Pure tetracyclo[6.2.1.$0^{2,7}$.$0^{3,5}$]undec-9-ene (XVIIb) was isolated in 2.5% yield (0.37 g.), b.p. 199° (microdetermination), n^{25}D 1.5069.

Anal. Calcd. for $C_{11}H_{14}$: C, 90.37; H, 9.63. Found: C, 89.99; H, 9.58.

Pure pentacyclo[6.3.1.$0^{2,7}$.$0^{3,5}$.$0^{9,11}$]dodecane (XVIII) was isolated in 52% yield (8.36 g.), b.p. 91° (8 mm.), n^{25}D 1.5184. The infrared spectra of the products were discussed above.

Anal. Calcd. for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 90.08; H, 10.18.

In separate experiments, both XVIIa and XVIIb were treated with reagent I and were converted in high yields to XVIII.

Reaction of XVIIb with Phenyl Azide.—Freshly distilled phenyl azide (0.081 g., 0.00069 mole) and XVIIb (0.100 g., 0.00069 mole) were dissolved in pentane (2 ml.). After standing overnight the mass of colorless crystals was filtered and weighed 0.147 g. (81%), m.p. 150–155°. Recrystallization from boiling hexane gave an analytical sample of **10-phenyl-10,11,12-triazapentacyclo[6.5.1.$0^{2,7}$.$0^{3,5}$.$0^{9,13}$]tetradec-11-ene (XIX)**, m.p. 154–155°. The infrared spectrum of XIX was discussed above. A mixture of XVIIa and phenyl azide in pentane solution was allowed to stand at 25° for 1 week with no evidence of reaction.

Anal. Calcd. for $C_{11}H_{19}N_3$: C, 76.95; H, 7.22; N, 15.83. Found: C, 76.81; H, 7.33; N, 15.91.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE 39, MASS.]

The Synthesis and Reactions of an α-Lactam, 1-*t*-Butyl-3,3-dimethylaziridinone

BY JOHN C. SHEEHAN AND ISTVAN LENGYEL

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1-*t*-Butyl-3,3-dimethylaziridinone (2) was prepared from 2-bromo-N-*t*-butyl-2-methylpropionamide (1) by dehydrobromination with potassium *t*-butoxide. In refluxing ether, this α-lactam isomerized to N-*t*-butylmethacrylamide (3, major product) and smaller amounts of acetone and *t*-butyl isocyanide. In the reactions with nonionic nucleophiles (water, *t*-butyl alcohol, benzylamine, α-toluenethiol, and ethyl glycinate) ring opening occurred preferentially with preservation of the amide linkage. Potassium *t*-butoxide converted N-*t*-butyl-2-chloropropionamide (11) into *t*-butyl 2-*t*-butylaminopropionate (13) in good yield. Similarly, the reaction of 2-bromo-2-methyl-N-*n*-propylpropionamide (7) with potassium *t*-butoxide produced *t*-butyl 2-methyl-2-*n*-propylaminopropionate (9) and 2-*t*-butoxy-2-methyl-N-*n*-propylpropionamide (10). In the latter two cases an intermediate α-lactam (12 and 8) was detected by the characteristic infrared band at 1840 cm.$^{-1}$.

In recent years there has been an increasing interest in α-lactams (aziridinones). In 1949, 1-phenylaziridinone was suggested as a possible intermediate in the reaction of phenyl isocyanate with diazomethane.[1] A claim that certain α-haloamides with sodium hydride produce aziridinones[2] has been questioned.[3] Hydrolysis of several dichloroaziridines lead to α-chloroamides with ring opening[4,5] rather than to α-lactams.

Baumgarten and co-workers were the first to find spectral evidence for the existence of an aziridinone,[6] and more recently reported in a short communication[7] the isolation of 1-*t*-butyl-3-phenylaziridinone from the interaction of potassium *t*-butoxide and N-chloro-N-*t*-butylphenylacetamide (prepared *in situ* and not characterized). No suggestion has been put forward as to the possible mechanism of the reaction.

