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

By J. S. MILLERSHIP and H. SUSCHITZKY*

(*Department of Chemistry and Applied Chemistry, University of Salford, Salford, Lancashire* M5 4WT)

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

PYROLYSIS of the 3-azidoazetidinone (**1a** or **1b**; $\mathrm{Ar}^1 = \mathrm{Ar}^2 = \mathrm{Ph}$) obtained by a reported method[1] 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**; $\mathrm{Ar}^1 = \mathrm{Ar}^2 = \mathrm{Ph}$), m.p. 140° separated in 70% yield. Its structure was supported by chemical and spectral evidence as follows: reduction under pressure (Pd–C; H_2; room temp.) of its methanolic solution gave phenylurea which is probably derived from the intermediate imidazolidinone (**3**; $\mathrm{Ar}^1 = \mathrm{Ar}^2 = \mathrm{Ph}$); 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**).

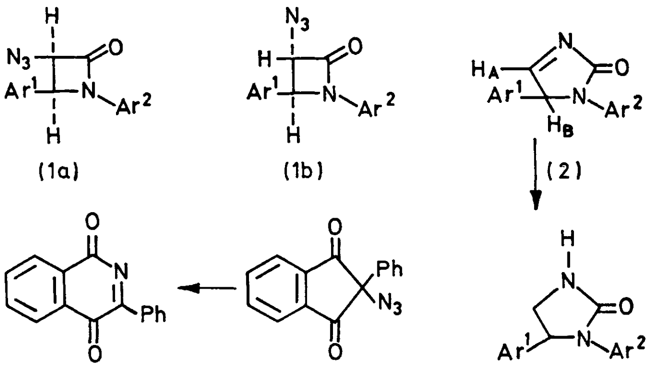
TABLE

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	*cis*	130°	Ph	Ph	70	140°
Ph	Ph	*trans*	82	Ph	Ph	20	140
p-$\mathrm{ClC_6H_4}$	p-$\mathrm{MeOC_6H_4}$[a]	*cis*	128	p-$\mathrm{ClC_6H_4}$	p-$\mathrm{MeOC_6H_4}$	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 alkylnitrene. While alkyl and aryl groups commonly migrate in the decomposition of alkyl azides[2] the only recorded case of an acyl shift takes place in the recently reported decomposition of the 2-azido-2-phenylindanedione[4] to give 2-aza-3-phenylnaphthaquinone (**4**) → (**5**). Some examples of imidazolinone formation from azides (**1**) are given in the Table.



(1a) (1b) (2) (5) (4) (3)

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**; NH_2 replaces N_3).

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

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