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.

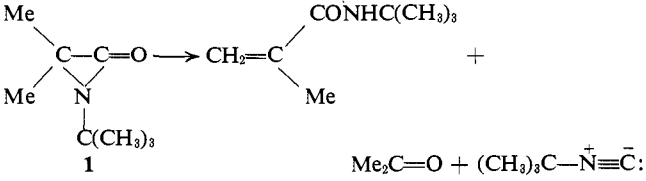
α-Lactams. V. The Pyrolysis and Nucleophilic Cleavage of Spiro-α-lactams[1]

John C. Sheehan and James H. Beeson[2]

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.

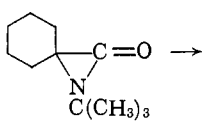
The thermal decomposition of an alkyl-substituted α-lactam, 1-*t*-butyl-3,3-dimethylaziridinone (**1**), has been shown to give N-*t*-butylmethacrylamide, acetone, and *t*-butyl isocyanide in yields of 65, 12, and



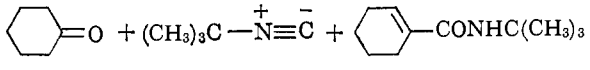
1

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

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.

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

(4) J. C. Sheehan and I. Lengyel, *ibid.*, **86**, 746 (1964).

α-lactams prompted the investigation of the pyrolyses (thermal decomposition) of two other spiro-α-lactams, 1-*t*-butyl-3,3-tetramethyleneaziridinone and 1-*t*-butyl-3,3-heptamethyleneaziridinone.

Results

The necessary α-lactam precursors, 1-bromo-1-(N-*t*-butylcarboxamido)cyclopentane (**3**) and 1-bromo-1-(N-*t*-butylcarboxamido)cyclooctane (**4**), were prepared by bromination of the corresponding cycloalkanecarbonyl chloride followed by treatment of the 1-bromocycloalkane-1-carbonyl chloride with *t*-butylamine. When the bromo amides were treated with potassium *t*-butoxide in an unreactive solvent (pentane, toluene, or ether), 1-*t*-butyl-3,3-tetramethyleneaziridinone (**3**) and 1-*t*-butyl-3,3-heptamethyleneaziridinone (**4**) were obtained. The relative instability and solubility (relative to starting material and by-products) of these α-lactams did not allow isolation in pure form. However, spectral evidence was obtained for the presence of the α-lactams. The α-lactam-containing mixtures were heated, and the pyrolysis[1] products were examined. Cyclopentanone (**6**), *t*-butyl isocyanide, and 1-(N-*t*-butylcarboxamino)-1-cyclopentene (**5**) were identified from the pyrolysis of **3**, and 1-(N-*t*-butylcarboxamido)-1-cyclooctene (**7**), cyclooctanone (**8**), and *t*-butyl isocyanide were obtained from the pyrolysis of **4**. Subsequent investigation of nucleophilic cleavage of these α-lactams indicated that no significant amounts of α,β-unsaturated amide were formed under the conditions of the α-lactam formation (*vide infra*). In both cases the yield of the α,β-unsaturated amide was greater than the yield of the cycloalkanone and *t*-butyl isocyanide pair. The ratio of the α,β-unsaturated amide to the ketone formed in the pyrolysis is given in Table I with the corresponding value from the pyrolysis of 1-*t*-butyl-3,3-pentamethyleneaziridinone.[3]

Table I

Ring size	(Amide): (ketone)	$k_{cyclic}/k_{acyclic}$[a]
8	2.5	100.0
6	0.15[3]	0.35
5	14.0	43.7

[a] Relative rates of solvolysis of methylcycloalkyl chlorides in 80% ethanol (*t*-butyl chloride = 1.0): H. C. Brown and M. Borkowski, *J. Am. Chem. Soc.*, **74**, 1894 (1952).

