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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



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on 88% of pyrolysed (1b)] and trace amounts of (6b) The compounds (1a, b) were characterized by 1 r and ¹H n m r spectroscopy as (3a) and (3b) (3a), v_{max} 1790 and 1642 cm⁻¹, δ (CDCl₃) 2 10 (m, Me), 3 00 (m, 5-H and 6-H₂) 4 15 (m, H-H₂), and 4·45 (m, 1-H), (**3b**), ν_{max} 1770 and 1600 cm⁻¹, δ (CDCl₃) 3 10 (m, 5-H and 6-H₂), 4 30 (m, 4-H₂), 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) $(51^{\circ}_{/\circ})$ the structures of which have been assigned by comparison of their ¹H chemical shifts with those of known $\hat{\Delta}^1$ -pyrrolines ² This behaviour is similar to that observed for bicyclo-[3 2 0]hept-4-en-7-one3 and thus confirms the assigned structures (3a, b)

At higher temperatures (450-470 °C) only the pyridine derivatives (6 a, b) are formed, in very low yields (10-20%), ¹H n m r † (CDCl₃) (**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 immoketens (2 a, b) obtained from (1 a, b) may undergo either intramolecular $[\pi 2_s + \pi 2_a]$ cycloaddition⁵ 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 $[\pi 2_s + \pi 4_s]$ cycloaddition¹ 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 NMR Spectra 1974-9-40 (Spectrum A)]

t 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