as well as being the focus of a number of mechanistic studies.[8]

The 3-aza-Cope rearrangement (**2** → **1**, Z = NR) is also well-known.[9] Because this sigmatropic shift is accelerated

(1) A portion of this work has appeared in a preliminary communication: Chu, M.; Wu, P-L.; Givre, S.; Fowler, F. W. *Tetrahedron Lett.* **1986**, *27*, 461.

(2) (a) Cope, A. C.; Hardy, E. M. *J. Am. Chem. Soc.* **1940**, *62*, 441. (b) Cope, A. C.; Hofmann, C. M.; Hardy, E. M. *Ibid.* **1941**, *63*, 1852. (c) Cope, A. C.; Levy, H. *Ibid.* **1944**, *66*, 1684.

(3) For reviews concerned with various aspects of the Cope rearrangement, see: (a) Gajewski, J. J. *Hydrocarbon Thermal Isomerization*; Academic: New York; pp 163–176. (b) Wehrli, R.; Hansen, H.-J.; Schmid, H. *Chimia* **1976**, *30*, 416. (c) Overman, L. E. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 579. (d) Lutz, R. P. *Chem. Rev.* **1984**, *84*, 205. (e) Rhoads, S. J.; Raulins, N. R. *Org. React. (N.Y.)* **1975**, *22*, 1.

(4) For a more complete analysis of possible geometries for the Cope rearrangement, see: Goldstein, M. J.; Benzon, M. S. *J. Am. Chem. Soc.* **1972**, *94*, 7149.

(5) Desimoni, G.; Tacconi, G.; Barco, A.; Pollini, G. P. *Natural Products Synthesis Through Pericyclic Reactions*; ACS Monograph 189; American Chemical Society: Washington, DC, 1983; p 443.

(6) The π-bond strengths for $CH_2{=}CH_2$, $CH_2{=}O$, and $CH_2{=}NH$ have been calculated to be 59.4, 72.4 and 74.3 kcal/mol, respectively (Shaw, R. In *The Chemistry of Double Bonded Functional Groups*; Patai, S., Ed.; Wiley: New York, 1977; p 131).

(7) (a) Ziegler, F. E. *Acc. Chem. Res.* **1977**, *10*, 227. (b) Bennett, G. B. *Synthesis* **1977**, 589. (c) Rhoads, S. J.; Raulins, N. R. *Org. React. (N.Y.)* **1975**, *22*, 1.

(8) For recent examples, see the following references and the work cited therein: (a) Coates, R. M.; Robers, B. D.; Hobbs, S. J.; Peck, D. R.; Curran, D. P. *J. Am. Chem. Soc.* **1987**, *109*, 1160. (b) Gajewski, J. J.; Jurayj, J.; Kimbrough, D. R.; Gande, M. E.; Ganem, B.; Carpenter, B. K. *J. Am. Chem. Soc.* **1987**, *109*, 1170. (c) Wilcox, C. S.; Babston, R. E. *J. Am. Chem. Soc.* **1986**, *108*, 6636.

(9) Although the terms 3-aza-Cope and 1-aza-Cope rearrangement are the most commonly used when Z = N, the term aza-Claisen has also been used for this process. This latter designation would be a misuse of the "replacement nomenclature" (For example, see: *Nomenclature of Organic Compounds. Principles and Practice*; Fletcher, J. H., Dermer, O. C., Fox, R. B., Eds.; American Chemical Society: Washington, DC, 1974; Chapter 7) since it would imply there is *both* a nitrogen and oxygen atom present in the six-atom chain. These latter compounds are known and undergo the Claisen rearrangement, but they are distinct from the class of compounds discussed in this paper. (a) Heimgartner, H.; Schmid, H. in *Advances in Organic Chemistry*; Taylor, E. C., Ed.; Academic: New York, 1979; Vol. 9, Part 2, p 656. (b) Winterfeldt, E. *Fortshr. Chem. Forsch.* **1971**, *16*, 75.

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when the nitrogen atom bears a formal positive charge, the 3-aza-Cope ammonium–iminium rearrangement has most frequently been studied. Although the 3-aza-Cope has achieved some importance in organic synthesis,[10] it has not gained the popularity of the Claisen rearrangement.

In contrast to the above transformations, there are very few examples of the hetero-Cope rearrangements **1** → **2** where Z is either oxygen or a nitrogen derivative. This is primarily due to unfavorable thermodynamics of the transformation; that is, the reactant is usually more stable than the product.[6] Therefore, in order to observe the hetero-Cope rearrangement (**1** → **2**), it is necessary to introduce a structural change to stabilize the product with respect to the reactant.

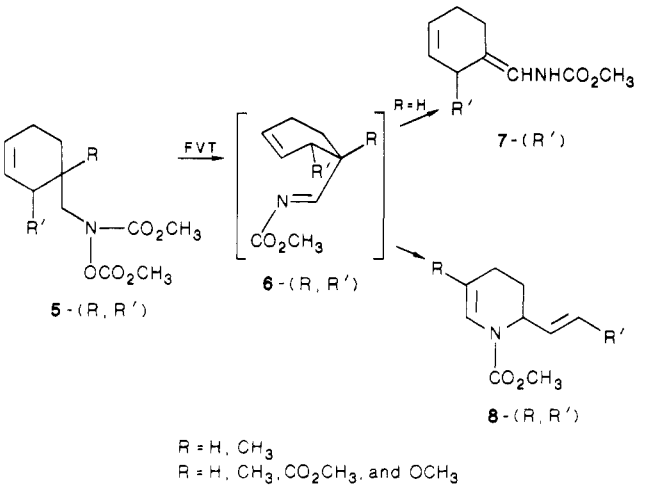
Because of an interest in the synthetic potential of the reaction **1** → **2**, where Z = O, Boeckmann and co-workers[11] considered driving this reaction using primarily steric effects. Their efforts were successful, in a few cases, giving us a better understanding of this problem and illustrating the synthetic potential of this transformation.

To our knowledge,[12] the only example of the reaction **1** → **2**, where Z = NR, is an aza analogue of the divinylcyclopropane rearrangement, a special case of the Cope rearrangement.[13] Although this reaction, driven by the relief of strain incorporated into the cyclopropane ring, is an interesting transformation it has limited synthetic potential.

We considered that a more general version of the 1-aza-Cope rearrangement would be possible if a carbonyl group were present on the nitrogen atom of the imine (**1**, Z = N–acyl). In contrast to the nitrogen atom in the reactant, where there is believed to be little interaction (ca. 4 kcal/mol)[14] between the carbonyl group and the imine nitrogen, the nitrogen atom of product forms part of an amide function with an associated stabilization of about 15–20 kcal/mol. Because it has been estimated[15] that the 1-aza-Cope is unfavorable by only 7–10 kcal/mol, the enamine product would be predicted to be more thermodynamically stable than the imine when the nitrogen atom carries a carbonyl group.

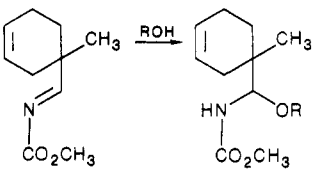
The Cope rearrangement of aza derivatives of the 4-vinylcyclohexene ring system is an interesting and a potentially valuable transformation in organic chemistry. The 1-aza 1,5-diene should be accessible from simple reactants by using a Diels–Alder reaction scheme as a key step (Scheme II). The product of the Cope rearrangement is a piperidine ring, a common structural feature of a large number of goal compounds. In addition, the endocyclic enamine derivative is present for further structural elaboration.

Scheme III



R = H, CH_3
R = H, CH_3, CO_2CH_3, and OCH_3

Scheme IV



Although all-carbon 4-vinylcyclohexene Cope rearrangements are rare, the simplest system has been extensively studied.[16] The Cope rearrangement of 4-vinylcyclohexene has a very large activation energy (52.3 kcal/mol) compared to simpler systems such as 1,5-hexadiene (35.5 kcal/mol). This high activation along with other data have led investigators to conclude that the Cope rearrangement of 4-vinylcyclohexene proceeds along a reaction pathway that is "not obviously concerted".[16a] The problem is that structural constraints require the concerted mechanism to pass through a boat transition state that possesses additional strain energy analogous to the bicyclo[2.2.2]octane ring system.

We considered that a suitable aza 1,5-diene to explore the 1-aza-Cope rearrangement is **6**-(H,H), which should be accessible from the hydroxamic acid derivative **5**-(H,H) (Scheme III). Flash vacuum thermolysis[17] would be used to both prepare the *N*-acyl imine as well as to induce the Cope rearrangement.[18]

However, evaporation of **5**-(H,H) through a hot tube did not produce the Cope rearranged product **8**-(H,H) but a stereoisomeric mixture of the enamides **7**-(H), the product of a hydrogen shift from the position α to the imine. This is a well-known reaction of *N*-acyl imines possessing α-hydrogens.[19]

(10) For a recent reference on the synthetic applications of the 3-aza-Cope rearrangement, see: Kurth, M. J.; Soares, C. J. *Tetrahedron Lett.* **1987**, *28*, 1031.

(11) Boeckman, R. K., Jr.; Flann, C. J.; Poss, K. M. *J. Am. Chem. Soc.* **1985**, *107*, 4359.

(12) We apply the term 1-aza-Cope rearrangement to those systems where only C-1 of the reacting carbon framework has been replaced by nitrogen. There are examples of this reaction known where C-1, in addition to other carbon atoms, has been replaced by heteroatoms. For examples, see ref 3c,d, 10b, and: Lipowitz, K. B.; Scarpone, S.; McCullough, D.; Barney, C. *Tetrahedron Lett.* **1979**, 2241.

(13) For example, see: Oehlschlager, A. C.; Zalkow, L. H. *J. Org. Chem.* **1965**, *30*, 4205.

(14) From rotational barriers it has been concluded that there is only a small stabilization due to the interaction of the nitrogen lone pair and the carbonyl group (Allmann, R.; Kupfer, R.; Nagel, M.; Wurthwein, E.-U. *Chem. Ber.* **1984**, *117*, 1597).

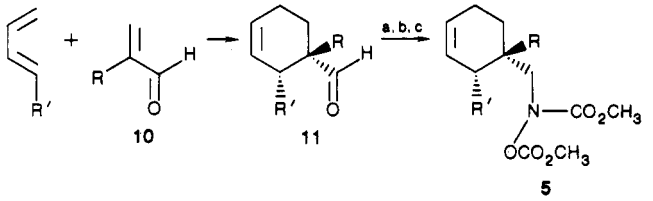
(15) This calculation is made by using enthalpy increments, see ref 9a, p 656.

(16) (a) Doering, W. v. E.; Brenner, D. M. *Tetrahedron Lett.* **1977**, 899. (b) Doering, W. v. E.; Granck-Newmann, M.; Hasselmann, D.; Kaye, R. L. *J. Am. Chem. Soc.* **1972**, *94*, 3833.

(17) The apparatus that we use is basically the same design as that described previously (Beeken, P.; Bonfiglio, J.; Hasan, I.; Piwinski, J.; Weinstein, B.; Zollo, K.; Fowler, F. W. *J. Am. Chem. Soc.* **1979**, *101*, 6677). The major difference is that a temperature controller (Omega Engineering Model D921K35F20) is used to maintain a constant temperature in the reaction tube.

(18) We have previously shown that *O*-acyl derivatives of hydroxamic acids readily produce, under thermal conditions, the *N*-acyl imine. (a) Lin, J.-M.; Koch, K.; Fowler, F. W. *J. Org. Chem.* **1986**, *51*, 167. (b) Wyle, M.; Fowler, F. W. *J. Org. Chem.* **1984**, *49*, 4025. (c) Cheng, Y.-S.; Lupo, A.; Fowler, F. W. *J. Am. Chem. Soc.* **1983**, *105*, 7696.

Scheme V[a]



[a] (a) NH_2OH; (b) reduction, $NaBH_4$/TFA or BH_3–pyridine/HCl; (c) $ClCO_2CH_3$.

In order to suppress the hydrogen migration, the hydroxamic acid derivative **5**-(CH_3,H) was prepared. Evaporation of this compound through the hot reaction tube led to a product mixture containing approximately 5% of 1-aza-Cope product **8**-(CH_3,H) in addition to 25% of the aza diene **6**-(CH_3,H) and/or its carbinol amide derivatives **9a,b**[20] (Scheme IV).

Raising the thermolysis oven temperature to 550 °C did not result in an increase in the amount of the 1-aza-Cope product but did give a more complex product mixture. Purification of the 1-aza-Cope product **8**-(CH_3,H) and passing it through the thermolysis oven at 525 °C resulted in its decomposition along with the formation of the carbinol amides **9a,b**. Apparently, equilibration of **6**-(CH_3,H) with **8**-(CH_3,H) is occurring at this temperature.

