THERMAL AND PHOTOCHEMICAL REACTIONS OF BICYCLO[3.2.0]-HEPTADIENES CONTAINING C=N-O GROUP

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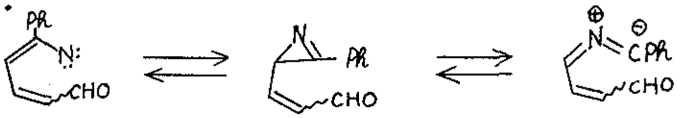
In 1973, we reported a novel photochemical transformation of 4-phenyl-2,3-oxazabicyclo[3.2.0]heptadiene (I) into 2-phenyl-1,3-oxazepine(II). In order to account for this intriguing rearrangement, 3-phenyl-2-(β-formylvinyl)-2H-azirine(III) was postulated as an intermediate. However, very recently Padwa et al. have argued for the intermediacy of III. In view of increasing interest of chemistry of III, we investigated the thermal and photochemical reactions of I and its isomer or 3-phenyl-2,4-oxazabicyclo[3.2.0]heptadiene(IV).

Pyrolysis of I at 450 or 550°C by means of the flow method afforded several pyrrole derivatives such as N-formyl-2-phenylpyrrole(V), 2-formyl-5-phenylpyrrole(VI), 4-formyl-2-phenylpyrrole(VII) and 2-phenylpyrrole(VIII) in addition to 6-phenyl-2-pyridone(IX). The same pyrrole derivatives were also formed in addition to 2-phenyl-3-hydroxypyridine by pyrolysis of IV. It was found that the relative yield of these pyrrole derivatives observed by the pyrolysis of both I and IV was the same , suggesting that a common intermediate may be involved in both reactions. Some additional experiments showed that VI, VII and VIII arose from V, and that V may be derived from 3-phenyl-1,2-oxazepine(X) and/or II which were formed from I and/or IV by the thermally induced cyclobutene ring opening, respectively. Based on some experimental evidence, azirine(III) or its isomeric nitrene(XI) was postulated as an intermediate to account for the thermal rearrangement of I and IV into V via X and II, respectively.

In contrast to the fact that I converted to II by photolysis with light of 2500 Å, photolysis of I with light longer than 3000 Å afforded VII and 3-formyl-2-phenylpyrrole (XII) in addition to a small amount of II and IV. The formation of VII and XII from I may also be explain by assuming III or its isomeric ylide(XIII) as an intermediate. On the other hand, irradiation of IV with light of 2500 Å resulted in the formation of its valence isomer(II).



XI III XIII