Maleic acid (0.1036 g) consumed 17.2 ml and fumaric acid (0.0872 g) consumed 14.7 ml; the permanganate was decolorized instantly in each case. Malic acid (0.1050 g) consumed 19.5 ml; the permanganate was decolorized slowly. DL-Aspartic acid did not consume permanganate under these conditions. Morpholinedione (**8**) dihydrate (0.0716 g) consumed 6.6 ml and the rate of decolorization of permanganate was similar to the rate of decolorization by malic acid. The consumption of permanganate was equivalent to 1 mole of malic acid per mole of **8** dihydrate. After permanganate titration, the solution gave an analysis equivalent to 1 mole of **8** dihydrate using the van Slyke method.[31] This indicates cleavage of the amide bond[32] to liberate a free amino group.

Acknowledgment.—The nmr data were obtained by Dr. Martin W. Dietrich and the optical rotations by Dr. Victor W. Saeger.

(32) A. Jolles [*J. Prakt. Chem.*, [2] **63**, 518 (1901)] found that in the oxidation of N-benzoylaspartic acid by potassium permanganate in boiling dilute sulfuric acid nitrogen is split out as urea.

α-Lactams. III. The Reaction of 1-*t*-Butyl-3,3-dimethylaziridinone with Lithium Aluminum Hydride

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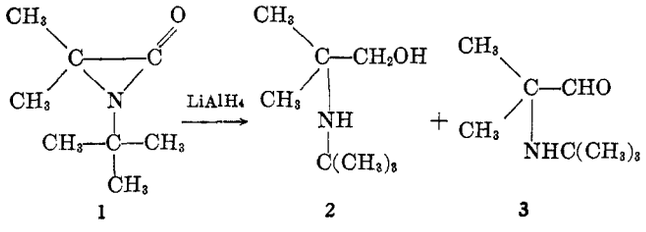
Received June 9, 1966

Recently, we reported a synthesis and some solvolytic reactions of 1-*t*-butyl-3,3-dimethylaziridinone (**1**).[1] It was pointed out that the products of solvolysis are α-substituted N-*t*-butylamides, except where the nucleophile was a strong ionic base (*e.g.*, *t*-butoxide). Now we wish to describe the lithium aluminum hydride ($LiAlH_4$) reduction of α-lactam **1**, a reaction in which cleavage of the ring occurs exclusively at the amide linkage. When a solution of **1** in ether or tetrahydrofuran is treated with $LiAlH_4$, and subsequently hydrolyzed, 2-*t*-butylamino-2-methyl-1-propanol (**2**) is formed in good yield, accompanied by a smaller amount of the corresponding aminoaldehyde, 2-*t*-butylamino-2-methylpropionaldehyde (**3**). The latter compound was isolated as the 2,4-dinitrophenylhydrazone. 1-*t*-Butyl-2,2-dimethylaziridine (**4**), an anticipated product, was not detected.



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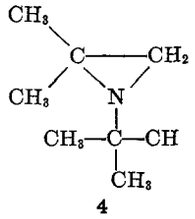

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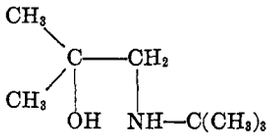
The structure assignment of the products is based on elemental analyses, infrared, nmr, and mass spectra. A picrate, an acetate, and a phenylurethan of the major product were also prepared. To corroborate further the structure of amino alcohol **2**, the structural isomer, 1-*t*-butylamino-2-methyl-2-propanol (**5**), was synthesized for comparison. The physical and spectral properties of this synthetic amino alcohol differed distinctly from those of compound **2**.



