

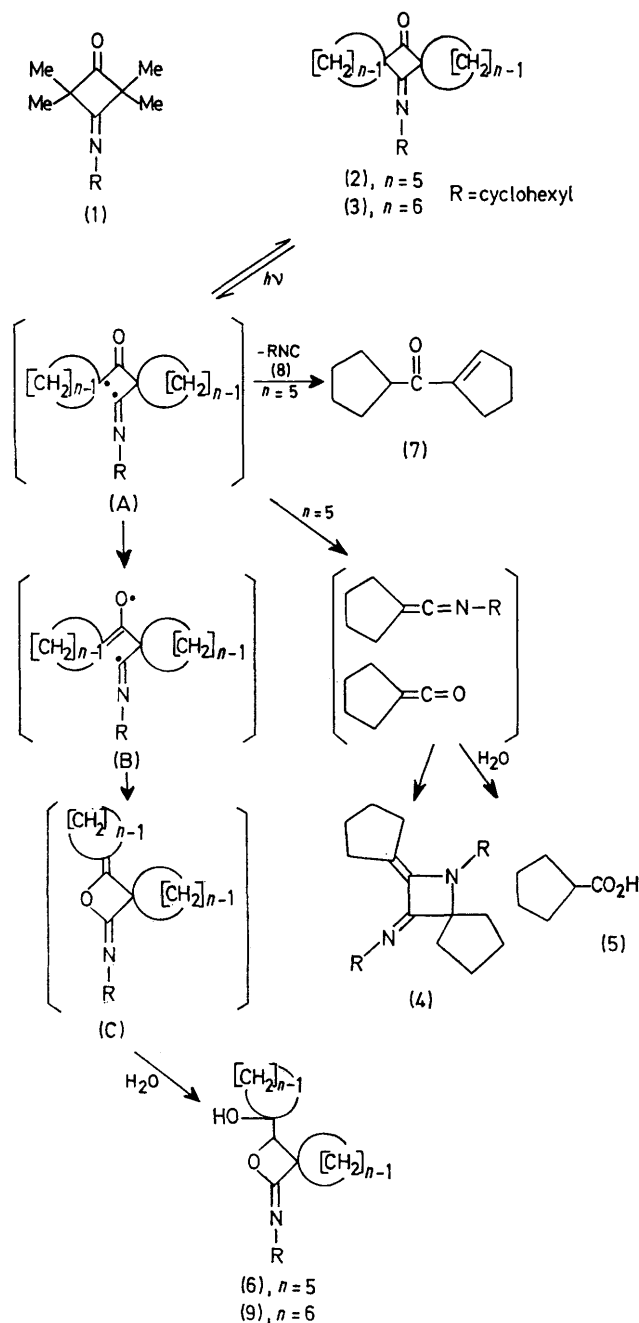
## Effect of Spiro-ring Size on the Photolysis of Dispiro-substituted 3-Iminocyclobutanones

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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<sup>1</sup> is ring expansion *via* a cyclic oxacarbene,<sup>2</sup> (**1**)



has also been reported to undergo a photoextrusion reaction at 254 nm leading to the formation of isocyanides.<sup>3</sup> In previous papers,<sup>4</sup> 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.<sup>†</sup>

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  $-70^{\circ}\text{C}$  for 3 h,  $\beta$ -cleavage took place to afford mainly the keten imine dimer (4) (62%)<sup>‡</sup> and tetramethyleneketene, which was characterised as cyclopentanecarboxylic acid (5) (50%). In addition, cyclopentenyl cyclohexyl 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%)<sup>¶</sup> 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  $\alpha$ -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 cyclopentenyl radical would decompose directly to form both tetramethyleneketene and the keten imine which would readily dimerize to form (4).\*

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<sup>†</sup> The absorption maxima at 317 ( $\epsilon$  31) or 314 ( $\epsilon$  24) and 326 ( $\epsilon$  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.

<sup>‡</sup> 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  $\alpha$ -cleavage on the carbonyl group side of the molecule cannot be ruled out.

<sup>1</sup> P. Yates and R. O. Loutfy, *Accounts Chem. Res.*, 1975, **8**, 209, and references therein.

<sup>2</sup> H. U. Hostettler, *Helv. Chim. Acta*, 1966, **49**, 2417.

<sup>3</sup> K. G. Srinivasan and J. H. Boyer, *J.C.S. Chem. Comm.*, 1974, 379.

<sup>4</sup> 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.