α-Lactams. VI.[1] Photochemistry of α-Lactams[2]

John C. Sheehan[3] and M. Mehdi Nafissi-V.

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.
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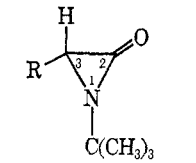
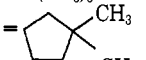
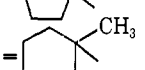
Abstract: Three α-lactams were found to possess a distinct absorption in the ultraviolet ($\lambda_{max}^{n\text{-hexane}}$ 250 mμ (ε ~10^2 l. mol^{-1} cm^{-1}), which exhibits a hypsochromic shift in going from *n*-hexane to ethanol as solvents. This type of absorption is characteristic of n → π* excitation. Irradiation of a pentane solution of 1,3-di-*t*-butylaziridinone (I), 1-*t*-butyl-3-(1-methylcyclopentyl)aziridinone (II), and 1-*t*-butyl-3-(1-methylcyclohexyl)aziridinone (III) in a quartz vessel by a uv light source produced carbon monoxide and the corresponding Shiff bases as the main products. This fragmentation formally resembles Norrish type I photodecarbonylation of amides, although the yields from α-lactams are strikingly higher. A radical mechanism on the basis of this similarity is suggested. Neither the uv spectra nor the photolysis of α-lactams have been reported previously.

The recent synthesis[4] of 1,3-di-*t*-butylaziridinone (I) demonstrated that low stability and high chemical reactivity are not inherent properties of three-membered cyclic lactams.[5] Compound I decomposes slowly at 170° and uncatalyzed solvolysis requires an elevated temperature and prolonged reaction time. The stability of α-lactams is, however, profoundly influenced by the nature of substituents on nitrogen and C-3. Thus it was noted[4,5] that the absence of hydrogen atoms on the carbon directly attached to C-3 of the ring results in a marked increase in thermal stability, since one mode of decomposition, namely eliminative isomerization to an open chain unsaturated amide, is blocked. This suggestion received further confirmation by the recently reported synthesis of several stable α-lactams.[6-9] In a continuing investigation of α-lactams reactions 1-*t*-butyl-3-(1-methylcyclopentyl)aziridinone (II) and 1-*t*-butyl-3-(1-methylcyclohexyl)aziridinone (III) were synthesized and subjected to photolysis.



I, R = $C(CH_3)_3$

II, R = 

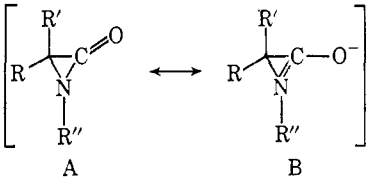
III, R = 

Synthesis

The synthesis of I has been reported previously.[4] α-Lactams II and III were synthesized from the corresponding cyclic ketones according to Scheme I. Both α-lactams show a band at 1835 cm^{-1} in the infrared, characteristic for aziridinone,[5] with no N-H-type absorption. The nmr (CCl_4) spectra possess a singlet, 1 H, at 164 Hz which is distinctive for C(3)-H in α-lactams.

Photolysis of α-Lactams

α-Lactams I, II, and III manifest a well-defined maximum in the ultraviolet at about 250 mμ, which shows a hypsochromic shift in going from *n*-hexane to ethanol as solvents (see Table I), a characteristic of n-π* transitions. The data in Table I are significant in that the n-π* absorption of cyclic[10] and open-chain amides lies below 220 mμ, which has been attributed to the interaction of lone-pair electrons on nitrogen with carbonyl π bonds.[11] In α-lactams, however, the amide resonance is sterically inhibited and form B is highly strained. Therefore, one might expect that



A B

α-lactams would exhibit the n-π* absorption band at nearly the same position as their cyclic ketone analogs, for example, cyclopropanones.[12,13] The fact that the n-π* band in α-lactams appears 600-1000 Å[14] lower than in cyclopropanones may indicate that the interaction of lone-pair electrons on nitrogen with the carbonyl π-orbital electrons is still significant.

