The Synthesis and Spectral Properties of a New Stable α-Lactam: 1-(1-Adamantyl)-3-t-butylaziridinone

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α-LACTAMS represent the only class of three-membered heterocyclic carbonyl compounds that have been synthesized.[1] Though interest in these compounds has increased,[2] the number of pure α-lactams reported to date is modest. With the recent synthesis[3] of 1,3-di-t-butylaziridinone, it became evident that high chemical reactivity and low thermal stability are not inherent properties of this class of compounds. Indeed, by proper selection of the substituents,† α-lactams with remarkable stability can be prepared. Based on the observation[3] that tertiary substituents markedly enhance the stability of α-lactams, we synthesized 1-(1-adamantyl)-3-t-butylaziridinone and investigated its spectral properties. We found this compound to have a stability comparable to that of common γ- or δ-lactams.

t-Butylacetyl chloride (52 mmoles) was converted into 2-bromo-3,3-dimethylbutyryl chloride by refluxing with bromine (58 mmoles). This was then added, without further purification, to a mixture of 1-adamantanamine (60 mmoles) and triethylamine (60 mmoles) in dichloromethane at 0°. After 30 min., the solution was washed with 2N-hydrochloric acid, 10% aqueous sodium hydrogen carbonate, and water. Evaporation of the solvent gave, after recrystallization from dichloromethane, 2-bromo-3,3-dimethyl-*N*-adamantylbutyramide‡ (82%), m.p. 173—174°; i.r. (in CCl_4); 3400 (NH), 2900 (CH), 1675 (CO of amide), and 1510 (amide II) cm.$^{-1}$; n.m.r. (in CCl_4): δ 1·08 (s, 9H), 1·60—2·20 (m, 15H), and 3·80 p.p.m. (s, 1H); mass spectrum§ (70 ev): 327, 329 (molecular ion), 271, 273 ($M - C_4H_8$) 248 (M − Br) and 214, 216 ($M - C_4H_8 - C_4H_9$).

The α-bromo-amide (30 mmoles), in ice-cold ether suspension, was cyclized by the addition of potassium t-butoxide[4] (38 mmoles) to give a 65% yield of 1-(1-adamantyl)-3-t-butylaziridinone,† m.p. 79°. The remarkable thermal stability of this α-lactam is shown by the fact that complete decomposition in refluxing toluene occurred only after 90 hr. To complete solvolysis in refluxing methanol required 48 hr. The compound is stable to water and after 200 hr. in aqueous suspension at room temperature there was no detectable change. The i.r. spectrum exhibits the characteristic α-lactam carbonyl band at 1835 cm.$^{-1}$ (CCl_4) or 1830 cm.$^{-1}$ (KBr) and shows no NH type absorption in the 3400 cm.$^{-1}$ region. The n.m.r. spectrum shows the expected singlet for the t-butyl group at δ 0·93 p.p.m., the complex multiplet due to the adamantane protons at δ 1·5—2·3, and a singlet for the methine proton at δ 2·62. The aziridinone shows a maximum in the u.v.: λ_{max} (n-hexane) 254nm. (ϵ 188) and λ_{max} (EtOH) 245 mμ (ϵ 290). The hypsochromic shift observed by changing the solvent from n-hexane to

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† For a detailed discussion fo how substituents influence the stability of α-lactams see reference 1.

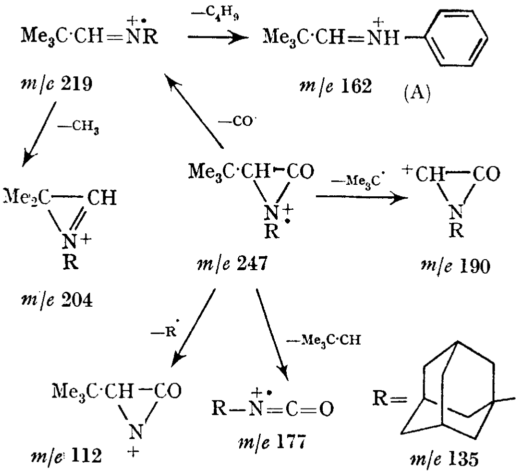
‡ Satisfactory elemental analyses were obtained for this compound.

§ The "low" resolution mass spectra were recorded on a CEC 21-103C instrument. High resolution data were obtained on a CEC 21-110B mass spectrometer using a direct probe, through the courtesy of Prof. K. Biemann, Department of Chemistry, Massachusetts Institute of Technology.

ethanol suggests an $n \rightarrow \pi^*$ transition. The major ions in the 70 ev mass spectrum are depicted in the Table. The primary step in the electron impact-induced fragmentation of this lactam is the ejection of carbon monoxide from the molecular ion.¶ This type of fragmentation is in sharp contrast with the thermal decomposition of α-lactams. The Scheme shows a partial fragmentation pattern of this compound. Unexpectedly, an $M + 1$ peak, proven to be genuine by pressure dependency, was noticed. Furthermore, abundant ions of type A were observed.[5]

TABLE

Nominal mass	Composition	Relative intensity (%)
57	C_4H_9	35
77	C_6H_5	15
93	C_7H_9	20
107	C_8H_{11}	18
112	$C_6H_{10}NO$	0·2
135	$C_{10}H_{15}$	100
161	$C_{10}H_{11}NO$	5
162	$C_{11}H_{16}N$	16
163	$C_{11}H_{15}O$	4
177	$C_{11}H_{15}NO$	10
190	$C_{12}H_{16}N$	0·5
204	$C_{14}H_{22}N$	17
219	$C_{15}H_{25}N$	18
247	$C_{16}H_{25}NO$	1
248	$C_{16}H_{26}NO$	2



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[1] The synthesis, chemical reactions, thermal decomposition products, and spectroscopic properties of α-lactams have been reviewed recently: I. Lengyel and J. C. Sheehan, *Angew. Chem.*, 1968, **80**, 27; *cf. Angew. Chem. Internat. Edn.*, 1968, **7**, 25.

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