ABOUT FOUR NEW TRITYL-SUBSTITUTED α-LACTAMS

Istvan Lengyel,* Victor Cesare, Ian Adam, and Tony Taldone

Department of Chemistry, St. John's University, Jamaica, New York 11439 USA

Abstract- This investigation comprises the synthesis, a description of the physical and spectroscopic properties, determination of the limits of thermal stability, and reactions with protic and aprotic nucleophiles of four new trityl-substituted α-lactams. With the exception of 3,3-dimethyl-1-tritylaziridin-2-one (4a), which is unstable at room temperature, all new compounds have been fully characterized.

INTRODUCTION

All stable, isolable α-lactams which have been prepared pure to date have a tertiary alkyl or cycloalkyl group attached to nitrogen (e.g. tert-butyl or 1-adamantyl). A further prerequisite of stability seems to be a tertiary alkyl or aryl group in position three. Two α-lactams with two methyl substituents at C-3 have been synthesized, but these are relatively less stable.

Because of these severe restrictions on stability, our attention fell on the trityl group as a potentially good stabilizing substituent. When this project was begun, no trityl-substituted α-lactams were known. During the course of this investigation, a report of one trityl-substituted α-lactam, 3-tert-butyl-1-tritylaziridin-2-one was published. The same compound was also prepared independently in our laboratory.

Here we report the synthesis, physical and spectral properties, and an investigation of the thermal decomposition, and some reactions with nucleophiles of four new trityl-substituted α-lactams, 3,3-dimethyl-1-tritylaziridin-2-one (4a), 3-(1-adamantyl)-1-tritylaziridin-2-one (4b), 1-tert-butyl-3-tritylaziridin-2-one (4c) and 1-(1-adamantyl)-3-tritylaziridin-2-one (4d) (Scheme 1).

The reaction of α-lactam (4a) with sodium methoxide in methanol gave an anomalous major product, N-triphenylmethyl-2-methoxy-2-methylpropanamide (15a), along with the expected methyl 2-methyl-2-triphenylmethylaminopropanoate (16a) as a minor product. This is the first reported example of the
formation of an \( \alpha \)-alkoxy amide as the main product, in high yield, by the action of an alkoxide upon an \( \alpha \)-lactam, resulting from C3-nitrogen bond cleavage (Scheme 9).

**Scheme 1.** The four new trityl-substituted \( \alpha \)-lactams comprising this investigation.

![Chemical structures](image)

**RESULTS AND DISCUSSION**

1. **Synthesis**

The synthesis of the four new aziridinones (4a-d) is outlined in Scheme 2. The commercially available carboxylic acids (1) were converted to the corresponding \( \alpha \)-bromo acid chlorides (2) following the procedure of Harpp *et al.*\(^8\) The \( \alpha \)-bromo acid chlorides (2) were then used to acylate the corresponding amine either by the procedure of Schlesinger and Prill\(^9\) or Lengyel and Aaronson.\(^10\) The resulting \( \alpha \)-bromo amides (3) were subsequently 1,3-dehydrobrominated by a variant of the general procedure of Sheehan and Lengyel,\(^3\) effecting ring closure to the \( \alpha \)-lactams (4), generally in good yield. Every new product, except 4a, which is unstable at room temperature, was fully characterized by IR, \(^1\)H-NMR, \(^13\)C-NMR, and MS spectra, mp, TLC, and elemental analysis.
Scheme 2. Synthesis of the aziridinones.

\[
\begin{align*}
1 & \quad \overset{(1) \ 	ext{SOCl}_2}{\rightarrow} \quad 2 \\
& \quad \overset{(2) \ 	ext{NBS}, \text{CCl}_4}{\rightarrow} \\
3 & \quad \overset{\text{NaO}t\text{-C}_4\text{H}_9}{\rightarrow} \\
& \quad \overset{\text{ether or THF}}{\rightarrow} \\
4 & \\
\end{align*}
\]