The reaction of each of these three spiro-α-lactams with nucleophiles was studied to determine whether any effect of ring geometry on these reactions could be observed. When **2**, **3**, and **4** were allowed to react with a representative nonionic nucleophile (methanol), the corresponding α-methoxy amides **9**, **10**, and **11** were the only methanolysis products isolated. Similarly, when each of the spiro-α-lactams was allowed to react with sodium methoxide, the only product of the reaction detected was the corresponding methyl ester (**12**, **13**, or **14**). Isolation of all of the methanolysis products by column chromatography produced no significant amounts of the α,β-unsaturated amide, indicating that the α,β-unsaturated amide formed previously was from pyrolysis of the α-lactam and not from dehydrohalogenation of the amide by potassium *t*-butoxide.[5]

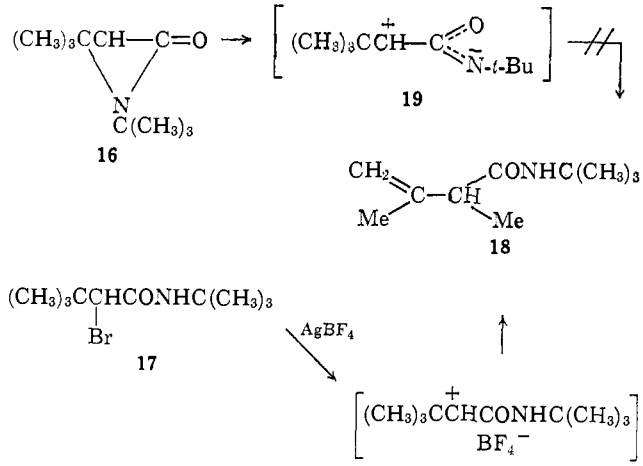
Discussion

When the thermal rearrangement of 1-*t*-butyl-3,3-pentamethyleneaziridinone (**2**) was reported, the oxirane structure **15** was postulated as a reaction intermediate to account for the formation of the ketone and isocyanide.[4] However, no mechanism for the transformation of **2** to **15** was suggested.

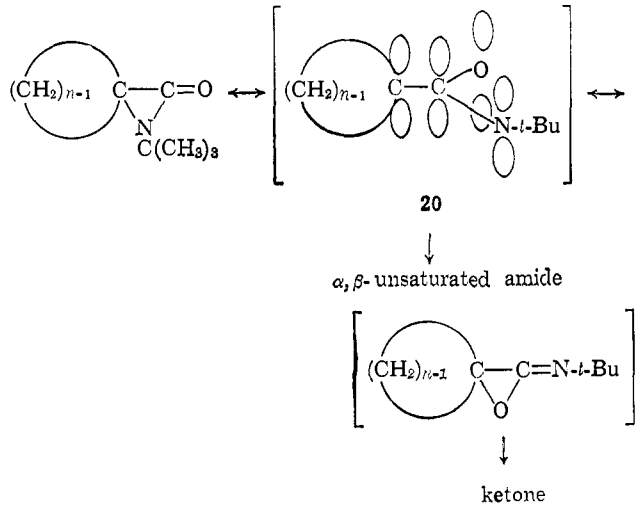
It has been reported that the pyrolysis of 1,3-di-*t*-butylaziridinone does not produce the neopentyl re-

(5) The observed impurities and by-products of the solvolysis reactions were the unreacted α-bromo amide and the α-*t*-butoxy amide and *t*-butyl ester from the reaction of the α-lactam with *t*-butyl alcohol and potassium *t*-butoxide.[3]

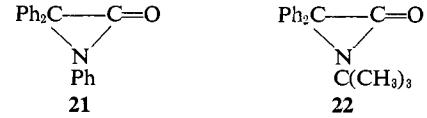
arrangement product 2,3-dimethyl-N-*t*-butyl-3-butenamide (**18**), which is produced by treatment of 2-bromo-3,3-dimethyl-N-*t*-butylbutyramide (**17**) with silver tetrafluoroborate.[1] This report may be taken as evidence that the rearrangement does not proceed *via* a dipolar transition state such as **19**.