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Scheme I

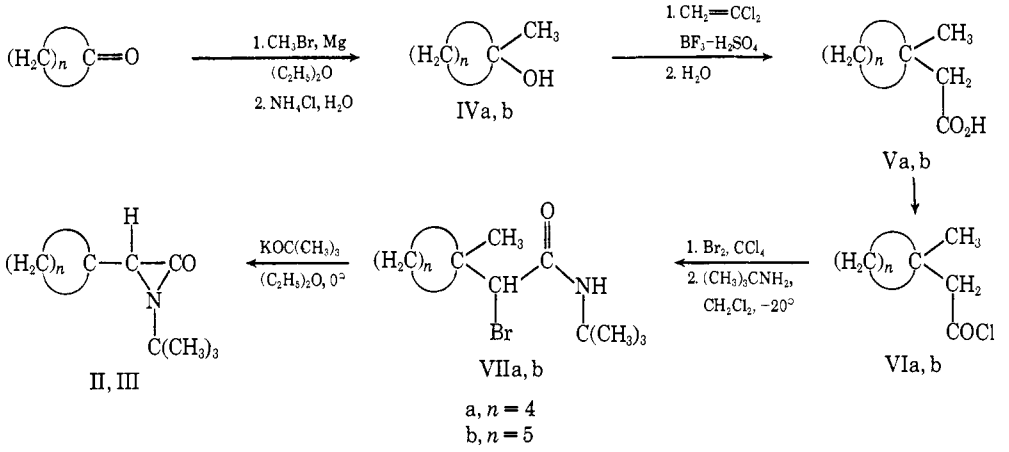
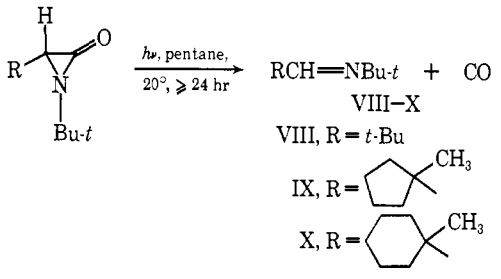


Table I. The n–π^* Band in the Uv Spectra of α-Lactams

Bu-*t*	λ_{max}, mμ (log ϵ) *n*-Hexane	Ethanol	Methanol
$C(CH_3)_3$	251 (2.03)	240 (2.19)	234 (1.98)
	246 (1.77)	233 (2.17)	
	247 (2.16)		

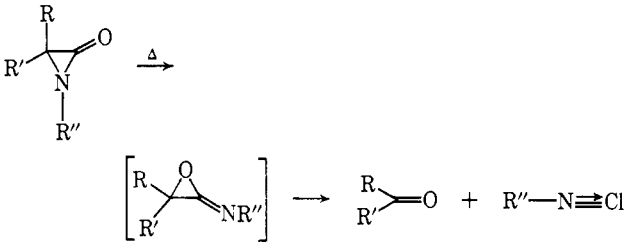
When a pentane solution of 1,3-di-*t*-butylaziridinone (I) in a quartz vessel was exposed to the radiation from a Hanovia 679 A 36 lamp for 24 hr complete decomposition occurred. No significant change was observed in the dark or in Pyrex glass, which is not transparent to light with wavelength shorter than 280 mμ, even in the presence of benzophenone. Carbon monoxide and N-*t*-butylneopentylidenimine (VIII), identical with a sample synthesized by an independent method,[4] were isolated in 97% yield.

The irradiation of 1-*t*-butyl-3-(1-methylcyclopentyl)-aziridinone (II) and 1-*t*-butyl-3-(1-methylcyclohexyl)-aziridinone (III) under the same conditions afforded similar products, namely, carbon monoxide (84–90%) and the corresponding imine. The complete decomposition of II and III, however, requires more than 24

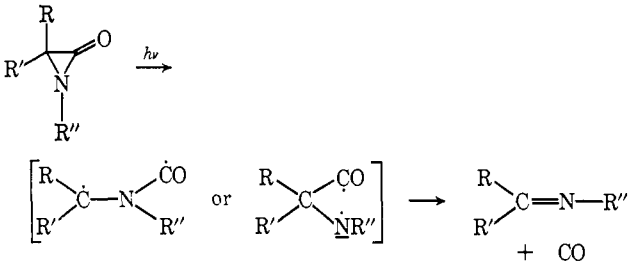


hr. The structure of imine IX was established by comparison with an authentic sample obtained from the condensation of 1-(1-methylcyclopentane)carboxaldehyde and *t*-butylamine in the presence of potassium hydroxide. The infrared and nmr spectra of imine X were consistent with the assigned structure.

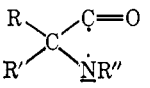
The photoinduced decomposition of α-lactams resembles Norrish type I photodecomposition of amides.[15] The main products of α-lactam reaction are carbon monoxide and the corresponding imines. This fragmentation is in sharp contrast with the thermal decomposition of these compounds,[4,16] which gives a carbonyl compound (aldehyde of ketone) and an isocyanide.