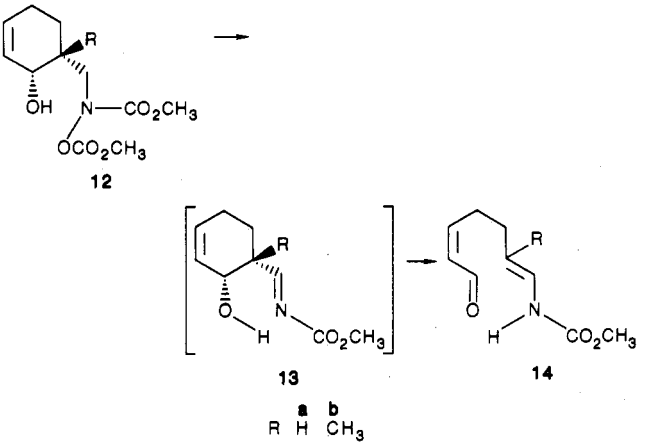
Although **8**-(CH_3,H) was formed in low yield, these were encouraging results because they demonstrated that *N*-acyl imines are capable of participating in the 1-aza-Cope rearrangement.

The Cope rearrangement is frequently accelerated by substituents on the saturated atoms between the reacting alkenes, C-3 and C-4 in **1**. Because these effects are sometimes dramatic, they have been the focus of a number of experimental as well as theoretical studies. In order to explore the effects of substituents[21] on the 1-aza-Cope rearrangement, the thermolysis of hydroxamic acid derivatives **5** were studied. The hydroxamic acid derivatives **5** were readily prepared from the appropriately substituted butadiene and acrolein derivative (Scheme V).

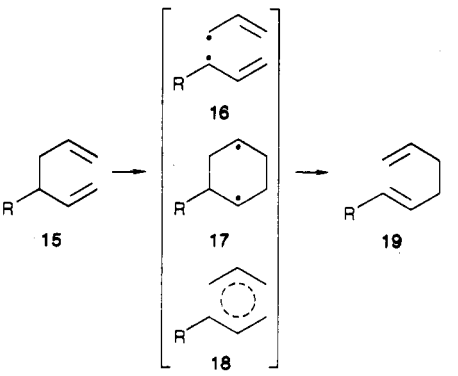
When **5**-(CH_3,CH_3) was evaporated through the thermolysis oven, a lowering (from 525 to 500 °C) of the reaction temperature required for the Cope rearrangement compared to **5**-(CH_3,H) and an increased yield (46%) of the Cope-rearranged product **8**-(CH_3,CH_3) were observed. A further decrease in the reaction temperature to 475 °C was observed for **5**-(CH_3,CO_2CH_3) to give the Cope-rearranged product **8**-(CH_3,CO_2CH_3) in 33% yield.

If a methyl substituent was not present α to the imine, **6**-(H,CH_3) and **6**-(H, CO_2CH_3), then a hydrogen shift occurred to produce a stereoisomeric mixture of the enamides **7**-(CH_3) and **7**-(CO_2CH_3). Although both the methyl and methoxycarbonyl substituents accelerate the 1-aza-Cope rearrangement, it is apparently not sufficient to compete with the hydrogen shift.

Scheme VI



Scheme VII



Further rate acceleration of the 1-aza-Cope rearrangement was anticipated for oxygen substituents. However, the presence of a hydroxyl group on the six-membered ring opened the possibility of an additional pericyclic reaction. The evaporation of either **12a** or **12b** through the thermolysis oven produced a stereoisomeric mixture of the enamides **14a** or **14b**, the products of retro-ene reactions involving the hydroxyl group and the *N*-acyl imine (Scheme VI).

The above retro-ene reactions could be suppressed and the effect of oxygen substituents was studied when the ring carried a methoxyl substituent. Evaporation of **5**-(CH_3,OCH_3) through the thermolysis oven produced the Cope-rearranged product **8**-(CH_3,OCH_3) in 61% yield at 475 °C, approximately 50 °C lower than was required for **5**-(CH_3,H).

The rate-accelerating effect of the methoxy group was also apparent for the 1-aza-Cope rearrangement **6**-(H,-OCH_3). Evaporation of **5**-(H,OCH_3) through the thermolysis oven gave the Cope-rearranged product along with *N*-(methoxycarbonyl)benzylamine.[22] Since the hydrogen shifts for all the **6**-(H,R′) aza dienes would be anticipated to occur at similar rates, the observation that only **6**-(H,OCH_3) participated in the 1-aza-Cope rearrangement suggests that the methoxy substituent has the greatest rate acceleration of the substituents we have studied.

It is important to recognize that the rate-determining step for the conversion of **5**-(R,R′) to **8**-(R,R′) appears to

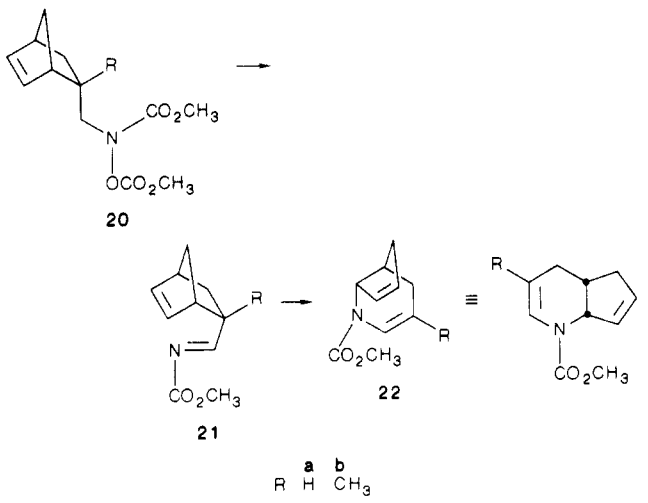
(19) We believe the rearrangement of the acyl imine to the more stable enamide is occurring in the gas phase and not in the condensed phase. Although this isomerization is a known transformation (Lenz, G. *Synthesis* **1978**, 489), the actual mechanism is obscure. The thermally forbidden suprafacial 1,3-hydrogen shift pathway can be avoided by using the orbitals involved with the nitrogen lone pair. Alternatively, a 1,5-hydrogen shift, involving the carbonyl π-bond, could occur to give, initially, the imide followed by tautomerization to the amide in the condensed phase.

(20) The aza dienes such as **6**-(CH_3,H) readily react with methanol (formed in the thermal elimination) or adventitious water present in the receiver to give the carbinol amide derivatives **9a,b**.

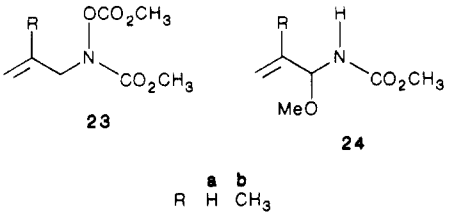
(21) There are two thermal reactions occurring, the elimination of methyl hydrogen carbonate to give the acyl imine and the Cope rearrangement. The elimination reaction occurs at a lower temperature (ca. 400–450 °C) than the Cope rearrangement. In some case, the acyl imine can be directly observed.

(22) The *N*-(methoxycarbonyl)benzylamine can arise by methanol elimination from either the *N*-acyl imine or enamide followed by tautomerization.

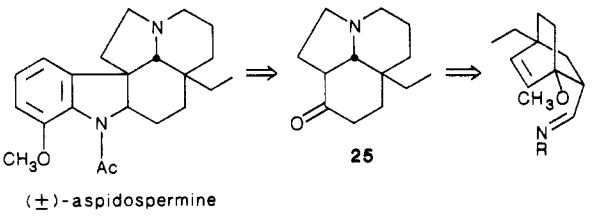
Scheme VIII



Scheme IX



Scheme X



be the Cope rearrangement and not the elimination step to produce the imine. The pyrolytic elimination occurs at a lower temperature (400–450 °C). The ^{1}H NMR spectrum of the crude pyrolysate at this temperature indicates the presence of the reactive imines **6**-(R,R′). This is not the situation with the more reactive bicyclic imines (see below), where the rate-determining step is the formation of the imine.

The three mechanisms[3a,b] most frequently discussed for the Cope rearrangement are (1) breaking of the bond between C-3 and C-4 to give two allyl radicals, (2) formation of a bond between C-1 and C-6 to give a 1,4-diradical, and (3) a combination of 1 and 2, where the bond making and bond breaking are occurring in concert (Scheme VII). Substituent effects have historically played an important role in the elucidation of reaction mechanisms. The difficulty of this approach with the Cope rearrangement is that substituents may significantly alter the reaction pathway.[23] Nevertheless, a recent study of substituent effects led to the conclusion that mechanism 2 is most consistent with the Cope rearrangement of substituted 1,5-hexadienes.[24] Examples relevant to our work are 3-methoxy, 3-methyl, and unsubstituted 1,5-hexadienes. A methyl and methoxy group were observed to have about the *same* effect on the rate of the Cope rearrangement of 1,5-hexadiene at 200 °C, increasing it by about a factor of two compared to the unsubstituted compound.[25]

We observed that methyl and methoxy substituents also accelerate the 1-aza-Cope rearrangement. However, the 1-aza-Cope rearrangement of vinylcyclohexene derivatives appears to be more sensitive to substituents than the Cope rearrangement of 1,5-hexadienes.[26] This observation and the fact that the methoxy substituent accelerates the reaction to a greater extent than the methyl group are consistent with the transition state of the rate-determining step having more character of mechanism 1 described above.[27] This would not be surprising because of the additional strain energy imposed on the transition state for the Cope rearrangement of vinylcyclohexene derivatives. Any breaking of the saturated bond between C-3 and C-4 of the vinylcyclohexene ring system in the transition state would relieve considerable strain energy compared to simple 1,5-hexadiene derivatives.

The Cope rearrangement of bicyclic derivatives of the 4-vinylcyclohexene rearrangement are more common. We extended our studies to the aza analogues of these ring systems because of their potential value in organic synthesis. The required aza diene precursor, hydroxamic acid **20b**, was readily prepared from cyclopentadiene by using the Diels–Alder reaction as the first step. Manipulation of the carbonyl group to give the hydroxamic acid **20b** was performed analogously to that described above. Evaporation of **20b** through the hot tube at 450 °C gave the pyrindine **22b** in 21% yield (Scheme VIII).

The aza diene **21a**, like the monocyclic aza diene **6**-(H,CH_3) has the possibility of the hydrogen shift competing with the Cope rearrangement. However, in contrast to the monocyclic derivative, evaporation of **20a** through the reaction tube at 450 °C gave, although in low isolated yield (11%), the Cope rearranged product **22**. No hydrogen-shifted enamide product analogous to **7** could be detected. The incorporation of the 1-aza diene into the bicyclo[2.2.1]heptane framework appears to be providing a further acceleration of the 1-aza-Cope rearrangement.

However, careful examination of the product mixtures revealed the presence of a small amount of *N*-allylhydroxamic acid derivatives **23** and a 7% yield of the carbinol amide derivatives **24** (Scheme IX). These latter compounds arise by the addition of methanol to the *N*-(methoxycarbonyl)-1-azabuta-1,3-diene. Both **23** and **24** are probably the result of initial retro-Diels–Alder reactions. The retro-Diels–Alder reaction of **20** would give **23**. The *N*-(methoxycarbonyl)-1-azabuta-1,3-diene can arise from the thermolysis of **23** or the retro-Diels–Alder reaction

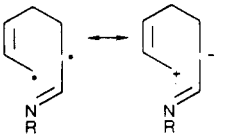
(23) For example, see: (a) Gajewski, J. J. *Acc. Chem. Res.* **1980**, *13*, 142. (b) See also ref 3b.

(24) Dollinger, M.; Henning, W.; Kirmse, W. *Chem. Ber.* **1982**, *115*, 2309.