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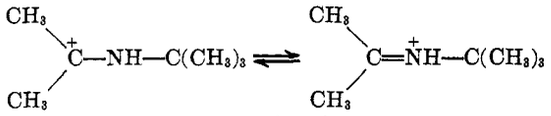
Elemental analysis and mass spectrometric molecular weight corresponded to the formula $C_8H_{19}NO$ for the major product of the reduction. The infrared spectrum showed the characteristic bands at 3600 and 3430 cm^{-1} expected for an alcohol. The nmr spectrum exhibited a singlet at 3.11 ppm (2 H), which indicates a CH_2 group next to an oxygen, thus pointing to a primary alcohol. The mass spectrum showed a very abundant ion at *m/e* 114, in agreement with structure **2**; amino alcohols of type **2** would be expected to lose CH_2OH to give the well-stabilized ion **6**.[2] A fragment with this *m/e* value cannot be derived from structure **5** and is indeed not found in the mass spectrum of **5**.



6, *m/e* 114

The product formed a monoacetate at room temperature with acetic anhydride, also indicating a *primary* alcohol. Phenyl isocyanate precipitated a phenyl urethan promptly.

For direct comparison, tertiary alcohol **5** was prepared from 1,2-epoxy-2-methylpropane[3] and *t*-butylamine by a procedure adapted from the literature.[4] The boiling point, infrared, and nmr spectra of amino alcohol **5** were different from those of compound **2**. The two picrates show a melting point difference of 50°.

Aldehyde **3**, constituting the minor product of the reduction, was isolated as the 2,4-dinitrophenylhydrazone. Elemental analysis and infrared and nmr spectra (see the Experimental Section) were in agreement with structure **3**.

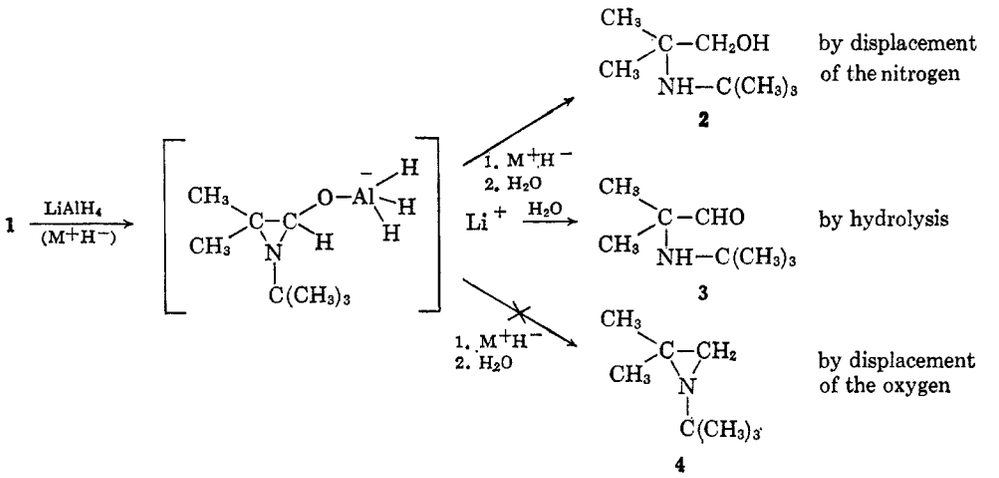
Even considerable variation in the ratio of $LiAlH_4$ to starting material or in the reaction conditions did not affect drastically the relative ratio of the observed products. The aforementioned results are in good agreement with what is known about the lithium alu-

(1) Part I: J. C. Sheehan and I. Lengyel, *J. Am. Chem. Soc.*, **86**, 1356 (1964).

(2) This fragmentation pattern is common for α-amino acid esters and α-amino alcohols; see, *e.g.*, K. Biemann, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 87–89.

(3) H. O. House, *J. Am. Chem. Soc.*, **77**, 5086 (1955).

