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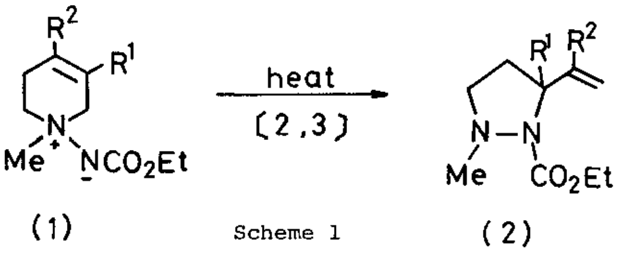
THERMAL REARRANGEMENTS OF 4- AND 6-VINYL-1,2,5,6-TETRAHYDROPYRIDINE AND 2-VINYLPIPERIDINE N-IMIDES

Takashi Tsuchiya* and Haruki Sashida

School of Pharmacy, Hokuriku University, Kanagawa-machi,
Kanazawa 920-11, Japan

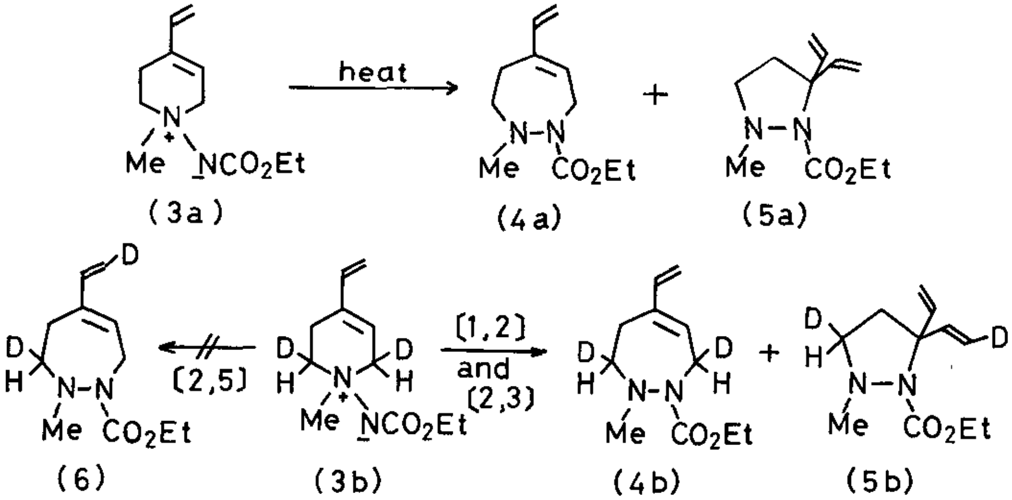
Abstract —— The thermolysis of the 4-vinyl-1,2,5,6-tetrahydropyridine N-imide (3) resulted in both [1,2]- and [2,3]-sigmatropic rearrangement to give the diazepine (4) and the pyrazole (5), respectively. This reaction mechanism was confirmed by a deuterium-labelling experiment. Whereas, in the thermolysis of the 2-vinyl derivatives (7 and 12), the [2,3]-rearrangement took place preferentially with the vinyl group to give the ring-expansion products (8 and 13).

In connection with the thermal rearrangements of various types of nitrogen[1-3] and sulfur[4,5] ylides, we were interested in examining such reaction of unsaturated cyclic amine N-imides, and already reported[6] that the thermolysis of the 1,2,5,6-tetrahydropyridine N-imides (1) resulted in the [2,3]-sigmatropic rearrangement to give the 3-vinyltetrahydropyrazoles (2). We report here the results of the thermolysis of the title cyclic amine N-imides (3, 7, and 12), which were expected to undergo different types of rearrangements from that observed for 1 because of the presence of the vinyl group.



Scheme 1

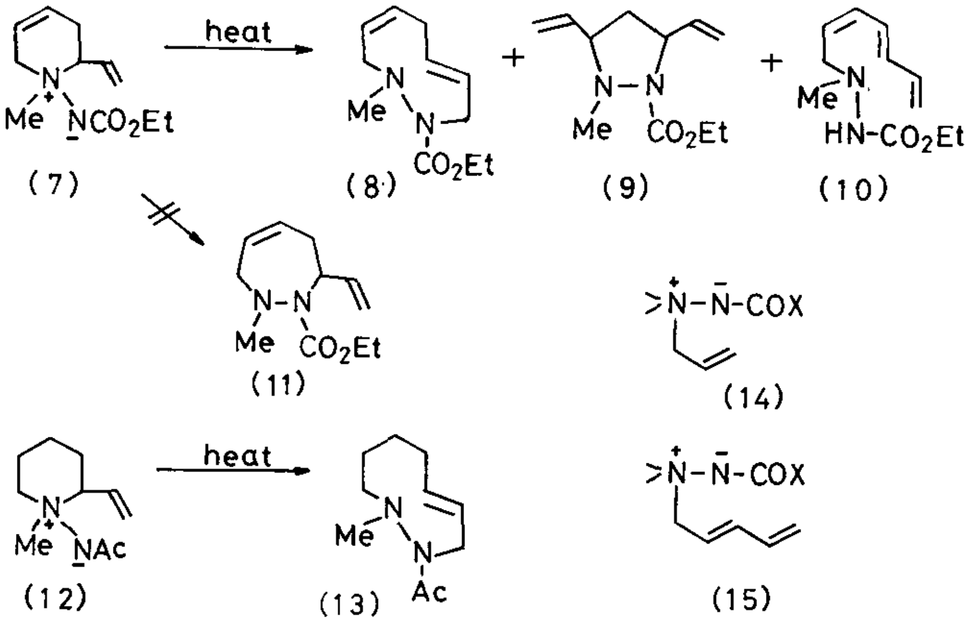
Thermolysis of the 4-vinyl-1,2,5,6-tetrahydropyridine N-imide (3a)[7] in xylene at 130-140 °C for *ca.* 6 hr and chromatography on silica gel gave the 5-vinyl-1,2,5,6-tetrahydro-1,2-diazepine (4a: 25%) and the 3,3-divinyltetrahydropyrazole (5a: 30%).[8] The formation of the ring-contraction product (5a) may involve a [2,3]-rearrangement occurred with the double bond in the ring by analogy with the case of 1.[6] However, two possible mechanisms; i.e., [1,2]- and [2,5]-rearrangements, have been considered for the formation of the ring-expansion product (4a). Therefore, the following deuterium-labelling experiment was carried out in order to clarify this mechanism.



