tions from 10% benzene–90% ligroin gave pure material, mp 144.5–145.0°; 70% yield. *Anal.* Calcd for $C_8H_7N_3O_4S$: C, 39.83; H, 2.93. Found: C, 40.08; H, 2.84.

1-Diphenylphoshinoxyaziridine (VI). The compound was prepared from diphenylphosphinous chloride (Stauffer Chemical Co.) by means of procedure B. The resulting oil was titrated with potassium permanganate in acetone to give aziridine VI. Six recrystallizations from 25% benzene–75% *n*-hexane gave pure material, mp 119.0–119.5°; 26% yield. *Anal.* Calcd for $C_{14}H_{14}NOP$: C, 69.13; H, 5.80. Found: C, 69.37; H, 5.94.

α-Lactams. IV.[1] A Stable α-Lactam, 1,3-Di-*t*-butylaziridinone[2]

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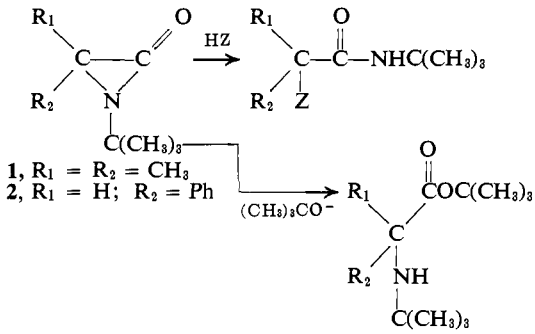
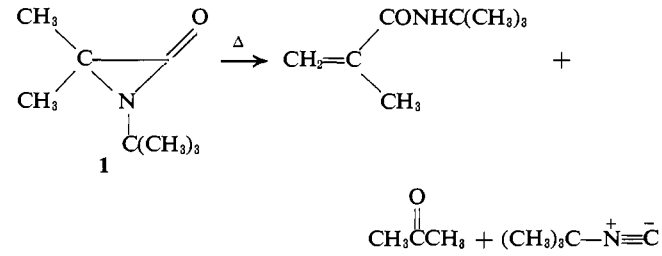
Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02319. *Received August 9, 1966*

Abstract: The dehydrobromination of 2-bromo-3,3-dimethyl-N-*t*-butylbutyramide with potassium *t*-butoxide has been found to give 1,3-di-*t*-butylaziridinone. This α-lactam has also been prepared by the addition of dichlorocarbene to N-neopentylidene-*t*-butylamine. The chemical properties of this α-lactam differ remarkably from other reported cases. It is cleaved only very slowly by refluxing methanol to give 2-methoxy-3,3-dimethyl-N-*t*-butylbutyramide and methyl 2-(N-*t*-butylamino)-3,3-dimethylbutyrate. The acidic and basic methanolyses of this α-lactam give the amide and methyl ester, respectively. Reaction of the aziridone with dimethylsulfoxonium methylide produces a carbonyl-stabilized ylide. At 450° pyrolysis of 1,3-di-*t*-butylaziridinone gives *t*-butyl cyanide and pivalaldehyde.

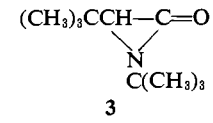
Since the suggestion in 1949 that 1-phenylaziridinone might be an intermediate in the reaction of phenyl isocyanate with diazomethane,[3] several attempts have led to the synthesis of three authentic α-lactams[1a,b,4] and the isolation and characterization of two of these, 1-*t*-butyl-3,3-dimethylaziridinone (**1**)[1b] and 1-*t*-butyl-3-phenylaziridinone (**2**).[4] Attack of nonionic nucleophiles (HZ = alcohols, amines, etc.) on the α-lactams **1** and **2** was found to proceed with cleavage of the alkyl–nitrogen bond to yield the corresponding α-substituted amide. Reaction of **1** or **2** with potassium *t*-butoxide produces the *t*-butyl ester from cleavage of the acyl–nitrogen bond.



In refluxing ether the thermal decomposition of the α-lactam **1** was complete in less than 1 hr, producing N-*t*-butylmethacrylamide, acetone, and *t*-butyl isocyanide in yields of 65, 12, and 12%, respectively.



If nucleophilic cleavage is retarded sterically and eliminative isomerization is avoided, then an α-lactam of greater stability should be obtained. Multiple phenyl substitutions appear to fulfill these requirements; however, attempts to produce 1,3,3-triphenylaziridinone by dehydrochlorination of 2-chloro-2,2-diphenylacetanilide have led only to rearranged products of the oxindole type.[5]



A more promising substitution pattern appeared to be that of 1,3-di-*t*-butylaziridinone (**3**). In this system one mode of decomposition, direct elimination to form an α,β-unsaturated amide, is blocked completely. There is precedent for the steric hindrance to nucleophilic attack at the α position in the failure of *n*-butyl 2-bromo-3,3-dimethylbutyrate to react with iodide ion in acetic acid or alcohol.[6] This hindrance should be

(1) (a) Part I: J. C. Sheehan and I. Lengyel, *J. Am. Chem. Soc.*, **86**, 746 (1964); (b) part II: J. C. Sheehan and I. Lengyel, *ibid.*, **86**, 1356 (1964); (c) part III: J. C. Sheehan and I. Lengyel, *J. Org. Chem.*, **31**, 4244 (1966).