(4) (a) K. Krassusky and A. Stepanoff, *J. Prakt. Chem.*, **115**, 321 (1927); (b) L. J. Kitchen and C. B. Pollard, *J. Org. Chem.* **8**, 342 (1943).



minum hydride reduction of tertiary amides[5] and N-alkyllactams.[6]

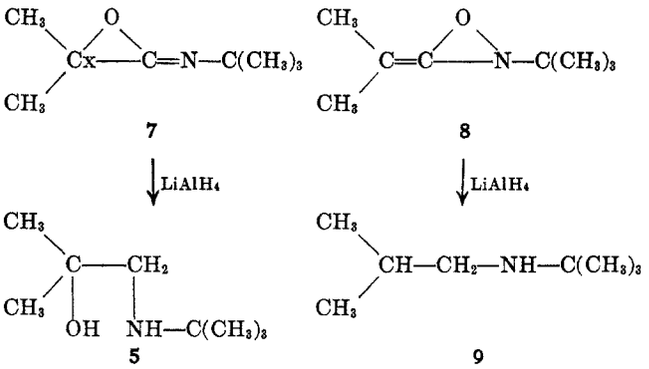
Medium sized N-alkyllactams (with five- to nine-membered rings) usually give the corresponding polymethylen imines upon lithium aluminum hydride reduction[6a-c,e] in excellent yield, with complete loss of the oxygen function. N-methylpyrrolidone and N-methylpiperidone have also been reduced to the corresponding aminoaldehydes.[6c] However, amino alcohols were the only products isolated from the $LiAlH_4$ reduction of a number of N-aryl-β-lactams.[6d]

In the mechanism commonly accepted for the reduction of tertiary amides by $LiAlH_4$,[5c,d] a nucleophilic attack of the metal hydride (M^+H^-) on the carbonyl group is postulated as the initial step, to form an ionic complex (see scheme pictured above).

Hydrolysis of this complex yields, in the case of lactams,[6c] an aminoaldehyde. Alternatively, further reduction may take place by displacement of either the oxygen atom or the nitrogen atom by a second hydride ion to produce a tertiary amine,[6a,b] *or* an amino alcohol,[6d,f,g] respectively.

The fact that aziridine **4** is not observed among the products of the reduction is not surprising. Displacement of the nitrogen should be a more favored process both for steric and for electronic reasons. The possibility that aziridine **4** was in fact formed but was transformed into other final products can be excluded, as it is known that 2,2-dimethyl-N-alkylaziridines are stable to even large excess of lithium aluminum hydride at reflux temperature of ether.[7]

The suggestion, that α-lactams in the ground state have indeed the true lactam structure,[8] seems to be supported by our finding that the lithium aluminum hydride reduction of **1** produces compounds **2** and **3**. If significant contributions of an epoxide (**7**)[9] or an oxazirane (**8**) were present in α-lactam **1**, the lithium aluminum hydride reduction products expected should contain amino alcohol **5** and/or secondary amine **9**, respectively.[10,11]



This work was supported by a contact with the Office of Naval Research, Biochemistry Branch.

Experimental Section[12]

Reduction of α-Lactam 1 with Lithium Aluminum Hydride. A. Reagent in Excess.—To a solution of lithium aluminum hydride (1.14 g, 30 mmole) in 300 ml of tetrahydrofuran was added a solution of α-lactam **1** (2.83 g, 20 mmoles) in 20 ml of tetrahydrofuran, dropwise, at 0°. The mixture was stirred at room temperature for 1 hr, then refluxed for 3 hr. After cooling to room temperature, 1.5 ml of water was added and the mixture was stirred for 1 hr. The salt was separated by filtration and was washed with tetrahydrofuran. Fractionation of the solu-

(5) (a) R. F. Nystrom and W. G. Brown, *J. Am. Chem. Soc.*, **70**, 3738 (1948); (b) V. M. Micovic and M. L. Mihailovic, *J. Org. Chem.*, **18**, 1190 (1953); (c) F. Weygand, *et al.*, *Angew. Chem.*, **65**, 525 (1953); (d) H. C. Brown and A. Tsukamoto, *J. Am. Chem. Soc.*, **83**, 2016, 4549 (1961).

(6) (a) R. Lukes and J. Malek, *Chem. Listy*, **45**, 72 (1951); (b) O. E. Schulz and J. Schneckenburger, *Arch. Pharm.*, **294**, 261 (1961); (c) F. Galinovsky and R. Weiser, *Experientia*, **6**, 377 (1950); (d) Al. Spasov and B. Panaiotova, *Godishnik Sofiiskiĭa Univ., Fiz.-Mat. Fak.*, **52** (3), 81 (1957–1958); *Chem. Abstr.*, **53**, 17992e; (e) P. G. Gassman and B. L. Fox, *J. Org. Chem.*, **31**, 982 (1966).