We now wish to report the preparation and some typical reactions of an α-lactam, 1-*t*-butyl-3,3-dimethylaziridinone (2).[8] In the choice of our precursor, we were influenced by the known stabilizing effect of substituents in the β-lactam[9] and β-thiolactone series.[10]

N-Carbobenzoxypenicillamine (β,β-dimethylcysteine) forms a thiolactone in high yield,[10] whereas N-carbobenzoxycysteine itself tends to polymerize[11] and the corresponding thiolactone was obtained only in very low yield.[12]

Preliminary experiments indicated that 2-bromo-2-methyl-N-*t*-butylpropionamide[13] (1) reacted with potassium *t*-butoxide to give a good yield of a product having the characteristic α-lactam band in the infrared at 1840 cm.$^{-1}$.[6,7] Substitution of potassium *t*-butoxide by metallic potassium as the base under otherwise identical conditions gave the same product but in lower yield. When the reaction was carried out in ether at −25°, the by-product formation could be practically eliminated. Separation from unchanged starting material was achieved by low-temperature fractional crystallization (only starting material precipitated from a *n*-pentane solution) and subsequent fractional low-temperature vacuum sublimation. By this technique we obtained a product with the chemical and spectral properties expected for an α-lactam: only one band was observed in the carbonyl region of the infrared (1837 cm.$^{-1}$; carbon tetrachloride); no band was detected in the 3100–3500 cm.$^{-1}$ region. The n.m.r. spectrum (carbon tetrachloride) had a singlet signal at 8.67 τ ascribable to the N-*t*-butyl group[14] and a singlet at 8.55 τ cor-

(1) J. C. Sheehan and P. T. Izzo, *J. Am. Chem. Soc.*, **71**, 4059 (1949).

(2) S. Sarel and H. Leader, *ibid.*, **82**, 4752 (1960).

(3) J. C. Sheehan and J. W. Frankenfeld, *ibid.*, **83**, 4792 (1961).

(4) E. K. Fields and J. M. Sandri, *Chem. Ind.* (London), 1216 (1959).

(5) A. G. Cook and E. K. Fields, *J. Org. Chem.*, **27**, 3683 (1962).

(6) H. E. Baumgarten, R. L. Zey, and U. Krolls, *J. Am. Chem. Soc.*, **83**, 4469 (1961).

(7) H. E. Baumgarten, *ibid.*, **84**, 4975 (1962).

(8) After the preparation of this manuscript, a short communication appeared: H. E. Baumgarten, *et al.*, *ibid.*, **85**, 3303 (1963), which described the preparation of an α-lactam (1-*t*-butyl-3-phenylaziridinone) by a very similar reaction. This type of reaction had been investigated previously by Sarel and Leader[2] and by Sheehan and Frankenfeld.[3] The former authors claimed isolation of an α-lactam, but the second investigators isolated only compounds of the oxindole and indoxyl type in the specific example mutually studied. The present authors (J. C. S. and I. L.) have prepared a number of α-lactams by the dehydrohalogenation of α-haloamides and have found that the substituents present profoundly affect the stability of α-lactams (Ph.D. Thesis, I. L., M.I.T., September, 1963, pp. 11, 12, and 19). In the case originally tried by Sarel and Leader (α-chloro-α,α-diphenylacetanilide) and reinvestigated by Sheehan and Frankenfeld, no α-lactam was isolated even by the recent modifications. There is still no independent, published confirmation of the alleged preparation of 1,3,3-triphenylaziridinone.

(9) J. C. Sheehan and E. J. Corey, "Organic Reactions," Vol. IX, John Wiley and Sons, Inc., New York, N. Y., 1957, p. 388.

(10) J. C. Sheehan, *Ann. N. Y. Acad. Sci.*, **88**, 665 (1960).

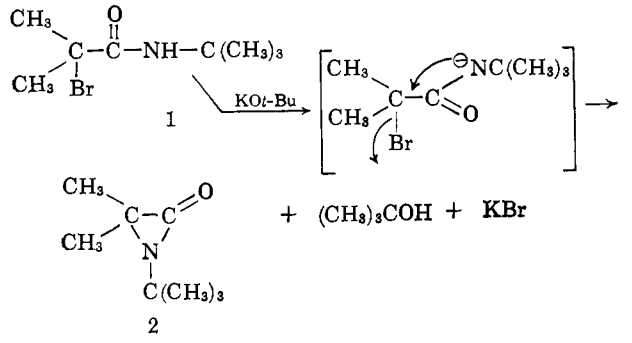
(11) J. C. Sheehan and I. Lengyel, unpublished results (1959–1960).

(12) M. Dadic, D. Fles, and A. Markovac-Prpic, *Croat. Chem. Acta*, **33**, 73 (1961).

(13) S. R. Safir, *et al.*, *J. Am. Chem. Soc.*, **77**, 4840 (1955).