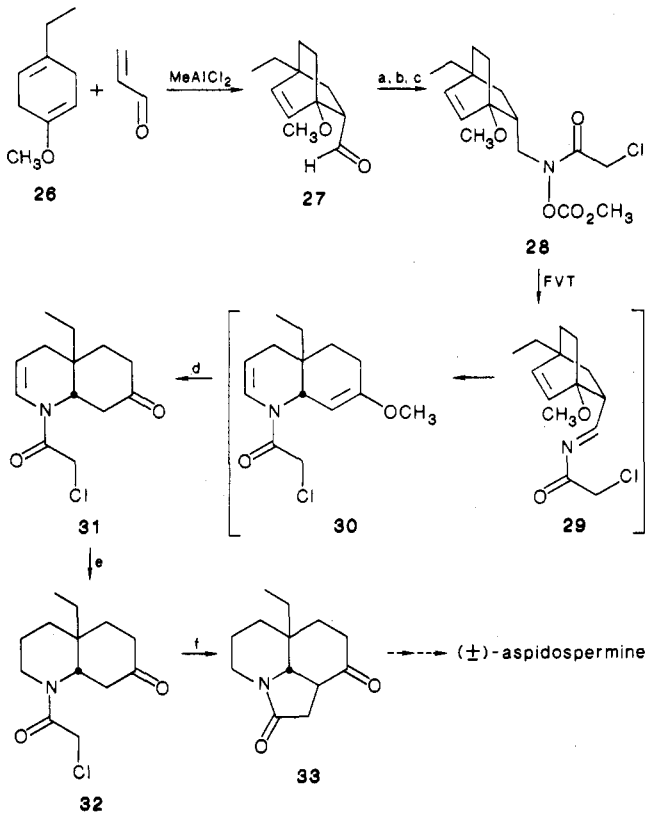
(25) The rates of these reactions at 200 °C for R = CH_3, OCH_3, and H have been reported to be (0.68, 0.60, and 0.33) × 10^5 (see ref 24).

(26) Equal rates at 525 and 475 °C for **6**-(CH_3,H) and **6**-(CH_3,OCH_3), respectively corresponds, very approximately, to relative rates of 1 to 25 at 200 °C.

(27) Because of the presence of the heteroatom, polar resonance structures should have significant contributions to species along the reaction pathway of the 1-aza-Cope rearrangement. Analogous species have often been postulated for the Claisen rearrangement (for example, see ref 8a,b).



Scheme XI[a]



[a] (a) NH_2OH–HCl; (b) (1) BH_3–pyridine/HCl, (2) chloroacetic anhydride/TEA; (c) methyl chloroformate/TEA; (d) oxalic acid/H_2O; (e) H_2–Rh/C; (f) potassium *tert*-butoxide.

of the aza diene **21**. Retro-Diels–Alder reactions of norbornene derivatives are facile processes. Reactive double bonds are often protected by using the Diels–Alder reaction with cyclopentadiene because the reaction is readily reversed thermally.[28] These observations demonstrate that the 1-aza-Cope rearrangement is competitive with the retro-Diels–Alder reaction. An analogous situation also appears to be operative with the cyclopentadiene dimer. That is, the retro-Diels–Alder reaction and the Cope rearrangement are competitive reactions.[28a]

The 1-aza-Cope rearrangements of simple 4-vinylcyclohexene derivatives are high-energy processes proceeding in low overall yield. Similar behavior has been observed for the Cope rearrangement of 4-vinylcyclohexene which has been reported to give at least 17 products.[29] The activation energy required for the 1-aza-Cope rearrangement can be lowered by the substitution of a methoxy substituent on C-4 of the aza diene or by the incorporation of the aza diene into a strained bicyclic ring system. These latter structural modifications enhance the synthetic potential of the process.

The hydrojulolidine **25** and related compounds have previously served as intermediates for the preparation of aspidosperma alkaloids[30] such as (±)-aspidospermine.[31]

The *cis*-hydroquinoline present in hydrojulolidine and aspidospermine is potentially accessible using the 1-aza-Cope rearrangement (Scheme X).

A suitable 1-aza-Cope product for the preparation of the hydrojulolidine **25** is the *cis*-hydroquinoline **30** (Scheme XI). This compound was prepared by evaporation of the hydroxamic acid derivative **28** through the thermolysis oven. It was not purified but was hydrolyzed directly to the ketone **31**. The overall yield for the three-step process from **28** to the ketone **31** was 31%. The preparation of the aza diene precursor was accomplished from the Diels–Alder adduct **27** by using standard procedures. The required endo Diels–Alder adduct **27** was readily prepared from the 1,4-cyclohexadiene **26**, the product of a Birch reduction, in 47% yield. We observed that methylaluminum dichloride could be used to catalyze both the isomerization of **26** to the 1,3-diene and the Diels–Alder reaction.

The preparation of the hydrojulolidine **33** was completed by reduction of the enamide double bond followed by cyclization using potassium *tert*-butoxide analogous to that previously reported.[32a]

In summary, this paper represents the first study concerned with the Cope rearrangement where C-1 has been replaced by a nitrogen atom (the 1-aza-Cope rearrangement). It has been shown that the normally thermodynamically unfavorable 1-aza-Cope reaction can occur when an acyl substituent is present on the nitrogen atom. Although simple aza analogues of vinylcyclohexenes rearrange with difficulty, substituents on C-4 and incorporation of the aza diene into a strained bicyclic ring system considerably enhance the reaction. Because the aza diene precursors are readily available by using the Diels–Alder reaction, the 1-aza-Cope rearrangement has potential for the preparation of nitrogen heterocycles.

Experimental Section

General. Melting points were recorded on a Fisher-Johns melting point apparatus and were uncorrected. Infrared spectra were recorded on a Perkin-Elmer 567 spectrometer as either thin films or KBr solid solutions. The absorption intensities were described as strong (s), medium (m), weak (w), or broad (br), and the absorption of polystyrene at 1944 or 1601 cm^{-1} was used as a reference. Proton NMR spectra were recorded on either a Varian HFT-80 or a Nicolet NT-300 spectrometer. Carbon NMR spectra were recorded on either a Varian CFT-20 or a Nicolet NT-300 spectrometer. All chemical shifts were reported in ppm from tetramethylsilane as internal standard and described as singlet (s), doublet (d), triplet (t), quartet (q), quintet (q'), multiplet (m), or broad (br). Low-resolution mass spectra were recorded on a Hewlett-Packard 5980A spectrometer. High-resolution mass spectra were recorded on an AEI MS-30 spectrometer. Elemental analyses were performed by MicAnal Organic Microanalysis, Tucson, AZ. Analytical gas chromatographic analyses were performed on a Hewlett-Packard 5710A chromatograph equipped with a flame ionization detector. Thin-layer chromatography was carried out with Analtech silica gel HLF precoated thin-layer chromatography plates. Flash column chromatography was carried out with 230–400 mesh silica gel 60 (E. Merck). Dry tetrahydrofuran and diethyl ether were freshly distilled over sodium benzophenone ketyl under nitrogen. 1-Methoxy-1,3-butadiene was bought from Aldrich.

***N,O*-Bis(methoxycarbonyl)-*N*-(3-cyclohexenylmethyl)-hydroxylamine (5-(H,H)).** To a solution of hydroxylamine hydrochloride (0.83 g, 12 mmol) in a minimum amount of water

(28) (a) The activation energies for the retro-Diels–Alder reactions involving cyclopentadiene are relatively low. For example, the E_a for the retro-Diels–Alder reaction of *endo*-bicyclo[2.2.1]hex-2-ene-5-carboxaldehyde is 33.6 kcal/mol (Wilcott, R. M.; Cargill, R. L.; Sears, A. B. *Prog. Phy. Org. Chem.* **1972**, *9*, 25). (b) For this reason, cyclopentadiene is often used as a protecting group for multibonded functional groups (Ripoll, J. L. *Synthesis* **1985**, 121).

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was added sodium carbonate (0.64 g, 6 mmol). Then 3-cyclohexene-1-carboxaldehyde (0.88 g, 8 mmol) in ethyl alcohol (2 mL) was added and stirred at room temperature for 3 h. The reaction mixture was extracted with diethyl ether. The combined extracts were washed with saturated sodium chloride solution, dried over anhydrous magnesium sulfate, and concentrated in vacuo. Flash column chromatography gave 3-cyclohexene-1-carbaldoxime[32] (0.90 g, 90% yield, major:minor = 3:1). Generally, this procedure produced a mixture of syn and anti isomers. These syn and anti isomers were not separated and were used for the further reaction. For the major oxime: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.90–2.21 (m, 6 H, 3 CH_2), 2.08–2.72 (m, 1 H, CH), 5.59–5.72 (m, 2 H, CH=CH), 7.41 (d, 1 H, CH=N, J = 7 Hz), 7.80 (br, 1 H, NOH); IR (film) 3360 (br), 3060 (w), 2960 (s), 1655 (m), 1445 (s), 1325 (m), 1150 (m), 1055 (m), 950 (s), 670 (s) cm^{-1}; ^{13}C NMR ($CDCl_3$, 20 MHz) δ 23.7, 26.0, 28.4, 34.3, 125.0, 126.8, 155.0. A mixture of oxime (0.25 g, 2 mmol) and pyridine–borane (0.37 g, 4 mmol) in ethyl alcohol (2 mL) was kept at 0 °C.[33] To this mixture, a 10% HCl solution (4 mL) was added dropwise, and the mixture was stirred for 20 min at room temperature. The solution was made alkaline with sodium carbonate (with cooling) and extracted with diethyl ether. The ether solution was dried ($MgSO_4$) and concentrated in vacuo to a volume of 20 mL. Triethylamine (0.40 g, 4 mmol) was added to the ether solution, then methyl chloroformate (0.38 g, 4 mmol) in dry diethyl ether (2 mL) was added dropwide at 0 °C. The mixture was stirred for 1.5 h at room temperature, then acidified with 10% HCl, and extracted with diethyl ether. These extracts were combined, dried over anhydrous magnesium sulfate, and concentrated in vacuo. The resulting crude product was purified by flash column chromatography to give **5**-(H,H) (0.35 g, 71% yield): ^{1}H NMR ($CDCl_3$, 80 MHz) δ 1.62–2.13 (m, 7 H, 3 CH_2 and CH), 3.53 and 3.62 (s, 2 H, CH_2N), 3.78 (s, 3 H, NCO_2CH_3), 3.90 (s, 3 H, OCO_2CH_3), 5.62–5.71 (m, 2 H, CH=CH); IR (film) 3050 (m), 2940 (s), 1795 (s), 1730 (s), 1450 (s), 1270 (s), 1210 (s), 1130 (m), 940 (m), 790 (m) cm^{-1}; ^{13}C NMR ($CDCl_3$, 20 MHz) δ 24.3, 25.9, 28.9, 31.7, 53.5, 55.8, 56.0, 125.4, 126.9, 154.8, 156.3.

Anal. Calcd for $C_{11}H_{17}NO_5$: C, 54.32; H, 7.00. Found: C, 54.47; H, 7.09.

***N,O*-Bis(methoxycarbonyl)-*N*-[(1-methyl-3-cyclohexenyl)methyl]hydroxylamine (5-(CH_3,H)).** The analogous procedure for the preparation of **5**-(H,H) was used. The oxime was obtained from 1-methyl-3-cyclohexene-1-carboxaldehyde[34] in 95% yield (major:minor = 4:1). For the major product: ^{1}H NMR ($CDCl_3$, 80 MHz) δ 1.10 (s, 3 H, CH_3), 1.12–2.10 (m, 6 H, 3 CH_2), 5.45–5.63 (m, 2 H, CH=CH), 7.34 (s, 1 H, CH=N), 7.62 (br, 1 H, NOH); IR (film) 3350 (br), 3040 (w), 2940 (s), 1650 (m), 1445 (s), 1380 (m), 1300 (w), 1160 (m), 950 (s), 750 (s) cm^{-1}; ^{13}C NMR ($CDCl_3$, 20 MHz) δ 22.4, 24.5, 32.1, 34.9, 35.1, 124.6, 126.3, 157.7. Then **5**-(CH_3,H) was obtained in 55% yield: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.96 (s, 3 H, CH_3), 1.38–2.08 (m, 6 H, 3 CH_2), 3.50 (br, 2 H, CH_2N), 3.77 (s, 3 H, NO_2CH_3), 3.90 (s, 3 H, OCO_2CH_3), 5.58–5.72 (m, 2 H, CH=CH); IR (film) 3040 (w), 2975 (m), 2930 (m), 1790 (s), 1730 (s), 1445 (s), 1380 (m), 1260 (s), 1240 (s), 1220 (s), 940 (w) cm^{-1}; ^{13}C NMR ($CDCl_3$, 20 MHz) δ 22.3, 23.2, 31.3, 33.3, 35.2, 53.7, 56.1, 60.5, 124.9, 125.9, 154.8, 156.7.

Anal. Calcd for $C_{12}H_{19}NO_5$: C, 56.03; H, 7.39. Found: C, 56.06; H, 7.42.