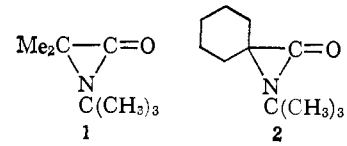
The ratio of α,β-unsaturated amide to ketone formed in the pyrolysis is compared to the relative rates of methylcycloalkyl chloride solvolysis in Table I. There is qualitative agreement between the numbers. The relative reaction rates of the methylcycloalkyl chlorides, according to the I-strain concept, are the result of changes in the bond hybridization in the transition state which in a cyclic system may produce concomitant changes in angle strain, torsional strain, and/or transannular strain.[6,7] It is apparent that if the α-lactam pyrolysis passes through a delocalized transition state such as **20**, I strain may well play a key role in the relative rates of ketone and olefin formation. Such a delocalized transition state (or metastable intermediate) is similar to that proposed for the Favorskii rearrangement.[8,9]



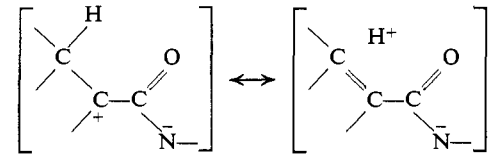
The large variation observed in the thermal stability of α-lactams is also compatible with a delocalized intermediate. Substituents which extend this delocalization promote formation of the delocalized transition state from the localized α-lactam structure and subsequent rearrangement of the α-lactam. Thus, **21** is so unstable that it has never been observed, and **22** has been observed only at low temperatures.[10]



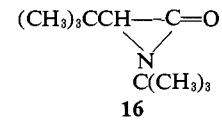
A vast improvement in thermal stability is achieved by replacing the phenyl groups of **22** with methyl (**1**) or methylene (**2**) groups. In these alkyl-substituted α-lactams, the delocalization may be extended only by



hyperconjugation, making such a transition state less energetically favorable than that of the phenyl-substituted α-lactams. When even hyperconjugation is



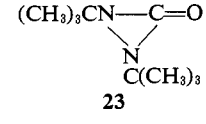
not allowed (*i.e.*, a *t*-butyl group is present), a very stable α-lactam (**16**) results.



The nucleophilic cleavage of α-lactams also resembles the behavior of the Favorskii intermediate described by Fort. The 2,6-lutidine-promoted methanolysis of α-chlorobenzyl benzyl ketone affords the α-methoxy ketone while the sodium methoxide promoted reaction gives the rearranged methyl ester.[9]

Summary

The ratio of α,β-unsaturated amide to ketone formed in the thermal decomposition of three spiro-α-lactams varies with the ring size of the spiro substituent, and the ratios are compatible with a delocalized transition state (or metastable intermediate) which is similar to the Favorskii intermediate described by House and Fort.[8,9] Generally, α-lactams seem to be intermediate in properties between a Favorskii intermediate and the very stable diaziridinone **23**.[11] The chemical properties of



α-lactams, however, resemble the Favorskii type more than the diaziridinone.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 237 spectrophotometer, and nuclear magnetic resonance spectra were

(6) See Table I, footnote *a*.
(7) E. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 265.
(8) H. O. House and W. F. Gilmore, *J. Am. Chem. Soc.*, **83**, 3980 (1961).
(9) A. W. Fort, *ibid.*, **84**, 2620 (1964).
(10) J. C. Sheehan and I. Lengyel, unpublished observation.
(11) F. D. Greene and J. C. Stowell, *J. Am. Chem. Soc.*, **86**, 3569 (1964).

determined on a Varian A-60 spectrometer. Melting points were determined on a Kofler hot-stage microscope, and the microanalyses were performed by Dr. S. M. Nagy and his associates at Massachusetts Institute of Technology.

1-Bromo-1-(N-*t*-butylcarboxamido)cyclopentane. A mixture of 5.0 g of cyclopentanecarboxylic acid (Aldrich) and 6.3 ml of thionyl chloride was warmed on a steam bath for 30 min, and the excess thionyl chloride was removed under reduced pressure. The acid chloride was warmed in an oil bath maintained at 90°, and 7.0 g (4.4 mmoles) of bromine was added in 0.5-ml portions. A small excess of bromine was added until the bromine color no longer disappeared. The crude product was distilled, bp 78° (1 mm), and the distillate was added slowly to an ice-cold solution of 6.4 g (88 mmoles) of *t*-butylamine in 50 ml of methylene chloride. After the addition, water was added, the layers were separated, and the organic layer was washed with dilute hydrochloric acid, aqueous sodium bicarbonate, and water. Evaporation of the methylene chloride gave 7.8 g (71%) of 1-bromo-1-(N-*t*-butylcarboxamido)-cyclopentane. An analytical sample was obtained by sublimation at 100° (760 mm): mp 93.5–94.5°; infrared (CCl_4): 3390, 2950, 1675, and 1515 cm^{-1}; nmr ($CDCl_3$): δ 1.38 (singlet, 9 H), 1.7–2.7 (complex, 8 H), 6.5 (broad singlet, 1 H).