Scheme 2

Thermolysis of the deuteriated N-imide (3b), prepared from 4-vinyl-N-ethoxycarbonyliminopyridinium ylide by successive $NaBD_4$ reduction, N-methylation, and base treatment in the manner described for 4a, yielded the labelled products (4b) and (5b), but no [2,5]-rearrangement product (6) as shown in Scheme 2.[9] This result clearly indicates that the formation of the diazepine (4) from 3 proceeds through a Stevens-type [1,2]-rearrangement and not [2,5]-rearrangement with the vinyl group.

Next, thermolysis of the 6-vinyl N-imide (7)[10] in refluxing xylene gave the 1,2-diazacyclononadiene (8: 20-25%),[11] the 3,5-divinyltetrahydropyrazole (9: *ca.* 1%), and the heptatrienyl hydrazine (10: 5-6%). The reaction of 7 may involve



Scheme 3

two different [2,3]-rearrangements to give 8 and 9, and a Hofmann-type cyclic elimination to give 11. This result shows that the [2,3]-rearrangement with the vinyl group predominates over that with the cyclic double bond. In this case, [1,2]-rearrangement products such as the 1,2-diazepine (11) could not be isolated.

Finally, the 2-vinylpiperidine N-imide (12) was heated to give the [2,3]-rearrangement product (13)[11] in 75-80% yield as the sole product, analogous for the 2-vinyl derivatives of thiane[5], and to give no [1,2]-rearrangement product.

Many studies on thermal reactions of the open chain allylic ylides (14) have shown that the [2,3]-rearrangement predominates over the [1,2]-rearrangement.[2,3] Whereas, the pentadienyl ylides (15) are known to undergo the [1,2]- and the [2,5]-rearrangement predominantly.[3] The results of the thermolysis of 7 and 12 are consistent with those of the ylides (14). However, the thermal behaviour of 3 is somewhat different from that of the open chain pentadienyl ylides (15), presumably because of steric effects. Studies on the detailed mechanisms and synthetic applications of the present results to other systems are under investigation.

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References and Footnotes

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7) The N-imide (**3a**: colorless viscous oil) was prepared from 4-vinylpyridine by successive N-amination by O-mesitylenesulfonylhydroxylamine, ethoxycarbonylation by ethyl chloroformate, $NaBH_4$ reduction, N-methylation by methyl iodide, and treatment with K_2CO_3. Satisfactory elemental analyses and spectral data (mass, n.m.r., and i.r.) were obtained for all new compounds reported herein.

8) **4a**: yellow oil, ν($CHCl_3$) 1690 cm^{-1}; δ($CDCl_3$) 4.10 (2H, m, 2-H_2), 5.74 (1H, m, 3-H), 2.50 (2H, m, 5-H_2), 3.10 (2H, m, 6-H_2), [3.75 (1H, dd, J=15 and 8 Hz), 4.95 (1H, d, J=8 Hz), 5.14 (1H, d, J=15 Hz), 4-CH=CH_2], 2.60 (3H, s, N-Me), [1.30 (3H, t) and 4.20 (2H, q), CO_2Et]. **5a**: yellow oil; ν($CHCl_3$) 1700 cm^{-1}; δ ($CDCl_3$) 2.30 (2H, t, 4-H_2), 3.09 (2H, t, 5-H_2), [6.16 (2H, dd, J=10 and 16 Hz), 5.16 (2H, d, J=16 Hz), 5.19 (2H, d, J=10 Hz), 2(3-CH=CH_2)], 2.61 (3H, s, N-Me), [1.28 (3H,t) and 4.20 (2H, q), CO_2Et].

9) The labelled compounds (**3b**, **4b**, and **5b**) were characterized by ^{1}H n.m.r. and mass spectroscopy.

10) The compound (**7**) was prepared from 2-vinylpyridine by the similar procedures described for 3.

11) The 9-membered ring compounds (**8** and **13**: colorless oil) are mixtures of conformational isomers on the n.m.r. spectra.

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