

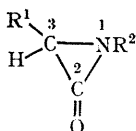
Ultraviolet Spectra and Photochemical and Electron-impact Induced Fragmentations of α -Lactams

By ERACH R. TALATY,* AUBRY E. DUPUY, JUN., and THOMAS H. GOLSON

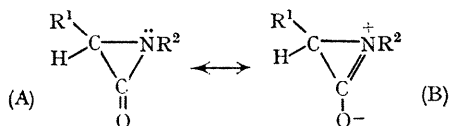
(Department of Chemistry, Louisiana State University in New Orleans, Lakefront, New Orleans, Louisiana 70122)

We have previously reported the isolation of the α -lactams (I),¹ (II),² and (III),³ which are remarkably stable, as is (IV).⁴

- (I) $R^1=R^2$ =Adamant-1-yl (Ad, $C_{10}H_{16}$)
 (II) R^1 =Ad, R^2 =Bu^t
 (III) R^1 =Bu^t, R^2 =Ad
 (IV) $R^1=R^2$ =Bu^t



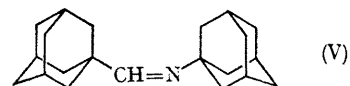
The u.v. spectra of α -lactams (I), (II), and (III) are characterized by a well-defined maximum of low intensity, whose position is solvent-dependent. In *n*-hexane, the maximum occurs at 252 nm. for all three compounds [$\log \epsilon$ 2.17, 2.13, and 2.16 for (I), (II), and (III), respectively]; in 95% ethanol, the corresponding positions are: 241 nm. ($\log \epsilon$ 2.34), 241.5 (2.27), and 240.5 (2.33). The hypsochromic shift noted in going from hexane to ethanol is characteristic of $n \rightarrow \pi^*$ transitions.^{5a} In the u.v. spectra of γ - and δ -lactams⁶ or open-chain amides,^{5b} by contrast, the $n \rightarrow \pi^*$ absorption occurs well below 220 nm; this has been attributed to the interaction of the lone-pair of electrons on the nitrogen atom with the carbonyl π -bond.^{5b,7} In the above α -lactams, because of the bulky substituents attached to the nitrogen atom and C-3 of the ring, and also because of increased strain in the ring, the canonical structure (B)



makes a smaller contribution to the resonance hybrid than

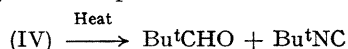
the corresponding structure in the other amides. Nevertheless, this resonance must still be important in these α -lactams, since their $n \rightarrow \pi^*$ maxima are far removed from those of cyclopropanones (310–354 nm.).⁸

When a solution of (I) (200 mg.) in pentane (55 ml.) was irradiated (12 hr.; primarily 2537 Å⁹), complete decomposition of (I) occurred. Evaporation of the reaction mixture, followed by sublimation (150°/0.2 mm.) and recrystallization from pentane, afforded a white, crystalline solid (>80%, m.p. 290–292° decomp.), *M* 297 (mass spectrometric); i.r. (KBr), 1653 cm^{-1} ; n.m.r. (CCl_4), τ 2.78 (s, 1H) and *ca.* 8.0 (m, 30H). This compound was identified as the hitherto unreported imine (V) by comparison with an authentic sample obtained by the condensation of 1-amino-

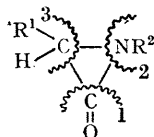


adamantane with adamantane-1-carbaldehyde in refluxing benzene (water was removed as an azeotrope). A small amount of polymer (<12%) of undetermined composition was also produced during the photolysis, together with a considerable amount of carbon monoxide. Hence, this fragmentation resembles, at least formally, the "Norrish-type I" photodecarbonylations of amides,^{5c,10} and seems to proceed with unusual facility in the highly strained α -lactam. A "Norrish-type II" decomposition, on the other hand, is blocked in compound (I) because of the impossibility of creating a double bond at the bridgehead position in the adamantyl moiety. Even in compounds (II) and

(III), where one of the adamantyl substituents of (I) is replaced by the *t*-butyl group, the photodecarbonylation to produce the corresponding imine appears to be the dominant process. The thermal fragmentation of (IV),⁴ by contrast, yields entirely different products:



We, as well as Lengyel and Uliss,¹¹ have examined the mass spectra† of the α -lactams, (I), (II), and (III) and the resemblance between the photo-chemical fragmentation of the α -lactams and one induced by electron impact (*cf.* ref. 12) is very strong. At 70 ev., all three compounds exhibit very weak or negligible peaks corresponding to the molecular ion, which has a strong tendency to lose carbon monoxide (cleavage 1). In fact, the strongest peak in all the spectra above *m/e* 135 (C₁₀H₁₅) occurs at (*M* - 28), and this mode of fragmentation is important even at 10–12 ev. This behaviour is in marked contrast to that of a β -lactam reported recently.¹³ Ions corresponding to the structures R¹CHO and R²NC (or R²CN) are also present in the spectra of all three α -lactams, but generally in low abundance: their



formation obviously involves a rearrangement of the molecular ion and corresponds to the thermal decomposition. Cleavage along line 2 is practically negligible, while cleavage along line 3 is noticeable when R² is adamantyl. This influence of the nature of the substituent, as well as its position, on the fragmentation of the molecular ion is revealed more clearly in a comparison of the relative tendencies of the isomeric molecular ions from (II) and (III) to lose a particular substituent, at least, formally. The (*M* - 57) peak, for example, is much stronger in the spectrum of (II) than in that of (III). Furthermore, the base peaks in the two spectra are different: *m/e* 57 in the former, and *m/e* 135 (C₁₀H₁₅) in the latter. Thus, mass spectrometry promises to be a useful method for the determination of the structures of, at least, the more stable α -lactams.

We thank the National Science Foundation for the award of a Graduate Traineeship to one of us (A.E.D.), and for a grant in aid of the purchase of the Hitachi-Perkin Elmer RMU-6E mass spectrometer used in this work. We also thank Mr. R. T. O'Connor and Miss D. Heinzelman, Southern Regional Laboratory, U.S. Dept. of Agriculture, for our earlier mass spectra obtained in summer, 1967, and Drs. K. Gerzon (Eli Lilly & Co., Indianapolis, Indiana) and H. E. Simmons (E. I. du Pont de Nemours & Co., Wilmington, Delaware) for some derivatives of adamantane.

(Received, October 24th, 1968; Com. 1444.)

† Preliminary results of our work were mentioned at the Southwest Regional Meeting of the American Chemical Society, Little Rock, Arkansas, December, 1967. (E. R. Talaty, A. E. Dupuy, jun. and A. E. Cancienne, jun., paper no. 167).

¹ E. R. Talaty, A. E. Dupuy, jun., and A. E. Cancienne, jun., *J. Heterocyclic Chem.*, 1967, **4**, 657.

² Footnote in E. R. Talaty and A. E. Dupuy, jun., *Chem. Comm.*, 1968, 790; K. Bott, *Angew. Chem. Internat. Edn.*, 1967, **6**, 946.

³ E. R. Talaty and A. E. Dupuy, jun., *J. Medicin. Chim.*, in the press.

⁴ J. C. Sheehan and J. H. Beeson, *J. Amer. Chem. Soc.*, 1967, **89**, 362; I. Lengyel and J. C. Sheehan, *Angew. Chem. Internat. Edn.*, 1968, **7**, 25.

⁵ J. G. Calvert and J. N. Pitts, jun., "Photochemistry," Wiley, 1966, (a) pp. 249–262; (b) p. 452; (c) pp. 460–462.

⁶ (a) Y. V. Moiseev, G. I. Batyukov, and M. I. Vinnik, *Zhur. fiz. Khim.*, 1963, **37**, 570, report a value of 208 nm. in water for both γ - and δ -lactams; (b) C. M. Lee and W. D. Kumler, *J. Amer. Chem. Soc.*, 1961, **83**, 4593.

⁷ S. F. Mason, *Quart. Rev.*, 1961, **15**, 287.

⁸ W. B. Hammond and N. J. Turro, *J. Amer. Chem. Soc.*, 1966, **88**, 2880; N. J. Turro and W. B. Hammond, *ibid.*, p. 3672; J. F. Pazos and F. D. Greene, *ibid.*, 1967, **89**, 1030.

⁹ J. H. Stocker and D. H. Kern, *J. Org. Chem.*, 1966, **31**, 3755.

¹⁰ G. H. Booth and R. G. W. Norrish, *J. Chem. Soc.*, 1952, 188.

¹¹ I. Lengyel and D. B. Uliss, Abstracts of 156th National Meeting of the Amer. Chem. Soc., Sept., 1968, ORGN 196.

¹² H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, 1967, p. 26.

¹³ E. J. Moriconi, J. F. Kelly, and R. A. Salomone, *J. Org. Chem.*, 1968, **33**, 3448.