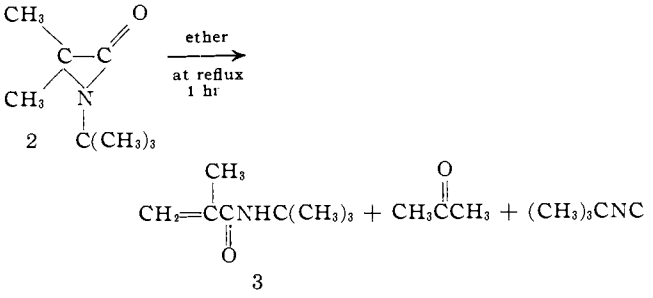
responding to the *gem*-dimethyl group. Analysis and molecular weight confirmed the $C_8H_{15}NO$ formula. The α-lactam 2 is a colorless liquid which crystallizes below room temperature (m.p. 22–24°) and can be stored in the frozen state (dry) at −78° indefinitely.

Although no mechanistic study was undertaken, a simple mechanism accounting for the product can be visualized by assuming the abstraction by the base of the N–H proton and subsequent intramolecular displacement of the bromine.



1 2

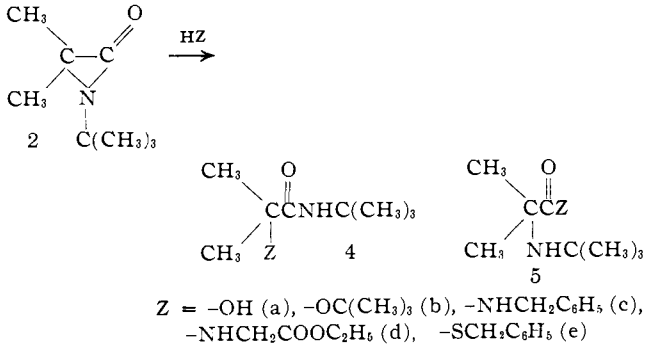
The α-lactam 2 decomposes on vacuum distillation (above 30°), on distillation at ordinary pressure, on column and thin layer chromatography (alumina, silicic acid, Florisil), and on vapor phase chromatography (5% Dow Corning silicone oil 710 on Anakrom support, room temperature). A short reflux period in ether produces the isomer, N-*t*-butylmethacrylamide (3) and smaller amounts of *t*-butylisonitrile and acetone. The former two were synthesized for comparison by independent methods.[15,16a,b]



2

3

Nonionic nucleophiles such as water, *t*-butyl alcohol, benzylamine, α-toluenethiol, and ethyl glycinate react smoothly with α-lactam 2 to produce α-substituted N-*t*-butylamides. Type 5 products were formed only in reactions where an *ionic* nucleophile (*t*-butoxide) was present.

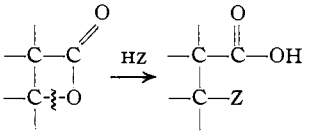


2

4 5

Z = –OH (a), –OC(CH3)3 (b), –NHCH2C6H5 (c), –NHCH2COOC2H5 (d), –SCH2C6H5 (e)

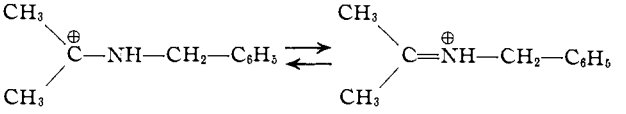
On the basis of these and other examples studied (*vide infra*) it is apparent that α-lactams differ markedly in their chemical reactions from monocyclic β-lactams which are heat stable and are solvolyzed (with relative difficulty) at the amide linkage.[17] Indeed, the chemical properties of α-lactams have more in common with β-lactones, which are opened preferentially by nonionic nucleophiles with cleavage of the alkyl–oxygen bond rather than the acyl–oxygen bond.[18]



HZ donates a nonionic nucleophile

The assignment of the structures to the products shown above was made on the basis of elemental analysis, molecular weight determination (where in doubt), infrared, n.m.r., and mass spectra (where the compounds did not decompose *before* entering the ionization chamber of the mass spectrometer).

