Retro-ene Reactions and 2-Alkylidenepyrrolidine Formation from Thermolyses of β-Amino-olefins and β-Aminoacetylenes†

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Thermolyses of β-aminoacetylenes with a terminal acetylenic bond and of β-amino-olefins afford retro-ene reactions in which nitrogen acts as the hydrogen donor, whereas alkyl substitution on the terminus of the acetylenic bond leads to a novel, facile cyclization to a 2-alkylidenepyrrolidine.

Although the presence of a nitrogen atom within the molecular framework presents no deterrent to pericyclic reactions such as the Claisen[1] or Cope[2] rearrangements, there are only few reports of nitrogen acting as the hydrogen donor in pericyclic reactions.[3] As part of our investigation of retro-ene reactions of acetylenic substrates, we have examined the thermal behaviour of β-aminoacetylenes and of their olefinic analogues.

Compounds (**1**)—(**6**) were prepared by a modification of the method of Wille and Goubeau,[4] *via* the reaction of the appropriate alkenyl or alkynyl bromide or tosylate with a five-fold excess of methylamine in a steel bomb.‡ Each compound was then thermolysed in a flow system at 400—460 °C, as well as in static tubes at 240 °C. With compounds (**1**)—(**5**) the flow system produced mainly the products expected from retro-ene reactions, although in the case of (**3**)

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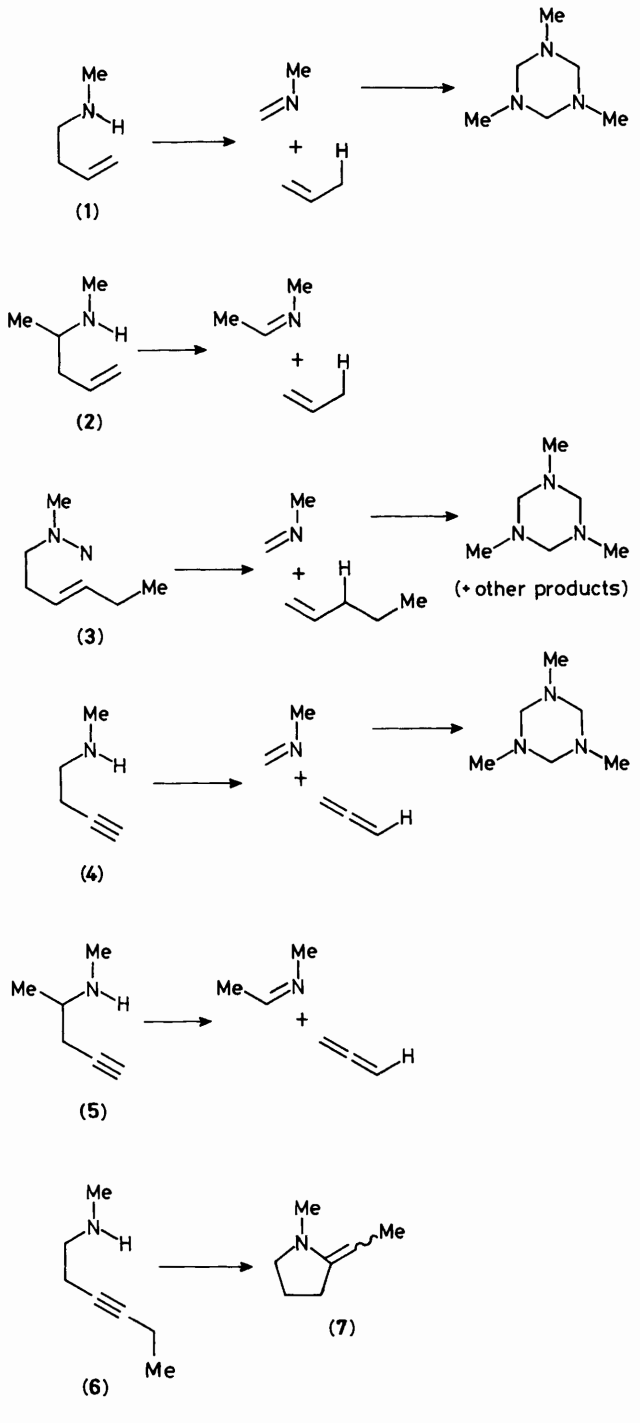
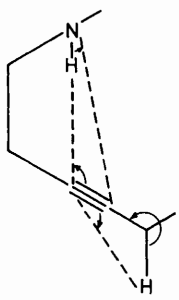
† For paper No. 9 in the series Intramolecular Pericyclic Reactions of Acetylenes, see ref. 5.

‡ All new compounds gave satisfactory C, H, and N combustion analyses.

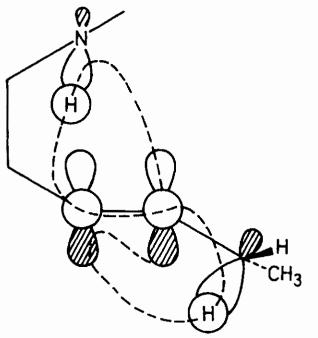


Flow system results (at 460 °C, 50 Torr).