(2) Taken in part from the Ph.D. Thesis of J. H. B., Massachusetts Institute of Technology, June 1966. This work was aided by National Institutes of Health Grant No. CA 02239-11,12 and a National Institutes of Health predoctoral fellowship (J. H. B.).

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

(4) (a) H. E. Baumgarten, *ibid.*, **84**, 4975 (1962); (b) H. E. Baumgarten, J. J. Fuerholzer, R. D. Clark, and R. D. Thompson, *ibid.*, **85**, 3303 (1963).

(5) (a) S. Sarel and H. Leader, *ibid.*, **82**, 4752 (1960); (b) J. C. Sheehan and J. W. Frankenfeld, *ibid.*, **83**, 4792 (1961); (c) S. Sarel, J. T. Klug, E. Breuer, and F. D'Angeli, *Tetrahedron Letters*, **No. 24**, 1553 (1964); (d) J. C. Sheehan and J. H. Beeson, *J. Org. Chem.*, **31**, 1637 (1966).

(6) E. Gryszkiewicz-Trochimowski and O. Gryszkiewicz-Trochimowski, *Bull. Soc. Chim. France*, 269 (1951).

$$(CH_3)_3CCHCO_3\text{-}n\text{-}C_4H_9 \xrightarrow[\text{or KI–ROH}]{\text{NaI–HOAc}} \text{no displacement}$$
(Br)

multiplied by the presence of the N-*t*-butyl group of the α-lactam, and the two *t*-butyl groups are well positioned, according to Newman's "rule of six," to provide maximum steric hindrance to attack on the acyl carbon.[7]

Results and Discussion

Synthesis. The precursor of this α-lactam, 2-bromo-3,3-dimethyl-N-*t*-butylbutyramide (**6**), was synthesized by bromination of 3,3-dimethylbutyryl chloride (**4**)[8] followed by treatment of **5** with *t*-butylamine.

$$(CH_3)_3CCH_2COCl \longrightarrow (CH_3)_3CCHCOCl \longrightarrow$$
4

(Br)
5

$$(CH_3)_3CCHCONH\text{-}t\text{-}Bu$$
(Br)
6

When **6** was treated with potassium *t*-butoxide in ether, the α-lactam **3** was obtained in good yield. Experimentation revealed that, unlike its predecessors,

$$(CH_3)_3CCHCONH\text{-}t\text{-}Bu \xrightarrow{t\text{-}BuO^-} (CH_3)_3CCH{-}C{=}O$$
(Br) **6** → N, $C(CH_3)_3$ **3**

3 was not destroyed by excess base and that, using 1.5 equiv of potassium *t*-butoxide, quantitative conversion could be obtained.

The purification of **3** can be achieved by distillation at low pressures, and this α-lactam can be analyzed for purity by gas chromatography on a column of silicone gum rubber. (On more polar columns decomposition of **3** is observed.) Although **3** does decompose slowly on silica gel, small samples of highly pure α-lactam may be obtained as the first fractions eluted from a column of silica gel with 95% benzene–5% ethyl acetate as the moving phase. No other α-lactam has been reported to withstand these conditions.

In a second synthesis of **3**, N-neopentylidene-*t*-butylamine (**7**), prepared from pivalaldehyde and *t*-butylamine, was allowed to react with dichlorocarbene generated by the reaction of potassium *t*-butoxide with chloroform. When the dichloroaziridine **8** produced was allowed to stand in contact with 5% aqueous sodium bicarbonate for 30 min, 1,3-di-*t*-butylaziridinone (**3**) was obtained, although in very low over-all yield (~1–5%).[9] The low yield is apparently due to steric hindrance of dichlorocarbene addition to the imine by the *t*-butyl groups.

$$(CH_3)_3CCH{=}NC(CH_3)_3 + CCl_2 \longrightarrow (CH_3)_3CCH{-}CCl_2$$
7 → N, $C(CH_3)_3$ **8**

$\xrightarrow{NaHCO_3,\ H_2O}$ $(CH_3)_3CCH{-}C{=}O$ (N, $C(CH_3)_3$) **3**

When phenyl(tribromomethyl)mercury[10] and sodium trichloroacetate[11] were employed as the dihalocarbene generators, no α-lactam was detected.