Anal. Calcd for $C_{10}H_{18}NOBr$: C, 48.39; H, 7.31; N, 5.65. Found: C, 48.50; H, 7.45; N, 5.83.

Preparation and Pyrolysis of 1-*t*-Butyl-3,3-tetramethyleneaziridinone (3). To a stirred solution of 1.0 g (4 mmoles) of 1-bromo-1-(N-*t*-butylcarboxamido)cyclopentane in 50 ml of pentane was added 0.45 g (4 mmoles) of potassium *t*-butoxide at 0°. The solution was stirred for 15 min and then concentrated to half-volume. Centrifugation gave a clear solution which on evaporation gave a mixture containing about 50–60% of the α-lactam (estimated from the infrared spectrum). The α-lactam mixture, under vacuum (0.5 mm), was plunged into an 80° oil bath, and the pyrolysis products were collected in a liquid nitrogen trap. Gas chromatographic analysis of the mixture on a 12 ft × 0.25 in. column of 10% Versamid 900 on Diatoport "W" indicated the presence of cyclopentanone (Eastman) and 1-(N-*t*-butylcarboxamido)-1-cyclopentene (**5**), with relative peak areas of 1:14 (corrected for the injection port pyrolysis of the α-bromo amide to give **5**).

1-(N-*t*-Butylcarboxamido)-1-cyclopentene (5). A solution of 2.0 g (8 mmoles) of 1-bromo-1-(N-*t*-butylcarboxamido)cyclopentane in 20 ml of pyridine was refluxed for 24 hr. The solution was poured into 80 ml of water and extracted with ether. The ether extract was washed with dilute hydrochloric acid, 5% aqueous sodium bicarbonate, and water. Evaporation of the extract gave 280 mg (21%) of **5**. An analytical sample was prepared by vacuum sublimation: mp 113–114°; infrared (CCl_4): 3410, 3040, 2950, 1670, 1630, and 1505 cm^{-1}; nmr ($CDCl_3$): δ 1.31 (singlet, 9 H), 1.55–2.60 (complex, 6 H), 5.4 (broad singlet, 1 H), and 6.32 (multiplet 1 H).

Anal. Calcd for $C_{10}H_{17}NO$: C, 71.81; H, 10.25; N, 8.38. Found: C, 71.81; H, 10.27; N, 8.44.

1-Bromo-1-(N-*t*-butylcarboxamido)cyclooctane. A mixture of 25 g (0.16 mole) of cyclooctanecarboxylic acid (prepared from cyclooctene[12] from City Chemical Co.) and 21.4 ml (0.3 mole) of thionyl chloride was allowed to stand until spontaneous bubbling ceased. After warming the solution for a few minutes on the steam bath, the excess thionyl chloride was removed under reduced pressure, and distillation gave 22.8 g (82%) of the acid chloride.

A solution of 4.57 g (27 mmoles) of cyclooctanecarbonyl chloride and 1.58 ml (29 mmoles) of bromine in 10 ml of carbon tetrachloride was refluxed gently until the bromine color disappeared. The solution was then cooled and added slowly to an ice-cold solution of 5.71 ml (54.4 mmoles) of *t*-butylamine in methylene chloride. After the addition, the solution was stirred a few minutes at room temperature. The resulting solution was washed with 6 *N* hydrochloric acid, 5% sodium hydroxide, and distilled water. Evaporation of the methylene chloride gave 7.02 g (93%) of the crude product. Chromatography of the material on 200 g of Mallinckrodt A.R. 100-mesh silicic acid with 95% benzene–5% ethyl acetate as the moving phase gave 6.75 g (89%) of the bromo amide. Low-temperature sublimation (40° with a Dry Ice condenser) gave a colorless crystalline solid, mp 38–40°. In spite of repeated sublimations, however, an analytically pure sample was not obtained; infrared (liquid film): 3400, 2925, 1675, and 1515 cm^{-1}; nmr ($CDCl_3$): δ 1.3 (singlet, 9 H), 1.4–2.4 (complex, 14 H), and 6.3 (broad singlet, 1 H).