***N,O*-Bis(methoxycarbonyl)-*N*-[(2-methyl-3-cyclohexenyl)methyl]hydroxylamine (5-(H,CH_3)).** The oxime was obtained from 2-methyl-3-cyclohexene-1-carboxaldehyde[35] in 83% yield (syn:anti = 1:1) by using the procedure for the preparation of **5**-(H,H): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.95 (d, 3 H, CH_3 of anti isomer, J = 7 Hz), 0.97 (d, 3 H, CH_3 of syn isomer, J = 8 Hz), 1.6–2.6 (m, 5 H, $CHCH_3$ and 2 CH_2), 3.3–3.4 (m, 1 H, CHC=N), 5.5–5.7 (m, 2 H, CH=CH), 6.73 (d, 1 H, CH=N of anti isomer, J = 8 Hz), 7.46 (d, 1 H, CH=N of syn isomer, J = 7 Hz), 8.3–8.5 (br, 1 H, NOH); IR (film) 3245 (br), 3035 (m), 2971 (s), 2935 (s), 1647 (w), 1452 (m), 942 (m), 711 (m) cm^{-1}. A solution of oxime (0.42 g, 3 mmol) in dry tetrahydrofuran (2 mL) was added to a solution of sodium borohydride (0.17 g, 4.5 mmol) and trifluoroacetic acid (1.03 g, 9 mmol) in dry tetrahydrofuran (3 mL) under nitrogen cooled in an ice bath.[36] Methyl chloroformate (0.85 g, 9 mmol) was then added slowly, and the resulting mixture was stirred at room temperature for 4 h. The excess reducing agent was decomposed by adding water. The mixture was extracted with diethyl ether, and the combined ethereal layers were washed with saturated sodium chloride solution, dried over anhydrous magnesium sulfate, concentrated in vacuo, and purified by flash column chromatography to give **5**-(H,CH_3) (0.49 g, 64% yield): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.90 (d, 3 H, CH_3, J = 7 Hz), 1.5–2.4 (m, 6 H, 2 CH and 2 CH_2), 3.59 and 3.61 (s, 2 H, NCH_2), 3.79 (s, 3 H, NCO_2CH_3), 3.91 (s, 3 H, OCO_2CH_3), 5.6 (m, 2 H, CH=CH); IR (film) 3.33 (m), 2975 (s), 1792 (s), 1758 (s), 1650 (w), 1449 (s), 1271 (s), 1233 (s), 1205 (s), 1125 (m), 995 (w), 938 (s), 790 (m) cm^{-1}; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.9, 21.0, 24.6, 30.5, 34.4, 52.7, 53.3, 55.8, 125.4, 132.2, 154.4, 156.1.

Anal. Calcd for $C_{12}H_{19}NO_5$: C, 56.02; H, 7.44. Found: C, 56.27; H, 7.67.

***N,O*-Bis(methoxycarbonyl)-*N*-[(1,2-dimethyl-3-cyclohexenyl)methyl]hydroxylamine (5-(CH_3,CH_3)).** The analogous procedure for the preparation of **5**-(H,CH_3) was used. The oxime was obtained from the aldehyde 11-(CH_3,CH_3) in 81% yield (major:minor = 6:1). For the major product: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.94 (d, 3 H, $CHCH_3$, J = 7 Hz), 1.15 (s, 3 H, CH_3), 1.5–2.2 (m, 4 H, 2 CH_2), 2.2–2.3 (m, 1 H, $CHCH_3$), 5.4–5.7 (m, 2 H, CH=CH), 7.46 (s, 1 H, CH=N), 7.80 (br, 1 H, NOH); IR (film) 3334 (br), 3034 (m), 2988 (s), 2940 (s), 1650 (w), 1453 (m), 1379 (m), 954 (s), 692 (s) cm^{-1}; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 16.7, 22.6, 23.4, 31.8, 38.1, 38.9, 125.5, 131.2, 156.2. Then **5**-(CH_3,CH_3) was obtained in 43% yield: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.93 (d, 3 H, $CHCH_3$, J = 7 Hz), 1.02 (s, 3 H, CH_3), 1.2–2.2 (m, 5 H, $CHCH_3$, and 2 CH_2), 3.4–3.8 (br, 2 H, CH_2N), 3.78 (s, 3 H, NCO_2CH_3), 3.91 (s, 3 H, OCO_2CH_3), 5.4–5.6 (m, 2 H, CH=CH); IR (film) 3033 (m), 2975 (s), 1790 (s), 1725 (s), 1450 (w), 1448 (s), 1378 (s), 1290 (s), 1245 (s), 1215 (s), 1100 (m), 938 (m), 785 (m) cm^{-1}; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 15.4, 22.2, 23.5, 29.5, 35.1, 38.6, 53.3, 55.3, 55.7, 124.9, 131.0, 154.3, 156.5.

Anal. Calcd for $C_{13}H_{21}NO_5$: C, 57.55; H, 7.80. Found: C, 57.77; H, 7.95.

***N,O*-Bis(methoxycarbonyl)-*N*-[(2-(methoxycarbonyl)-3-cyclohexenyl)methyl]hydroxylamine (5-(H,CO_2CH_3)).** The oxime was obtained from 2-(methoxycarbonyl)-3-cyclohexene-1-carboxaldehyde[37] in 79% yield (major:minor = 6:1) by using the procedure for the preparation of **5**-(H,H). For the major product: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.7–2.3 (m, 4 H, 2 CH_2), 2.88 (m, 1 H, $CHCH_2$), 3.33 (m, 1 H, $CHCO_2CH_3$), 3.68 (s, 3 H, CO_2CH_3), 5.75–5.95 (m, 2 H, CH=CH), 6.83 (br, 1 H, NOH), 7.48 (d, 1 H, CH=N, J = 6 Hz); IR (film) 3370 (br), 3035 (w), 2958 (m), 1730 (s), 1440 (m), 1200 (s), 1180 (s), 920 (m), 740 (m) cm^{-1}; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 23.4, 24.4, 36.1, 44.6, 52.0, 122.9, 129.1, 152.9, 173.6. A mixture of oxime (0.92 g, 5 mmol) and pyridine–borane (0.58 g, 6.25 mmol) in ethyl alcohol (3 mL) was cooled in an ice bath. To this mixture, 10% HCl solution (6 mL) was added dropwise, and the mixture was stirred for 20 min at room temperature. The solution was concentrated in vacuo to remove ethanol and washed with diethyl ether. Methyl chloroformate (0.95 g, 10 mmol) was added into the aqueous solution, and then sodium bicarbonate (1.68 g, 20 mmol) was added slowly to the mixture cooled in an ice bath. The mixture was stirred for 1 h at room temperature, acidified with 10% HCl solution, and extracted with diethyl ether. These extracts were combined, dried over anhydrous magnesium sulfate, and concentrated in vacuo. The crude product was purified by flash column chromatography to give **5**-(H,CO_2CH_3) (0.36 g, 24% yield): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.6–2.2 (m, 5 H, $CHCH_2$ and 2 CH_2), 3.25 (m, 1 H, $CHCO_2CH_3$), 3.65 (s, 3 H, CO_2CH_3), 3.65–3.75 (br, 2 H, NCH_2), 3.75 (s, 3 H, NCO_2CH_3), 3.82 (s, 3 H, OCO_2CH_3), 5.7–5.9 (m, 2 H, CH=CH); IR (film) 3040 (w), 2960 (m), 1795 (s), 1735 (s), 1445 (s), 1270 (s), 1237 (s), 1198 (s), 1125 (m), 940 (m), 785 (m) cm^{-1}; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 23.7, 32.9, 42.2, 51.1, 51.4, 53.2, 54.8, 55.7, 122.9, 129.5, 154.2, 156.1, 172.7; MS, m/z (relative intensity)

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269 (4, $M^+ - CH_3OH$), 242 (2), 226 (10), 194 (14), 166 (50), 154 (33), 93 (81), 91 (73), 88 (61), 79 (94), 77 (55), 59 (100).

***N,O*-Bis(methoxycarbonyl)-*N*-[(1-methyl-2-(methoxycarbonyl)-3-cyclohexenyl)methyl]hydroxylamine (5-(CH_3,CO_2CH_3)).** The analogous procedure for the preparation of 5-(H,CO_2CH_3) was used. The oxime was obtained from aldehyde 11-(CH_3,CO_2CH_3) in 86% yield (major:minor = 4:1). For the major product: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.23 (s, 3 H, CH_3), 1.5–2.2 (m, 4 H, 2 CH_2), 3.05 (m, 1 H, $CHCO_2CH_3$), 3.68 (s, 3 H, CO_2CH_3), 5.6–5.9 (m, 2 H, CH=CH), 7.51 (s, 1 H, CH=N), 8.42 (br, 1 H, NOH); IR (film) 3400 (br), 3038 (w), 2940 (m), 1730 (s), 1448 (m), 1330 (w), 1170 (s), 1030 (w), 950 (s) cm^{-1}; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.9, 23.9, 30.6, 37.0, 50.1, 51.7, 122.3, 128.8, 155.5, 172.9. Then 5-(CH_3,CO_2CH_3) was obtained in 14% yield: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.91 (s, 3 H, CH_3), 1.5–2.2 (m, 4 H, 2 CH_2), 3.15 (m, 1 H, $CHCO_2CH_3$), 3.64 (br, 2 H, NCH_2), 3.65 (s, 3 H, CO_2CH_3), 3.76 (s, 3 H, NCO_2CH_3), 3.89 (s, 3 H, OCO_2CH_3), 5.6–5.9 (m, 2 H, CH=CH); IR (film) 3035 (m), 2970 (s), 1790 (s), 1725 (s), 1450 (s), 1390 (s), 1240 (s), 1032 (m), 938 (s), 785 (m) cm^{-1}; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.7, 21.8, 35.3, 35.5, 47.1, 48.4, 51.4, 53.6, 56.0, 122.8, 129.0, 154.4, 156.5, 173.2; MS, *m/z* (relative intensity) 283 (4, $M^+ - CH_3OH$), 240 (5), 208 (8), 180 (11), 121 (30), 107 (38), 105 (22), 93 (100), 91 (47), 88 (49), 79 (33), 77 (32), 59 (66).

***N,O*-Bis(methoxycarbonyl)-*N*-[(2-methoxy-3-cyclohexenyl)methyl]hydroxylamine (5-(H,OCH_3)).** The analogous procedure for the preparation of 5-(H,H) was used. The oxime was obtained from 2-methoxy-3-cyclohexene-1-carboxaldehyde[38] in 84% yield (major:minor = 2:1). For the major product: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.6–2.2 (m, 4 H, 2 CH_2), 2.68–2.78 (m, 1 H, CHCH=N), 3.34 (s, 3 H, OCH_3), 3.77 (m, 1 H, $CHOCH_3$), 5.86 (m, 2 H, CH=CH), 7.54 (d, 1 H, CH=N, J = 7 Hz), 9.0 (br, 1 H, NOH); IR (film) 3300 (br), 3047 (w), 2948 (s), 1651 (w), 1458 (m), 1201 (m), 1110 (s), 923 (m) cm^{-1}; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.3, 23.4, 38.1, 56.3, 74.6, 125.7, 130.6, 152.6. Then 5-(H,OCH_3) was obtained in 37% yield: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.5–2.1 (m, 4 H, 2 CH_2), 2.1–2.2 (m, 1 H, $CHCH_2N$), 3.35 (s, 3 H, OCH_3), 3.68 (m, 2 H, CH_2N), 3.76 (m, 1 H, $CHOCH_3$), 3.78 (s, 3 H, NCO_2CH_3), 3.90 (s, 3 H, OCO_2CH_3), 5.90 (m, 2 H, CH=CH); IR (film) 3039 (w), 2947 (s), 2839 (m), 1788 (s), 1725 (s), 1445 (s), 1275 (s), 1237 (s), 1200 (s), 1121 (s), 1090 (s), 1001 (w), 938 (m), 790 (m) cm^{-1}; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.9, 24.7, 36.2, 51.8, 53.4, 55.9, 56.2, 73.0, 125.6, 131.4, 154.8, 156.3.

Anal. Calcd for $C_{12}H_{19}NO_6$: C, 52.74; H, 7.01. Found: C, 52.64; H, 7.12.