(7) (a) H. M. Kissman and D. S. Tarbell, *J. Am. Chem. Soc.*, **74**, 4317 (1952); (b) A. T. Bottini and J. D. Roberts, *ibid.*, **80**, 5203 (1958).

(8) H. E. Baumgarten, J. F. Fuerholzer, R. D. Clark, and R. D. Thompson, *ibid.*, **85**, 3303 (1963).

(9) Recently, an intermediate of similar type has been postulated (part II of this series) [J. C. Sheehan and I. Lengyel, *ibid.*, **86**, 746 (1964)] in the reaction of 1-bromo-1-N-*t*-butylcarboxamidocyclohexane with potassium *t*-butoxide and subsequent warming.

(10) In the lithium aluminum hydride reduction of *gem*-substituted epoxides the oxygen function is retained in the product and the oxiran ring is opened at the less-substituted carbon to give a tertiary alcohol as the predominant product, *e.g.*, reduction of 2,3-epoxy-2-methylpropane gave an excellent yield of *t*-butyl alcohol: E. L. Eliel and D. W. Delmonte, *ibid.*, **80**, 1744 (1958).

(11) It was demonstrated by W. D. Emmons [*ibid.*, **79**, 5744 (1957)] that oxaziranes on reduction with lithium aluminum hydride retain the original carbon skeleton but lose the oxygen function, to give a Schiff base or the corresponding secondary amine.

(12) Microanalyses were performed by Dr. S. M. Nagy and associates at Massachusetts Institute of Technology. Melting points were determined on a Kofler hot stage and are uncorrected. 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 (nmr) spectra. Peak positions are given in ppm values downfield from tetramethylsilane. The molecular weight determinations were carried out by mass spectrometry using a CEC 21-103C mass spectrometer equipped with a stainless steel heated inlet system. Vapor phase chromatography (vpc) was carried out on an F & M Model 720 dual column programmed temperature gas chromatograph. A 2 ft × 0.25 in. stainless steel column was used packed with 20% silicone gum rubber (GE SE-30) on Diatoport P support.

tion gave 2.20 g (76%), bp 55–58° (2.5 mm), of a colorless liquid, which was identified as **2-*t*-butylamino-2-methyl-1-propanol (2)**.

Anal. Calcd for $C_8H_{19}NO$: C, 66.15; H, 13.19; N, 9.64; mol wt, 145.24. Found: C, 66.48; H, 12.98; N, 9.56; mol wt, 146 (M + 1) by mass spectrometry.

The infrared spectrum (CCl_4) showed 3610 and 3430 (wide) (OH), 2980, 2880 (CH), 1370, 1220 (*t*-butyl), and 1065 (CO stretching of a primary alcohol) cm^{-1}. The nmr spectrum (CCl_4) showed 1.14 (6 H), *gem*-dimethyl; 1.20 (9 H), *t*-butyl; 2.25 (1 H); NH and 3.11 ppm (2 H), methylene next to oxygen. All signals are singlets. The OH proton does not show up directly A **picrate** of 2 had mp 159–160°, unchanged after recrystallization from ethanol–water.

Anal. Calcd for $C_{14}H_{22}N_4O_8$: C, 44.92; H, 5.92; N, 14.97; mol wt, 374.35. Found: C, 45.11; H, 6.18; N, 14.83.

An **acetate** was prepared from a distilled sample of amino alcohol 2 (2.90 g, 20 mmoles) which was dissolved in 20 ml of acetic anhydride, causing an exothermic reaction. After 1 day of storage at room temperature, ice–water (25 ml) and ether (25 ml) were added, the pH was adjusted to 8 with potassium carbonate, and after a thorough shaking the two layers were separated. The organic layer was washed with water, dried over sodium sulfate, and distilled. The major portion (3.04 g, 81%) had bp 50–55° (8 mm) or 111–112° (60 mm). The boiling point at atmospheric pressure was 189–190° with partial decomposition.