1-(N-*t*-Butylcarboxamido)-1-cyclooctene (7). Cyclooctanecarbonyl chloride (22.8 g, 0.131 mole) was heated in a 110° oil bath, and 8.1 ml (0.15 mole) of bromine was added slowly. The liquid was heated for 30 min after the addition was complete, and then it was poured into 300 ml of ice water. Extraction with ether and distillation of the extract gave 18.0 g (89%) of cyclooctenecarboxylic acid, bp 125° (0.8 mm). The acid was converted to the N-*t*-butylamide *via* the acid chloride: mp 100–101.5° (from aqueous methanol); infrared (CCl_4): 3400, 2930, 1670, 1630, and 1500 cm^{-1}; nmr ($CDCl_3$): δ 1.35 (singlet, 9 H), 1.4–2.5 (complex, 12 H), 5.6 (broad singlet, 1 H), and 6.36 (triplet, 1 H, J = 9 cps).

Anal. Calcd for $C_{13}H_{23}NO$: C, 74.59; H, 11.08; N, 6.69. Found: C, 74.58; H, 11.15; N, 6.45.

Preparation and Pyrolysis of 1-*t*-Butyl-3,3-heptamethyleneaziridinone (4). To a stirred ice-cold solution of 1.39 g (4.8 mmoles) of the α-bromo amide was added 0.53 g (4.8 mmoles) of potassium *t*-butoxide, and the resulting suspension was stirred for 15 min. The pentane solution was concentrated to half-volume and filtered. The resulting pentane solution exhibited a single carbonyl absorption in the infrared spectrum at 1835 cm^{-1}. Evaporation of the remainder of the solvent gave the crude α-lactam. The flask containing the α-lactam was placed under vacuum (0.5 mm) and plunged into an oil bath at 100°. The volatile material (151 mg) was trapped in a liquid nitrogen trap. Gas chromatographic analysis on a 6 ft by 0.25-in. column of 10% silicone gum rubber (GE SE-30) on Diatoport "W" indicated that the volatile material consisted of a mixture of *t*-butyl isocyanide[4] and cyclooctanone[13] (17% yield).

Column chromatography of the nonvolatile residue on Mallinckrodt A.R., 100-mesh silicic acid with 97.5% benzene–2.5% ethyl acetate as the moving phase gave 360 mg (42%) of 1-(N-*t*-butylcarboxamido)-1-cyclooctene (**7**).

Reaction of Spiro-α-lactams with Methanol. The 1-bromo-1-(N-*t*-butylcarboxamido)cycloalkane was mixed with 1.1 equiv of potassium *t*-butoxide in enough dry toluene to make a 5% solution and stirred for 30 min at 0°. The toluene was then removed under reduced pressure at a temperature not exceeding 10°. The residue was taken up in petroleum ether, transferred to a centrifuge tube, and placed in the freezer (−20°) for 30 min. Centrifugation gave a clear solution which was mixed with excess methanol and allowed to stand for 1 hr. The petroleum ether and excess methanol were removed under reduced pressure, and the methanolysis product was isolated by column chromatography on Mallinckrodt A.R. 100-mesh silicic acid using 95% benzene–5% ethyl acetate as the moving phase. Only the products listed below were obtained from the methanolysis Other chromatography fractions were examined by nmr and were found to contain no OMe group.

1-Methoxy-1-(N-*t*-butylcarboxamido)cyclopentane (9) had the following properties: mp 69–71°; infrared (CCl_4): 3400, 2950, 1680, and 1510 cm^{-1}; nmr ($CDCl_3$): δ 1.35 (singlet, 9 H), 1.5–2.2 (complex, 8 H), 3.2 (singlet, 3 H), and 6.3 (broad singlet, 1 H).