The known 2-hydroxy-2-methyl-N-*t*-butylpropionamide (4a)[19] was identified by m.p. and infrared spectrum. The product of solvolysis in *t*-butyl alcohol, 2-*t*-butoxy-2-methyl-N-*t*-butylpropionamide (4b), showed the O-*t*-butyl signal at 8.66 τ. The isomer, *t*-butyl 2-*t*-butylamino-2-methylpropionate (5b), was prepared directly from 1 and showed the O-*t*-butyl signal at 8.50 τ. The product of the reaction of 2 with benzylamine (4c) had a signal in the n.m.r. at 8.62 τ, the expected shift for the N-*t*-butyl group of an N-*t*-butylamide (see Experimental for examples). The alternative structure 5c (not found in the product) would be expected to give the *t*-butyl signal at about 8.8–8.9 τ[20] (see examples in Experimental). The given structural assignment can also be verified by the mass spectrum of product 4c which shows an extraordinarily strong peak at *m/e* −148. Although a very likely major fragment of structure 4c would be the well-stabilized cation 6,[21] it is impossible to derive a fragment of this mass number from structure 5c.



6, *m/e* = 148

Reaction with ethyl glycinate also leads to the formation of the corresponding *t*-butylamide 4d rather than to the possible alternative, a dipeptide (5d; signal for N-*t*-butyl group at 8.65 rather than at 8.8–8.9 τ). Similarly, α-toluenethiol opens the α-lactam ring to the α-benzylthio-*t*-butylamide 4e; none of the

(14) Identical with the chemical shift reported by Baumgarten[7] for the *t*-butyl group in 1-*t*-butyl-3-phenylaziridinone.

(15) J. Heyboer and A. J. Staverman, *Rec. trav. chim.*, **69**, 787 (1950).

(16) (a) I. Ugi and R. Meyr, *Chem. Ber.*, **93**, 239 (1960); (b) J. Casanova, R. E. Schuster, and N. D. Werner, *J. Chem. Soc.*, 4280 (1963).

(17) See, for example, Th. Wieland, in Houben-Weyl, "Methoden der Organischen Chemie," G. Thieme, Stuttgart, 1958, Band 11/2, pp. 526–528.

(18) H. E. Zaugg in "Organic Reactions," Vol. VIII, John Wiley and Sons, Inc., New York, N. Y., 1954, pp. 322–328.

(19) R. F. Rekker and W. T. Nauta, *Rec. trav. chim.*, **70**, 241 (1951).

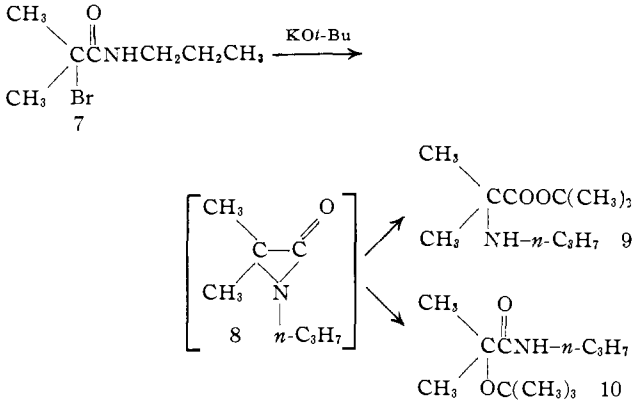
(20) *t*-Butylamine itself shows a signal at 8.85 τ: "Varian High Resolution NMR Spectra Catalog," Varian Associates, Palo Alto, Calif., 1962, Spectrum No. 90.

(21) K. Biemann, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp. 88–89 (general discussion) and p. 288 (fragmentation of amino acids and peptides).

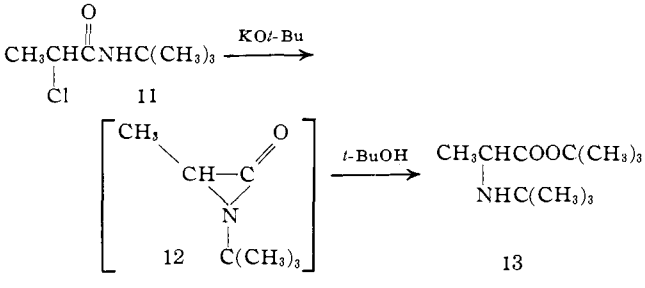
alternative thioester 5e was found (signal in n.m.r. for N-*t*-butyl at 8.62 τ).

Diazomethane, dimethyl acetylenedicarboxylate, and dimethyl fumarate did not react with α-lactam 2 under the very mild conditions employed (inert, nonpolar solvents at 0°).

To ascertain the effect of substituents on the ease of formation, the stability, and the type of chemical reactivity of the α-lactam 2, we prepared two analogs of precursor 1. As expected, replacement of the bulky *t*-butyl group for an N-*n*-propyl group in the starting material enhanced the reactivity of the corresponding aziridinone. 2-Bromo-2-methyl-N-*n*-propylpropionamide[13] (7) reacted smoothly with potassium *t*-butoxide. The intermediate α-lactam 8 was detected by infrared. The two final products, *t*-butyl 2-methyl-2-*n*-propylaminopropionate (9) and 2-*t*-butoxy-2-methyl-N-*n*-propylpropionamide (10), were obtained in isolated yields of 41 and 24%, respectively. It appears that α-lactam 8 opens easier and less selectively than α-lactam 2.