<table>
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<tr>
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<th>R_1</th>
<th>R_2</th>
<th>R_3</th>
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<td>a</td>
<td>CH₃</td>
<td>CH₃</td>
<td>Tr</td>
</tr>
<tr>
<td>b</td>
<td>Ad</td>
<td>H</td>
<td>Tr</td>
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<tr>
<td>c</td>
<td>Tr</td>
<td>H</td>
<td>t-C₄H₉</td>
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<tr>
<td>d</td>
<td>Tr</td>
<td>H</td>
<td>Ad</td>
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* Ad denotes 1-adamantyl, C₁₀H₁₅

2. Thermal Decomposition

While \(\alpha\)-lactams (4b, 4c, and 4d) are extraordinarily stable to heat (Scheme 3), \(\alpha\)-lactam (4a) rearranges at room temperature in ether solution in a few minutes to its isomer, \(N\)-tritylmethacrylamide (5) (Scheme 4). The structure of the rearrangement product of \(\alpha\)-lactam (4a) was confirmed by an independent synthesis of \(N\)-tritylmethacrylamide (5) from methacryloyl chloride and tritylamine (see EXPERIMENTAL).

Quast et al.¹¹ state that pure 1-\(t\)-ert-butyl-3,3-dimethylaziridin-2-one³ quantitatively decomposes at 40°C into acetone and \(t\)ert-butyl isocyanide. Eliminative isomerization to the \(\alpha\), \(\beta\)-unsaturated amide³ is not a pure thermal process, but is probably caused by difficult-to-exclude impurities, in particular bases, i.e. "must be regarded as a base-catalyzed eliminative ring opening."

We agree with this interpretation, persuaded by the evidence offered in the analogous autocatalytic rearrangement of aziridinimines (12) to \(\alpha\), \(\beta\)-unsaturated amidines (13), in which the amidine product (13) is believed to act as the ring-opening base catalyst¹² (Scheme 5).
α-Lactam (4b) must be refluxed in n-octane for one hour to bring about complete thermal decomposition, α-lactam (4c) required 75 min of reflux in n-nonane, and α-lactam (4d) is even more stable: it required one hour of reflux in n-decane to cause complete thermal decomposition. In each case, the decomposition products are the corresponding aldehyde (6 and 8) and isonitrile (7, 9, and 10) (Scheme 3). This path of thermal decomposition of α-lactams was first observed and reported by Sheehan and Lengyel, who
Scheme 5. Base-catalyzed isomerization of aziridinimines (12) to $\alpha, \beta$-unsaturated amidines (13).

![Scheme 5](image)

proposed an imino-oxirane (14) as a likely intermediate in this fragmentation (Scheme 6). In the case of 4c, the heat and duration required to bring about complete decomposition also causes extensive isomerization of the isonitrile to the more stable nitrile (9 $\rightarrow$ 11).

Scheme 6. The main path of thermal decomposition of $\alpha$-lactams.

![Scheme 6](image)

It is interesting to note that the thermal decomposition products of $\alpha$-lactams do not correspond to the fragments obtained upon electron bombardment. The electron impact-induced predominant primary fragmentation pathway of all $\alpha$-lactams investigated to date is decarbonylation$^{14,15}$ to the corresponding Schiff bases.

3. Reactions

The non-ionic nucleophile methanol, and the ionic nucleophile sodium methoxide (in methanol) were chosen for this study.

a) Reaction with methanol

The direct relationship between thermal stability and reactivity with nucleophiles has been established.$^{1,2}$ Thus, for example, 1,3-di-tert-butylaziridin-2-one decomposes only slowly at $140^\circ$C and requires 87 h refluxing in methanol (pK$_a$ 15.5) to react completely (leading to a mixture of products).$^{16}$ In contrast, 1-tert-butyl-3,3-dimethylaziridin-2-one decomposes completely after refluxing for one hour in ether and
requires only two hours to react completely with tert-butyl alcohol (pK\textsubscript{a} 18.0) at 50°C, to give only one product, the α-tert-butoxy amide.\textsuperscript{3}

Therefore, we were not all too surprised to find enormous differences in the rate of reaction of these α-lactams with the very weak nucleophile methanol, from almost instantaneous in the case of 4a, yielding one product (15a), to refluxing for several days and leading to a mixture of products for 4c and 4d. The two methanolyses we found preparatively feasible are reported here, Scheme 7. The others (4c and 4d), achieved under forced conditions and therefore giving multiple products, are omitted.