Nucleophilic Cleavage. In the reaction with nucleophiles, 1,3-di-*t*-butylaziridinone differs remarkably from other α-lactams. While other reported α-lactams react swiftly with methanol at 0° to give the α-methoxy amide, **3** requires several days in refluxing methanol to complete the solvolysis. The reaction was found to give 40% methyl 2-(N-*t*-butylamino)-3,3-dimethylbutyrate (**9**) and 60% 2-methoxy-3,3-dimethyl-N-*t*-butylbutyramide (**10**). This is the first report of an α-amino ester obtained from the "uncatalyzed" methanolysis of an α-lactam.

$$(CH_3)_3CCH{-}C{=}O$$
(N, $C(CH_3)_3$)

MeOH, MeO^- → $(CH_3)_3CCHCO_2CH_3$ ($NHC(CH_3)_3$) **9**

MeOH → $(CH_3)_3CCHCONHC(CH_3)_3$ (OCH_3) **10**

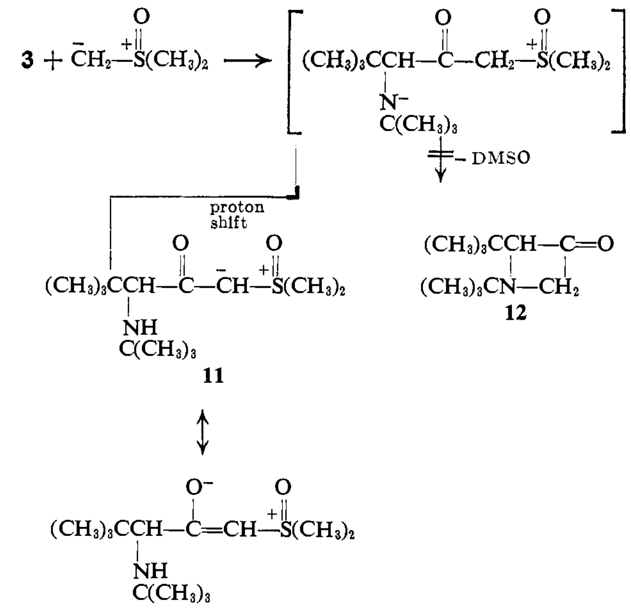
MeOH, TsOH

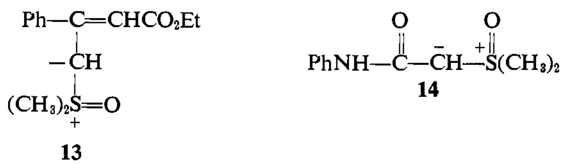
The sodium methoxide catalyzed methanolysis of **3** is complete in less than 2 hr in refluxing methanol, and only the methyl ester **9** is obtained. Similarly, when a trace of *p*-toluenesulfonic acid is added, the methanolysis produces only the amide **10**.

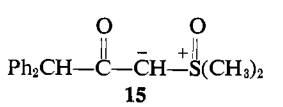
When **3** was stored at 25° with a dimethyl sulfoxide solution of dimethylsulfoxonium methylide for 18 hr in the hope of obtaining a ring expansion product (**12**), the stable ylide, dimethylsulfoxonium 2-(N-*t*-butylamino)-3,3-dimethylbutyrylmethylide (**11**), was obtained. The formation of **11** is similar to the previously reported formation of **13**, **14**, and **15** by the reaction of dimethylsulfoxonium methylide with ethyl propiolate, phenyl isocyanate, and diphenylketene, respectively.[12]

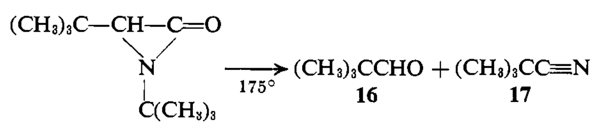
Thermal Decomposition. Perhaps the most remarkable property of 1,3-di-*t*-butylaziridinone (**3**) is its thermal stability. Other reported α-lactams undergo thermal decomposition rapidly at temperatures of 105° or less.[1a,b,13] However, the α-lactam **3** decomposes only slowly at 140° and, when the decomposition was carried out at 175° in a sealed tube, a complex mixture was obtained containing pivalaldehyde (**16**) and *t*-butyl cyanide (**17**) (from the thermal rearrangement of *t*-butyl isocyanide[14]) as the major products.