***N,O*-Bis(methoxycarbonyl)-*N*-[(1-methyl-2-methoxy-3-cyclohexenyl)methyl]hydroxylamine (5-(CH_3,OCH_3)).** The analogous procedure for the preparation of 5-(H,H) was used. The oxime was obtained from aldehyde 11-(CH_3,OCH_3) in 91% yield (major:minor = 2:1). For the major product: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.15 (s, 3 H, CH_3), 1.6–2.2 (m, 4 H, 2 CH_2), 3.39 (s, 3 H, OCH_3), 3.43 (m, 1 H, $CHOCH_3$), 5.82 (m, 2 H, CH=CH), 7.55 (s, 1 H, CH=NOH), 7.7 (br, 1 H, NOH); IR (film) 3320 (br), 3047 (w), 2940 (s), 1651 (w), 1450 (m), 1107 (s), 952 (s) cm^{-1}; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.8, 22.4, 29.5, 39.6, 57.3, 81.1, 124.8, 129.6, 155.4. Then 5-(CH_3,OCH_3) was obtained in 37% yield: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.97 (s, 3 H, CH_3), 1.6–2.2 (m, 4 H, 2 CH_2), 3.33 (s, 3 H, OCH_3), 3.6–3.8 (m, 3 H, CH_2N and $CHOCH_3$), 3.77 (s, 3 H, NCO_2CH_3), 3.90 (s, 3 H, OCO_2CH_3), 5.84 (m, 2 H, CH=CH); IR (film) 3039 (w), 2985 (m), 2941 (m), 2838 (w), 1789 (s), 1730 (s), 1450 (s), 1390 (m), 1248 (s), 1220 (s), 1105 (s), 998 (w), 939 (s) cm^{-1}; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.6, 22.4, 27.7, 37.4, 37.7, 53.3, 55.5, 55.7, 79.3, 124.4, 130.0, 154.5, 156.6.

Anal. Calcd for $C_{13}H_{21}NO_6$: C, 54.35; H, 7.37. Found: C, 54.03; H, 7.44.

General Method for the Flash Vacuum Thermolysis (FVT). The reactant (20–200 mg) was added to the evaporating flask and cooled in liquid nitrogen. A vacuum was applied, and when the pressure was reduced to ca. 10^{-3} Torr, the heater was turned on. When the thermolysis oven had stabilized at the desired temperature, the receiver was cooled in a liquid nitrogen bath. The temperature of the reaction tube was regulated by an Omega D-921 K controller. The reactant was evaporated through the thermolysis oven, often requiring the application of heat. The product was washed out of the receiver with diethyl ether or methylene chloride. After removal of the solvent, the crude product was purified by flash column chromatography. All yields are reported for the pure products.

1-[(*N*-(Methoxycarbonyl)amino)methylene]-3-cyclohexene (7-(H)). This compound was obtained from 5-(H,H) according to the general thermolysis procedure (500 °C, 30% yield): ^{1}H NMR ($CDCl_3$, 80 MHz) δ 2.00–2.68 (m, 6 H, 3 CH_2), 3.72 (s, 3 H, NCO_2CH_3), 5.52–5.72 (m, 2 H, CH=CH), 5.68 (br, 1 H, NH), 6.01–6.43 (m, 1 H, C=CHN); IR (film) 3340 (br), 3040 (m), 2930 (m), 1710 (s), 1520 (s), 1450 (m), 1370 (m), 1250 (s), 1070 (s), 790 (m) cm^{-1}; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 24.5, 26.4, 30.6, 52.4, 115.9, 117.0, 125.7, 127.5, 154.4; MS, *m/z* (relative intensity) 167 (62, M^+), 92 (68), 91 (100), 88 (56), 76 (62), 69 (25); HRMS, *m/e* 167.0962 ($C_9H_{13}NO_2$ requires 167.0946).

1-[(*N*-(Methoxycarbonyl)amino)methylene]-2-methyl-3-cyclohexene (7-(CH_3)). This compound was obtained from 5-(H,CH_3) as a mixture of cis and trans isomers according to the general thermolysis procedure (475 °C, 58% yield): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.09 and 1.11 (d, 3 H, CH_3 of cis and trans isomers, J = 7 Hz), 1.9–2.3 (m, 4 H, 2 CH_2), 2.7–2.9 (m, 1 H, $CHCH_3$), 3.72 (s, 3 H, NCO_2CH_3), 5.5–5.8 (m, 2 H, CH=CH), 6.1–6.4 (m, 2 H, CHN and NH); IR (film) 3320 (br), 3030 (w), 2963 (m), 2935 (m), 1690 (s), 1505 (s), 1455 (m), 1365 (m), 1240 (s), 1060 (m), 772 (m) cm^{-1}; MS, *m/z* (relative intensity) 181 (29, M^+), 166 (30), 106 (52), 91 (100), 88 (39), 59 (15); HRMS, *m/e* 181.1110 ($C_{10}H_{15}NO_2$ requires 181.1103).

***trans*-1-[(*N*-(Methoxycarbonyl)amino)methylene]-2-(methoxycarbonyl)-3-cyclohexene (*trans*-7-(CO_2CH_3)).** This compound was obtained from 5-(H, CO_2CH_3) according to the general thermolysis procedure (450 °C, 32% yield): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.0–2.4 (m, 4 H, 2 CH_2), 3.6 (m, 1 H, $CHCO_2CH_3$), 3.66 (s, 3 H, CCO_2CH_3), 3.70 (s, 3 H, NCO_2CH_3), 5.7–5.9 (m, 2 H, CH=CH), 6.37 (br, 1 H, NH), 6.52 (br, 1 H, C=CHN); IR (film) 3340 (br), 3030 (m), 2958 (s), 1710 (s), 1510 (s), 1440 (s), 1350 (m), 1230 (s), 1050 (s), 780 (m), 745 (s) cm^{-1}; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.5, 25.4, 46.8, 52.1, 52.4, 114.0, 119.3, 123.9, 129.6, 154.3, 173.0; MS, *m/z* (relative intensity) 225 (7, M^+), 193 (17), 166 (100), 150 (10), 134 (19), 106 (20), 91 (96), 88 (36), 79 (23), 77 (24), 59 (19); HRMS, *m/e* 225.1005 ($C_{11}H_{15}NO_4$ requires 225.1001).

***cis*-1-[(*N*-(Methoxycarbonyl)amino)methylene]-2-(methoxycarbonyl)-3-cyclohexene (*cis*-7-(CO_2CH_3)).** This compound was obtained from 5-(H,CO_2CH_3) according to the general thermolysis procedure (450 °C, 16% yield): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.0–2.3 (m, 4 H, 2 CH_2), 3.65 (br, 1 H, $CHCO_2CH_3$), 3.71 (s, 6 H, 2 CO_2CH_3), 5.6 (br, 1 H, C=$CHCCO_2CH_3$), 6.0 (m, 1 H, CH=$CCCO_2CH_3$), 6.48 (br, 1 H, C=CHN), 7.15 (br, 1 H, NH); IR (film) 3340 (br), 3025 (w), 2950 (m), 2840 (w), 1710 (s), 1500 (s), 1435 (m), 1330 (w), 1230 (s), 1053 (s), 1018 (m), 920 (w), 738 (m) cm^{-1}; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 25.7, 26.6, 42.5, 52.4, 52.5, 114.0, 120.2, 121.8, 130.6, 154.5, 172.3; MS, *m/z* (relative intensity) 225 (6, M^+), 193 (15), 166 (100), 134 (14), 106 (15), 91 (96), 88 (35), 79 (19), 77 (18), 59 (17).

***N*-(Methoxycarbonyl)-2-vinyl-5-methyl-1,2,3,4-tetrahydropyridine (8-(CH_3,H)).** This compound was obtained from 5-(CH_3,H) according to the general thermolysis procedure (525 °C, 4% yield): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.76–1.30 and 1.70–1.92 (m, 4 H, 2 CH_2), 1.65 (s, 3 H, CH_3), 3.75 (s, 3 H, NCO_2CH_3), 4.75 (br, 1 H, CHN), 4.93–5.12 (m, 2 H, CH_2=C), 5.60–5.81 (m, 1 H, C=CHC), 6.62 (br, 1 H, C=CHN); IR (film) 3010 (w), 2980 (m), 1710 (s), 1450 (s), 1400 (m), 1375 (m), 1350 (m), 1325 (m), 1200 (m), 970 (w), 780 (m) cm^{-1}; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.9, 23.2, 25.5, 52.0, 52.8, 114.8, 118.8, 130.9, 135.5, 154.1; MS, *m/z* (relative intensity) 181 (100, M^+), 166 (57), 154 (32), 152 (48), 122 (30), 106 (47), 96 (36), 59 (20); HRMS, *m/z* 181.1136 ($C_{10}H_{15}NO_2$ requires 181.1103).

The ^{1}H NMR spectrum indicated the crude product contained a mixture of the aza diene 6-(CH_3,H), **9a**, and **9b**. The aza diene 6-(CH_3,H) was unstable and could not be purified. Its presence was inferred from the ^{1}H NMR spectrum, particularly the characteristic absorption at δ 8.20 for the aldimine hydrogen. Also, this compound is the major product when the thermolysis is performed at lower temperature (450 °C). Flash chromatography (ether/hexane (1:1)) of the crude product gave the pure com-

(38) Makin, S. M.; Boiko, I. I.; Berezhnaya, M. I.; Boiko, T. N. *J. Org. Chem., USSR (Engl. Transl.)* **1974**, *10*, 21.

pounds **9a** and **9b**. **9a**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.94 (s, 3 H, CH_3), 1.4–2.3 (m, 6 H, 3 CH_2), 3.5–3.7 (br, 1 H, OH), 3.70 (s, 3 H, NCO_2CH_3), 4.95–5.05 (br, 1 H, CH), 5.4–5.6 (br, 1 H, NH), 5.6–5.8 (m, 2 H, CH=CH); IR (film) 3360 (br), 3020 (w), 2920 (m), 2840 (w), 1700 (s), 1510 (s), 1455 (m), 1350 (m), 1245 (s), 1025 (s), 780 (w) cm^{-1}; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.2, 21.4, 29.4, 33.0, 35.8, 52.0, 80.8, 124.6, 125.9, 157.0; MS, *m/z* (relative intensity) 124 (100), 95 (78), 81 (67), 67 (75), 55 (40). Anal. Calcd for $C_{10}H_{17}NO_3$: C, 60.28; H, 8.60. Found: C, 60.09; H, 8.45. **9b**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.89 (s, 3 H, CH_3), 1.3–2.4 (m, 6 H, 3 CH_2), 3.34 (s, 3 H, OCH_3), 3.71 (s, 3 H, NCO_2CH_3), 4.6–4.7 (br d, 1 H, CH), 4.9–5.1 (br, 1 H, NH), 5.5–5.8 (m, 2 H, CH=CH); IR (film) 3340 (br), 3020 (w), 2920 (m), 2840 (w), 1705 (s), 1500 (s), 1450 (m), 1350 (m), 1235 (s), 1085 (s), 660 (m) cm^{-1}; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.4, 21.9, 29.5, 33.1, 36.7, 52.0, 56.0, 89.0, 124.8, 126.0, 157.2; MS, *m/z* (relative intensity) 198 (0.3, M^+), 181 (26), 118 (100), 106 (21), 91 (16), 59 (16).

***N*-(Methoxycarbonyl)-2-propenyl-5-methyl-1,2,3,4-tetrahydropyridine (8-(CH_3,CH_3)).** This compound was obtained from 5-(CH_3,CH_3) according to the general thermolysis procedure (500 °C, 46% yield): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.6–1.7 (br, 6 H, 2 CH_3), 1.7–2.1 (m, 4 H, 2 CH_2), 3.72 (s, 3 H, NCO_2CH_3), 4.5–4.7 (br d, 1 H, CH=CCH_3), 5.3–5.6 (br, 2 H, C=$CHCH_3$ and C=CCH), 6.5–6.7 (br, 1 H, C=CHN); IR (film) 2940 (m), 2910 (m), 1700 (s), 1445 (s), 1340 (s), 1195 (s), 970 (m) cm^{-1}; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.5, 20.8, 23.1, 25.9, 51.2, 52.6, 114.2, 118.3, 125.9, 128.2, 153.9; MS, *m/z* (relative intensity) 195 (100, M^+), 180 (44), 154 (26), 152 (48), 136 (25), 128 (23), 120 (46), 105 (51), 96 (30), 68 (69), 67 (52), 59 (20); HRMS, *m/e* 195.1250 ($C_{11}H_{17}NO_2$ requires 195.1260).