Anal. Calcd for $C_{11}H_{21}NO_2$: C, 66.29; H, 10.62; N, 7.03. Found: C, 66.26; H, 10.51; N, 7.11.

1-Methoxy-1-(N-*t*-butylcarboxamido)cyclohexane (10) had the following properties: mp 82–84°; infrared (Nujol): 3310, 1660, and 1510 cm^{-1}; nmr ($CDCl_3$): δ 1.35 (singlet, 9 H), 1.2–2.1 (complex, 10 H), 3.17 (singlet, 3 H), and 6.2 (broad singlet, 1 H).

Anal. Calcd for $C_{12}H_{23}NO_2$: C, 67.56; H, 10.87; N, 6.57. Found: C, 67.87; H, 11.11; N, 6.53.

1-Methoxy-1-(N-*t*-butylcarboxamido)cyclooctane (11) had the following properties: infrared (Nujol): 3340, 1660, and 1525 cm^{-1}; nmr ($CDCl_3$): δ 1.35 (singlet, 9 H), 1.35–2.4 (complex, 14 H), 3.18 (singlet, 3 H), and 6.2 (broad singlet, 1 H).

Anal. Calcd for $C_{14}H_{27}NO_2$: C, 69.66; H, 11.28; N, 5.80. Found: C, 69.65; H, 11.08; N, 5.82.

Reaction of Spiro-α-lactams with Sodium Methoxide. Petroleum ether solutions of the crude spiro-α-lactams obtained by the previously described procedure were mixed with a fourfold excess of sodium methoxide and stirred for 1 hr at room temperature. The petroleum ether solution was then extracted with 6 *N* hydrochloric acid. Neutralization of the acid solution with 20% sodium hydroxide followed by extraction with methylene chloride gave the α-amino esters listed below. These esters were distilled in a Hickman apparatus for analysis. The acid–neutral fraction from the

(12) (a) R. Willstätter and E. Waser, *Chem. Ber.*, **43**, 1176 (1910); (b) A. C. Cope, M. Burg, and S. W. Fenton, *J. Am. Chem. Soc.*, **74**, 173 (1952).

(13) An authentic sample was obtained from the laboratories of Professor A. C. Cope.

extraction was examined by nmr in each case, and no OMe-containing compounds were observed.

Methyl 1-(N-*t*-butylamino)cyclopentane-1-carboxylate (12) showed: bp 50° (0.1 mm); infrared (CCl_4): 2950 and 1735 cm^{-1}; nmr ($CDCl_3$): δ 1.03 (singlet, 9 H), 1.4–2.2 (complex, 8 H), and 3.6 (singlet, 3 H).

Anal. Calcd for $C_{11}H_{21}NO_2$: C, 66.29; H, 10.62; N, 7.03. Found: C, 66.35; H, 10.68; N, 7.07.

Methyl 1-(N-*t*-butylamino)cyclohexane-1-carboxylate (13) showed: bp 70° (0.1 mm); infrared (liquid film): 2950 and 1740 cm^{-1}; nmr ($CDCl_3$): δ 1.05 (singlet, 9 H), 1.1–2.2 (complex, 10 H), and 3.6 (singlet, 1 H).

Anal. Calcd for $C_{12}H_{23}NO_2$: C, 67.56; H, 10.87; N, 6.57. Found: C, 67.45; H, 10.70; N, 6.41.

Methyl 1-(N-*t*-butylamino)cyclooctane-1-carboxylate (14) showed: bp 90° (0.1 mm); infrared (liquid film): 2950 and 1740 cm^{-1}; nmr ($CDCl_3$): δ 1.03 (singlet, 9 H), 1.1–2.1 (complex, 14 H), and 3.6 (singlet, 3 H).

Anal. Calcd for $C_{14}H_{27}NO_2$: C, 69.66; H, 11.28; N, 5.80. Found: C, 69.68; H, 11.10; N, 6.09.

