HETEROCYCLES, Vol. 14, No. 12, 1980

THERMAL REARRANGEMENT OF 2-VINYLPIPERIDINE AND 6-VINYL-1,2,5,6-TETRAHYDROPYRIDINE N-OXIDES: FORMATION OF 1,2-OXAZEPINE DERIVATIVES

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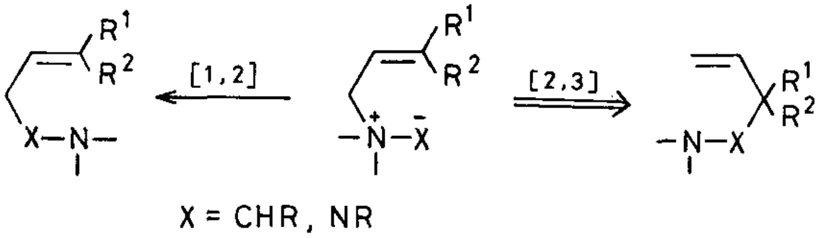
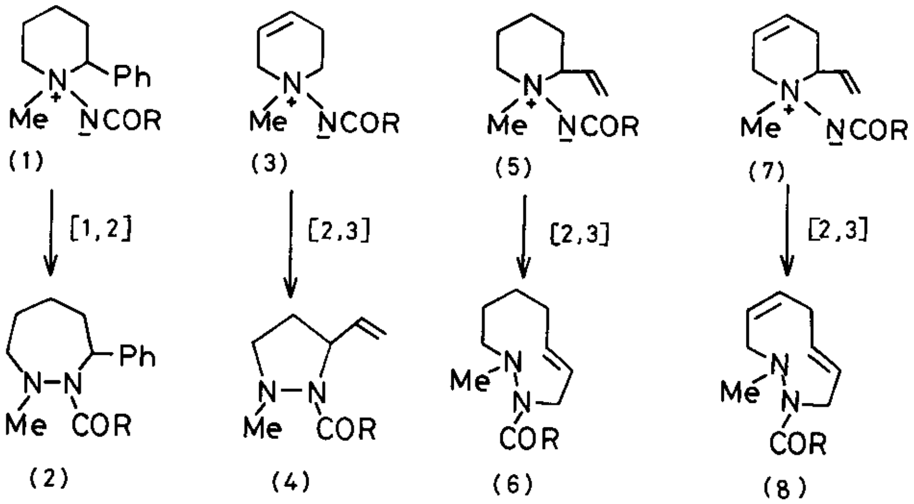
Abstract —— The thermolysis of both 2-vinyl piperidine N-oxides (9 and 12) and 1,2,5,6-tetrahydropyridine N-oxides (15) resulted in the Meisenheimer-type [1,2] rearrangement to give the corresponding 1,2-oxazepine derivatives (10, 13, 16, and 17). In the thermolysis, the involvement of [2,3]-sigmatropic rearrangement could not be observed in contrast to the cases of the analogous cyclic amine N-imides (3, 5, and 7).

Thermal reactions of aminimides have been well documented[1] and allyl-N-acylammonium ylides are known to undergo competing [1,2]- and [2,3]-sigmatropic rearrangements to give the corresponding products in a ratio that depends upon the ylide structure and the reaction conditions (Scheme 1).[2] On the other hand, the piperidine N-imide (1)[3] undergoes the Stevens-type [1,2] rearrangement to give the ring expansion product (2), whereas both β,γ-unsaturated six-membered cyclic amine N-imides (3)[4] and (5)[5] undergo the [2,3]-sigmatropic rearrangement