Anal. Calcd for $C_{10}H_{21}NO_2$: C, 64.13; H, 11.30; N, 7.48; mol wt, 187.28. Found: C, 63.95; H, 11.26; N, 7.52.

The infrared spectrum (CCl_4) showed no OH and NH bands in the 3600–3100-cm^{-1} region, 2970 (aliphatic CH), 1737 (ester carbonyl), 1375 + 1385 (dimethyl), and 1235 (CO stretching of acetate and *t*-butyl skeletal vibration) cm^{-1}. The lack of NH stretching vibrations, commonly observed in this series, is probably due to the strong steric hindrance of the highly substituted amine group.

A **phenylurethan** was prepared in the following way. To a solution of 1.45 g (10 mmoles) of distilled 2-*t*-butylamino-2-methyl-1-propanol (2) in 10 ml of *n*-pentane was added phenyl isocyanate (1.43 g, 12 mmoles) and the solution was maintained for 3 days at 0°. The crystalline product was collected and washed with cold *n*-pentane. Recrystallization from hot *n*-pentane afforded needles (2.22 g, 84%), mp 95–96°.

Anal. Calcd for $C_{15}H_{24}N_2O_2$: C, 68.15; H, 9.15; N, 10.60; mol wt, 264.37. Found: C, 68.24; H, 8.82; N, 10.54.

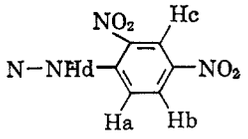
The infrared spectrum (CH_2Cl_2) showed 3400 (NH), 2960 (CH), 1725 (carbonyl of urethan), 1600 (phenyl), and 1525 (amide II) cm^{-1}.

B. Reduction with 0.25 Equiv of Lithium Aluminum Hydride.—To a solution of α-lactam 1 (2.82 g, 20 mmoles) in 30 ml of ether was added 10 ml of a 0.50 *M* solution of lithium aluminum hydride in ether, dropwise, at 0° with stirring. After 30 min of stirring at 0°, water (0.6 ml) was added, and the mixture was stirred for another 0.5 hr. After filtration the inorganic precipitate was washed with ether. The filtrate and washings were evaporated to dryness. To the residual liquid was added a solution of 2,4-dinitrophenylhydrazine (prepared freshly in the following way. 2,4-Dinitrophenylhydrazine (2.0 g, Eastman) was dissolved in 10 ml of concentrated sulfuric acid, then 15 ml of water and 20 ml of alcohol were added. Within 10 min, yellow crystals precipitated. After 12 hr of storage in a refrigerator, the crystals were collected, washed with 95% ethanol, and dried over concentrated sulfuric acid. Recrystallization from hot ethanol–water yielded 1.94 g (23%) of bright yellow crystals, mp 193–194°, characterized as the **2,4-dinitrophenylhydrazone sulfate of aldehyde 3.**

Anal. Calcd for $C_{14}H_{23}N_5O_8S$: C, 39.90; H, 5.50; N, 16.72; S, 7.61; mol wt, 421.42. Found: C, 39.65; H, 5.91; N, 16.68; S, 7.28.

The infrared spectrum (KBr) showed 3275 (NH), 2975, 2810 (CH), 1620, 1590, 1520 (CNO_2), 1335 (CNO_2), 1150, 1080, and 1060 cm^{-1}.

