Acetylenes as Potential *Antarafacial* Components in Concerted Reactions. Formation of Pyrroles from Thermolyses of Propargylamines, of a Dihydrofuran from a Propargylic Ether, and of an Ethylidenepyrrolidine from a β-Amino Acetylene

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A thermal cyclization of acetylenic compounds provides evidence for the ability of acetylenic links to act as *antarafacial* components in [2 + 2] processes. The cyclization competes with the normally favored acetylenic retro-ene reaction. Propargylic amines, without substituents whose presence would hinder a tight cyclic transition state, yield intermediate pyrrolines whose subsequent hydrogen elimination affords pyrroles in small amounts. The same process in 2-ethynyltetrahydropyran affords 8-oxabicyclo[3.2.1]octane in 35% yield. A related thermal reaction of *N*-methyl-3-hexyn-1-amine provides a quantitative transformation to *N*-methyl-2-ethylidenepyrrolidine in a nominal [$2_s + 2_a + 2_s + 2_s$] Möbius process, wherein the acetylenic unit is the *antarafacial* component. Evidence for concertedness in these reactions is discussed.

During our investigations into thermal intramolecular reactions of acetylenic compounds which require cyclic transition states,[1] we have encountered three reaction processes indicative of the ability of acetylenic bonds to act as *antarafacial* components in pericyclic reactions. Although in none of the three cases can we clearly delineate the mechanism of the reaction, a consideration of all three processes provides compelling evidence that the small select group of components, known or suspected of being capable to act in that manner, must be expanded to include the acetylenic linkage.

The three cyclizations, which are the subject of this report, occurred on thermolyses of a variety of substrates (see Table I). The contributions of this pathway varied widely, from the formation of minor byproducts in the thermolyses of propargylic amines **1–5**, to a substantial component in the thermolysis of propargylic ether **6**, and to a quantitative transformation of β-amino acetylene **7** (see Table II). These unexpected reactions are best explained as concerted cyclizations involving the *antarafacial* addition of a C–H or N–H bond to an acetylenic π-bond. In addition, since our preliminary accounts,[1–3] Dreiding[4] has concluded that such a mechanism is also responsible for the formation of some of the products obtained from the cyclizations of α-alkynones (Scheme I). Furthermore, an *antarafacial* reaction mode has been implicated for a [2 + 2] cycloaddition of cyclopentyne, although the nature of that acetylenic bonding system remains open for discussion.[5]

Concerted thermal [2 + 2] reactions require the two approaching bonding systems to assume an orthogonal orientation for the symmetry-allowed *supra-antara* process and are known only for a few $_\pi 2_a$ components: singlet oxygen,[6] cumulative π-bonded systems,[7] a few highly constrained cyclic olefins wherein available choices for potential reaction pathways are severely limited,[8] and possibly vinyl cations.[9] Other nominal [$_\pi 2_a + 2_s$] processes

Table I. Flow System Thermolyses

	retro-ene products	cyclization product(s)
1	[a] + H	8
2	+ H	9
3	+ H	10
4	[a] + H	11
5	[a] + H	12 + 13
6	+	14
	15	
7		16

[a] These imines are the primary reaction products, but were isolated as their cyclic trimers.

(1) For a review, see: Viola, A.; Collins, J. J.; Filipp, N. *Tetrahedron* **1981**, *37*, 3765–3811.
(2) Viola, A.; Locke, J. S. *J. Chem. Soc., Chem. Commun.* **1984**, 1429–1431.
(3) Viola, A.; Collins, J. J. *J. Chem. Soc., Chem. Commun.* **1980**, 1247–1248.
(4) Koller, M.; Karpf, M.; Dreiding, A. S. *Helv. Chim. Acta* **1986**, *69*, 560–579.
(5) Gilbert, J. C.; Baze, M. E. *J. Am. Chem. Soc.* **1984**, *106*, 1885–1886.
(6) Bartlett, P. D.; Schaap, A. P. *J. Am. Chem. Soc.* **1970**, *92*, 3223–3225. Frimer, A. A.; Bartlett, P. D.; Boschung, A. F.; Jewett, J. G. *J. Am. Chem. Soc.* **1977**, *99*, 7977–7986.

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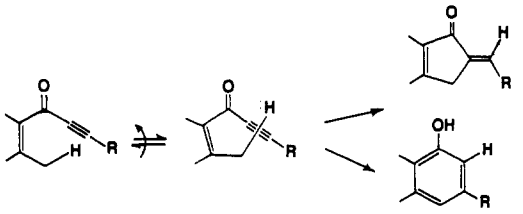
Table II. Contribution of Cyclization Pathways[a]

compd	temp (°C)	pressure (Torr)	cyclization[b] (%)
1	420	24	3.8
	450	24	4.3
2	450	24	3.6
3	400	24	trace
	450	24	3.8
4	450	1	5.8
	450	50	5.8
	480	36	6.0
5	450	12	4.7[c]
	450	35	4.7[d]
6	420	63	35
7	400	50	100

[a] Based on 100% conversion of starting material. The remainder of the product mixture is ascribable to the retro-ene cleavage. [b] Based upon GLPC analysis with an internal standard. [c] Composed of 2.7% pyrroline 12 and 2.0% pyrrole 13. [d] Composed of 0.7% pyrroline 12 and 4.0% pyrrole 13.

Scheme I



have usually, on closer inspection, been found to proceed via nonconcerted diradical pathways.[10] Virtually all of the known $_{\pi}2_{a}$ components possess an unhindered linearity, free of interfering hydrogen atoms, such as to permit a facile orthogonal approach to the other reaction component—this requisite geometry also holds true for the acetylenic bond.

We have investigated the retro-ene reactions of β-hydroxy acetylenes,[1] propargylic ethers,[1] propargylic amines,[1] and β-amino acetylenes.[2] In the first three cases the corresponding olefinic retro-ene reactions are well known, and we have reported the thermolysis of β-amino olefins to result primarily in a retro-ene fragmentation.[2] In all acetylenic retro-ene reactions for which kinetic determinations have been reported, the reactions strictly follow the first-order rate law, their energies and entropies of activation are in accord with concerted processes, and in the one case of an optically active acetylenic substrate, the formation of an optically active allene meets the chirality transfer criterion for concertedness.[11] The fact that acetylenes almost invariably react faster than do their olefinic analogs has been explained, in part, on the basis of increased aromaticity in the transition state, which results from a planar array of the six-atom reaction system, as opposed to the preferred chairlike olefinic transition state. When molecular constraints prevent the attainment of the requisite planarity in the acetylenic substrates, then the retro-ene process is inhibited, or, in the extreme case, is prevented altogether.[3] As is frequently the case in pericyclic reactions, the process is also hindered by terminal substitution on the acetylenic unit. If the retro-ene pathway is sufficiently encumbered, then other processes may compete with the normally favored retro-ene reaction.