Structural Effects in Solvolytic Reactions. II. Nature of the Intermediates Involved in the Solvolysis of Symmetrically Substituted β-Anisylethyl Derivatives

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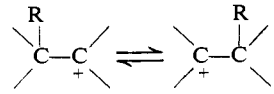
Abstract: The rates of reaction of sodium borohydride in isopropyl alcohol with 1-*p*-anisyl-2-propanone, 3-*p*-anisyl-2-butanone, and 3-methyl-3-*p*-anisyl-2-butanone were measured. An examination of a linear free energy plot of these quantities *vs.* the rates of solvolysis of the related toluenesulfonic acid esters reveals deviations from the linear relationship previously noted for the phenyl derivatives. These deviations support the presence of moderate participation by the anisyl substituents in the solvolysis of the tosylates. The rates of formolysis of β-phenylethyl, β-*m*-tolylethyl, β-*p*-tolylethyl, and β-*p*-anisylethyl tosylates were determined. The data are not correlated by the σ^+ constants, suggesting that only a small amount of the developing positive charge in the transition state is transmitted to the aromatic ring. On the other hand, the rates of acetolysis and formolysis of substituted benzyl tosylates do give satisfactory correlations with the σ^+ constants. The observation that a *p*-methoxy group enhances the rate of solvolysis of a benzyl tosylate by a factor in the neighborhood of 100,000, as compared to a factor of only 76 for the formolysis of β-*p*-anisylethyl tosylate, is indicative of the large difference in the amount of the developing charge which is delocalized into the aromatic ring and the *p*-methoxy substituent in the two systems. It is pointed out that neighboring groups may be classified into three types: *n*-, such as RS–, R_2N–, I–, Br–, Cl–; π-, such as $CH_2{=}CH$–, *p*-$^-OC_6H_4$–, *p*-$CH_3OC_6H_4$–, C_6H_5–; and σ-, such as H_3C–. In the *n* class we have a transition between excellent groups, such as neighboring iodide (rate enhancement of 10^6), bromide (rate enhancement of 800), and chloride (negligible rate enhancement). Here current theory recognizes the possibility that there is a transition between the formation of a bridged species for a group with a large rate enhancement, such as iodine, and the absence of a bridged species in the case of a poor neighboring group, such as chlorine. In the π group we observe similar large changes in the effect of the neighboring group: β-*p*-$^-OC_6H_4$–, 10^8, β-*p*-$CH_3OC_6H_4$–, 160, β-C_6H_5–, 2.1. Yet in this π class current theory does not recognize the possibility for a similar transition in the structure of the intermediate. It is suggested that in the case of β-arylethyl derivatives current theory must be revised to consider fully bridged intermediates (arylonium ions), unsymmetrical π-bridged equilibrating cations, equilibrating essentially unbridged cations, and static classical cations. In other words, the sharp dichotomy exhibited by the present theory would appear to be better replaced by an essentially continuous spectrum of cations whose precise structure will depend upon the height of the central barrier for interconversion and the nature of its environment.

The current treatment of carbonium ions[4] appears to involve two major anomalies.[5] First, practically all carbonium ions (or ion pairs[6]) for which structures have been proposed are considered to be static classical or static bridged species. Second, the formation of stable bridged species has been frequently proposed in solvolytic reactions in cases where no significant rate enhancement is indicated.

As was pointed out,[5a] systematic lowering of the potential barrier separating two equivalent cations[6] would



be expected to result in an essentially continuous spectrum of such cations, of which three main classes may be distinguished: (A) essentially static classical ions, which can be formed and transformed into products without significant equilibration; (B) equilibrating

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(3) Post-doctorate research associate, 1964–1965, on Grant G 19878 supported by the National Science Foundation.

(4) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

(5) (a) H. C. Brown, K. J. Morgan, and F. J. Chloupek, *J. Am. Chem. Soc.*, **87**, 2137 (1965). (b) See this source and D. J. Cram, *ibid.*, **86**, 3767 (1964), for leading references to the voluminous prior literature dealing with the parent β-phenylethyl derivatives.

(6) In many instances the data do not permit one to distinguish between the formation and reactions of ions or of ion pairs. Consequently, in the subsequent discussion the use of the term cation or carbonium ion shall be understood to include either the free cation or the corresponding ion pair.