***N*-(Methoxycarbonyl)-2-[2-(methoxycarbonyl)vinyl]-5-methyl-1,2,3,4-tetrahydropyridine (8-(CH_3,CO_2CH_3)).** This compound was obtained from 5-(CH_3,CO_2CH_3) according to the general thermolysis procedure (475 °C, 23% yield): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.65 (s, 3 H, CH_3), 1.8–2.0 (m, 4 H, 2 CH_2), 3.71 (s, 3 H, CCO_2CH_3), 3.75 (s, 3 H, NCO_2CH_3), 4.9 (br, 1 H, $CHCH_2$), 5.75 (d, 1 H, C=$CHCO_2CH_3$, J = 16 Hz), 6.6 (br, 1 H, C=CHN), 6.8 (dd, 1 H, CH=CCO_2CH_3, J = 4, 16 Hz); IR (film) 3030 (w), 2960 (m), 1710 (s), 1448 (s), 1440 (m), 1320 (m), 1280 (m), 1195 (s), 1040 (w), 775 (w) cm^{-1}; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.7, 23.2, 24.9, 50.7, 51.5, 52.9, 114.6, 118.0, 121.0, 145.5, 153.3, 166.5; MS, *m/z* (relative intensity) 239 (40, M^+), 207 (10), 206 (9), 180 (100), 152 (37), 148 (73), 132 (44), 120 (35), 95 (20), 81 (27), 59 (39); HRMS, *m/e* 239.1153 ($C_{12}H_{17}NO_4$ requires 239.1158).

***N*-(Methoxycarbonyl)-2-(2-methoxyvinyl)-1,2,3,4-tetrahydropyridine (8-(H,OCH_3)).** This compound was obtained from 5-(H,OCH_3) according to the general thermolysis procedure (475 °C, 18% yield): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.7–2.2 (m, 4 H, 2 CH_2), 3.50 (s, 3 H, OCH_3), 3.74 (s, 3 H, NCO_2CH_3), 4.7–5.0 (br, 3 H, CHN and CH=CN and CH=$CHOCH_3$), 6.5 (br, 1 H, C=$CHOCH_3$), 6.7 (br, 1 H, C=CHN); IR (film) 2972 (m), 2863 (w), 1713 (s), 1649 (s), 1447 (s), 1413 (m), 1362 (s), 1214 (s), 1123 (m), 948 (m), 772 (s) cm^{-1}; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.6, 27.1, 49.5, 52.8, 55.9, 100.2, 105.8, 123.9, 149.6, 154; MS, *m/z* (relative intensity) 197 (54, M^+), 139 (43), 138 (50), 122 (57), 84 (100), 69 (59), 59 (12); HRMS, *m/e* 197.1073 ($C_{10}H_{15}NO_3$ requires 197.1067).

***N*-(Methoxycarbonyl)-2-(2-methoxyvinyl)-5-methyl-1,2,3,4-tetrahydropyridine (8-(CH_3,OCH_3)).** This compound was obtained from 5-(CH_3,OCH_3) according to the general thermolysis procedure (475 °C, 61% yield): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.67 (s, 3 H, CH_3), 1.6–2.2 (m, 4 H, 2 CH_2), 3.49 (s, 3 H, OCH_3), 3.72 (s, 3 H, NCO_2CH_3), 4.6–4.8 (br, 2 H, CHN and CH=$COCH_3$), 6.4–6.7 (br, 2 H, C=CHN and C=$CHOCH_3$); IR (film) 2970 (s), 2940 (s), 2855 (m), 1705 (s), 1645 (s), 1442 (s), 1325 (s), 1218 (s), 1195 (s), 945 (m), 772 (m) cm^{-1}; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.8, 23.0, 27.2, 48.7, 52.6, 55.9, 100.5, 114.3, 118.6, 149.4, 153.5; MS, *m/z* (relative intensity) 211 (47, M^+), 152 (28), 136 (46), 118 (19), 84 (100), 69 (50); HRMS, *m/e* 211.1224 ($C_{11}H_{17}NO_3$ requires 211.1209).

1,2-Dimethyl-3-cyclohexene-1-carboxaldehyde (11-(CH_3,CH_3)). Methacrolein (0.32 g, 45 mmol) was added to a suspension of $SnCl_4 \cdot 5H_2O$ (0.7 g) in benzene (6 mL) over 10 min at 20 °C. Then the mixture was cooled in an ice bath and a solution of piperylene (2.04 g, 30 mmol) in benzene (4 mL) was added over 30 min. The mixture, cooled in an ice bath, was stirred for 3 h, then 10 mL of 3% HCl was added, and the mixture was washed with water, dried with anhydrous magnesium sulfate, and concentrated in vacuo. The crude product was purified by flash column chromatography to give the pure compound 11-(CH_3,CH_3) as a colorless liquid (2.24 g, 54% yield): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.01 (d, 3 H, CH_3CH, J = 7 Hz), 1.09 (s, 3 H, CCH_3), 1.5–2.2 (m, 4 H, CH_2), 2.2–2.3 (m, 1 H, $CHCH_3$), 5.6–5.7 (m, 2 H, CH=CH), 9.67 (s, 1 H, CHO); IR (film) 3015 (m), 2983 (s), 2940 (s), 2702 (w), 1723 (s), 1650 (w), 1457 (m), 1379 (m), 913 (m), 720 (m) cm^{-1}; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 16.3, 19.5, 21.8, 26.6, 36.2, 46.5, 125.2, 205.7.

1-Methyl-2-(methoxycarbonyl)-3-cyclohexene-1-carboxaldehyde (11-(CH_3,CO_2CH_3)). Methacrolein (4.20 g, 60 mmol), methyl 2,4-pentadienoate (3.36 g, 30 mmol), hydroquinone (10 mg), and benzene (30 mL) were placed in a tube, which was then sealed. The tube was heated at 120 °C for 3 days. The resulting solution was concentrated in vacuo. Flash chromatography gave the product 11-(CH_3,CO_2CH_3) as a colorless liquid (2.40 g, 44% yield): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.13 (s, 3 H, CH_3), 1.6–2.2 (m, 4 H, 2 CH_2), 3.16 (m, 1 H, $CHCO_2CH_3$), 3.70 (s, 3 H, CO_2CH_3), 5.75–5.95 (m, 2 H, CH=CH), 9.6 (s, 1 H, CHO); IR (film) 3030 (w), 2955 (m), 2850 (w), 2710 (w), 1725 (s), 1435 (m), 1325 (m), 1195 (m), 1170 (m), 1032 (m), 920 (w) cm^{-1}; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.9, 21.6, 27.0, 45.6, 47.8, 51.8, 122.0, 129.0, 172.6, 204.3.

1-Methyl-2-methoxy-3-cyclohexene-1-carboxaldehyde (11-(CH_3,OCH_3)). 1-Methoxy-1,3-butadiene (1.68 g, 20 mmol) was added to a solution of methacrolein (2.10 g, 30 mmol) and hydroquinone (5 mg). The reaction mixture was refluxed for 2 h and concentrated in vacuo. Flash column chromatography gave the pure product 11-(CH_3,OCH_3) (2.28 g, 74% yield): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.04 (s, 3 H, CH_3), 1.9–2.2 (m, 4 H, 2 CH_2), 3.38 (s, 3 H, OCH_3), 3.64 (m, 1 H, $CHOCH_3$), 5.9–6.0 (m, 2 H, CH=CH), 9.68 (s, 1 H, CHO); IR (film) 3042 (m), 2948 (s), 2834 (s), 2704 (w), 1722 (s), 1646 (w), 1452 (m), 1398 (m), 1192 (m), 944 (m), 725 (m) cm^{-1}; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.7, 20.1, 25.4, 48.2, 56.8, 78.8, 123.9, 130.9, 205.6.

***N*,*O*-Bis(methoxycarbonyl)-*N*-[(2-hydroxy-3-cyclohexenyl)methyl]hydroxylamine (12a).** The analogous procedure for the preparation of 5-(H,H) was used. The oxime was obtained from 2-[(trimethylsilyl)oxy]-3-cyclohexene-1-carboxaldehyde[39] in 82% yield (major:minor = 5:1). For the major product: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.11 (s, 9 H, OTMS), 1.6–2.2 (m, 4 H, 2 CH_2), 2.5–3.2 (m, 1 H, CHC=N), 4.2–4.3 (m, 1 H, CHOTMS), 5.65–5.85 (m, 2 H, CH=CH), 7.46 (d, 1 H, CH=N, J = 8 Hz), 8.2–8.6 (br, 1 H, NOH); IR (film) 3250 (br), 3040 (m), 2950 (s), 1645 (w), 1450 (m), 1250 (s), 1095 (s), 1020 (s), 840 (s) cm^{-1}; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 0.2, 21.4, 24.1, 40.5, 66.1, 128.7, 129.8, 154.0. Then **12a** was obtained in 40% yield: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.4–2.2 (m, 4 H, 2 CH_2), 2.65 (m, 1 H, CHCN), 3.44 and 3.93 (dd, 2 H, CH_2N, J = 6, 15 Hz, and 10, 15 Hz), 3.77 (s, 3 H, NCO_2CH_3), 3.88 (s, 3 H, OCO_2CH_3), 3.97 (br, 1 H, OH), 4.08 (m, 1 H, CHO), 5.85 (m, 2 H, CH=CH); IR (film) 3450 (br), 3010 (m), 2955 (m), 2910 (m), 1785 (s), 1720 (s), 1430 (s), 1265 (s), 1220 (s), 1195 (s), 1110 (m), 925 (m), 725 (m) cm^{-1}; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.1, 25.4, 37.6, 52.6, 53.8, 56.2, 62.8, 127.6, 131.2, 154.7, 156.5; MS, *m/z* (relative intensity) 183 (8, $M^+ - HOCO_2CH_3$), 166 (18), 104 (63), 93 (53), 91 (50), 88 (35), 79 (100), 77 (53), 59 (40).

***N*,*O*-Bis(methoxycarbonyl)-*N*-[(1-methyl-2-hydroxy-3-cyclohexenyl)methyl]hydroxylamine (12b).** The analogous procedure for the preparation of 5-(H,H) was used. The oxime was obtained from 1-methyl-2-[(trimethylsilyl)oxy]-3-cyclohexene-1-carboxaldehyde in 85% yield (major:minor = 3:1). For the major product: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.12 (s, 9 H, OTMS), 1.10 (s, 3 H, CH_3), 1.5–2.2 (m, 4 H, 2 CH_2), 3.93 (s, 1 H, CHOTMS), 5.5–5.8 (m, 2 H, CH=CH), 7.56 (s, 1 H, CH=N), 7.65 (br, 1 H, NOH); IR (film) 3300 (br), 3020 (w), 2953 (s), 2905 (m), 1647 (w), 1446 (m), 1247 (s), 1085 (s), 840 (s) cm^{-1}; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 0.2, 22.5, 22.5, 29.8, 40.2, 73.1, 128.5, 129.5, 155.9. Then **12b** was obtained in 47% yield: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.95 (s, 3 H, CH_3), 1.6–2.1 (m, 4 H, 2 CH_2), 3.3 (br, 1 H, OH), 3.76 (m, 2 H, CH_2N), 3.79 (s, 3 H, NCO_2CH_3), 3.91 (s, 3 H, OCO_2CH_3), 4.1 (br, 1 H, *C*HOH), 5.7–5.9 (m, 2 H, CH=CH); IR (film) 3450 (br), 3035 (m), 2975 (m), 2935 (m), 1790 (s), 1725

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(s), 1450 (s), 1390 (s), 1245 (s), 1100 (m), 935 (m), 740 (m) cm^{-1}; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.1, 22.3, 26.1, 37.9, 53.9, 56.2, 58.1, 68.7, 126.9, 129.6, 154.4, 157.1; MS, *m/z* (relative intensity) 197 (7, $M^+ - HOCO_2CH_3$), 180 (8), 104 (63), 94 (58), 93 (100), 91 (68), 88 (62), 79 (95), 77 (64), 59 (60).

7-[*N*-(Methoxycarbonyl)amino]-2,6-heptadienal (14a). This compound was obtained as a mixture of cis and trans isomers from **12a** according to the general thermolysis procedure (475 °C, 5% yield): ^1H NMR ($CDCl_3$, 300 MHz) δ 2.2–2.5 (m, 4 H, 2 CH_2), 3.70 and 3.72 (s, 3 H, NCO_2CH_3 of cis and trans isomers), 4.5–5.1 (m, 1 H, CH=CN), 6.1–6.3 (m, 2 H, C=C*H*CHO and NH), 6.3–6.4 (br, 1 H, C=CHN), 6.4–6.6 (br d, 1 H, C=CHN), 6.6–6.8 (m, 1 H, C*H*=CCHO) 9.48 and 9.49 (d, 1 H, CHO of cis and trans isomers, J = 14 Hz); IR (film) 3300 (br), 3025 (w), 2920 (m), 2845 (w), 2740 (w), 1720 (s), 1680 (s), 1520 (s), 1450 (m), 1340 (m), 1240 (s), 1130 (m), 1050 (m), 715 (m) cm^{-1}; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 28.0, 33.1, 52.6, 108.2, 124.9, 133.4, 154.1, 157.3, 193.9; MS, *m/z* (relative intensity) 183 (2, M^+), 114 (100), 82 (59), 59 (28); HRMS, *m/e* 183.0897 ($C_9H_{13}NO_3$ requires 183.0896).