Replacement of one of the two α-methyl groups by hydrogen (while keeping the N-*t*-butyl group) in the starting material also leads to substantial change in the reactivity of the corresponding α-lactam formed. Reaction of 2-chloro-N-*t*-butylpropionamide (11)[22] with potassium *t*-butoxide gave *t*-butyl 2-*t*-butylaminopropionate (*t*-butyl N-*t*-butylalaninate) (13) as the only major product in excellent yield. The *t*-butyl ester signal was at 8.50 τ, the expected shift for this structure. The intermediate α-lactam 12 was detected at low temperature by infrared (1840 cm.$^{-1}$ band) but was not isolated in pure form.



Experimental[23]

2-Bromo-2-methyl-N-*t*-butylpropionamide (1)[13] was prepared from 2-bromo-2-methylpropionyl bromide (Eastman) and *t*-butylamine (Eastman) in 92–96% yield, m.p. 85–86°,[25] using a method similar to that used by Schlesinger and Prill for the preparation of a series of 2-chloro-N-alkylamides.[22] Purification by vacuum sublimation (80° (0.01 mm.)) gave m.p. 87–89°.

1-*t*-Butyl-3,3-dimethylaziridinone (2).—To a solution of 1 (4.44 g., 20 mmoles) in 200 ml. of dry ether, cooled to −25° by means of Dry Ice–acetone, was added with stirring under a dry nitrogen stream, potassium *t*-butoxide (2.23 g., 10.9 mmoles, MSA Research Corp., sublimed, dry, free of *t*-butyl alcohol) in one portion. The suspension was stirred at −25° for 1 hr. and centrifuged, the ether solution was decanted, and the solid residue washed with ether. The ether and the *t*-butyl alcohol formed were evaporated quickly at 0°. The residue, a clear liquid, showed a strong band in the infrared at 1840 cm.$^{-1}$ (methylene chloride or chloroform) and a weak one at 1675 cm.$^{-1}$. The product was stored in *n*-pentane solution in the freezer for 2 days. The precipitated crystals collected (0.750 g., 17%, m.p. 85–87°) were unchanged starting material. After removal of the solvent the filtrate was subjected to fractional sublimation (0–25° (0.005 mm.)). After two fractional vacuum sublimations the receiver contained 1.57 g. (54%) of 1-*t*-butyl-3,3-dimethylaziridinone (2). The product crystallized in an ice bath; m.p. 22–24°; infrared spectrum (CCl_4): one single, strong carbonyl band at 1837 cm.$^{-1}$, no band in the N–H region; n.m.r.: a singlet at 8.67 (N-*t*-butyl group) and a singlet at 8.55 τ (*gem*-dimethyl group).

Anal. Calcd. for $C_8H_{15}NO$: C, 68.09; H, 10.64; N, 9.93; mol. wt., 141.2. Found: C, 67.78; H, 10.53; N, 9.95; mol. wt., 145 ± 5 (by the vapor pressure method).

If the reaction is carried out at room temperature, by-products arise (3, 4b, 5b) the separation of which requires low temperature countercurrent distribution technique. It is important to use dry apparatus and dry solvents. A considerable decrease in yield was observed when the base was exposed to moist air before use.

Reaction of 2-Bromo-2-methyl-N-*t*-butylpropionamide (1) **with Metallic Potassium.**—Potassium (0.39 g., 0.9 g.-atom, Mallinckrodt) was powdered under dry toluene. The suspension was cooled to room temperature and the toluene was decanted and replaced by dry ether (100 ml.). To this suspension 2.22 g. (10 mmoles) of 1 was added in 50 ml. of dry ether at 0°. After shaking vigorously for 1 hr. at 0° the suspension was centrifuged and the ether was evaporated from the clear solution. The liquid residue contained about 45% of α-lactam as estimated by infrared (CCl_4; 1840 cm.$^{-1}$ band) and by chemical reactions (*vide infra*).[26]

Thermal Decomposition of 2.—A solution of the α-lactam 2 (1.41 g., 10 mmoles) in 20 ml. of ether was refluxed for 1 hr. Removal of ether and the other volatile components left behind a crystalline solid. Column chromatography[27] with benzene as eluent gave 0.92 g. (65%) of N-*t*-butylmethacrylamide (3), m.p. (after sublimation *in vacuo*) 58–59° (in a sealed tube 63–64°); reported m.p. 59°,[15] 57.5°.[28] Mixture m.p. with a sample of 3 synthesized by a known method[15] was undepressed; n.m.r.: 4.32 (1H), 4.64 (1H), the two olefinic protons; 8.03 (3H), the methyl group next to the carbonyl; 8.57 τ (9H), the N-*t*-butyl group.

