Intramolecular Cycloaddition of (Allylimino)ketens: Access to 3-Azabicyclo-[3.2.0]hept-2-en-7-ones

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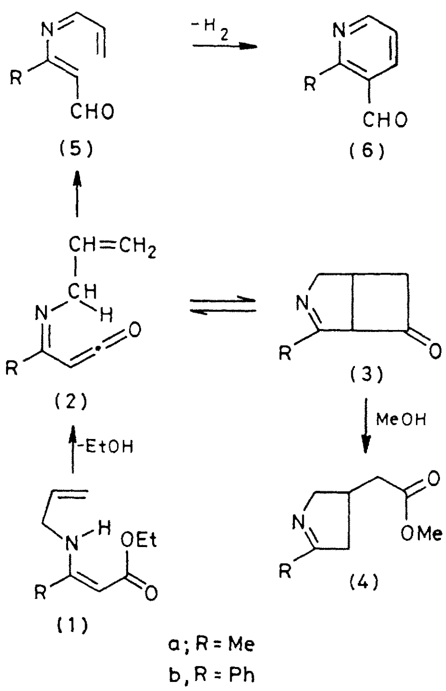
Summary Pyrolysis of the enamino esters (**1 a**,**b**) leads to the (allylimino)keten intermediates (**2 a**,**b**) which by cycloaddition and 1,5-sigmatropic hydrogen shift are converted into the new bicyclic heterocycles (**3 a**,**b**), respectively, and, *via* the azatrienals (**5**), to the formylpyridines (**6 a**,**b**).

LITTLE attention has been paid to the use of iminoketens as synthetic intermediates. We have recently reported the formation of these derivatives from *N*-alkyl enamino esters and their easy isomerization to azadienals by a 1,5-sigmatropic hydrogen shift.[1] In an extension of this work, we have now found that *N*-allyl enamino esters give thermal intramolecular cycloadducts which prove the intermediacy of (allylimino)ketens and allow access to new bicyclic heterocycles

When a carbon tetrachloride solution of (**1a**) was subjected to flow pyrolysis (400 °C, 15 Torr), 2-methyl-3-azabicyclo[3 2 0]hept-2-en-7-one (**3a**) was formed [46% yield based on 89% of pyrolysed (**1a**)] accompanied by (**6a**) in 10% yield Similarly, (**1b**) afforded (**3b**) [45% yield based on 88% of pyrolysed (**1b**)] and trace amounts of (**6b**) The compounds (**1a,b**) were characterized by i r and ^{1}H n m r spectroscopy as (**3a**) and (**3b**) (**3a**), ν_{max} 1790 and 1642 cm^{-1}, δ ($CDCl_3$) 2 10 (m, Me), 3 00 (m, 5-H and 6-H_2) 4 15 (m, H-H_2), and 4·45 (m, 1-H), (**3b**), ν_{max} 1770 and 1600 cm^{-1}, δ ($CDCl_3$) 3 10 (m, 5-H and 6-H_2), 4 30 (m, 4-H_2), and 4 90 (m 1-*H*)



The bicyclic compounds (**3a,b**) are easily opened by hydroxylic solvents at room temperature Treatment with methanol yields the Δ^1-pyrroline esters (**4a**) (56%) and (**4b**) (51%) the structures of which have been assigned by comparison of their ^{1}H chemical shifts with those of known Δ^1-pyrrolines [2] This behaviour is similar to that observed for bicyclo-[3 2 0]hept-4-en-7-one[3] and thus confirms the assigned structures (**3a,b**)

At higher temperatures (450—470 °C) only the pyridine derivatives (**6 a**,[4]**b**) are formed, in very low yields (10—20%), ^{1}H n m r † ($CDCl_3$) (**6a**) δ 2·82 (s, 3H), 7 3 (m, 1H), 8 05 (dd, 1H, *J* 1 5 and 7·5 Hz), 8 3 (dd, 1H, *J* 2 and 5 Hz), and 10 3 (s, 1H) (**6b**) δ 7 40 (m, 6H), 8 33 (dd, 1H, *J* 1 and 8 Hz), 8 90 (dd, 1H, *J* 1 and 5 Hz), and 10 05 (s, 1H) Dihydropyridines arising from the electrocyclisation of (**5 a,b**) were not detected ‡

It appears that the initial iminoketens (**2 a,b**) obtained from (**1 a,b**) may undergo either intramolecular [$_\pi2_s + _\pi2_a$] cycloaddition[5] or a 1,5 hydrogen shift to give the hexatrienals (**5 a,b**) followed by electrocyclisation to (**6 a,b**) The first reaction is favoured at 'low' temperatures and the formation of (**3 a,b**) is reversible since these compounds give (**6 a,b**) when they are pyrolysed at higher temperatures It is likely that the intramolecular [$_\pi2_s + _\pi4_s$] cycloaddition[1] is affected by steric interactions, this possibility is presently being tested with a longer ethylenic chain

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† Similar chemical shifts and coupling constants have been observed for 3-formylpyridine [The Aldrich Library of N M R Spectra 1974-9-40 (Spectrum A)]

‡ Evidence for an intramolecular [1,5] shift of a formyl group was not found (see P Schiess, P Funfschilling, *Tetrahedron Letters*, 1972, 5191)

[1] A Maujean, G Marcy, and J Chuche, submitted for publication

[2] J I Seeman, *Synthesis*, 1977, **7**, 498

[3] J J Beereboom, *J Amer Chem Soc*, 1963 **85** 3525

[4] E B Sanders H V Secor, and J I Seeman *J Org Chem* 1976 **41**, 2658

[5] I Fleming, 'Frontier Orbitals and Organic Chemical Reactions,' Wiley-Interscience, London, 1976, 143