7-[*N*-(Methoxycarbonyl)amino]-6-methyl-2,6-heptadienal (14b). This compound was obtained from **12b** according to the general thermolysis procedure (450 °C, 6% yield): ^1H NMR ($CDCl_3$, 300 MHz) δ 1.57 (s, 3 H, CH_3), 2.19 (t, 2 H, CCH_2, J = 7 Hz), 2.4–2.5 (m, 2 H, CCH_2), 3.70 (s, 3 H, NCO_2CH_3), 6.09 (dd, 1 H, C=C*H*CHO and NH, J = 8, 16 Hz), 6.1–6.3 (br, 1 H, NH), 6.3–6.4 (br, 1 H, C=CHN), 6.79 (dt, 1 H, C*H*=CCHO, J = 7, 16 Hz), 9.48 (d, 1 H, CHO, J = 8 Hz); IR (film) 3300 (br), 3010 (w), 2910 (m), 2840 (m), 2720 (w), 1720 (s), 1680 (s), 1500 (m), 1440 (m), 1260 (s), 1050 (s), 775 (w) cm^{-1}; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.2, 31.1, 34.7, 52.4, 114.0, 119.2, 133.2, 154.2, 157.5, 193.9; MS, *m/z* (relative intensity) 197 (8, M^+), 128 (100), 96 (64), 59 (29), 42 (30); HRMS, *m/e* 197.1056 ($C_{10}H_{15}NO_3$ requires 197.1052).

***N,O*-Bis(methoxycarbonyl)-*N*-(bicyclo[2.2.1]hept-5-en-*endo*-2-ylmethyl)hydroxylamine (20a).** The analogous procedure for the preparation of **5**-(H,H) was used. The oxime was obtained from 5-norbornene-2-carboxaldehyde in 90% yield (major:minor = 3:1). For the major product: ^1H NMR ($CDCl_3$, 300 MHz) δ 0.98–1.47 (m, 4 H, 2 CH_2), 1.87–3.03 (m, 3 H, 3 CH), 5.95–6.23 (m, 2 H, CH=CH), 7.05 (d, 1 H, CH=N, J = 8 Hz), 7.92 (br, 1 H, NOH); IR (film) 3500 (br), 3040 (w), 2980 (s), 1670 (m), 1460 (m), 1350 (m), 1310 (m), 1250 (m), 960 (m), 780 (m), 750 (s) cm^{-1}; ^{13}C NMR ($CDCl_3$, 20 MHz) δ 30.8, 38.9, 42.6, 46.8, 49.5, 132.4, 138.7, 156.4. Then **20a** was obtained in 54% yield: ^1H NMR ($CDCl_3$, 300 MHz) δ 0.46–2.92 (m, 7 H, 2 CH_2 and 3 CH), 3.35 (m, 2 H, CH_2N), 3.77 (s, 3 H, NCO_2CH_3), 3.91 (s, 3 H, OCO_2CH_3), 5.76–6.24 (m, 2 H, CH=CH); IR (film) 3080 (w), 2980 (s), 1790 (s), 1730 (s), 1450 (s), 1350 (m), 1250 (s), 1230 (s), 1200 (m), 1110 (m), 940 (m) cm^{-1}; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 30.1, 36.9, 42.4, 44.6, 49.5, 53.6, 54.5, 56.1, 132.3, 137.7, 154.8, 156.1.

Anal. Calcd for $C_{12}H_{17}NO_5$: C, 56.47; H, 6.67. Found: C, 56.17; H, 6.85.

***N,O*-Bis(methoxycarbonyl)-*N*-[(2-methylbicyclo[2.2.1]-hept-5-en-*endo*-2-yl)methyl]hydroxylamine (20b).** the analogous procedure for the preparation of **5**-(H,H) was used. The oxime was obtained from 2-methyl-5-norbornene-2-carboxaldehyde[40] in 90% yield (major:minor = 3:1). For the major product: ^1H NMR ($CDCl_3$, 80 MHz) δ 1.12–1.72 (m, 4 H, 2 CH_2), 1.34 (s, 3 H, CH_3), 2.58 and 2.87 (br, 2 H, 2 CH), 5.98–6.20 (m, 2 H, CH=CH), 7.26 (s, 1 H, CH=N), 7.82 (br, 1 H, NOH); IR (film) 3500 (br), 3060 (w), 2980 (s), 1680 (m), 1450 (m), 1380 (m), 1340 (m), 1260 (m), 950 (m), 770 (m), 730 (s) cm^{-1}. Then **20b** was obtained in 56% yield: ^1H NMR ($CDCl_3$, 300 MHz) δ 0.08–2.76 (m, 6 H, 2 CH_2 and 2 CH), 1.25 (s, 3 H, CH_3), 3.32 (m, 2 H, CH_2N), 3.77 (s, 3 H, NCO_2CH_3), 3.92 (s, 3 H, OCO_2CH_3), 5.82–6.20 (m, 2 H, CH=CH); IR (film) 3080 (w), 2980 (s), 1795 (s), 1730 (s), 1450 (s), 1380 (m), 1310 (m), 1285 (m), 1265 (s), 1240 (s), 1220 (s), 1190 (s), 1150 (m), 940 (m) cm^{-1}; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 25.2, 38.3, 41.9, 42.3, 47.6, 50.9, 53.4, 56.0, 58.9, 135.2, 136.5, 154.5, 156.3.

Anal. Calcd for $C_{13}H_{19}NO_5$: C, 57.97; H, 7.06. Found: C, 58.12; H, 7.21.

***N*-(Methoxycarbonyl)-1,4,8,9-tetrahydropyrindine (22a).** This compound was obtained from **20a** according to the general thermolysis procedure (450 °C, 11% yield): ^1H NMR ($CDCl_3$, 300 MHz) δ 1.73–2.59 (m, 5 H, 2 CH_2 and CH), 3.77 (s, 3 H, NCO_2CH_3), 4.79–4.96 (m, 2 H, CHN and CH=CH), 5.78–5.81 (m, 2 H, CH=CH), 6.88 (br, 1 H, C=CHN); IR (film) 3110 (w), 2960 (s), 1715 (s), 1450 (s), 1410 (m), 1360 (s), 1270 (m), 1140 (m), 790 (m) cm^{-1}; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 24.2, 34.1, 38.4, 52.9, 60.5, 105.3, 125.3, 130.9, 133.7, 154.4; MS, *m/z* (relative intensity) 179 (85, M^+), 164 (32), 114 (76), 104 (88), 78 (55), 66 (100), 59 (24); HRMS, *m/e* 179.0954 ($C_{10}H_{13}NO_2$ requires 179.0947).

***N*-(Methoxycarbonyl)-3-methyl-1,4,8,9-tetrahydropyrindine (22b).** This compound was obtained from **20b** according to the general thermolysis procedure (450 °C, 21% yield): ^1H NMR ($CDCl_3$, 300 MHz) δ 1.67 (s, 3 H, CH_3), 1.68–2.63 (m, 5 H, 2 CH_2 and CH), 3.77 (s, 3 H, NCO_2CH_3), 4.73–4.90 (m, 1 H, CHN), 5.72–5.91 (m, 2 H, CH=CH), 6.65 (m, 1 H, C=CHN); IR (film) 3080 (w), 2940 (s), 1710 (s), 1450 (s), 1400 (m), 1350 (m), 1320 (m), 1200 (m), 780 (m) cm^{-1}; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.9, 30.0, 34.8, 38.5, 52.8, 59.8, 114.9, 119.9, 131.2, 133.6, 154.3; MS, *m/z* (relative intensity) 193 (60, M^+), 178 (34), 128 (60), 118 (33), 117 (30), 96 (35), 66 (100), 59 (28); HRMS, *m/e* 193.1099 ($C_{11}H_{15}NO_2$ requires 193.1103).

***N,O*-Bis(methoxycarbonyl)-*N*-prop-2-enylhydroxylamine (23a).** A trace amount of this compound was produced from the thermolysis of **20a**. It was independently prepared from hydroxylamine according to the following procedure. Allyl chloride (0.77 g, 10 mmol) and *N,O*-bis(methoxycarbonyl)hydroxylamine[18b] (1.49 g, 10 mmol) were dissolved in 3 mL of dimethylformamide at room temperature. The solution was stirred while potassium carbonate (1.38 g, 10 mmol) was added and mixing continued 1 day at room temperature. The mixture was washed into a separatory funnel with 10 mL of diethyl ether and extracted once with 10% hydrochloric acid. The ether layer was dried with magnesium sulfate and concentrated in vacuo. Flash column chromatography furnished **23a** (0.83 g, 44% yield): ^1H NMR ($CDCl_3$, 80 MHz) δ 3.80 (s, 3 H, NCO_2CH_3), 3.89 (s, 3 H, OCO_2CH_3), 4.24 (d, 2 H, CH_2N, J = 6 Hz), 5.1–5.9 (m, 3 H, 3 CH=C); IR (film) 3080 (w), 2980 (m), 2860 (w), 1790 (s), 1730 (s), 1650 (w), 1440 (s), 1360 (s), 1260 (s), 1215 (s), 1145 (s), 1098 (s), 1045 (m), 990 (m), 932 (s), 845 (m), 780 (m) cm^{-1}; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 53.0, 53.4, 55.8, 118.9, 130.6, 154.3, 155.7.

***N,O*-Bis(methoxycarbonyl)-*N*-(2-methylprop-2-enyl)-hydroxylamine (23b).** A trace amount of this compound was produced from the thermolysis of **20b**. It was prepared according to the procedures for the preparation of **23a**. Methallyl chloride, instead of allyl bromide, was used. Flash column chromatography provided, in 51% yield, **23b**: ^1H NMR ($CDCl_3$, 300 MHz) δ 1.78 (s, 3 H, CH_3), 3.80 (s, 3 H, NCO_2CH_3), 3.89 (s, 3 H, OCO_2CH_3), 4.19 (s, 2 H, CH_2N), 4.94 (s, 2 H, CH_2=C); IR (film) 3080 (w), 2970 (m), 2860 (w), 1795 (s), 1730 (s), 1615 (w), 1450 (s), 1380 (s), 1270 (s), 1220 (s), 1110 (s), 940 (m), 835 (w), 788 (m), 765 (m) cm^{-1}; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.3, 53.2, 55.5, 56.2, 114.0, 138.8, 154.1, 155.6.

***N*-(1-Methoxyprop-2-enyl)-*N*-(methoxycarbonyl)amine (24a):** ^1H NMR ($CDCl_3$), 300 MHz) δ 3.38 (s, 3 H, OCH_3), 3.72 (s, 3 H, NCO_2CH_3), 5.27 (dd, 1 H, cis of CH_2=C, J = 1, 11 Hz), 5.40 (dd, 1 H, trans of CH_2=C, J = 1, 17 Hz), 5.1–5.5 (br, 2 H, CH and NH), 5.83 (ddd, 1 H, C=CH, J = 5, 11, 17 Hz); IR (film) 3310 (br), 2958 (m), 2830 (w), 1710 (s), 1515 (s), 1450 (m), 1340 (m), 1245 (s), 1080 (s), 783 (w) cm^{-1}; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 52.1, 54.9, 82.9, 117.0, 135.1, 156.4.

***N*-(1-Methoxy-2-methylprop-2-enyl)-*N*-(methoxycarbonyl)amine (24b):** ^1H NMR ($CDCl_3$, 300 MHz) δ 1.75 (s, 3 H, CH_3), 3.36 (s, 3 H, OCH_3), 3.72 (s, 3 H, NCO_2CH_3), 4.96 and 5.13 (s, 2 H, CH_2=C), 5.0–5.3 (br, 2 H, CH and NH); IR (film) 3330 (br), 3080 (w), 2960 (m), 2840 (w), 1720 (s), 1660 (w), 1520 (s), 1455 (m), 1340 (m), 1245 (s), 1088 (s), 972 (m), 915 (m), 782 (w) cm^{-1}; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.6, 52.0, 55.1, 85.2, 112.7, 141.7, 156.4.