A radical mechanism similar to photoinduced decarbonylation of amides[15] can be formulated for the decomposition of α-lactams by uv light, although other mechanisms (*e.g.*, ionic or concerted) cannot be excluded on the basis of present evidence.



An intermediate of the type



has been suggested for the photorearrangement of certain anilides.[17a]

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Experimental Section

Melting points were determined on a Kofler hot-stage microscope. The infrared spectra were recorded on a Perkin-Elmer 237 spectrophotometer, and nmr spectra were obtained on a Varian A-60 and/or T-60 spectrometer. Refractive indices were determined by a Zeiss Opton Abbe refractometer. Ultraviolet spectra were recorded on a Cary 14 spectrophotometer. Microanalyses were performed by Dr. S. M. Nagy and his associates at Massachusetts Institute of Technology. All melting points and boiling points are uncorrected.

Preparation of N-*t*-Butyl-2-(1-methylcyclopentyl)-2-bromoacetamide (VIIa). 1-Methylcyclopentan-1-ol, mp 36°, bp 140° (lit.[17b] mp 36°, bp 135–136°), was converted to 1-methylcyclopentylacetic acid by the method described by Bott[18] in 33% yield: bp 112–113° (11 mm) (lit.[18] 131–132° (20 mm)); n^{25}D 1.4554; infrared (neat) 1705 cm^{-1}; nmr (CCl_4) 739 (singlet, 1 H), 140 (singlet, 2 H), 96 (multiplet, 8 H), and 67 Hz (singlet, 3 H). This acid was converted to the acid chloride by thionyl chloride in amost quantitative yield: bp 63–65° (10 mm); n^{29}D 1.4608; infrared (neat) 1800 cm^{-1}. The acid chloride was brominated in refluxing carbon tetrachloride, and the α-bromo acid chloride, bp 62° (0.5 mm), $n^{24.7}$D 1.555, was treated with *t*-butylamine in methylene chloride at −20°. VIIa was isolated with an over-all yield of 72%: mp 98–99°; infrared (KBr disk) 3310, 1663, and 1555 cm^{-1}; nmr (CCl_4) 378 (broad, 1 H), 252 (singlet, 1 H), 101 (multiplet, 8 H), 91 (singlet, 9 H), and 67 Hz (singlet, 3 H).

Anal. Calcd for $C_{12}H_{22}BrNO$: C, 52.36; H, 8.0; N, 5.09; Br, 28.7. Found: C, 52.70; H, 8.46; N, 4.81; Br, 27.94.

Preparation of N-*t*-Butyl-2-(1-methylcyclohexyl)-2-bromoacetamide (VIIb). 1-Methylcyclohexan-1-ol, bp 170° (lit.[19] 168°), was converted to 1-methylcyclohexylacetic acid according to the method described by Bott[18] in 45% yield: bp 104–105° (1.3 mm) (lit.[18] bp 148–150° (20 mm)); $n^{25.5}$D 1.4673; infrared (neat) 1710 cm^{-1}; nmr (CCl_4) 730 (singlet, 1 H), 132 (singlet, 2 H), 84 (broad, 10 H), and 62 Hz (singlet, 3 H). This acid was converted to acid chloride by thionyl chloride in 97% yield: bp 49° (0.6 mm); n^{26}D 1.4723; infrared (neat) 1800 cm^{-1}. The acid chloride was brominated in refluxing carbon tetrachloride and the α-bromo acid was treated with *t*-butylamine in methylene chloride at −20°. VIIb was isolated in an over-all yield of 84%; mp 124–125°; infrared (KBr disk) 3305, 1665, and 1557 cm^{-1}; nmr (CCl_4) 366 (broad, 1 H), 250 (singlet, 1 H), 88 (broad, 10 H), 80 (singlet, 9 H), and 64 Hz (singlet, 3 H).

Anal. Calcd for $C_{13}H_{24}BrNO$: C, 53.79; H, 8.33; N, 4.82; Br, 27.53. Found: C, 54; H, 8.23; N, 5; Br, 27.55.

Preparation of N-*t*-Butyl-1-(1-methylcyclopentyl)methylidenimine (IX). 1-(1-Methylcyclopentyl)carbinol, bp 75.6° (6 mm), n^{25}D 1.4592 (lit.[20] bp 168°; n^{20}D 1.4586) (2.28 g), was converted to 1-(1-methylcyclopentane)carboxaldehyde by the method described by Holum.[21] The yield was 1.85 g (82%): bp 141–142° (lit.[22] 142–143°); n^{25}D 1.4562 (lit.[23] n^{25}D 1.4560); infrared (neat) 2700 and 1715 cm^{-1}.