Pyrrole Formation from Propargylic Amines. In the flow-system vapor-phase thermolyses of propargylic amines 1–5, the major retro-ene pathway was accompanied by varying amounts of pyrrole formation,[12] which ranged from 3 to 7% of the total conversion at 450 °C. Table II indicates the effects of reaction time (i.e., pressure within the flow system) and of temperature on product partitioning. These effects indicate this cyclization to be a primary reaction of the propargylic amines, which is competitive with the concerted retro-ene cleavage. Thus, a 50-fold variation in the reaction time for the thermolysis of 4 afforded product mixtures with identical ratios of pyrrole to retro-ene components, whereas a significant change in this ratio would be expected from any sequential process.

The homogeneous nature of the cyclization pathway is implicated by kinetic measurements in a static system. Of the five propargylic amines which afforded pyrroles in the flow system at 450 °C, only in the cases of 1 and 4 were cyclization products observed at the considerably lower temperatures used for kinetic determinations. Although the contributions of this pathway were smaller at these lower temperatures, in both cases the disappearance rate of starting material strictly followed the first-order rate law. Packing of the individual glass tubes with glass wool, which increases the surface-to-volume ratio by several orders of magnitude, affected neither the pyrrole/retro-ene ratio nor the first-order rate constants for the overall disappearance of starting material. Further, the use of toluene in place of octane as the diluent during kinetic determinations did not alter the product ratio, no trace of bibenzyl could be detected in the product mixtures, and the first-order rate constants were unaffected. Likewise, a 6-fold change in the concentration of starting material affected neither the product ratios nor the rate constants.

The results clearly indicate that both retro-ene cleavage and cyclization are primary reactions of the initial substrates. The pyrroles formed are thermally stable and are not intermediates in the formation of retro-ene products. The retro-ene products do not undergo any bimolecular additions which could result in the formation of the observed cyclization products.

No pyrroles are formed at the lower temperatures utilized for kinetic determinations of 2, 3, and 5, and, in general, pyrrole formation increases with increasing temperature (see Table II). The cyclization must therefore require a higher energy of activation than does the competing retro-ene cleavage. Of these five propargylic amines, 1 is the only one without substituents which accelerate the retro-ene process and has the lowest retro-ene reaction rate constant.[12] Consequently, the cyclization is able to compete. In 2 and 3 the retro-ene reaction rate is enhanced by the fact that the transferring hydrogen atom is secondary rather than primary, and the cyclization cannot compete at lower temperatures.

Compounds 4 and 5 permit an interesting comparison.

(7) For a listing of such cumulative π-bond systems see ref 4 in: Borisenko, A. A.; Nikulin, A. V.; Wolfe, S.; Zefirov, N. S.; Zyk, N. V. *J. Am. Chem. Soc.* **1984**, *106*, 1074–1079.

(8) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Academic Press: New York, 1970.

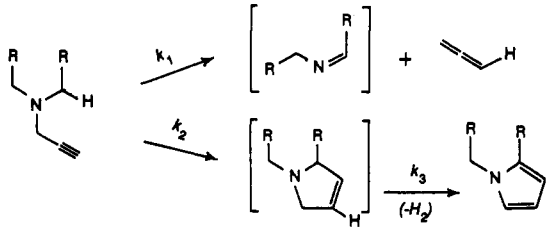
(9) Griesbaum, K.; Seiter, W. *J. Org. Chem.* **1976**, *41*, 937–939 and references cited therein. It has been suggested that these reactions are probably concerted.[8]

(10) Padwa, A.; Blacklock, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 3390–3392.

(11) Viola, A.; Dudding, G. F.; Proverb, R. J. *J. Am. Chem. Soc.* **1977**, *99*, 7390–7392.

(12) Our studies of the retro-ene reactions of propargylic amines and ethers will be reported separately.

Scheme II

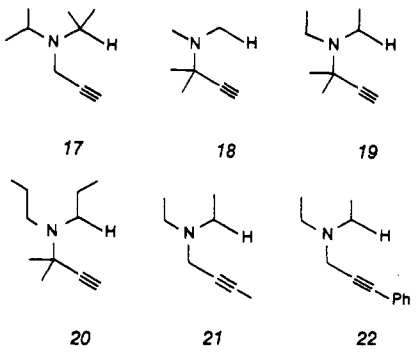


The predominant acetylenic retro-ene pathway requires the participating six-atom system to assume a planar orientation.[1] When planarity of the acetylenic retro-ene transition state is restricted, then the reaction is hindered. Consequently, in this competitive reaction system any substituents which restrict planarity of the retro-ene portion of the molecule can be expected to hinder that pathway and thereby increase the contribution from any alternate reaction component. Due to the preferred chair conformation of the piperidine ring, the propargyl group in **4** can only attain coplanarity with an α C–H bond if the ring first assumes a higher energy boat conformation. By contrast, the propargyl group in **5** is already eclipsed, or nearly so, with an α C–H bond in the preferred ground-state conformation of the pyrrolidine ring. These differences are reflected in the activation energies for the two retro-ene processes in **4** and **5**, which are 42.6 and 38.9 kcal/mol, respectively.[1] It is the activation energy for **4**, the highest found for any of these amines, which allows the cyclization reaction to compete to the largest extent (see Table II).

The stoichiometry of the cyclization suggests the intermediacy of pyrrolines with subsequent hydrogen elimination to afford pyrroles (see Scheme II). The thermal elimination of hydrogen from 3-pyrroline has been reported as a concerted homogeneous reaction, with E_a = 44.6 kcal/mol and $\Delta S^{\ddagger}$ = –5.8 eu.[13] Evidence for this sequential process is provided by thermolysis of **5**, which afforded a mixture of pyrroline **12** and pyrrole **13**, whose ^{1}H NMR spectra were identical to those of authentic **12** and **13**.[14] As shown in Table II, an increase in the reaction time, i.e., pressure, leads to an increase in pyrrole formation at the expense of pyrroline. In amines **1–4** $k_3 > k_2$ and no intermediate pyrroline can be detected. However, conformational restraint resulting from the fusion of two five-membered rings in **12** increases the energetic requirement of hydrogen elimination, a process which has been reported to involve a bending mode of the pyrroline ring.[13] As a result, k_3 is decreased and the intermediate **12** becomes detectable. The fact that shorter reaction time results in a greater proportion of **12** is only in accord with a sequential process involving the pyrroline as the intermediate in pyrrole formation.

Although it should be possible to arrest the cyclization sequence at the pyrroline stage by geminal substitution at either position α to the nitrogen atom, such that no dehydrogenation step is possible, compounds **17–20** failed to give any cyclized products and reacted solely via the retro-ene path. Compounds **21** and **22**, whose terminal acetylenic substituents should hinder the retro-ene fragmentation, also failed to provide any cyclized products and reacted solely via the retro-ene pathway.

