Thermal Decomposition of α-Lactams: a New Ring Expansion of an α-Lactam to a β-Lactam System

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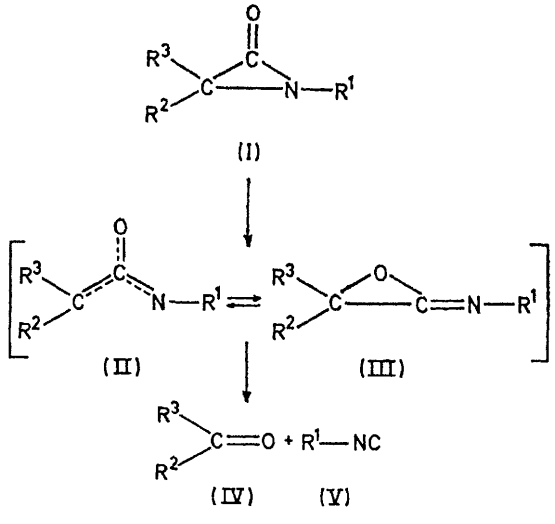
Summary The pyrolysis of 1,3-di-(1-adamantyl)aziridin-2-one in a sealed tube leads to a 4-iminoazetidin-2-one (VI) the structure of which is established by degradation as well as by an independent synthesis.

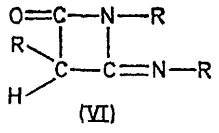
ALTHOUGH several α-lactams have been prepared, few reactions of these compounds have been studied in detail.[1] Among the unsuccessful reactions recorded are attempted ring expansions with diazomethane and dimethylsulphoxonium methylide.[1a] We now report a detailed study of the



a; $R^1 = R^2 =$ 1-adamantyl, $R^3 = H$
b; $R^1 = R^2 = Bu^t$, $R^3 = H$
c; $R^1 = Bu^t$, $R^2 = R^3 = Ph$

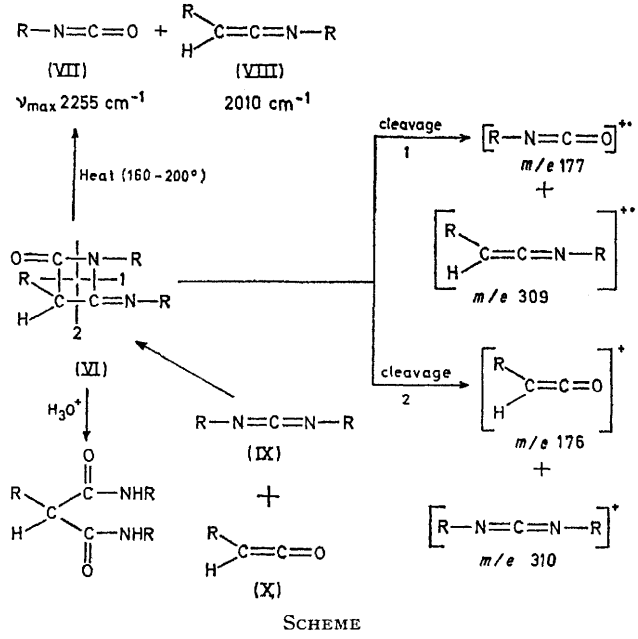
pyrolysis of 1,3-di-(1-adamantyl)aziridin-2-one (Ia) in a sealed tube and the isolation of a ring-expansion product.

Previous studies showed that the thermal decomposition of all α-lactams involves fragmentation to a carbonyl compound and an isocyanide,[1a,1b,2] presumably *via* (II)[1a,2b] and (III)[2] as intermediates. However, complex mixtures of additional, unidentified products have also been observed during the pyrolysis of (Ib) in a sealed tube[3] and the slow decomposition of (Ic).[1b] In order to resolve the nature of these complex mixtures, we have studied the pyrolysis of (Ia).



R = 1-adamantyl

When (Ia) was heated in a sealed tube for 3 h at 115—160°, the reaction mixture was complex in that its i.r. spectrum



SCHEME

(KBr) exhibited six bands in the region 1650—2150 cm^{-1}. Two of these bands (1720 and 2140 cm^{-1}) were assigned to (IVa)[4] and (Va),[5] the expected products, by comparison with authentic samples. Of the remaining four peaks, two (1675 and 1788 cm^{-1}) declined in intensity above 160°, while the other two (2010 and 2255 cm^{-1}) increased in intensity.

The major component was isolated by fractional crystallization from pentane; m.p. > 200° (decomp.); ν_{max} 1675s and 1788w, but no N–H absorption; τ 6·92 (1H, s), and 7·50—8·55 (45H, m); M^+ 486. Moreover, when equimolecular mixtures of (Ia) and (Va) were heated, the same product was produced (71% yield), but at temperatures well below 115°. This observation suggests that the compound is produced by cycloaddition of (Va) to either (Ia) or an isomer obtained by thermal rearrangement of (Ia), which may be the elusive imino-oxiran (IIIa).

We assign structure (VI) to the adduct because it is the only one that is consistent with the thermal, hydrolytic, and electron-impact induced cleavages shown in the Scheme, and because its m.p. and spectral characteristics are identical with those of an adduct which we have obtained, albeit in low yield (<20%), by the reaction of di-(1-adamantyl)carbodi-imide (IX) with a large excess of 1-adamantylketen (X).

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