1-(1-Methylcyclopentane)carboxaldehyde (1 g) was condensed with *t*-butylamine (5 ml) in the presence of potassium hydroxide (2 g) in 15 hr to give 0.9 g (70%) of IX: bp 156–157°; infrared (neat) 2960, 2875, and 1665 cm^{-1}; nmr (CCl_4) 448 (singlet, 1 H), 98 (multiplet, 8 H), 66 (singlet, 9 H), and 63 Hz (singlet, 3 H).

Preparation of 1-*t*-Butyl-3-(1-methylcyclopentyl)aziridinone (II). N-*t*-Butyl-2-bromo-2-(1-methylcyclopentyl)acetamide (VIIa) was converted to aziridinone II by the general method described in ref 4 in 77% yield: bp 72–73° (0.4 mm); infrared (neat) 1835 cm^{-1}; nmr (CCl_4) 164 (singlet, 1 H), 98 (multiplet, 8 H), 88 (singlet, 9 H), and 64 Hz (singlet, 3 H); uv, λ_{max}^{hexane} 246 mμ (log ε 1.770).

Anal. Calcd for $C_{12}H_{21}NO$: C, 73.7; H, 10.83; N, 7.172. Found: C, 73.93; H, 10.98; N, 7.36.

Preparation of 1-*t*-Butyl-3-(1-methylcyclohexyl)aziridinone (III). N-*t*-Butyl-2-(1-methylcyclohexyl)-2-bromoacetamide (VIIb) was converted to aziridinone III by the general method described in ref 4 in 90.5% yield: bp 81.2° (0.35 mm); infrared (neat) 1835 cm^{-1}; nmr (CCl_4) 164 (singlet, 1 H), 95 (broad, 10 H), 84 (singlet, 9 H), and 67 Hz (singlet, 3 H); uv, λ_{max}^{hexane} 247 mμ (log ε 2.16).

Anal. Calcd for $C_{13}H_{23}NO$: C, 74.64; H, 11; N, 6.7. Found: C, 74.71; H, 11.06; N, 6.8.

Photolysis of 1,3-Di-*t*-butylaziridinone (I). A solution of 1,3-di-*t*-butylaziridinone (I),[4] 0.521 g, in pentane (25 ml) contained in a quartz test tube was placed in a water bath at a distance of 5 cm from the radiation source. After attachment of a gas collection bulb, the solution was irradiated by a Hanovia 679 A 36 (450 W) lamp for 24 hr at 20°. After filtration, the solvent was evaporated at 0° under reduced pressure. The residue, which was a colorless liquid, bp 120°; infrared (neat) 1670 cm^{-1}; nmr (CCl_4) 437 (singlet, 1 H), 63 (singlet, 9 H), and 59 Hz (singlet, 9 H), was identical with the synthetic N-*t*-butylneopentylidenimine.[4]

In addition to this liquid, 85 ml of gas was collected. A 67-ml portion of this gas was absorbed by an acidic solution of cuprous chloride (a reagent for carbon monoxide).[24] This represents a yield of 97% of carbon monoxide. A minor quantity of solid polymer, the structure of which was not determined, was also separated from the reaction mixture.

Photolysis of 1-*t*-Butyl-3-(1-methylcyclopentyl)aziridinone (II). A solution of 0.67 g of II in pentane (25 ml) contained in a quartz test tube was irradiated by uv light as described previously. Imine IX and carbon monoxide were the only products detected; the yield was 90% based on carbon monoxide.

Photolysis of 1-*t*-Butyl-3-(1-methylcyclohexyl)aziridinone (III). A solution of 1-*t*-butyl-3-(1-methylcyclohexyl)aziridinone (III), 0.5 g, in pentane (25 ml) contained in a quartz test tube was irradiated by uv light as described before; 45 ml (corrected volume) of carbon monoxide was collected which represents 84% yield. The liquid was filtered and the solvent was evaporated at 0°. A colorless liquid was obtained: infrared (neat) 1675 cm^{-1} (C=N); nmr (CCl_4) 448 (singlet, 1 H), 96 (multiplet, 10 H), 67 (singlet, 9 H), and 63 Hz (singlet, 3 H).

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