Because of the small amount of pyrrole formation, it was not possible to determine kinetic parameters for the cyclization process with sufficient accuracy. Therefore,



the evidence for the first-order nature of the cyclization process remains circumstantial: (a) for any of the propargylic amines the total disappearance rate strictly obeys the first-order rate equation; (b) the product ratio of cyclization/retro-ene remains constant at any given temperature with varying reaction time; and (c) total disappearance rates and product ratios are independent of starting concentrations.

The energy of activation for cyclization, although not directly determinable, can be estimated by two different comparisons. Both the cyclization and the retro-ene pathways may be assumed to have similar entropies of activation, since most rotational degrees of freedom will be lost in the rigid transition state of either process. The partitioning of the two pathways, about 96:4 at 450 °C (see Table II) corresponds to a $\Delta\Delta G^{\ddagger}$ of about 4 kcal/mol. Since the retro-ene reaction has an activation energy of about 41 kcal/mol,[1] it follows that for the cyclization $E_a \approx 45$ kcal/mol.

Another estimate comes from the second step in pyrrole formation. In the absence of constraints resulting from a fused ring system such as in **12**, dehydrogenation is faster than cyclization. Since it has been reported[13] that for dehydrogenation $E_a \approx 44.5$ kcal/mol, E_a for cyclization can only be slightly higher, assuming similar rigid transition states, if a small additional strain is to render the two reaction rates comparable.

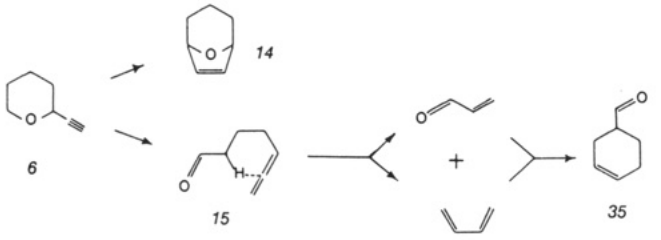
Radical pathways are unlikely for this cyclization since (a) E_a is lower than any single BDE in the molecule, (b) substantial changes in surface-to-volume ratios have no effect, (c) the addition of toluene has no effect on the reaction rate and no detectable bibenzyl is produced, (d) there are no products from H-migration to the thermodynamically and sterically favored terminal acetylenic carbon, (e) there are no products involving the more highly activated propargylic hydrogens, (f) there is no detectable cyclization in compounds with terminal acetylenic (**21**, **22**) or geminal substituents (**17–20**), even though such substituents would stabilize radical intermediates, and (g) no similar reactions are observable in analogous olefins although the competing retro-ene reactions are less facile in olefins.

The methylenecarbene–acetylene interconversion represents an unlikely pathway since this reaction normally requires considerably higher reaction temperatures and an sp^2-hybridized center α to the acetylenic bond and is not inhibited by substituents.[15]

(13) Thomas, A. C.; Wellington, C. A. *J. Chem. Soc. A* **1969**, 2895–2896.

(14) We thank Professor K. Grant Taylor (University of Louisville) for providing us with the ^{1}H NMR spectra of authentic 1,2,5,8-tetrahydro-3*H*-pyrrolizine, **12**, and 2,3-dihydro-1*H*-pyrrolizine, **13**.

Scheme III



We favor a concerted [$2_a + 2_s$] group migration as the most likely alternative because (a) of the apparent homogeneous, first-order nature of the process, (b) of the unlikely participation of radical or carbenoid pathways, (c) of the energetic similarity to two known, concerted processes, (d) the reaction is hindered by substituents which would sterically crowd a tight, cyclic transition state (i.e., **17–22**), and (e) *antarafacial* participation is a structural requirement of the reaction product since the two newly formed bonds must have a *trans* relationship.

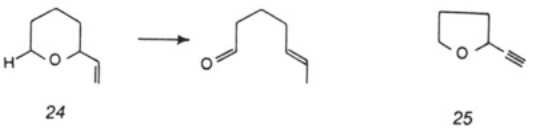
Although acetylenes are linear in the ground state, the sp bond angle is readily distorted without a prohibitive energetic requirement. It is such distortions which make possible the large number of reactions of acetylenic substrates which are known to proceed via cyclic transition states.[1] The molecules involved in this reaction can readily assume a bent conformation, such as illustrated in **23**, which leads to the requisite transition state for this reaction.

The Cyclization of 2-Ethynyltetrahydropyran. In the propargylic ether series,[12] formation of dihydofuran **14** during thermolysis of **6** (see Table I) provides additional evidence for the initial formation of a dihydro derivative. In this instance dehydrogenation is blocked by the trimethylene bridge. Propargylic ether **6** was originally intended to show the effect of ring strain on the retro-ene transition state. The retro-ene path is indeed encumbered by the bicyclic nature of that transition state, since **6** is the only ether in our study whose olefinic analog reacted at a comparable rate and is also the only ether from which a cyclization component was produced.

Thermolysis of **6** affords a single retro-ene product, **15**, which, although thermally unstable, is not responsible for the formation of **14**. Instead, **15** undergoes a sequential retro-ene cleavage to produce butadiene and acrolein, a recombination of which via their known Diels–Alder pathway[16] affords only **35** (Scheme III). The evidence for this reaction manifold is described in the Experimental Section. The partitioning of products between the two pathways is independent of reaction time, since substantial pressure variations during flow system thermolyses did not affect the ratio of products from each path and since the ratio of cyclization to retro-ene products remained constant during kinetic runs in the static system. At 420 °C the partitioning between cyclization and retro-ene pathways is 35:65.

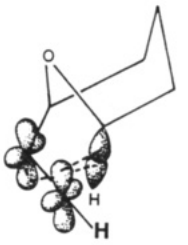
The structure determination of **14** is described in the Experimental Section. Accurate kinetic data for the thermolysis of **6** was unobtainable since the number of secondary products arising from thermally unstable **15** prevented sufficiently accurate product analyses.

As is the case with allylic amines, thermolysis of allylic ether **24** leads only to the expected retro-ene product.



2-Ethynyltetrahydrofuran, **25**, has been reported[3] to be essentially thermally stable under flow-system thermolysis conditions at 470 °C. The rigid structure of **25** precludes the distortion of the molecular framework essential for the formation of either transition state.

Apparently, with propargylic ethers the cyclization can compete with the more facile retro-ene reaction only if the latter is encumbered by steric restraints and/or if the molecular geometry is favorable for the requisite orthogonal approach of reacting components. As indicated in **23** the participating bonds in **6** can assume this orientation

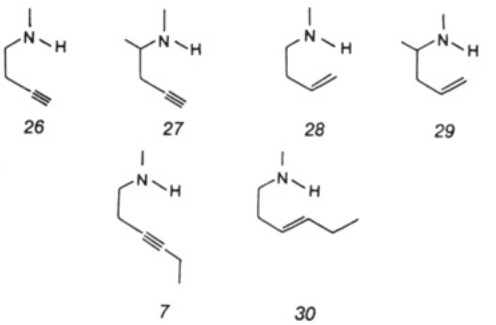


23

with a moderate deformation of the sp bond angle, which is readily attainable,[17] and which would aid the concerted addition of a C–H bond to an acetylenic π-lobe if the hydrogen transfers with hydride character.[18]

Cyclization of *N*-Methyl-3-hexyn-1-amine, 7. β-Amino acetylenes and β-amino olefins give mainly retro-ene reactions on flow-system thermolysis over the temperature range of 400–460 °C and in the static system at 240 °C,[2] with one exception. The β-amino acetylene **7** exhibits a unique behavior on thermolysis, quite apart from that of any of the other 3,4-unsaturated amines investigated.