(7) M. S. Newman, *J. Am. Chem. Soc.*, 72, 4783 (1960).
(8) E. Berliner and F. Berliner, *ibid.*, 72, 222 (1950).
(9) The addition of dichlorocarbene to imines was first reported by Fields and Sandri, who isolated 2,2-dichloro-1,3-diphenylaziridine from the reaction of benzalaniline with dichlorocarbene. However, they were only able to isolate 2-chloro-2-phenylacetanilide from hydrolysis of the aziridine and no observation of an α-lactam was reported: E. K. Fields and J. M. Sandri, *Chem. Ind.* (London), 1216 (1959); also see A. G. Cook and E. K. Fields, *J. Org. Chem.*, 27, 3686 (1962).
(10) D. Seyferth, J. M. Burlitch, R. J. Minasz, J. Yick-Pui Mui, H. D. Simmons, Jr., A. J. H. Treiber, and S. R. Dowd, *J. Am. Chem. Soc.*, 87, 4259 (1965).
(11) W. M. Wagner, H. Kloosterziel, and S. Van Der Ven, *Rec. Trav. Chim.*, 80, 740 (1961).
(12) C. Kaiser, B. M. Trost, J. Beeson, and J. Weinstock, *J. Org. Chem.*, 30, 3972 (1965).
(13) J. J. Fuerholzer, Ph.D. Thesis, The University of Nebraska, 1965.
(14) (a) J. D. Roberts and M. C. Caserio, "Basic Principals of Organic Chemistry," W. A. Benjamin, Inc., New York, N. Y., 1964, p 685; (b) C. R. Noller, "Chemistry of Organic Compounds," 2nd ed, Philadelphia, Pa., 1957, p 257.

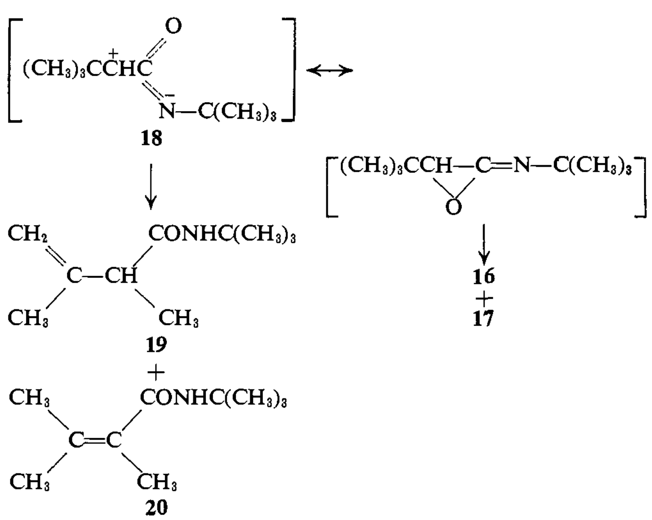






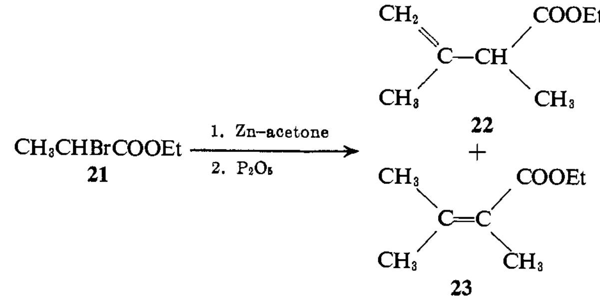


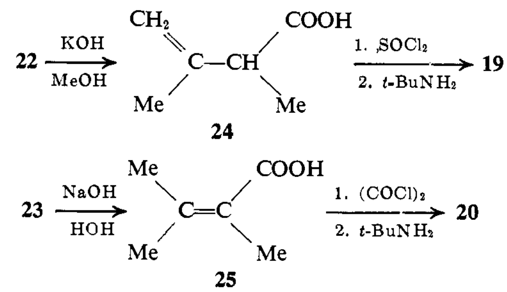
It was thought that if the pyrolytic rearrangement proceeded by way of a zwitterion intermediate (**18**), 2,3-dimethyl-N-*t*-butyl-3-butenamide (**19**) and 2,3-dimethyl-N-*t*-butylcrotonamide (**20**), the products of a neopentyl rearrangement, might be observed in the pyrolysis mixture. For comparison, **22** and **23** were prepared from ethyl 2-bromopropionate (**21**) by means of the Reformatsky reaction.[15] Saponification of the esters gave the acids **24** and **25**,[16] which were converted



(15) R. C. Huston and G. L. Goerner, *J. Am. Chem. Soc.*, **68**, 2504 (1946).

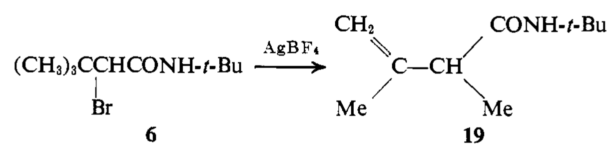
(16) H. J. Boonstra and J. F. Arens, *Rec. Trav. Chim.*, **79**, 866 (1960)





to the desired amides, **19** and **20**. Gas chromatographic analysis of the pyrolysis mixture using these standards revealed that the pyrolysis did not produce either **19** or **20** in detectable quantities.

A neopentyl rearrangement of a similar system was demonstrated when **6** was treated with silver tetrafluoroborate, and the rearrangement product **19** was isolated.



The gas-phase pyrolysis of **3** at 450° in a hot tube is a clean reaction giving rise to pivalaldehyde and *t*-butyl cyanide. This indicates that the complex mixture obtained from the sealed tube may consist of secondary products from the reactions of the aldehyde and the cyanide at that temperature.