To remove the sulfuric acid from this salt the following procedure was employed. To a suspension of the salt (100 mg) in water (5 ml) and methylene chloride (10 ml) sodium carbonate was added with stirring until pH 9 was reached; the salt dissolved. After thorough shaking the two layers were separated. The aqueous phase was extracted with two 10-ml portions of methylene chloride. The combined methylene chloride extracts were washed with water, dried over sodium sulfate, and evaporated to dryness, leaving an orange, crystalline residue, 70 mg, mp 125–125.5°. The infrared spectrum (CH_2Cl_2) showed 3290 (NH), 2960 (CH), 1620, 1595, 1520 (CNO_2), 1340 (CNO_2), 1225 (*t*-butyl), 1150, and 1080 cm^{-1}. The nmr spectrum ($CDCl_3$) showed 1.18 (9 H), *t*-butyl; 1.43 (6 H), *gem*-dimethyl; 1.7-1.8 (1 H), NH-*t*-butyl; 7.54 (1 H), CH=N; 7.91 (H_a) doublet, J = 9.5 cps; 8.31 (H_b), two doublets, J_1 = 9.5 cps, J_2 = 2.5 cps; 9.10 (H_c), doublet, J = 2.5 cps, and 11.0 ppm (H_d).



The signals at lower field represent the standard pattern for 2,4-dinitrophenylhydrazones.

1-*t*-Butylamino-2-methyl-2-propanol (5).—The starting material, 1,2-epoxy-2-methylpropane, was prepared[3] from 1-chloro-2-methyl-2-propanol (Chemical Intermediates and Research Laboratories sample) in 91% yield, bp 50–52°, $n^{25}D$ 1.3690. A general procedure was followed[4b] for the opening of the epoxide ring with *t*-butylamine. To a 70% aqueous *t*-butylamine solution (36.5 g, 0.5 mole of *t*-butylamine and 15.7 ml of water) was added 1,2-epoxy-2-methylpropane (6.29 g, 0.10 mole) during the period of 1 hr. The solution was refluxed for 1 hr (oil-bath temperature 120°) and then fractionated, to give 11.5 g (79.3%) of **5**, bp 103–105° (100 mm) or 45° (3 mm), mp 21–23°, $n^{25.5}D$ 1.4240.

Anal. Calcd for $C_8H_{19}NO$: C, 66.15; H, 13.19; N, 9.64; mol wt, 145.24. Found: C, 66.26; H, 13.00; N, 9.35.

The infrared spectrum (CCl_4) showed 3600 (unassociated OH), 3450 (wide band, associated OH, possibly covering the NH band), 2850–3000 (aliphatic CH), 1375 + 1395 (dimethyl group), 1225 + 1245 (*t*-butyl group), and 1175 (CO stretching of a tertiary alcohol) cm^{-1}. The nmr spectrum ($CDCl_3$) showed 1.10 (9 H), *t*-butyl; 1.16 (6 H), *gem*-dimethyl; 2.47 (2 H), methylene next to nitrogen and 3.64 ppm (1 H), a broad signal, probably NH. All signals are singlets. The OH proton does not show up directly; its presence, however, can be concluded from the integration; the combined signals at 1.20–1.10 ppm integrate for 16 protons, possibly containing the OH proton. The **picrate** had mp 210–211°.

Anal. Calcd for $C_{14}H_{22}N_4O_8$ (picrate): C, 44.92; H, 5.92; N, 14.97; mol wt, 374.35. Found: C, 45.17; H, 6.01; N, 15.07.

The Isolation of Dehydroabietic Acid from Disproportionated Rosin

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Received June 17, 1966

The disproportionation of the acids of rosin, in the presence of catalytic quantities of palladium, to a mixture of dehydro- and dihydroabietic acids is a well-known reaction.[2,3] However, the methods for isolating pure dehydroabietic acid from this mixture have been quite tedious, involving its conversion to some derivative, recrystallization of the derivative, and then the regeneration of the acid from the derivative.[2,4–6]

(1) One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

(2) E. E. Fleck and S. Palkin, *J. Am. Chem. Soc.*, **60**, 921 (1938).

(3) V. M. Loeblich and R. V. Lawrence, *J. Am. Oil Chemists' Soc.*, **33**, 320 (1965).

(4) L. F. Fieser and W. P. Campbell, *J. Am. Chem. Soc.*, **60**, 159 (1938).

(5) L. F. Fieser and W. P. Campbell, *ibid.*, **60**, 2631 (1938).

(6) A. W. Burgstahler and L. W. Warden, *ibid.*, **86**, 96 (1964).