Although amines **26–29** gave clean retro-ene reactions, it was anticipated that the retro-ene reactions of both **7** and **30** would be retarded by their terminal ethyl substituents, due to the normal steric and/or electronic effects associated with such substituents in pericyclic reactions.



Indeed, the retro-ene reaction of olefinic amine **30** was substantially retarded. In the thermolysis of acetylenic

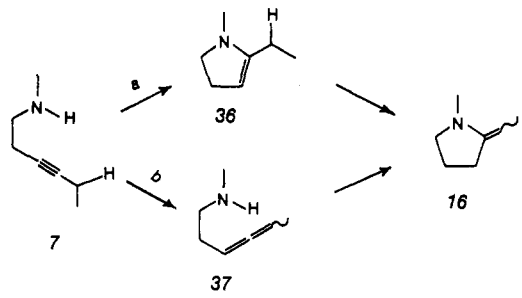
(15) For a full discussion of the unlikelihood of this pathway, see ref 4.

(16) Shortridge, R. W.; Craig, R. A.; Greenlee, K. W.; Derfer, J. M.; Boord, C. E. *J. Am. Chem. Soc.* **1948**, *70*, 946–949.

(17) Viola, A.; MacMillan, J. H.; Proverb, R. J.; Yates, B. L. *J. Am. Chem. Soc.* **1971**, *93*, 6967–6974.

(18) Strozier, R. W.; Caramella, P.; Houk, K. N. *J. Am. Chem. Soc.* **1979**, *101*, 1341–1343.

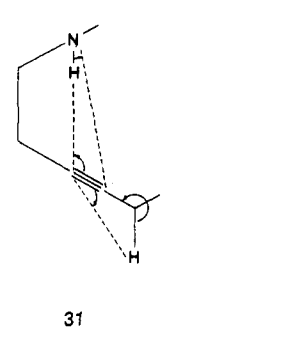
Scheme IV

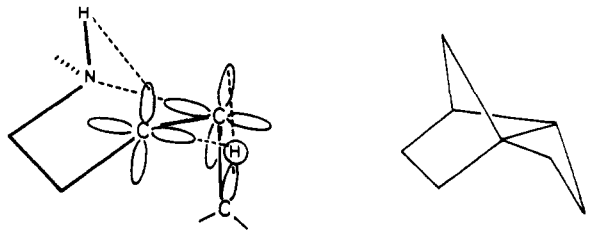


amine **7** no traces of retro-ene products were observable, and **16** was the sole product obtained (Table I). Furthermore, under the much milder conditions of the static system, **16** was still produced readily and, indeed, even the conditions of preparative GLPC consistently led to partial **7** → **16** conversion. The structure of **16**, which has been previously reported,[19] was assigned on the basis of its IR, ^{1}H NMR, and ^{13}C NMR spectra. The NMR spectra, as well as the GLPC behavior of **16**, indicated that only a single isomer of **16** was produced, but the available data do not permit the assignment of configuration of that isomer.

The **7** → **16** transformation requires not only bond formation between the nitrogen atom and the far terminus of the acetylenic unit, but also the migration of two hydrogen atoms. Two step-wise processes can be envisaged to accomplish the required bond changes (Scheme IV). These reaction sequences differ only in the occurrence of symmetry-forbidden [1,3] hydrogen migrations and can thus be assumed to require catalysis or liquid-phase bimolecular reactions. Path a represents an initial group-transfer reaction, similar to that discussed for thermolyses of propargylic amines and ethers (*vide supra*). A symmetry-forbidden [1,3] shift would then have to produce **16** quantitatively, since none of the endocyclic product of the initial cyclization, **36**, can be observed. Pathway b involves an initial [1,3] hydrogen migration to produce allenic amine **37**, followed by a group transfer, similar to that above, to provide **16**. Here again the second step in the reaction path would have to be rapid and quantitative since none of the intermediate **37** is observed. The intermediacy of **37** seems particularly unlikely, however, since the central atom of the allenic system is known to be a ready hydrogen acceptor in pericyclic reactions such as the vinyl allene rearrangement[20] and the retro-ene reaction of β-hydroxyallenes.[21]

The ease of the **7** → **16** transformation, under the variety of conditions observed, militates against the occurrence of a symmetry-forbidden [1,3] hydrogen migration. Both of the processes considered above, which depend upon such a "forbidden" step, are also unlikely because of the total absence of either intermediate which should be observable under the conditions utilized. A concerted, one-step alternative is therefore more attractive, in which all the bonding changes shown in **31** occur in concert. The orbital interactions required for this process are depicted in **32** and represent a symmetry-allowed [$2_s + 2_a + 2_s$ + 2_s] eight-electron Möbius process.[22] The necessary conformation leading to the requisite transition state, **33**,





tricyclo [3.2.1.0^{1,4}] octane

requires considerable distortion of the acetylenic sp bond angle, but the resultant atomic framework does not appear excessively strained and is comparable to its all-carbon analog, tricyclo[3.2.1.0^{1,4}]octane, **34**. An eight-electron pericyclic process is thermally allowed when there is an odd number of *suprafacial* involvements, and this criterion is met in **32** by the *antarafacial* involvement of an acetylenic π-bond. The H migration depicted in **32**, from C-5 to C-3, does not constitute a [1,3] shift since it does not involve the same acetylenic π-lobe for hydrogen transfer as it does for formation of the new olefinic π-bond. Such a reaction step is only possible with an acetylenic bond, wherein there are two differing π-orbitals on the same carbon center, and this factor may be the reason why such a pathway is not observed with olefinic compounds. The *antarafacial* involvement of one π-bond is also necessitated on steric grounds, since the developing C–N and C–H bonds, involving the same acetylenic π-bond, must approach their respective receptor sites from opposite sides of the former π-bond, since otherwise the approaching hydrogen atom would have to do so from within the forming ring structure; the addition to this acetylenic π-bond is therefore a trans addition, although the olefinic structure normally resulting from such a step is lost due to the involvement of the second acetylenic π-bond in the same reaction process.

Conclusions

The role of the heteroatom in these reactions is not clear. Previous investigations of retro-ene reactions have indicated them to be concerted but nonsynchronous processes, in line with recent theoretical calculations on most pericyclic reactions in general.[1] In a nonsynchronous

(19) (a) Dedek, V.; Barta, M. *Sb. Vys. Sk. Chem.-Tekhnol. Praze, Org. Technol.* **1966**, *8*, 89–95; *Chem. Abstr.* **1967**, *67*, 73469. (b) Lukes, R.; Dedek, V.; Novotny, L. *Chem. Listy.* **1958**, *52*, 654–662; *Chem. Abstr.* **1958**, *52*, 13705b.