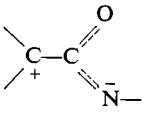
Summary

The substitution of *t*-butyl groups on the 1 and 3 positions of the aziridinone ring produces an α-lactam which is relatively resistant to nucleophilic cleavage and has relatively high thermal stability. The resistance to nucleophilic cleavage can be attributed to the steric hindrance provided by the *t*-butyl groups.

Analysis of the product ratio of the thermal rearrangement of 1-*t*-butyl-3,3-dimethylaziridinone indicates that, in the case of aliphatic acyclic substituents, elimination to form an α,β-unsaturated amide is the preferred mode of decomposition. In 1,3-di-*t*-butylaziridinone, where no β-hydrogen atoms are available, eliminative decomposition is not allowed and an increase in stability is anticipated. However, the thermal stability of this α-lactam (**3**) is far greater than can be explained on this basis alone.

The failure of 1,3-di-*t*-butylaziridinone to form the products of a neopentyl rearrangement during pyrolysis has been demonstrated. Since the treatment of 2-bromo-3,3-dimethyl-N-*t*-butylbutyramide with silver tetrafluoroborate does lead to a neopentyl rearrangement, this may be taken as evidence that formation of

the oxirane intermediate (necessary for formation of



aldehyde and isonitrile) does not arise *via* a dipolar intermediate (zwitterion) of significant lifetime.

A detailed discussion of the factors affecting α-lactam stability appears in a later paper.[17]

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 spectrometer. Vapor phase chromatograms were obtained on an F & M 720 gas chromatograph. Microanalyses were performed by Dr. S. M. Nagy and his associates at Massachusetts Institute of Technology.

2-Bromo-3,3-dimethyl-N-*t*-butylbutyramide (6). Bromine (1.6 ml, 29 mmoles) was added to a solution of 3.5 g (26 mmoles) of 3,3-dimethylbutyryl chloride[8,18] in 7 ml of carbon tetrachloride, and the resulting solution was refluxed until the bromine color disappeared (about 2.5 hr). The solution was then added to an ice-cold solution of 6.3 ml (60 mmoles) of *t*-butylamine in methylene chloride. When the addition was complete, water was added and the layers were separated. The methylene chloride solution was washed with hydrochloric acid, aqueous sodium hydroxide, and distilled water. Evaporation of the methylene chloride solution gave 5.28 g (82%) of **6**: mp 156–157°; infrared (CCl_4): 3400, 2950, 1675, and 1515 cm^{-1}; nmr ($CDCl_3$): δ 1.13 (singlet, 9 H), 1.35 (singlet, 9 H), 4.0 (singlet, 1 H), and 6.0 (broad singlet, 1 H).

Anal. Calcd for $C_{10}H_{20}BrNO$: C, 48.00; H, 8.06; N, 5.60; Br, 31.94. Found: C, 48.07; H, 7.93; N, 5.81; Br, 32.11.

1,3-Di-*t*-butylaziridinone (3). A solution of 18.7 g (0.075 mole) of the α-bromo amide **6** in 500 ml of ether was cooled to 0° in an ice bath, and 12.08 g (0.107 mole) of potassium *t*-butoxide (MSA Research Corp.) was added. After 15 min of stirring, an infrared spectrum of the solution indicated that the α-lactam formation was complete. The solution was filtered under nitrogen pressure and the resulting cloudy solution was evaporated. The residue was taken up in petroleum ether, placed in centrifuge tubes, and cooled to −20°. Centrifugation gave a clear solution which on evaporation yielded 8.0 g (68%) of the α-lactam. Further purification could be obtained by distillation, bp 38° (0.4 mm), or column chromatography on a column of Mallinckrodt "AR" 100 mesh silicic acid with 95% benzene–5% ethyl acetate as the moving phase. For most purposes, however, such further purification was not necessary. Spectral data showed: infrared (liquid film): 2960 and 1835 cm^{-1}; nmr ($CDCl_3$): δ 0.98 (singlet, 9 H), 1.25 (singlet 9 H), and 2.61 (singlet, 1 H).

Anal. Calcd for $C_{10}H_{19}NO$: C, 70.96; H, 11.32; N, 8.28. Found: C, 70.68; H, 11.26; N, 8.29.