A quantitative analysis of the volatile fraction removed and trapped with the solvent by vapor phase chromatography (v.p.c.)[29] showed besides ether 0.10 g. (12%) of *t*-butyl isocyanide and 0.070 g. (12%) of acetone. The identity of the *t*-butyl isocyanide was established by direct comparison of retention time on v.p.c. with an authentic sample synthesized by a known method[16a] and by infrared (a 2135 cm.$^{-1}$ band in CCl_4). The

(22) A. H. Schlesinger and E. J. Prill, *J. Am. Chem. Soc.*, **78**, 6123 (1956).

(23) Microanalyses were performed by Dr. S. M. Nagy and associates, at M. I. T., or by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. Melting points were determined on a Kofler hot-stage microscope. The infrared spectra were measured on a Perkin-Elmer Model 237 recording spectrophotometer. A Varian Associates A-60 instrument was used for recording nuclear magnetic resonance (n.m.r.) spectra ($CDCl_3$); peak positions are given in τ values.[24] The molecular weight determinations were carried out either by mass spectrometry or on a Mechrolab Vapor Pressure Osmometer, Model 301A, in benzene. The mass spectra were recorded on a Consolidated Electrodynamics Corp. mass spectrometer Type 21-103C with a 21-013 heated inlet system.

(24) G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

(25) Reported[13] yield 35%, m.p. 85–88°.

(26) Reactions performed on 2 can also be carried out with a sample prepared by the potassium method. In this case the yields are lower.

(27) The column chromatographic purifications in this experiment were carried out using Woelm, neutral alumina, activity grade 1, deactivated further by the addition of water: 3 ml. of water/100 g. of alumina.

(28) H. Plaut and J. J. Ritter, *J. Am. Chem. Soc.*, **73**, 4076 (1951).

(29) The instrument used was an F and M Model 720 dual column programmed temperature gas chromatograph. Column: 20% silicone gum rubber [GE SE-30] on Diatoport P support, 2 ft. × 0.25 in. stainless steel, programmed from room temperature to 300°.

identity of acetone was also shown by direct comparison with an analytical sample (Fisher).

Hydrolysis of 2.—A sample of 2 (1.41 g., 10 mmoles) was shaken with 10 ml. of distilled water for 15 min. The mixture was extracted with methylene chloride, the solution was dried over sodium sulfate, and the solvent was evaporated. The residue crystallized spontaneously. Recrystallization from benzene–petroleum ether gave 2-hydroxy-2-methyl-N-*t*-butylpropionamide (4a), 1.21 g. (76%), m.p. 95–96° (reported[19] 94°); infrared (CCl_4): 3600 (OH), 3400 (NH), 2975 (aliphatic CH), 1675 and 1658 (shoulder) (α-hydroxyamide carbonyl), and 1520 cm.$^{-1}$ (amide II).

Solvolysis of 2 in *t*-Butyl Alcohol.—A sample of 2 (1.41 g., 10 mmoles) in 1.48 g. (20 mmoles) of *t*-butyl alcohol on heating for 20 min. at 50° or on storage at room temperature for 24 hr. produced 2-*t*-butoxy-2-methyl-N-*t*-butylpropionamide (4b), 1.66 g. (77%), b.p. 68–70° (3 mm.); infrared (CCl_4): 3400 (NH), 1675 (amide carbonyl), and 1512 cm.$^{-1}$ (amide II); n.m.r.: 3.3 (1H), NH; 8.55 (6H), *gem*-dimethyl; 8.62 (9H), N-*t*-butyl group; and 8.66 τ (9H), O-*t*-butyl group.

Anal. Calcd. for $C_{12}H_{25}NO_2$: C, 66.92; H, 11.70; N, 6.51. Found: C, 66.69; H, 11.75; N, 6.51.