(20) Wu, K.-M.; Midland, M. M.; Okamura, W. H. *J. Org. Chem.* **1990**, *55*, 4381–4392.

(21) Unpublished results, this laboratory.

(22) For examples of other suggested 8-electron Möbius processes see: Pasto, D. L.; Borchardt, J. K. *J. Am. Chem. Soc.* **1974**, *96*, 6944–6948. Duncan, J. A.; Bohle, D. C.; Blanchard, C. A.; Bosse, M. L.; Noland, T. W.; Ford, C. M.; Powell, M. A.; Sutton, M. C.; Eggleston, A. C.; Klevit, R. E.; Krueger, S. M. *J. Am. Chem. Soc.* **1982**, *104*, 2837–2839.

process the presence of polar bonds in the vicinity of heteroatoms may aid in the initial polarizations which trigger the reaction process. It is well established that the all-carbon retro-ene process is a high-energy reaction in comparison with any of its heteroatom analogs. That nitrogen compounds participate in these reactions more readily than do their oxygen analogs may reflect differing bond energies. The BDE's for α C–H bonds in ethers and in amines, 93.9 *vs* 86.6 kcal/mol in the *anti* conformation and 102.5 *vs* 99.8 kcal/mol in the *gauche* conformation, respectively,[23] indicate an energetic bias favoring reactions of amines in any path involving rupture of that C–H bond. A further factor favoring the participation of nitrogen compounds over that of their oxygen analogs, in reactions requiring considerable bond angle distortions, is the more facile distortion of bond angles around the N atom, as evidenced by the lower energy C–N–C bending mode, 366 cm^{-1}, as opposed to that for C–O–C, 418 cm^{-1}. Thus, no furans have been detected in the thermolyses of acyclic propargylic ethers analogous to amines **1–3**.

The three cyclization reactions discussed herein are unique for the acetylenic bond, for there are no traces of similar reactions in analogous olefins. These examples, together with that reported by Dreiding, *et al.*,[4] provide substantial evidence for the ability of the acetylenic bond to act as an *antarafacial* component in pericyclic reactions and are ample reason to look for further instances of this reaction mode which utilize the unique bonding features of the acetylenic structure.

Experimental Section

General. All melting points and boiling points are uncorrected. ^{1}H NMR spectra (60 MHz) are from $CDCl_3$ solutions in ppm downfield from TMS. IR spectra were obtained on neat liquid samples between sodium chloride plates. Elemental analyses were performed by Galbraith Laboratories, Inc., or Spang Microanalytical Laboratories.

GLPC analyses were performed with 20% UCON LB-550-X/20% KOH on Chromosorb-P in 18-in. × 1/8-in. or 5-ft × 1/8-in. stainless steel columns for amines and on 10% SE-30 on Chromosorb P in 2-ft × 1/8-in. copper columns for other compounds. Preparative GLPC was performed using similarly packed 2-ft × 1/4-in. stainless steel or 6-ft × 1/4-in. copper columns.

Preparation of Starting Materials. *N,N*-Dimethyl-2-propynylamine (1) was purchased from Aldrich Chemical Co. and distilled prior to use.

***N,N*-Diethyl-2-propynylamine (2)** was prepared by the method of Brandsma.[24] From 39.1 g (0.54 mol) diethylamine in 60 mL of ether and 28.4 g (0.24 mol) of propargyl bromide (Aldrich Chemical Co.) was obtained a yield of 13.6 g (71%) of **2** after distillation, bp 65–70 °C/100 Torr (lit.[24] bp 50 °C/70 Torr, lit.[25] bp 60–62 °C/85 Torr). The ^{1}H NMR is in agreement with that reported[26] previously: δ 1.05 (6H, t, J = 7 Hz, methyl), 2.12 (1H, t, J = 2 Hz, acetylenic), 2.58 (4H, q, J = 7 Hz, methylene), 3.40 (2H, d, J = 2 Hz, propargylic); IR 3310 (s, ≡CH), 2100 (w, C≡C) cm^{-1}.

***N,N*-Dipropyl-2-propynylamine (3)** was prepared by the same method as **2**. From 51.9 g (0.51 mol) of dipropylamine and 26.0 g (0.22 mol) of propargyl bromide was obtained a yield of 3.7 g (12%) of pure **3** after fractional distillation: bp 80–85 °C/65 Torr (lit.[27] bp 157.5–158.5 °C); ^{1}H NMR δ 0.92 (6H, t, J = 7 Hz, methyl), 1.48 (4H, sextet, J = 7 Hz, methylene), 2.14 (1H, t, J = 2 Hz, acetylenic), 2.46 (4H, t, J = 7 Hz, methylene), 3.39 (2H, d, J = 2 Hz, propargylic); IR 3310 (s, ≡CH), 2100 (w, C≡C) cm^{-1}.

1-(2-Propynyl)piperidine (4) was prepared by the method of Mochalin and Minervina.[28] From 21.8 g (0.26 mol) of piperidine and 10.1 g (0.086 mol) of propargyl bromide was obtained a yield of 5.9 g (56%) of **4** after distillation, bp 74–75 °C/36 Torr (lit.[28] bp 72–73 °C/35 Torr). The ^{1}H NMR spectrum is in agreement with that reported[29] previously: δ 1.5 (6 H, m, $-CH_2CH_2CH_2-$), 2.24 (1 H, t, J = 2 Hz, acetylenic), 2.5 (4H, m, $-CH_2NCH_2-$), 3.30 (2H, d, J = 2 Hz, propargylic); IR 3310 (s, ≡CH), 2100 (w, C≡C) cm^{-1}.

1-(2-Propynyl)pyrrolidine (5) was prepared by the method of Biel and DiPierro.[30] From 19.6 g (0.27 mol) of pyrrolidine and 16.0 g (0.13 mol) of propargyl bromide was obtained a yield of 4.5 g (32%) of **5** after distillation: bp 65–67 °C/53 Torr (lit.[30] bp 74–77 °C/85 Torr); ^{1}H NMR δ 1.8 (4H, m, $-CH_2CH_2-$), 2.27 (1H, t, J = 2 Hz, acetylenic), 2.6 (4H, m, $-CH_2NCH_2-$), 3.34 (2H, d, J = 2 Hz, propargylic); IR 3300 (s, ≡CH), 2100 (w, C≡C) cm^{-1}.

2-Ethynyltetrahydropyran (6). (a) Ethynylmagnesium bromide was prepared by a modification of the procedure of Landor.[31] Acetylene gas, generated by the addition of a solution of 50 mL of water and 50 mL of THF to calcium carbide, 120 g, and passed through a 14 in. drying tube containing Indicator Drierite, was slowly passed into 120 mL of anhydrous THF, while a filtered solution of ethylmagnesium bromide, prepared from 7.63 g (0.317 mol) of magnesium turnings and 34.6 g (0.319 mol) of ethyl bromide in THF, was simultaneously added over a 5-h period during which time the temperature was maintained at 25–30 °C. The acetylene gas flow was continued for a further 1.5 h.