N-Neopentylidene-*t*-butylamine (7). A solution of 21.7 ml (0.2 mole) of pivalaldehyde (Aldrich) and 21.0 ml of *t*-butylamine in 100 ml of benzene was refluxed under a water separator until no more water was collected. The solution was then distilled through a helices-packed column giving 13.3 g (47%) of the pure imine **7**: bp 120°;[19] infrared (CCl_4): 2960 and 1670 $cm.^{-1}$

Reaction of N-Neopentylidene-*t*-butylamine (7) with Dichlorocarbene.[8] A solution of 5.3 g (48 mmoles) of N-neopentylidene-*t*-butylamine (**7**) in 50 ml of pentane was mixed with 18.8 g (0.17 mole) of potassium *t*-butoxide (MSA Research Corp.). The slurry was cooled to 0° in an ice bath, and 13.4 ml (0.17 mole) of chloroform was added slowly. After the addition, the ice bath was removed and the mixture was stirred for 18 hr. The solution was filtered and evaporated. Distillation of the residue gave starting material and 400 mg (5%) of a viscous oil. This oil was taken up in ether and stirred in contact with 5% aqueous sodium bicarbonate for 2 hr. The solution was evaporated, and the residue upon evaporative vacuum distillation gave 60 mg (1%) of nearly pure 1,3-di-*t*-butylaziridinone (**3**). The product was identified by infrared spectrum and gas chromatographic retention time on a column of 10% silicone gum rubber (GE SE-30) on Diatoport "W."

Reaction of 1,3-Di-*t*-butylaziridinone (3) with Methanol. A solution of 434 mg (2.6 mmoles) of **3** in 10 ml of methanol was refluxed for 87 hr. The solution was cooled and evaporated. The residue was dissolved in methylene chloride and extracted with 20 ml of 6 *N* hydrochloric acid. Neutralization of the acid solution and extraction with methylene chloride gave 134.1 mg (26%) of methyl 2-(N-*t*-butylamino)-3,3-dimethylbutyrate (**9**): infrared (liquid film): 3300 (vw), 2950, and 1735 cm^{-1}; nmr (CCl_4): δ 0.89 (singlet, 9 H), 1.00 (singlet, 9 H), 1.48 (broad singlet, 1 H), 2.80 (singlet, 1 H), and 3.62 (singlet, 3 H).

Anal. Calcd for $C_{11}H_{23}NO_2$: C, 65.63; H, 11.52; N, 6.96. Found: C, 65.82; H, 11.72; N, 6.89.

Evaporation of the neutral fraction gave 234 mg (45%) of 2-methoxy-3,3-dimethyl-N-*t*-butylbutyramide (**10**): mp 56–58°; infrared (Nujol): 3300, 1660, and 1540 cm^{-1}; nmr ($CDCl_3$): δ 0.96 (singlet, 9 H), 1.38 (singlet, 9 H), 3.05 (singlet, 1 H), 3.36 (singlet, 3 H), and 6.1 (broad singlet, 1 H).

Anal. Calcd for $C_{11}H_{23}NO_2$: C, 65.63; H, 11.52; N, 6.96. Found: C, 65.49; H, 11.51; N, 6.85.

Reaction of 1,3-Di-*t*-butylaziridinone (3) with Methanolic Sodium Methoxide. A solution of 547 mg (3.2 mmoles) of the α-lactam **3** and 0.4 g of sodium methoxide (Matheson Coleman and Bell) in 12 ml of methanol was refluxed for 2 hr. The solution was cooled and concentrated under reduced pressure. The residue was taken up in methylene chloride and extracted with 6 *N* hydrochloric acid. The acid solution was made alkaline wth 20% aqueous sodium hydroxide and extracted with methylene chloride, yielding 336 mg (52%) of methyl 2-(N-*t*-butylamino)-3,3-dimethylbutyrate (**9**), bp 120° (30 mm). The physical properties of this material were identical with those of the ester isolated from the reaction of **3** with methanol.

Acid-Catalyzed Reaction of 1,3-Di-*t*-butylaziridinone (3) with Methanol. To a solution of 1.65 g (9.75 mmoles) of **3** in 25 ml of methanol were added a few small crystals of *p*-toluenesulfonic acid. The solution was refluxed for 72 hr. Evaporation of the methanol gave 2-methoxy-3,3-dimethyl-N-*t*-butylbutyramide (**10**), mp 56–58° (from aqueous methanol). This compound was identical with that previously obtained from the methanolysis of **3**.

Dimethylsulfoxonium 2-(N-*t*-butylamino)-3,3-dimethylbutyrylmethylide (11). To a solution of 608 mg (3 mmoles) of trimethylsulfoxonium iodide[20] in dimethyl sulfoxide was added 66 mg (3 mmoles) of a 50.9% dispersion of sodium hydride in mineral oil (Metal Hydrides, Inc.). The solution was stirred in a nitrogen atmosphere for 30 min, and a solution of 467 mg of 1,3-di-*t*-butylaziridinone (**3**) in 6 ml of dimethyl sulfoxide was then added. After stirring for 18 hr at ambient temperature, the solution was warmed to 60° for 2 hr and then poured into 80 ml of water. The aqueous mixture was extracted with four 20-ml portions of ether. Evaporation of the ether extract gave 623 mg (86%) of the stabilized ylide; mp 162–163° (from chloroform–hexane); infrared (Nujol): 1560 cm^{-1}; nmr ($CDCl_3$): δ 0.92 (singlet, 9 H), 1.03 (singlet, 9 H), 1.92 (broad singlet, 1 H), 3.72 (singlet, 1 H), 3.37 (singlet, 3 H), 3.40 (singlet, 3 H), and 4.45 (singlet, 1 H).