Scheme 1



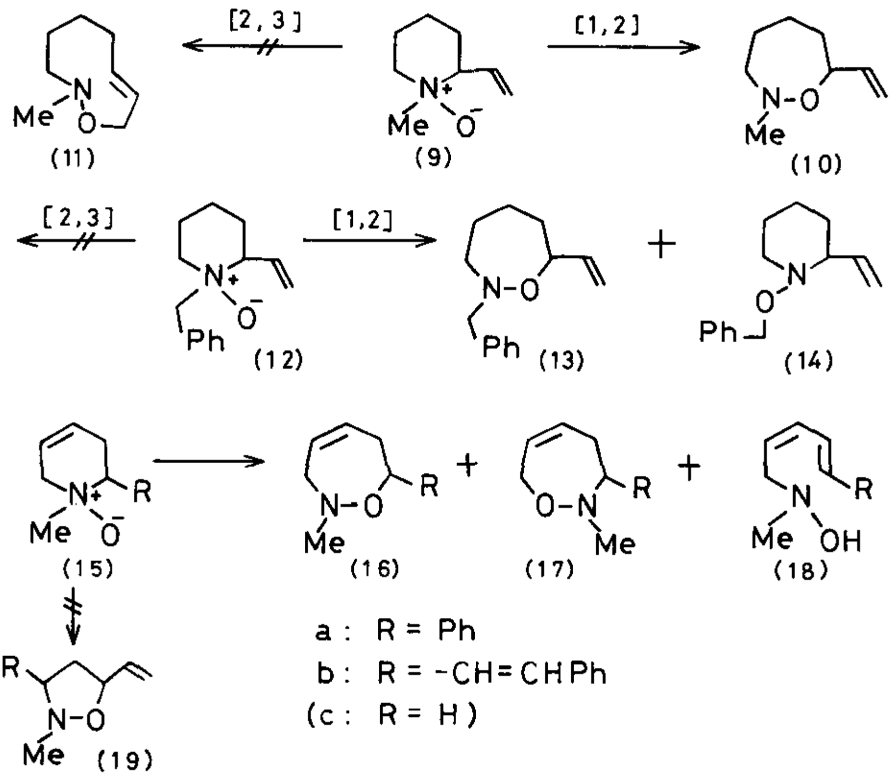
Scheme 2

with the double bonds to give the corresponding products (4) and (6). We have also reported that the [2,3] rearrangement with the vinyl group predominates over that with the cyclic double bond to give the tetrahydrodiazonine (8) in the thermolysis of the N-imide (7).[5]

In connection with these results and the rearrangements of open-chain allylamine N-oxides,[6] we were interested in examining the thermal behavior of the title cyclic amine N-oxides and present here the formation of novel tetra- and pentahydro-1,2-oxazepine derivatives by the Meisenheimer-type [1,2] rearrangement in contrast to the cases of the N-imides (3, 5, and 7).

Thermolysis of 1-methyl-2-vinylpiperidine 1-oxide (9) in toluene at 110 °C for ca. 1 hr resulted in the Meisenheimer-type [1,2] rearrangement to give the hexahydro-1,2-oxazepine (10) in 40-45% yield as the sole product.[7] In the reaction, the expected [2,3] rearrangement product, oxazonine derivative (11), could not be isolated. Heating of the benzyl derivative (12) under the same conditions gave the oxazepine derivative (13: 20%) and the N-benzyloxypiperidine (14: 55%). This result clearly indicates that the [1,2] rearrangement takes place to either carbon having vinyl or phenyl group and the latter predominates.

Next, thermolysis of the 1,2,5,6-tetrahydropyridine N-oxides (15a,b) gave the tetrahydrooxazepines (16: a, 12%; b, 10%) and (17: a, 15%; b, trace), and the Hofmann-type cyclic elimination products (18: a, 30%; b, 53%). However, the



Scheme 3

formation of the [2,3] rearrangement product, isoxazole derivative (19), was not observed. In addition, the N-oxide (15c) having no substituent in the 2-position gave only the elimination product (18c) and did not give any rearrangement product. The result of the thermolysis of 15a,b also shows that the [1,2] rearrangement occurs to either side of the tetrahydropyridine ring , however the expected [2,3] rearrangement does not occur either with the double bond in the ring or with the 2-vinyl group.

It is already known that allyl[6] and prop-2-ynyl[8] amine N-oxides undergo preferentially the [2,3]-sigmatropic rearrangement analogous to those observed for open-chain allylamine N-imides.[2] However, the thermal behavior of the present cyclic amine N-oxides (9, 12, and 15) is different from those of the open-chain amine N-oxides and the analogous cyclic amine N-imides (3, 5, and 7). Studies on the detailed mechanisms and synthetic applications of the present results to other systems are under investigation.

A part of this work was supported by a Grant-in-Aid for Special Project Research from the Ministry of Education, Science and Culture, Japan, which is gratefully acknowledged.

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Received, 31st July, 1980