(b) 2-Chlorotetrahydropyran was prepared by a modification of the method of Ficini.[32] Dry HCl gas was passed into a solution of 17.1 g (0.204 mol) of 3,4-dihydro-2*H*-pyran in 70 mL of anhydrous diethyl ether, cooled in a dry ice/acetone bath. A slow, steady stream of HCl gas, generated by addition of excess concentrated sulfuric acid to 22.2 g (0.380 mol) of sodium chloride and bubbled through concentrated sulfuric acid before addition to the reaction vessel, was maintained for 8 h. After removal of the ether, fractional distillation of the residue under reduced pressure yielded 18.6 g (0.155 mol, 76%) of product: bp 36–38 °C/22 Torr, n^{22}_D 1.4655 (lit.[33] bp 35–36 °C/12 Torr, n^{20}_D 1.4676); ^{1}H NMR δ 1.4–2.4 (6H, m, methylenes), 3.5–4.2 (2H, m, $-OCH_2-$), 6.25 (1H, m, methine); IR 2950 (s), 1260 (s), 1195 (s), 1130 (s), 1085 (s), 1055 (s), 1040 (s), 1015 (s), 885 (s), 875 (s), 815 (s), and 700 (s) cm^{-1}.

Since this compound showed evidence of decomposition during the purification process and also on standing, the purification step was omitted before its immediate use in subsequent reactions.

(c) 2-Ethynyltetrahydropyran (6) was prepared by a modification of the method of Gouin.[34] A solution of 2-chlorotetrahydropyran, prepared from 20.8 g (0.242 mol) of dihydropyran as described above, in anhydrous diethyl ether was slowly added to the solution of ethynylmagnesium bromide in THF prepared above, while the reaction flask was cooled in an ice/water bath. The resultant solution was stirred at room temperature overnight and then poured onto 125 mL of saturted ammonium chloride solution. The organic phase was separated, washed with 150 mL water, dried with anhydrous magnesium sulfate, and distilled to yield 14.3 g (0.13 mol, 54%) of **6**: bp 145–146 °C, n^{25}_D 1.4562 (lit.[34] bp 50–51 °C/20 Torr, n^{15}_D 1.4603); ^{1}H NMR δ 1.33–2.00 (6H, m, methylenes), 2.56 (1 H, d, J = 2 Hz,

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acetylenic), 3.1–4.1 (2H, m, $-CH_2O-$), 4.18–4.37 (1H, m, methine); IR 3280 (s, ≡CH), 2940 (s), 2100 (w, C≡C), 1085 (s, CO) cm^{-1}.

***N*-Methyl-3-hexyn-1-amine (7). (a) 3-Hexyn-1-yl tosylate** was prepared by the addition of 50 g (0.26 mol) of *p*-toluenesulfonyl chloride, in two equal portions, to 25 g (0.255 mol) of 3-hexyn-1-ol (Farchan) in 300 mL of dry pyridine at 0 °C. Workup in the usual manner yielded 46.8 g (73%) of crude product: ^1H NMR δ 1.0–1.35 (t, 3H, alkyl methyl), 1.95–2.75 (m, 7H, propargylic methylenes, aromatic methyl), 3.90–4.13 (t, 2H, tosyl methylene), 7.20–7.65 (m, 4H, aromatic).

(b) *N*-Methyl-3-hexyn-1-amine (7). An 80-mL steel bomb was charged with 20.0 g (0.079 mol) of 3-hexyn-1-yl tosylate and 18 mL (12.4 g, 0.395 mol) of methylamine, added from a chilled container. The bomb was sealed and allowed to stand at room temperature for 4 days. The bomb was emptied and rinsed with three 20-mL portions of ether and a small amount of water to dissolve any solid residue, and the combined solutions were allowed to separate. The organic layer was dried with $MgSO_4$ and fractionally distilled to yield 5.0 g (57%) of product. GLPC analysis indicated this material to contain about 2% of 3-hexyn-1-ol and a compound subsequently identified as *N*-methyl-2-ethylidenepyrrolidine, 16. Attempted preparative GLPC failed to remove the latter impurity, and the slightly impure 7 was subjected to thermolysis without further purification: bp 157 °C/760 Torr; $n^{27.5}_D$ 1.4465; ^1H NMR δ 0.97–1.22 (t, 3H, methyl), 1.80 (s, 1H, NH), 1.90–2.87 (m, 9H, methylenes, *N*-methyl at δ 2.42); deuterium exchange resulted in the disappearance of the singlet at δ 1.80; IR 3300 (m), 2970 (s), 2200 (w), and 1440 (s) cm^{-1}.

Anal. Calcd for $C_7H_{13}N$: C, 75.60; H, 11.81; N, 12.60. Found: C, 75.66; H, 11.86; N, 12.27.

Thermolyses Products. For preparative purposes thermolyses were carried out in a vapor-phase flow system, in a nitrogen atmosphere, over the temperature range of 350–450 °C. For kinetic purposes thermolyses were carried out in small static tubes, in either vapor or solution phases, over the range of 200–260 °C. The apparatus used for flow-system thermolyses has been described previously,[35] as has the static system.[36] Routinely the results obtained from the flow system were taken as an indication of the feasibility of utilizing the compound in question for kinetic determinations. Only when the flow system indicated thermolyses to be sufficiently clean processes were kinetic determinations at substantially lower temperatures attempted.

The large capacity of the flow system facilitated the isolation and subsequent identification of thermolysis products. The wide range of temperatures available in this system permitted the determination of temperature dependency of product distribution. Variation of reaction time, by adjustment of the nitrogen carrier gas pressure, provided a means for detection of secondary vapor phase reactions of the primary products. Products were normally isolated and purified from flow-system thermolyses by preparative GLPC. Amounts produced in the thermolyses as well as conditions used are summarized in Table II.

1-Methylpyrrole (8) was isolated from numerous thermolyses of *N,N*-dimethyl-2-propynylamine, 1, performed under a variety of conditions at rates determined by vaporization from the dropping funnel.

GLPC analyses of condensed product mixtures indicated formation of three new substances, along with unreacted 1. The receiving flask was removed from the dry ice/acetone bath and slowly warmed to room temperature, and the volatile components were trapped by bubbling the effluent into $CDCl_3$. The ^1H NMR spectrum of the resultant solution contained a sharp singlet at δ 4.67, indicative of the formation of allene.[37] The other two components were isolated by micropreparative GLPC. Of these, the major component, which had the shorter retention time, had ^1H NMR and IR spectra identical to those of an authentic sample of hexahydro-1,3,5-trimethyl-*s*-triazine, prepared according to Hinze and Curl.[38] The component with the longest retention time was identified as 1-methylpyrrole by its ^1H NMR spectrum, δ 3.66 (3H, s), 6.15 (2H, d of d), 6.60 (2H, d of d), and by its IR spectrum, which was identical to that reported[39] for 1-methylpyrrole.