Anal. Calcd for $C_{13}H_{27}NO_2S$: C, 59.73; H, 10.41; N, 5.47; S, 12.27. Found: C, 59.68; H, 10.44; N, 5.32; S, 11.90.

Sealed Tube Pyrolysis of 1,3-Di-*t*-butylaziridinone (3). A 226-mg sample of **3** was sealed in an 8 × 80 mm Pyrex tube. The tube was placed in an electric oven at 175 ± 5° for 12 hr. The tube was cooled and opened. Gas chromatographic analysis of the liquid product on an 8 ft by 0.25 in. column of 10% Carbowax 20M on Diatoport "W" showed a complex mixture. Co-injection of authentic standards indicated that pivalaldehyde (Aldrich) and *t*-butyl cyanide (obtained from the phosphorous pentoxide dehydration of pivalamide[21]) comprised about 60% of the total chromatogram area.

Ethyl 2,3-Dimethyl-3-butenoate (22) and Ethyl 2,3-Dimethylcrotonate (23). These compounds were prepared *via* the Reformatsky reaction utilizing the procedure described by Huston and Goerner.[15]

Ethyl 2,3-dimethyl-3-butenoate (22) showed spectral peaks at: infrared (CCl_4): 3070, 2980, 1735, and 1650 cm^{-1}; nmr (CCl_4): δ 1.22 (doublet, 3 H, J = 7 cps), 1.23 (triplet, 3 H, J = 7 cps), 2.27 (triplet, 3 H, J = 1.5 cps), 3.04 (quartet, 1 H, J = 7 cps),

(17) J. C. Sheehan and J. H. Beeson, *J. Am. Chem. Soc.*, **89**, 366 (1967).

(18) The 3,3-dimethylbutyric acid was obtained from K & K Rare and Fine Chemicals.

(19) R. Bonnett, *J. Chem. Soc.*, 2313 (1965).

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4.07 (quartet, 2 H, J = 7 cps), and 4.79 (slightly split, 2 H, J = 1.5 cps).

Ethyl 2,3-dimethylcrotonate (23) showed spectral peaks at: infrared (CCl_4): 2980, 1715, and 1640 cm^{-1}; nmr (CCl_4): δ 1.25 (triplet, 3 H, J = 7 cps), 1.8 (singlet, 6 H), 1.98 (singlet, 3 H), and 4.10 (quartet, 2 H, J = 7 cps).

2,3-Dimethyl-N-*t*-butyl-3-butenamide (19). 2,3-Dimethyl-3-butenoic acid (534 mg, 4.7 mmoles) (from saponification of **22**[16]) was mixed with 0.4 ml (5.5 mmoles) of thionyl chloride, and the solution was allowed to stand for 30 min. The resulting mixture was taken up in ether and added to an ice-cold excess of *t*-butylamine in ether. The ether solution was washed with dilute hydrochloric acid, dilute sodium hydroxide, and water. Evaporation of the ether gave 340 mg (45%) of **19**. An analytical sample was obtained by vacuum sublimation: mp 76°; infrared (CCl_4): 3400, 3060, 1685, 1640, and 1505 cm^{-1}; nmr (CCl_4): δ 1.13 (doublet, 3 H, J = 7 cps), 1.28 (singlet, 9 H), 1.69 (slightly split, 3 H, J = 1.5 cps), 2.83 (quartet, 1 H, J = 7 cps), 4.80 (slightly split, 2 H, J = 1.5 cps).

Anal. Calcd for $C_{10}H_{19}NO$: C, 70.96; H, 11.32; N, 8.28. Found: C, 71.09; H, 11.42; N, 8.33.

2,3-Dimethylcrotonic Acid (25). Ethyl 2,3-dimethylcrotonate (6.2 g, 44 mmoles) was mixed with 50 ml of 20% aqueous sodium hydroxide and the resulting suspension was refluxed with stirring for 12 hr. The alkaline solution was washed with methylene chloride and then acidified. Extraction of the acidified solution gave 4.82 g (97%) of the acid, mp 71–72° (from aqueous methanol).[16]

2,3-Dimethyl-N-*t*-butylcrotonamide (20). A solution of 500 mg (4.4 mmoles) of 2,3-dimethylcrotonic acid (**25**) and 0.56 ml (6.6 mmoles) of oxalyl chloride in 10 ml of benzene was allowed to stand until the spontaneous bubbling ceased and was then refluxed for 1 hr. The excess oxalyl chloride and benzene were removed under reduced pressure, and the acid chloride, dissolved in ether, was added to an ice-cold solution of 0.9 ml (8.8 mmoles) of *t*-butylamine in 30 ml of ether. Water was added, and the layers were separated. The organic layer was washed with dilute hydrochloric acid, sodium bicarbonate, and distilled water. Evaporation gave 504 mg (68%) of **20**. A sample was sublimed for analysis: mp 83–86°; infrared (CCl_4): 3400, 2950, 1670, and 1500 cm^{-1}; nmr ($CDCl_3$): δ 1.40 (singlet, 9 H), 1.65 (singlet, 3 H), 1.80 (singlet, 6 H), 5.4 (broad singlet, 1 H).