1-Methoxy-4-ethyl-1,4-cyclohexadiene (26). A solution of 4-ethylanisole (2.04 g, 15 mmol) in dry THF (5 mL) and absolute ethyl alcohol (5 mL) was added liquid ammonia (50 mL). Sodium (2 g) was added in small pieces with good stirring as rapidly as possible without the reaction becoming uncontrollable. When the blue color had disappeared, the reaction mixture was decomposed by cautious addition of water and extracted with

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pentane. The combine extracts were dried over anhydrous magnesium sulfate and concentrated in vacuo. Vacuum distillation gave pure product as a colorless liquid (1.67 g, 81% yield; bp 47–48 °C (0.25 mm)): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.01 (t, 3 H, CH_3, J = 7.5 Hz), 1.99 (q, 2 H, CH_2, J = 7.5 Hz), 2.71 (br, 4 H, 2 CH_2), 3.54 (s, 3 H, OCH_3), 4.62 and 5.36 (br, 2 H, 2 CH=C); IR (film) 3040 (w), 3000 (w), 2970 (s), 2880 (s), 2835 (s), 1698 (s), 1668 (s), 1450 (m), 1390 (s), 1216 (s), 1175 (s), 1018 (m), 790 (m), 688 (w) cm^{-1}; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.1, 29.0, 29.2, 53.5, 90.2, 115.8, 136.8, 153.0.

1-Methoxy-4-ethylbicyclo[2.2.2]oct-5-ene-*endo*-2-carboxaldehyde (27). Methylaluminum dichloride (0.3 mmol) was added into a solution of the 1,4-diene **26** (2.07 g, 15 mmol) in dry chloroform (15 mL) cooled in an ice bath. Then acrolein (0.84 g, 15 mmol) was added. After stirring for 2 h, the mixture was decomposed with water, dried over anhydrous magnesium sulfate, and concentrated in vacuo. Flash column chromatography and then vacuum distillation gave pure Diels–Alder adduct **27** (1.36 g, 47% yield; bp 80–82 °C (0.1 mm)): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.93 (t, 3 H, CH_3, J = 7.5 Hz), 1.2–1.8 (m, 8 H, 4 CH_2), 2.75–2.85 (m, 1 H, CH), 3.37 (s, 3 H, OCH_3), 6.08 and 6.22 (d, 2 H, CH=CH, J = 9 Hz), 9.48 (d, 1 H, CHO, J = 4 Hz); IR (film) 3040 (w), 2960 (s), 2865 (m), 2830 (m), 2730 (w), 1725 (s), 1460 (m), 1378 (m), 1210 (m), 1138 (m), 1105 (s), 695 (m) cm^{-1}; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 8.8, 28.5, 30.1, 30.2, 32.9, 37.2, 50.6, 54.3, 79.1, 131.8, 136.7, 203.9.

***O*-(Methoxycarbonyl)-*N*-(chloroacetyl)-*N*-[(1-methoxy-4-ethylbicyclo[2.2.2]oct-5-en-*endo*-2-yl)methyl]hydroxylamine (28).** The analogous procedure for the preparation of **5**-(H,H) was used. The oxime was obtained from the aldehyde **27** in 89% yield: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.90 (t, 3 H, CH_3, J = 7.5 Hz), 1.45 (q, 2 H, CH_2, J = 7.5 Hz), 1.0–2.0 (m, 6 H, 3 CH_2), 2.85–2.95 (m, 1 H, CH), 3.31 (s, 3 H, OCH_3), 6.05 and 6.10 (d, 2 H, CH=CH, J = 9 Hz), 7.14 (d, 1 H, CH=N, J = 8 Hz); IR (film) 3300 (br), 3040 (w), 2940 (s), 2865 (m), 1650 (w), 1460 (m), 1380 (m), 1210 (m), 1140 (m), 1110 (s), 940 (m), 700 (m) cm^{-1}. Treatment of the oxime by using 1 equiv of chloroacetic anhydride as acylating agent instead of methyl chloroformate gave, in 44% yield, *N*-(chloroacetyl)-*N*-[(1-methoxy-4-ethylbicyclo[2.2.2]oct-5-en-*endo*-2-yl)methyl]hydroxylamine: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.90 (t, 3 H, CH_3, J = 7.5 Hz), 1.45 (q, 2 H, CH_2, J = 7.5 Hz), 0.6–1.8 (m, 6 H, 3 CH_2), 2.25–2.4 (m, 1 H, CH), 2.90 and 3.82 (dd, 2 H, CH_2N, J = 11, 15 Hz and 3, 15 Hz), 3.40 (s, 3 H, OCH_3), 4.21 and 4.29 (d, 2 H, CH_2Cl, J = 13 Hz), 6.06 and 6.12 (d, 2 H, CH=CH, J = 9 Hz), 8.95 (br, 1 H, NOH); IR (film) 3200 (br), 3040 (w), 2940 (s), 2860 (m), 1635 (s), 1455 (m), 1380 (w), 1230 (m), 1140 (s), 1108 (m), 790 (w), 695 (m) cm^{-1}; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 8.5, 28.1, 29.9, 30.3, 36.3, 36.8, 39.5, 41.1, 50.6, 51.8, 80.5, 130.5, 136.2, 165.5. Then addition of 2 equiv of methyl chloroformate and 2 equiv of triethylamine in dry diethyl ether at room temperature for 2 h gave **28** in 83% yield after flash column chromatography: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.89 (t, 3 H, CH_3, J = 7.4 Hz), 1.2–1.6 (m, 8 H, 4 CH_2), 2.3–2.4 (m, 1 H, CH), 3.28 (s, 3 H, OCH_3), 3.4 and 3.75 (br, 2 H, CH_2N), 3.93 (s, 3 H, OCO_2CH_3), 4.07 (s, 2 H, CH_2Cl), 6.03 and 6.12 (d, 2 H, CH=CH, J = 9 Hz); IR (film) 3040 (w), 2960 (s), 2870 (m), 1795 (s), 1690 (s), 1440 (s), 1380 (m), 1250 (s), 1225 (s), 1108 (s), 925 (m), 778 (m), 698 (m) cm^{-1}; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 8.3, 28.6, 30.2, 30.4, 36.7, 37.0, 39.0, 40.8, 50.3, 51.9, 56.5, 79.0, 131.5, 136.1, 154.0; MS, m/z (relative intensity) 272 (0.4), 270 (1.6), M^+ – OCO_2CH_3), 150 (30), 138 (100), 123 (47), 121 (22), 109 (34), 91 (13), 77 (16).

Anal. Calcd for $C_{16}H_{24}NO_5Cl$: C, 55.57; H, 7.00. Found: C, 55.62; H, 6.84.

1-(Chloroacetyl)-7-oxo-10-ethyl-1,4,5,6,7,8,9,10-octahydroquinoline (31). The Cope product was obtained from **28** (200 mg, 0.58 mmol) according to the general thermolysis procedure (425 °C): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.80 (t, 3 H, CH_3, J = 7.5 Hz), 1.2–2.3 (m, 8 H, 4 CH_2), 3.47 (s, 3 H, OCH_3), 4.18 (s, 2 H, CH_2Cl), 4.29 (br, 1 H, CHN), 4.87 (br, 1 H, CH=CO), 4.95–5.02 (m, 1 H, CH=CN), 6.42 and 6.45 (br, 1 H, C=CHN); IR (film) 3070 (w), 3040 (w), 2925 (s), 2860 (m), 1650 (s), 1450 (m), 1420 (s), 1370 (s), 1250 (m), 1230 (s), 1205 (s), 1175 (m), 1130 (s), 1005 (w), 988 (m), 790 (m), 700 (m) cm^{-1}; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 7.6, 24.3, 25.2, 29.0, 30.0, 32.9, 41.2, 53.4, 54.3, 94.9, 108.8, 121.9, 155.9, 164.3; MS, m/z (relative intensity) 271 (4), 269 (15, M^+), 242 (10), 240 (28), 234 (54), 186 (14), 184 (42), 164 (58), 150 (7), 147 (24), 138 (57), 137 (48), 136 (56), 133 (37), 123 (47), 121 (44), 109 (72), 108 (100), 98 (38), 77 (45). It was hydrolyzed without purification by 1% oxalic acid in acetone–water (10:1) solution to give **31** as a solid (45 mg, 31% yield in two steps; mp 116–117 °C): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.82 (t, 3 H, CH_3, J = 7.5 Hz), 1.3–2.5 (m, 10 H, 5 CH_2), 4.12 (s, 2 H, CH_2Cl), 4.54 (dd, 1 H, CHN, J = 5, 12 Hz), 5.08 (ddd, 1 H, CH=CN, J = 2, 5, 12 Hz), 6.45 and 6.47 (br, 1 H, C=CHN); IR (KBr) 3030 (w), 2960 (m), 2865 (w), 1710 (s), 1645 (s), 1438 (m), 1420 (m), 1370 (s), 1255 (m), 1150 (m), 1000 (m), 930 (w), 735 (m), 665 (m) cm^{-1}; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 7.3, 25.6, 29.7, 30.7, 33.7, 36.6, 40.7, 41.0, 53.0, 107.7, 121.7, 163.6, 207.8; MS, m/z (relative intensity) 257 (6), 255 (17, M^+), 228 (5), 226 (17), 220 (43), 186 (5), 184 (18), 178 (30), 150 (84), 124 (52), 108 (100), 96 (44), 93 (43), 82 (75), 79 (62), 77 (60), 67 (70), 56 (56).

Anal. Calcd for $C_{13}H_{18}NO_2Cl$: C, 61.05; H, 7.09. Found: C, 60.86; H, 7.15.

1-(Chloroacetyl)-7-oxo-10-ethyldecahydroquinoline (32). Hydrogenation of **31** (38 mg, 0.15 mmol) with 5% of Rh/C (8 mg) as catalyst in ethyl acetate (5 mL) at room temperature for 1 day and chromatography gave **32** (31 mg, 81% yield) as a solid [mp 78–79 °C (lit. mp 75–77[31a] or 122–122.5 °C[31b])]: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.82 (t, 3 H, CH_3, J = 7.5 Hz), 1.1–2.8 (m, 12 H, 6 CH_2), 2.9–3.3 and 3.6–3.8 (m, 2 H, CH_2N), 4.01 and 4.09 (d, 2 H, CH_2Cl, J = 12 Hz), 4.66 (dd, 1 H, CHN, J = 5, 13 Hz); IR (KBr) 2965 (s), 2930 (s), 2865 (m), 1710 (s), 1640 (s), 1630 (s), 1450 (s), 1370 (w), 1342 (w), 1280 (s), 1152 (s), 915 (m), 783 (w), 658 (s) cm^{-1}; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 7.2, 20.6, 24.0, 28.7, 32.8, 34.9, 36.5, 39.6, 40.4, 41.4, 54.0, 165.5, 208.6; MS, m/z (relative intensity) 231 (2), 230 (2), 229 (5), 228 (5, $M^+ - C_2H_5$), 222 (100), 180 (61), 152 (19), 135 (19), 124 (27), 110 (34), 96 (36), 81 (21), 79 (25), 77 (26), 67 (30), 55 (41), 41 (23).

Anal. Calcd for $C_{13}H_{20}NO_2Cl$: C, 60.59; H, 7.82. Found: C, 60.18; H, 7.71.

6a-Ethyl-9-oxodecahydro-4*H*-pyrrolo[3,2,1-*ij*]quinoline (33).[31a] Added potassium *tert*-butoxide (22.4 mg, 0.2 mmol) into a solution of **32** (25.8 mg, 0.1 mmol) in 5 mL of benzene. The reaction mixture was stirred at room temperature for 1 h, then neutralized with 10% HCl solution. The benzene solution was dried over anhydrous magnesium sulfate and concentrated in vacuo. Recrystallized from diethyl ether to give pure **33** (16 mg, 72% yield; mp 118–119 °C (lit. mp 116–118[31a] or 165–166 °C[31b])): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.94 (t, 3 H, CH_3, J = 7.5 Hz), 1.2–3.0 (m, 14 H, 6 CH_2, CH, and 1 of CH_2N), 3.39 (dd, 1 H, CHN, J = 2, 6 Hz), 4.02 (br d, 1 H, 1 of CH_2N); IR (KBr) 2945 (s), 2860 (m), 1705 (s), 1690 (s), 1415 (s), 1300 (m), 1155 (w), 935 (w) cm^{-1}; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 6.87, 18.83, 24.00, 29.14, 32.56, 32.98, 34.10, 35.39, 40.42, 42.46, 65.76, 174.34, 208.97.

Anal. Calcd for $C_{13}H_{19}NO_2$: C, 70.56; H, 8.65. Found: C, 70.61; H, 8.66.

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