***t*-Butyl 2-*t*-butylamino-2-methylpropionate (5b)** was detected as a minor by-product of 2 when the reaction was carried out at room temperature. To obtain it in isolable amounts, the following modification was made: to a solution of 2.22 g. (10 mmoles) of 1 in 30 ml. of ether was added 1.40 g. (12.5 mmoles) of potassium *t*-butoxide. The mixture was stirred under reflux for 1 hr. After centrifugation and evaporation of the solvent, the residue was analyzed by v.p.c. The product consisted of about 8:4:1 mixture of 3, 5b, and 4b.[30] An attempt to separate these by fractional vacuum distillation gave no pure products, but a pure sample was collected by v.p.c.; infrared (CCl_4): no pronounced N–H band, 1725 (ester carbonyl), 1260 and 1220 (*t*-butyl groups), and 1140 cm.$^{-1}$ (C–O bond of ester); n.m.r.: 8.04 (1H), NH; 8.50 (9H), O-*t*-butyl group; 8.68 (6H), *gem*-dimethyl group; and 8.82 τ (9H), N-*t*-butyl group. All signals are singlets as expected.

Anal. Calcd. for $C_{12}H_{25}NO_2$ (215.328): C, 66.92; H, 11.70; N, 6.51. Found: C, 66.67; H, 11.85.

Reaction of 2 with Benzylamine.—To a solution of 1.41 g. (10 mmoles) of 2 in 4 ml. of dioxane was added (exothermic reaction) 1.07 g. (10 mmoles) of freshly distilled benzylamine (Eastman). After 30 min. the solution was freeze-dried, leaving a crystalline solid, which upon chromatography[27] afforded 1.77 g. (71.5%) of crystalline 2-benzylamino-2-methyl-N-*t*-butylpropionamide (4c), m.p. 85–86° (with sintering from 76°); infrared (CCl_4): 3350 (NH), 1680 (amide carbonyl), and 1515 cm.$^{-1}$ (amide II); n.m.r.: 2.55 (5H), phenyl group; 6.29 (2H), benzylic methylene; 8.60 (6H), *gem*-dimethyl; and 8.62 τ (9H), N-*t*-butyl group.

Anal. Calcd. for $C_{15}H_{24}N_2O$ (248.368): C, 72.52; H, 9.74; N, 11.28. Found: C, 72.59; H, 9.89; N, 11.32; mol. wt., 249 (mass spectrometrically: M + 1).

Reaction of 2 with Ethyl Glycinate.—The α-lactam 2 (1.41 g., 10 mmoles) was dissolved in 1 ml. of dioxane and 1.03 g. (10 mmoles) of ethyl glycinate (freshly prepared from its hydrochloride)[31] was added (exothermic reaction). After 24 hr. the dioxane and excess ethyl glycinate were evaporated at 25° (0.01 mm.). The residue, a clear, colorless liquid, was chromatographed[27] with benzene as eluent. The main fraction obtained by chromatography was vacuum distilled, yielding 1.64 g. (67.5%), b.p. 108–110° (0.05 mm.), of 2-(carbethoxymethylamino)-2-methyl-N-*t*-butylpropionamide (4d); infrared (CCl_4): 3400 and 3350 (NH), 1745 (ester carbonyl), 1677 (amide carbonyl), and 1515 cm.$^{-1}$ (amide II); n.m.r.: 2.58 (1H), NH of amide; 5.70 (2H), quartet (*J* 7 c.p.s.), methylene group of alcohol; 6.64 (2H), methylene group next to carbonyl; 8.3 (1H), NH of glycine; 8.65 (9H), N-*t*-butyl; 8.68 (3H), triplet (*J* 7 c.p.s.), methyl group of alcohol; and 8.70 τ (6H), *gem*-dimethyl group.

(30) Temperature of column 130°, injection port 210°, detector 230°, He pressure 20 p.s.i.

(31) E. Fischer, *Ber.*, **34**, 436 (1901).

Anal. Calcd. for $C_{12}H_{24}N_2O_3$: C, 58.98; H, 9.89; N, 11.46. Found: C, 58.99; H, 9.94; N, 11.51.

Reaction of 2 with α-Toluenethiol.—To a solution of the α-lactam 2 (1.41 g., 10 mmoles) in 1 ml. of dioxane was added in one portion α-toluenethiol (Eastman, 1.24 g., 10 mmoles). There was no observable heat evolution. After 24 hr. the reaction was over. The dioxane and the unreacted α-toluenethiol were evaporated. The liquid residue (2.62 g.) was distilled under reduced pressure; b.p. of the main fraction 150–155° (2.2 mm.). The product, 1.6 g. (62%), 2-benzylthio-2-methyl-N-*t*-butylpropionamide (4e), is a colorless, viscous oil with a penetrant odor; infrared (CCl_4): 3360 (NH), 1675 (amide carbonyl), 1510 (amide II), and 750 cm.$^{-1}$ (phenyl); n.m.r.: 2.58 (5H), phenyl group; 2.92 (1H), NH; 6.20 (2H), methylene; 8.45 (6H), *gem*-dimethyl group; and 8.62 τ (9H), N-*t*-butyl group. All signals are singlets.

