

Pyrolysis of 3-Azidoazetidiones: A New Route to Δ^3 -Imidazolin-2-one

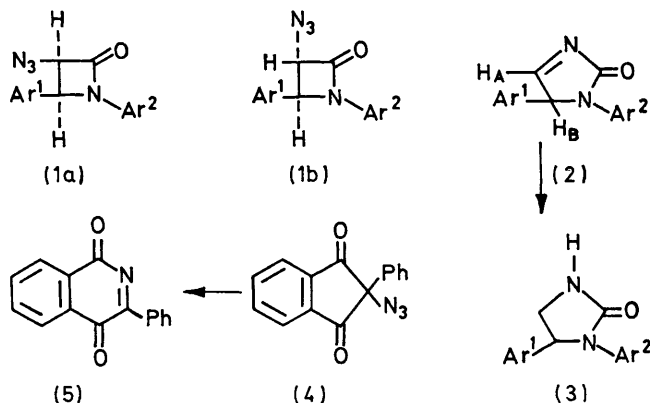
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Summary Pyrolysis of the *cis*- or *trans*-isomers of various 3-azidoazetidiones occurs with evolution of nitrogen and ring expansion to give diaryl- Δ^3 -imidazolin-2-ones.

Pyrolysis of the 3-azidoazetidione (**1a** or **1b**; Ar¹ = Ar² = Ph) obtained by a reported method¹ in boiling chlorobenzene occurred very slowly, but under reflux in diglyme evolution of nitrogen was complete in 1 h. On cooling Δ^3 -imidazolin-2-one (**2**; Ar¹ = Ar² = Ph), m.p. 140° separated in 70% yield. Its structure was supported by chemical and spectral evidence as follows: reduction under pressure (Pd-C; H₂; room temp.) of its methanolic solution gave phenylurea which is probably derived from the intermediate imidazolidinone (**3**; Ar¹ = Ar² = Ph); this result is clearly indicative of the product (**2**); its i.r. spectrum showed bands at 1645 (C=N) and at 1720 cm⁻¹ (>C=O) while the azide band at 2100 and the β -lactam CO peak at 1760 cm⁻¹ observed in (**1**) had disappeared; a molecular ion peak (M⁺ 236) and a breakdown pattern similar to that of the starting azide (**1**) after loss of nitrogen (M-28) were observed. The similarity in the fragmentation patterns of product and starting material is undoubtedly due to the fact that the azide (**1**) loses nitrogen and then rearranges into product (**2**). The n.m.r. spectrum of the product showed resonances at τ 2.4-2.9 [11H, 10 ArH + H^B in (**2**)] and (on expansion) a quartet at τ 1.75 (H^A). Double irradiation at τ 2.48 (H^B) caused collapse of this signal to a singlet. The quartet is presumably due to coupling of H^A with H^B in a *cis* and *trans*-configuration, a situation also observed in the n.m.r. spectra of (**1a**) and (**1b**).

nitrene. While alkyl and aryl groups commonly migrate in the decomposition of alkyl azides² the only recorded case



of an acyl shift takes place in the recently reported decomposition of the 2-azido-2-phenylindanedione⁴ to give 2-aza-3-phenylnaphthaquinone (**4**) \rightarrow (**5**). Some examples of imidazolinone formation from azides (**1**) are given in the Table.

Photolysis of the azido-lactams (**1**) over prolonged periods in various solvents with or without sensitizers was completely abortive.

Decomposition of the azides (**1**) in hot ethanol in presence of copper yielded the corresponding amines (**1**; NH₂ replaces N₃).

TABLE

Pyrolysis of 3-azido- β -lactams (**1**) in diglyme at 156° to give the imidazolinones (**2**)

Lactam (1)				Imidazolinone ^a (2)			
Ar ¹	Ar ²	Stereoisomer	M.p.	Ar ¹	Ar ²	Yield (%)	M.p.
Ph	Ph	<i>cis</i>	130°	Ph	Ph	70	140°
Ph	Ph	<i>trans</i>	82	Ph	Ph	20	140
<i>p</i> -ClC ₆ H ₄	<i>p</i> -MeOC ₆ H ₄ ^a	<i>cis</i>	128	<i>p</i> -ClC ₆ H ₄	<i>p</i> -MeOC ₆ H ₄	40	197

^a All new compounds gave satisfactory analyses and spectra.

The ring-expansion brought about by heating the azido- β -lactams is of preparative interest since it yields substituted imidazolinones of a type which is novel as far as we know. Moreover, the reaction occurs with acyl migration (from carbon to nitrogen) in an intermediate alkyl-

The scope of expansion of 4-membered rings by azide decomposition is under investigation.

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¹ A. K. Bose, B. Anjaneyulu, S. K. Bhattacharya, and M. S. Manhas, *Tetrahedron*, 1967, **23**, 4769.

² (a) F. D. Lewis and W. H. Saunders jun., in 'Nitrenes', ed. W. Lwowski, Interscience, New York, 1970, p. 47; (b) R. A. Abramovitch and E. P. Kyba, *J. Amer. Chem. Soc.*, 1971, **93**, 1537.

³ Ref. 2(a), p. 72.

⁴ H. W. Moore and D. S. Pearce, *Tetrahedron Letters*, 1971, 1621.