For quantitative determinations, a solution of 15 drops of nonane, used as internal standard, in 40 drops of 1 was thermolyzed. Thus, at 450 °C/24 Torr GLPC analysis of the thermolysate indicated formation of 8 to represent 4.3% of the total reaction manifold.

1-Ethyl-2-methylpyrrole (9) was isolated from numerous thermolyses of *N,N*-diethyl-2-propynylamine, 2, performed under a variety of conditions. GLPC analyses of the condensed product mixtures indicated two major products with low retention times, unreacted 2, and a minor product with a long retention time. The component with the lowest retention time was identified as allene as described above in the thermolysis of 1. The remainder of the thermolysate was subjected to micropreparative GLPC. The major product with the longer retention time was identified as *N*-ethylideneethylamine by its IR and previously reported[40] ^1H NMR spectra. The minor product, which had the longest GLPC retention time, was identified as 1-ethyl-2-methylpyrrole, 9, by its IR and previously reported[41] ^1H NMR spectra: ^1H NMR δ 1.33 (3H, t, J = 7 Hz), 2.24 (3H, s), 3.84 (2H, q, J = 7 Hz), 5.87 (1H, m), 6.04 (1H, d of d), 6.57 (1H, d of d); IR 3100 (m), 2980 (s), 2940 (s), 1550 (m), 1490 (s), 1450 (s), 1420 (s), 1295 (s), and 700 (s) cm^{-1}.

For quantitative determinations, a solution of 40 drops of 2 and 15 drops of undecane, used as internal standard, in 50 drops of dodecane was thermolyzed at 450 °C/24 Torr, with a drop rate of 1 drop/22 s. GLPC analysis of the thermolysate indicated that 9 represented 3.6% of the total reaction manifold. Identical results were obtained in the absence of the dodecane diluent.

1-Propyl-2-ethylpyrrole (10), previously reported,[42] was isolated from numerous thermolyses of *N,N*-dipropyl-2-propynylamine, 3, performed under a variety of conditions. Allene was isolated and identified as described above in the thermolysis of 1. The remaining thermolysate was subjected to micropreparative GLPC. The major product with the longer retention time was identified as *N*-propylidenepropylamine by its IR and previously reported[43] ^1H NMR spectra.

The minor product, which had the longest GLPC retention time, was identified as 1-propyl-2-ethylpyrrole, 10, on the basis of its IR and ^1H NMR spectra and its combustion analysis: ^1H NMR δ 0.93 (3H, t, J = 7 Hz), 1.28 (3H, t, J = 7 Hz), 1.3–2.0 (2H, m), 2.57 (2H, q, J = 7 Hz), 3.37 (2H, t, J = 7 Hz), 5.92 (1H, m), 6.05 (1H, d of d), 6.57 (1H, d of d); IR 3100 (m), 2970 (s), 2930 (s), 2880 (m), 1630 (w), 1545 (w), 1490 (s), 1420 (s), 1290 (s), and 700 (s) cm^{-1}. Anal. Calcd for $C_9H_{15}N$: C, 78.77; H, 11.02. Found: C, 79.03, H, 11.15

For quantitative determinations, a solution of 25 drops of 3 in 17 drops of tetradecane, used as internal standard, was thermolyzed at 450 °C/24 Torr at a drop rate of 1 drop/20 s. GLPC analysis of the condensed thermolysate indicated that 10 represented 3.8% of the total reaction manifold.

5,6,7,8-Tetrahydroindolizine (11), previously reported,[44] was isolated from numerous thermolyses of 1-(2-propynyl)piperidine, 4, performed under a variety of conditions. Allene was isolated and identified as described above for the thermolysis of 1. The remaining thermolysate was placed in a refrigerator for several hours, after which a white precipitate had formed. The liquid portion was decanted, and the precipitate was recrystallized from acetone to yield α-tripiperidein, mp 58–59 °C, which showed no

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melting point depression on admixture with an authentic sample and whose ^{1}H NMR and IR spectra were identical to those of that authentic sample.[45]

The minor product in the thermolysate, isolated by micropreparative GLPC, was identified as 5,6,7,8-tetrahydroindolizine, **11**, on the basis of its IR and previously reported[44] ^{1}H NMR spectra: ^{1}H NMR δ 1.84 (4H, m), 2.75 (2H, broad t), 3.93 (2H, broad t), 5.84 (1H, m), 6.10 (1H, d of d), 6.49 (1H, d of d); IR 3110 (w), 2950 (s), 2870 (s), 1545 (w), 1490 (s), 1389 (s), 1382 (s), 1255 (s), 1082 (s), 765 (s), and 705 (s) cm^{-1}.

For quantitative determinations, a solution of 30 drops of **4** in 30 drops of dodecane, used as internal standard, was thermolyzed at a rate of 1 drop/18 s under a variety of conditions. Thus, at 450 °C/36 Torr GLPC analysis of the condensed thermolysate indicated that **11** represented 5.8% of the total reaction manifold.

1,2,5,8-Tetrahydro-3*H*-pyrrolizine (12) and 2,3-dihydro-1*H*-pyrrolizine (13) were isolated from numerous thermolyses of 1-(2-propynyl)pyrrolidine, **5**, performed under a variety of conditions at a rate of 1 drop/20 s.

Allene was isolated from the thermolysate and identified as described above for the thermolysis of **1**. The remainder of the thermolysate was separated by micropreparative GLPC. The major product was identified as α-tripyrroline on the basis of its ^{1}H NMR and previously reported[46] IR spectra. The thermolysate also contained two minor components. The one with the shorter GLPC retention time was identified as **12** on the basis of its complex ^{1}H NMR spectrum, which was identical to that kindly provided us by Professor K. Grant Taylor, University of Louisville: ^{1}H NMR δ 1.2–2.0 (m), 1.9–2.3 (m), 2.3–2.8 (m), 2.8–3.3 (m), 3.4 (m), 3.7 (d), 3.9–4.4 (m), 5.68 (s); IR 3060 (m), 2950 (s), 2860 (s), 1615 (w), and 700 (s) cm^{-1}.

The minor component with the longer GLPC retention time was identified as **13** on the basis of its ^{1}H NMR spectrum, which was also identical to that kindly provided us by Professor K. Grant Taylor: ^{1}H NMR δ 2.2–3.0 (4H, m), 3.90 (2H, t, J = 7 Hz), 5.74 (1H, m), 6.17 (1H, d of d), 6.53 (1H, m); IR 3110 (m), 3090 (m), 2950 (s), 2880 (s), 1540 (m), 1488 (s), 1462 (s), 1300 (s), 1283 (s), 1052 (s), 760 (s), and 695 (s) cm^{-1}.