Anal. Calcd. for $C_{15}H_{23}NOS$ (265.398): C, 67.88; H, 8.73; N, 5.28; S, 12.08. Found: C, 68.14; H, 8.84; N, 5.20; S, 11.76.

t*-Butyl 2-*t*-Butylaminopropionate (12)** (t*-Butyl N-*t*-Butylalaninate**).—To a solution of 2-chloro-N-*t*-butylpropionamide[22] (16.3 g., 0.10 mole) in 300 ml. of dry ether, potassium *t*-butoxide (11.2 g., 0.10 mole) was added. The mixture was stirred for 1 hr. at 0°, centrifuged, the solvent evaporated and the liquid residue distilled through a 30-cm. Vigreux column; b.p. 26–28° (0.05 mm.) or 43–45° (2.0 mm.), $n^{23}D$ 1.4155, yield 17.58 g. (87.3%); infrared (CCl_4): no pronounced NH type band around 3200–3500, only one carbonyl at 1728 (ester), and 1160 cm.$^{-1}$ (C–O bond of ester); n.m.r.: 6.67 (1H), a quartet (*J* 7 c.p.s.), the CH group; 8.22 (1H), N–H; 8.50 (9H), O-*t*-butyl group; 8.77 (3H), a doublet (*J* 7 c.p.s.), the methyl group; and 8.91 τ (9H), N-*t*-butyl group.

Anal. Calcd. for $C_{11}H_{23}NO_2$ (201.298): C, 65.64; H, 11.51; N, 6.96. Found: C, 65.91; H, 11.48; N, 7.05.

Reaction of 2-Bromo-2-methyl-N-*n*-propylpropionamide (7) with Potassium *t*-Butoxide.—To a solution of 5.50 g. (0.0264 mole) of the bromoamide 7[13] in 500 ml. of dry ether was added potassium *t*-butoxide (2.90 g., 0.0257 mole) in one portion. After 40 min. of stirring at room temperature the mixture was centrifuged and the solvent was removed. The residue yielded on vacuum distillation two fractions: fraction 1, b.p. 58–60° (3.8 mm.), 2.18 g. (41%) of **t-butyl 2-methyl-2-*n*-propylaminopropionate (9)**; infrared (CCl_4): no pronounced N–H type band, only weak absorption in the 3200–3500 cm.$^{-1}$ range, 1725 (ester carbonyl), and 1145 cm.$^{-1}$ (C–O bond of ester); n.m.r.: 7.47 (2H), triplet (*J* 7 c.p.s.), methylene next to NH; 8.3 (1H), NH; 8.4–8.7 (2H), center methylene in propyl group, covered by other signals; 8.50 (9H), O-*t*-butyl group; 8.72 (6H), *gem*-dimethyl; and 9.05 τ (3H), a triplet (*J* 7 c.p.s.), methyl in propyl group.

Anal. Calcd. for $C_{11}H_{23}NO_2$ (201.298): C, 65.63; H, 11.51; N, 6.96. Found: C, 65.96; H, 11.86; N, 7.24.

Fraction 2 of the distillation, b.p. 80–83° (3.5 mm.), 1.27 g. (24%), was identified as **2-*t*-butoxy-2-methyl-N-*n*-propylpropionamide (10)**; infrared (CCl_4): 3400 (NH), 1676 (amide carbonyl), and 1517 cm.$^{-1}$ (amide II); n.m.r.: 3.0 (1H), NH; 6.70 (2H), a quartet (*J* 7 c.p.s.), methylene next to NH; 8.38 (2H), quartet partly covered by dimethyl signal, the center methylene in propyl group; 8.48 (6H), *gem*-dimethyl group; 8.63 (9H), O-*t*-butyl; and 9.02 τ (3H), a triplet (*J* 7 c.p.s.), methyl in propyl group.

Anal. Calcd. for $C_{11}H_{23}NO_2$ (201.298): C, 65.63; H, 11.51; N, 6.96. Found: C, 65.32; H, 11.59; N, 6.65.

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