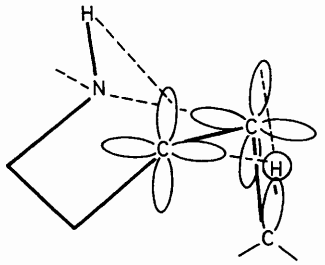
there were also a number of minor low-molecular weight products. Compound (**6**), on the other hand, produced no retro-ene products but instead afforded a quantitative conversion into (**7**). The structures of all retro-ene products were assigned on the bases of their known spectral characteristics and/or their conversion into known derivatives, or in the case of *N*-methylenemethanamine on the basis of the properties of its trimer, hexahydro-1,3,5-trimethyl-*s*-triazine. The structure of (**7**) is based on its i.r. and ^{1}H n.m.r. spectra and its decoupled and off-resonance ^{13}C n.m.r. spectra. Although only a single stereoisomer of (**7**) appeared to be present, no configurational assignment can be made on the basis of the available data.



(**8**)



(**9**)



(**10**)

The retro-ene reactions of β-hydroxyacetylenes and of prop-2-ynylic ethers are reported[5] to proceed at higher rates than those of their olefinic analogues, except in a few cases of steric inhibition.[6] Also, alkyl substitution at any internal carbon atom increases the reactivities of acetylenic as well as of olefinic substrates, while terminal substitution on the unsaturated bond decreases the reactivity.[5] The results of thermolyses of these amines closely parallel those observations. Thus, under similar conditions acetylenic substrates (**4**)—(**6**) reacted at higher rates than did olefinic amines (**1**)—(**3**). Methyl substituted substrates (**2**) and (**5**) reacted more rapidly than did (**1**) and (**4**) respectively, and with both (**3**) and (**6**) the ethyl group substituted on the terminus of the unsaturation had a detrimental effect on the retro-ene process. In the case of (**3**) the retro-ene reaction was hindered, either sterically or electronically, to the point where homolytic processes could compete with the normally favoured concerted hydrogen transfer to afford some low-molecular weight fragments. In the case of (**6**) the reaction took a completely different course; instead of the expected decrease in the rate of the retro-ene process, the observed reaction was quantitative under conditions much milder than those necessary for the retro-ene process, and even an attempted preparative g.l.c. purification led to partial transformation to (**7**).

The lower reactivities of the olefinic substrates were particularly noticeable at the lower temperature utilized for static thermolyses. At 240 °C compounds (**1**)—(**3**) gave virtually no observable reaction after 73 h, while (**4**) and (**5**) were converted into retro-ene products to the extent of 40 and 70% respectively. By contrast, the conversion of (**6**) into (**7**) was quantitative under these conditions, and even after only 16 h the conversion into (**7**) was already 70% complete.

The novel, facile conversion of (**6**) into (**7**) deserves further comment. Since catalysed processes appear unlikely under the variety of conditions utilized (flow and static systems, g.l.c.), an appealing alternative is the symmetry-allowed,[7] concerted, 8-electron [$_{\sigma}2_s + {}_{\pi}2_a + {}_{\pi}2_s + {}_{\sigma}2_s$] process depicted in (**8**), in which one acetylenic π-lobe participates in an antarafacial manner to provide the Möbius orbital interaction shown in (**9**). The resultant transition state is illustrated by (**10**). It is the unique cylindrical symmetry of the acetylenic π-system which permits the conformational orientation of a π-lobe such that its antarafacial participation becomes possible. While (**10**) requires considerable distortion from the linear ground-state acetylenic system, such distortions do not present an excessive energy demand.[8] This facile process is not explicable solely on the basis of hindrance of the competing retro-ene reaction by the terminal ethyl group, since the cyclization proceeds more rapidly than the retro-ene process observed in any of the other substrates utilized.

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References

1 For a review, see: S. J. Rhoads and N. R. Raulins, *Org. React.*, 1975, **22**, 1.

2 L. E. Overman and L. T. Mendelson, *J. Am. Chem. Soc.*, 1981, **103**, 5579.

3 For two reports proposing the intermediacy of such processes, see: R. L. Danheiser and D. J. Carini, *J. Org. Chem.*, 1980, **45**, 3925; A. Maujean, G. Marcy, and J. Chuche, *Tetrahedron Lett.*, 1980, **21**, 519.

4 H. Wille and J. Goubeau, *Chem. Ber.*, 1972, **105**, 2166.

5 A. Viola, J. J. Collins, and N. Filipp, *Tetrahedron*, 1981, **22**, 3768, 3771.

6 A. Viola and J. J. Collins, *J. Chem. Soc., Chem. Commun.*, 1980, 1247.

7 R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, 1969, **8**, 781.

8 A. Viola, J. H. MacMillan, R. J. Proverb, and B. L. Yates, *J. Am. Chem. Soc.*, 1971, **93**, 6967; D. B. Bigley and R. H. Weatherhead, *J. Chem. Soc., Perkin Trans. 2*, 1976, 592.