Anal. Calcd for $C_{10}H_{19}NO$: C, 70.96; H, 11.32; N, 8.28. Found: C, 71.20; H, 11.24; N, 8.14.

Reaction of N-*t*-Butyl-2-bromo-3,3-dimethylbutyramide (6) with Silver Tetrafluoroborate. Silver tetrafluoroborate (10.5 g, 54 mmoles) and 9.0 g (36 mmoles) of the amide **6** were mixed in 150 ml of methylene chloride and stirred for 4 hr. A black precipitate accumulated during this time. The solution was filtered and washed with sodium bicarbonate. Evaporation gave 6.4 g of crystalline material. Column chromatography of 2.0 g of this material on Mallinckrodt A.R. 100-mesh silicic acid with 95% benzene–5% ethyl acetate as the moving phase gave 1.38 g of pure starting material (6) and 0.536 g of 2,3-dimethyl N-*t*-butyl-3-butenamide (**19**) which was identical with the synthetic sample (*vide supra*).

Hot-Tube Pyrolysis of 1,3-Di-*t*-butylaziridinone (3). A tube packed with 3-mm glass beads (15-ml volume) was heated in a 480° furnace, and 1.09 g of the α-lactam **3** was slowly dropped into the tube in a 100 cc/min nitrogen stream. In a Dry Ice–acetone trap, 615 mg of a condensate was collected. Gas chromatography on an 8 ft by 0.25 in. column of 10% Carbowax 20M on Diatoport "W" revealed that pivalaldehyde and *t*-butyl cyanide comprised 93% of the total product.

α-Lactams. V. The Pyrolysis and Nucleophilic Cleavage of Spiro-α-lactams[1]

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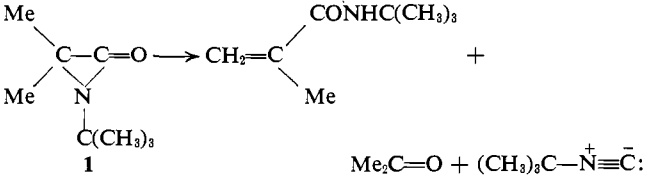
Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. *Received August 9, 1966*

Abstract: The thermal decomposition of three spiro-α-lactams has been found to produce the corresponding α,β-unsaturated amide and the corresponding cycloalkanone with an equivalent amount of *t*-butyl isocyanide. The ratio of amide to ketone was found to be dependent upon the ring size of the spiro substituent. Spiro-α-lactams react with methanol to form the corresponding 1-methoxy-1-(N-*t*-butylcarboxamido)cycloalkane. Reaction with sodium methoxide yields the methyl 1-(N-*t*-butylamino)cycloalkane-1-carboxylate. These nucleophilic cleavages are independent of the ring size of the spiro moiety. The ratio of products from thermal decomposition can be related to the geometry of the transition state.

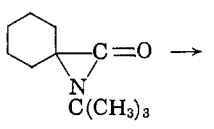
The thermal decomposition of an alkyl-substituted α-lactam, 1-*t*-butyl-3,3-dimethylaziridinone (**1**), has been shown to give N-*t*-butylmethacrylamide, acetone, and *t*-butyl isocyanide in yields of 65, 12, and



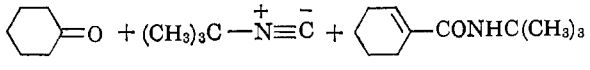
1

$Me_2C{=}O + (CH_3)_3C{-}\overset{+}{N}{\equiv}\overset{-}{C}$:

12%, respectively.[3] A subsequent study has demonstrated that the spiro-α-lactam, 1-*t*-butyl-3,3-pentamethyleneaziridinone (**2**), undergoes thermal rearrangement to give similar products; however, the product ratios are reversed. Cyclohexanone and *t*-butyl isocyanide were isolated in about 65% yield, and 11%



2



1-(N-*t*-butylcarboxamido)-1-cyclohexene was isolated.[4] This apparent dichotomy of two alkyl-substituted

(1) Part IV: J. C. Sheehan and J. H. Beeson, *J. Am. Chem. Soc.*, **89**, 362 (1967).

(2) National Institutes of Health Predoctoral Fellow, 1963–1966. This work is taken in part from the Ph.D. thesis of J. H. B., Massachusetts Institute of Technology, Cambridge, Mass., June 1966. See ref 1.

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