In order to determine the effect of reaction time on the amounts of **12** and **13** produced, samples of **5** were thermolyzed at 450 °C/12 Torr and 450 °C/35 Torr. In both cases the combined amounts of **12** and **13** represented 4.7% of the total reaction manifold. However, at the shorter reaction time (lower pressure) the thermolysate contained 2.7% **12** and 2.0% **13**, while at the longer reaction time there were 0.7% **12** and 4.0% **13**.

8-Oxabicyclo[3.2.1]oct-6-ene (14) was isolated from numerous thermolyses of 2-ethynyltetrahydropyran, **6**, performed under a variety of conditions, at a rate of 1 drop/14 s. The five products in the thermolysate were isolated by micropreparative GLPC and identified as follows.

The product with the shortest retention time was identified as 1,3-butadiene via its IR spectrum and its tetrabromo derivative, mp 116–117 °C (lit.[47] mp 118 °C).

The second product with a short retention time was identified as acrolein by its characteristic odor, its IR spectrum which was identical to that of an authentic sample, and its 2,4-dinitrophenylhydrazone, mp 164–5 °C (lit.[47] mp 165 °C) which showed no melting point depression on admixture with an authentic sample.

The third product was identified as 1,2,3,4-tetrahydrobenzaldehyde by its IR and ^{1}H NMR spectra, which were identical to those of an authentic sample, and by its 2,4-dinitrophenylhydrazone, mp 172–3 °C, which showed no melting point depression on admixture with an authentic sample.

The fourth product was identified as 5,6-heptadienal: ^{1}H NMR δ 1.33–2.66 (6H, m, $-CH_2CH_2CH_2-$), 4.63 (2H, t of d, J_t = 3.5 Hz, J_d = 7 Hz, terminal allene), 5.06 (1H, m, internal allene), 9.72 (1H, t, aldehydic); IR 3020 (w), 2940 (s), 2720 (m), 1950 (s), 1720 (vs), 845 (s) cm^{-1}. This compound gave a 2,4-dinitrophenylhydrazone, mp 70–71.5 °C. Anal. Calcd for $C_{13}H_{14}N_4O_4$: C, 53.79; H, 4.86. Found: C, 53.65; H, 4.80.

The fifth product was assigned the 8-oxabicyclo[3.2.1]oct-6-ene structure, **14**, based on the following evidence: mp 58–59 °C; ^{1}H NMR δ 1.02–1.77 (6H, m, $-CH_2CH_2CH_2-$), 4.54 (2H, m, allylic methine), 6.20 (2H, m, vinylic); IR 3075 (w, =CH), 2940 (s), 1030 (s, bicyclic COC), 970 (s), 865 (s), and 705 (s) cm^{-1}. Anal. Calcd for $C_7H_{10}O$: C, 76.33; H, 9.15. Found: C, 76.14; H, 9.10. The absence of any observable IR absorption in the C=C stretch region is indicative of a symmetrical alkene or *cis* double bond.[48] **14** readily decolorized a dilute solution of bromine in carbon tetrachloride. A sample of **14** was hydrogenated (Pd/C) to produce a compound whose GLPC retention time and IR spectrum were identical to those of authentic 8-oxabicyclo[3.2.1]-octane, prepared and isolated according to the procedure of Cope *et al.*[49]

Interrelationships among these five products were established by numerous thermolyses of **6** at varying temperatures. The amount of **14**, which first appeared at 420 °C, increased with increasing temperature. The amount of 5,6-heptadienal, which first appeared at 380 °C, initially increased with increasing temperature, reached a maximum, and then decreased. The amount of tetrahydrobenzaldehyde, present in trace amounts at 380 °C, increased steadily with increasing temperatures. Thermolyses of tetrahydrobenzaldehyde and of **14** at 480 °C/65 Torr indicated these compounds to be essentially thermally stable even under these vigorous conditions. Thermolysis of a sample of 5,6-heptadienal, with tetradecane as internal standard, under similar conditions followed by immediate GLPC analysis of the thermolysate, indicated a 70% decomposition into 1,3-butadiene and acrolein, with a trace amount of 1,2,3,4-tetrahydrobenzaldehyde also present. When samples of this thermolysate, containing acrolein and butadiene, were sealed in melting point capillaries and stored at room temperatures for 1, 2, and 3 days, increasing amounts of 1,2,3,4-tetrahydrobenzaldehyde were detected by GLPC as storage time lengthened. This behavior is in accord with the known facile Diels–Alder reaction of these two components.[50]

The experimental findings described above are best explained on the basis of the reaction sequence depicted in Scheme III. Obviously, the product distribution from the thermolysis of **6** is highly dependent on temperature and reaction time. Thermolysis at 420 °C/63 Torr, with a rate of 1 drop/24 s and tetradecane as internal standard, provided a thermolysate which upon immediate GLPC analysis was found to consist of 33% acrolein and butadiene, 30% **14**, 23% heptadienal, 14% unreacted **6**, and a trace of 1,2,3,4-tetrahydrobenzaldehyde. The conversion to **14** was therefore 35%.

***N*-Methyl-2-ethylidenepyrrolidine (16)**, which has been previously reported,[19] was the major product from the thermolysis of *N*-methyl-3-hexyn-1-amine, **7**. Sequential attempts to purify **7** by micropreparative GLPC gave mixtures with increasing amounts of **16**, which constituted up to 95% of the material collected, and which was apparently produced in the heated thermal conductivity detector just prior to exiting the instrument. Due to the difficulties encountered in the purification of **7**, samples thermolyzed contained small amounts of 3-hexyn-1-ol, which is known to fragment to 1,2-pentadiene and formaldehyde under the thermolysis conditions used,[17] and trace amounts of both these compounds were present in the thermolysate. The structure of **16** is based on its IR and NMR spectra. IR 3020 (w, =CH), 2960 (m, sat. CH), 1660 (s, C=C), 1260 (s) cm^{-1}; ^{1}H NMR δ 1.35–2.08 (5H, m, H_a and H_b), 2.08–2.55 (2H, m, H_c), 2.42 (3H, s, H_d), 2.85 (2H, t, H_e), 3.52–4.08 (1H, m, H_f). ^{13}C NMR assignments are based on both decoupled and off-resonance spectra: δ 13.4 (q, C_a), 22.0 (t, C_b), 28.1 (t, C_c), 34.5 (q, C_d), 55.0 (t, C_e), 83.6 (d, C_f), 148.0 (s, C_g).

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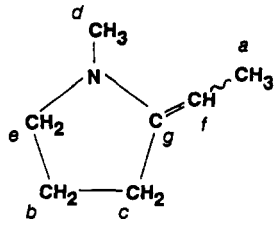

When a solution of **7**, containing a small impurity of 3-hexyn-1-ol, in undecane as an internal standard was thermolyzed at 400 °C/50 Torr, the resulting thermolysate contained 75% **16** and 25% unreacted **7**, plus traces of 1,2-pentadiene and formaldehyde.

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