was obtained. Washing of this residue once with 20 ml. of cold ethanol gave 9.0 g. (62% yield) of the desired product, m.p. 114–115° (reported[2] m.p. 116.5–118°, reported[3] 114°).

N-Alkyl Cleavage in Acid Hydrolysis of Norbornane γ-Lactams

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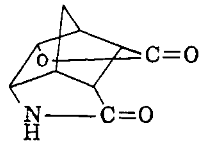
When the lactone-lactam I previously described by Worrall,[2] was refluxed in 5% hydrochloric acid, N-alkyl cleavage occurred and the product, isolated in 85% yield, was found to be identical with an authentic sample of the nortricyclenic acid lactone II.[3,4] In a similar manner III was found to give IV which was converted into II by reduction with sodium borohydride followed by heating. The ketone IV had been previously prepared by oxidation of II.[4] The amino acid lactone V,[5] is converted into its hydrochloride under the conditions mentioned above, indicating that the N-alkyl cleavages observed occur in the lactams instead of the amino acids. The unusual N-alkyl cleavages observed are considered to proceed *via* an intermediate bridged carbonium ion such as VI. In a similar manner N-*t*-butylisobutyramide, VII, evolved isobutylene when refluxed in 20% hydrochloric acid.



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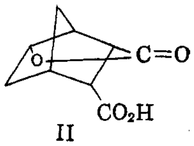

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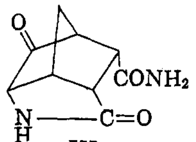

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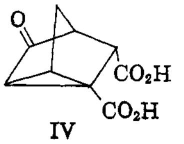

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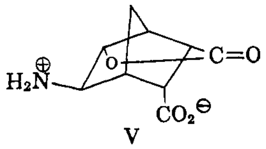

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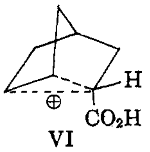
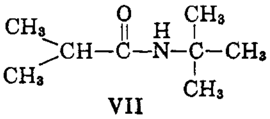


VI



$$\begin{matrix}CH_3\\ CH_3\end{matrix}\!\!>CH-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-CH_3$$

VII

Experimental[6]

Hydrolysis of Lactone-lactam of *endo-cis*-2,3-Dicarboxy-*endo*-5-amino-*endo*-6-hydroxynorbornane (I).—The lactone-lactam I (0.75 g., m.p. 191–192.5°) prepared as previously described[7] was refluxed in 20 ml. of 5% hydrochloric acid for 12 hr. The product was isolated as long white needles by concentrating the solution to a small volume and cooling. Recrystallization from water gave 0.61 g. (81%), m.p. 207–207.5°, alone and on admixture with an authentic sample of II.[7] Its infrared spectrum was identical with that of the authentic sample.

Anal. Calcd. for $C_9H_8O_4$: C, 60.00; H, 4.47. Found: C, 59.90; H, 4.75.

The aqueous solution remaining after the removal of II was made basic and steam distilled. The ammonia liberated was titrated with standard acid using a modified micro-Kjeldahl procedure[8] and 99% of the theoretical nitrogen content resulting from N-alkyl cleavage was detected.

Acid Hydrolysis of III.—The keto-lactam, III (0.10 g., m.p. 234–236°) prepared as previously described[2] was refluxed for 6 hr. in 20 ml. of 10% hydrochloric acid. After work-up as described above, a 70% yield of pure IV was obtained, m.p. 238–238.5° (reported[3] 239°), $\nu_{\max}^{\mathrm{KBr}}$ 1780, 1710, 1690 cm.$^{-1}$. Nitrogen analysis, as described above, indicated quantitative N-alkyl cleavage.

Conversion of IV into II.—The ketone, IV (0.048 g.), was added to a solution of 0.056 g. of sodium borohydride in 1 ml. of 50% ethanol. After standing at room temperature for 2 hr. the solution was made acidic with dilute hydrochloric acid and continuously extracted with ether for 10 hr. Evaporation of the ether left a solid which was heated in a sublimation tube at 170° and 40 mm. for 3 hr. The unszblimed residue (0.010 g.) was identical in melting point and infrared spectrum with an authentic sample of II.

Hydrolysis of N-*t*-butylisobutyramide.—N-*t*-Butylisobutyramide[9] (0.800 g., m.p. 115–117°) was added to a refluxing solution of 20 ml. of 20% hydrochloric acid in a closed system containing a gas burette. After 1 hr. 94 ml. (75% yield) of gas was evolved. The gas was identical in its infrared spectrum (10-cm. gas cell) with isobutylene.

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[1] National Defense Education Act Fellow, 1959–1962.

[2] W. S. Worrall, *J. Am. Chem. Soc.*, **82**, 5707 (1960).

[3] K. Alder and F. Brockhagen, *Ber.*, **87**, 167 (1954).

[4] A. Winston and P. Wilder, Jr., *J. Am. Chem. Soc.*, **76**, 3045 (1954).

[5] L. H. Zalkow and C. D. Kennedy, the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., September 9–14, 1962, Abstracts, 94Q.

[6] All melting points were taken on a Fisher–Johns melting point apparatus and are uncorrected. Analyses were done by Dr. A. Bernhardt (Mulheim, Germany). Infrared spectra were recorded on a Beckman IR-5 spectrophotometer.

[7] The authors thank Dr. P. Wilder, Jr., for an authentic sample of II.

[8] L. Miller and J. A. Houghton, *J. Biol. Chem.*, **159**, 373 (1945).

[9] Kindly supplied by Dr. R. C. Freeman, Monsanto Chemical Co., St. Louis, Mo.

The Effect of Coördination on the Reactivity of Aromatic Ligands. VII. Specific Ion Effects on Diazo Coupling Rates[1]

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The effect of coördination to zinc ion on the rate of coupling of a phenolic chelating agent with a diazonium salt has been reported in a previous paper in this series.[2] The present work was undertaken to extend these rate studies to complexes of a number of other metal ions. The metal ions selected for this work were restricted to those which exhibit only one oxidation state in aqueous solution. In this way, side reactions of the metal ions with the diazonium salt were minimized.

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[1] We wish to acknowledge, with thanks, the financial assistance of the U. S. Army Research Office (Durham).

[2] K. D. Maguire and M. M. Jones, *J. Am. Chem. Soc.*, in press.