THERMALLY INDUCED REARRANGEMENT OF 1,3-OXAZEPINES

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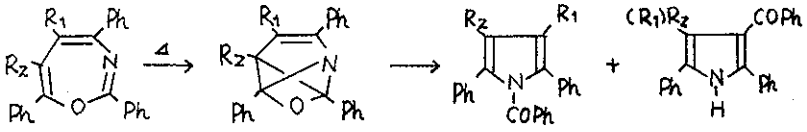
In 1975, we proposed that 2-phenyl-1,3-oxazepine, upon pyrolysis at 450° in vapor phase, underwent a deep-seated rearrangement leading to N-formyl-2-phenylpyrrole and 2-phenyl-3-hydroxypyridine as primary products. The formation of the latter could be reasonably explained by the intermediacy of 1-phenyl-2-aza-7-oxabicyclo[4.1.0]hepta-2,4-diene. On the other hand, 3-(3-phenyl-2H-azirinyl)acrolein has been proposed as a key intermediate for the formation of N-formyl-2-phenylpyrrole. However, some ambiguities remained how the azirinylacrolein was derived from 2-phenyl-1,3-oxazepine.

In order to verify this proposal, we re-examined the reaction path from the 1,3-oxazepine to the N-formylpyrrole using various substituted 1,3-oxazepines. At first, we have chosen 2,4,5,7- and 2,4,6,7-tetraphenyl-1,3-oxazepines as convenient model compounds for the mechanistic studies, and obtained N-benzoyl-2,3,5-triphenylpyrrole and 3-benzoyl-2,4,5-triphenylpyrrole in almost the same ratio in both cases. Futhermore, an easy conversion of N-formyl-2,3,5-triphenylpyrrole to the corresponding 3-benzoyl derivative, namely, benzoyl migration, is also established under the same conditions (450°, v.p.). This rearrangement can not be explained by the intermediacy of triphenyl-substituted azirinylstyrylketone unless a benzoyl migration on the pyrrole ring occurs. An attractive pathway to explain this fact is that proceeding via cross-linked structure shown below.



R_1 or R_2 = Ph or H

To prove the assumption of such a cross-linked structure, additional pyrolysis experiments have been carried out using 2-cyano-, 2-phenylbenzo[d]1,3-oxazepines, and 2-cyanobenz[f]1,3-oxazepine. Pyrolyses of benzo[d]-derivatives provide the rearranged products such as indole and 3-hydroxyquinoline derivatives. Contrary to this, benzo[f]-derivative is completely recovered under the same pyrolysing conditions. These observations might be accomodated in terms of the stability of the corresponding cross-linked structures formed from each reactant.