Effect of Spiro-ring Size on the Photolysis of Dispiro-substituted 3-Iminocyclobutanones

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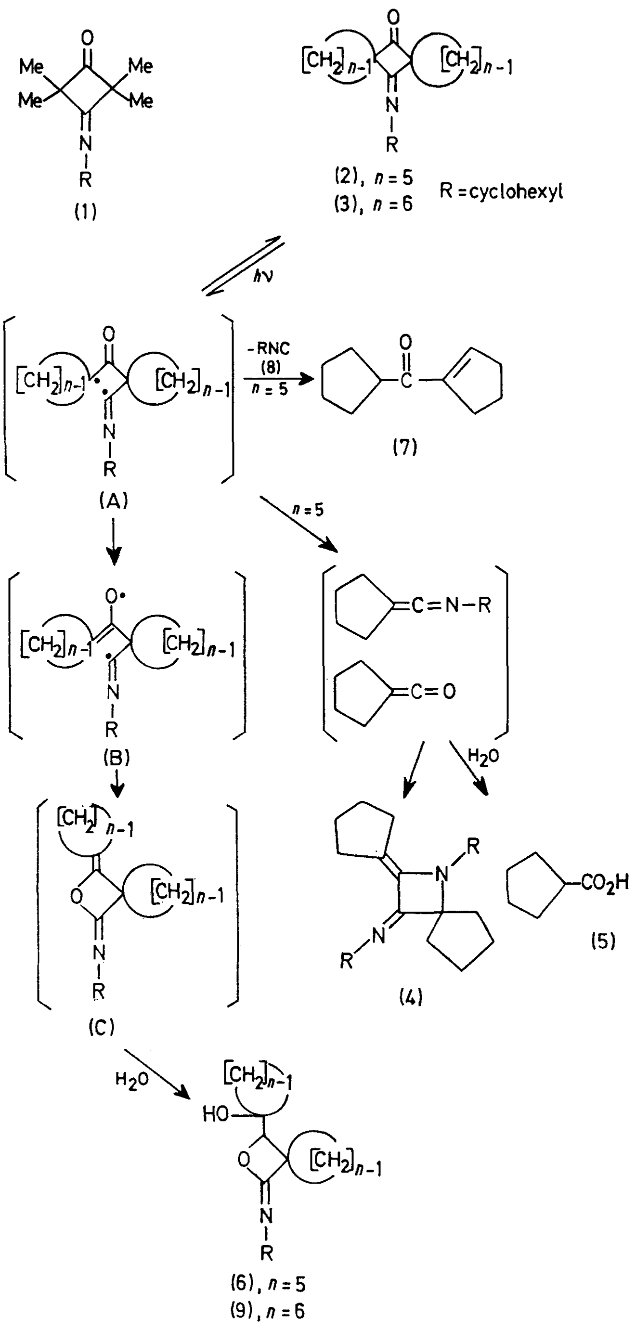
Summary The spiro-ring size markedly affects the products formed in photolyses of dispiro-substituted 3-iminocyclobutanones.

While the principal pathway in the photochemical reaction of the tetramethyl 3-iminocyclobutanones (**1**) and of cyclobutanones[1] is ring expansion *via* a cyclic oxacarbene,[2] (**1**)



has also been reported to undergo a photoextrusion reaction at 254 nm leading to the formation of isocyanides.[3] In previous papers,[4] we pointed out that the photochemical process of dispiro-substituted cyclobutanones (of cyclobutane-1,3-diones in particular) was dependent on the spiro-ring size of the substrate. Here we report the prominent effect of spiro-ring size on the photolysis of dispiro-substituted 3-iminocyclobutanones at longer wavelengths.[†]

Irradiation of both the dispiro-compounds (**2**) and (**3**) in methanol led to the formation of the corresponding ring-expanded acetals in good yields. On the other hand, marked differences were observed in the photolytic behaviour of (**2**) and (**3**) when the reactions were carried out in ether. When (**2**) was irradiated in ether in a Pyrex vessel at −70 °C for 3 h, β-cleavage took place to afford mainly the keten imine dimer (**4**) (62%)[‡] and tetramethyleneketen, which was characterised as cyclopentanecarboxylic acid (**5**) (50%). In addition, cyclopentenyl cyclopentyl ketone (**7**) (7%) and cyclohexyl isocyanide (**8**),[§] derived from the photoextrusion reaction of the isocyanide, were obtained as minor products along with a small amount of the imino-oxetan (**6**).

In contrast, irradiation of (**3**) under similar conditions gave the imino-oxetan (**9**) (84%)[¶] as the major product and the keten imine dimer was not formed. A trace of (**8**) was detected, however.

This remarkable effect of the spiro-ring size may be interpreted in terms of the stability of the 1,4-biradical intermediate derived from α-cleavage on the imino-group side of the molecule. In the case of (**3**), an intermediate biradical (A) comprised of an unstable cyclohexyl radical would isomerize instantly to a more stable isomeric biradical (B), which would be followed by ring closure to give cyclohexylidene imino-oxetan (C) which would add water to form (**9**). In the case of (**2**), on the other hand, an intermediate biradical (A) comprised of a more stable cyclopentyl radical would decompose directly to form both tetramethyleneketen and the keten imine which would readily dimerize to form (**4**).[**]

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[†] The absorption maxima at 317 (ϵ 31) or 314 (ϵ 24) and 326 (ϵ 25) nm in the u.v. spectrum of (**2**) or (**3**) in methanol suggest that the mixing of carbonyl- and imino-orbitals occurs albeit with relative inefficiency.

[‡] All new compounds were characterised by spectral properties (n.m.r., i.r., and mass) and elemental analyses.

[§] Cyclohexyl isocyanide (**8**) could not be quantified.

[¶] In the cases of both (**3**) in furan and (**1**) in ether, the corresponding imino-oxetans were formed preferentially.

[**] Concerning the formation of (**4**) and (**5**), the possibility of α-cleavage on the carbonyl group side of the molecule cannot be ruled out.

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[3] K. G. Srinivasan and J. H. Boyer, *J.C.S. Chem. Comm.*, 1974, 379.
[4] K. Kimura, M. Takamura, A. Kunai, and Y. Odaira, *J.C.S. Chem. Comm.*, 1974, 685; K. Kimura, S. Koshibe, M. Juro, Y. Fukuda, and Y. Odaira, *Bull. Chem. Soc. Japan*, 1976, **49**, 741.