**Scheme 7.** Reaction of α-lactams (4a) and (4b) with methanol.

\[
\begin{array}{cccccc}
R_1 & R_2 & \text{Temp, °C} & \text{Time, h} & \text{Yield %} & \text{mp, °C} \\
15a & \text{CH}_3 & \text{CH}_3 & -20 & 1 & 63.0 & 127-129 \\
15b & \text{Ad} & \text{H} & +65 & 24 & 89.4 & 131-133 \\
\end{array}
\]

b) Reaction with sodium methoxide

Reaction of α-lactams with the powerful ionic nucleophile methoxide (CH\textsubscript{3}ONa in methanol) has been known\textsuperscript{1,2} to result in acyl nitrogen (1,2-) bond cleavage and the formation of α-alkylamino acid methyl esters (Scheme 8). Indeed, α-lactam (4b) with sodium methoxide in methanol at rt gave an 81 % yield of crystalline methyl 2-(1-adamantyl)-2-triphenylmethylaminoacetate (16b), mp 188-189°C, α-lactam (4c) a 78 % yield of pure methyl 2-tert-butylamino-3,3,3-triphenylpropanoate (16c), mp 116-118°C, and α-lactam (4d), under similar reaction conditions, yielded 70 % of pure methyl 2-(1-adamantylamino)-3,3,3-triphenylpropanoate (16d), mp 165-166°C. All three products are stable colorless crystalline compounds. Each has been fully characterized by IR, \textsuperscript{1}H-NMR, \textsuperscript{13}C-NMR, and MS spectra, mp, TLC, and a correct elemental analysis.
Scheme 8. Reaction of α-lactams (4b, 4c, and 4d) with sodium methoxide in methanol.

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<tr>
<th></th>
<th>R₁</th>
<th>R₂</th>
<th>R₃</th>
<th>Yield %</th>
<th>mp, °C</th>
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<tbody>
<tr>
<td>16b</td>
<td>Ad</td>
<td>H</td>
<td>Tr</td>
<td>81</td>
<td>188-189</td>
</tr>
<tr>
<td>16c</td>
<td>Tr</td>
<td>H</td>
<td>t-C₄H₉</td>
<td>78</td>
<td>116-118</td>
</tr>
<tr>
<td>16d</td>
<td>Tr</td>
<td>H</td>
<td>Ad</td>
<td>70</td>
<td>165-166</td>
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To our bafflement, however, α-lactam (4a) reacted with sodium methoxide in methanol-THF at 0°C to give a mixture of N-triphenylmethyl-2-methoxy-2-methylpropanamide (15a) and methyl 2-methyl-2-triphenylmethylaminopropanoate (16a) in a relative ratio of about eight to one (Scheme 9).

The major product (15a) obtained from the sodium methoxide reaction is identical in every respect (IR, NMR, and MS spectra, and mp) with the product of the methanolysis. This is the first reported example of an α-lactam undergoing alkoxide-promoted nucleophilic ring opening by C₃-nitrogen bond cleavage.

Scheme 9. Reaction of α-lactam (4a) with sodium methoxide in methanol.

Compound (16a) was also obtained by an independent synthesis from 2-aminoisobutyric acid (17) according to Scheme 10. The 2-aminoisobutyric acid (17) was first converted to its methyl ester hydrochloride (18) in nearly quantitative yield by the general procedure of Boissonas et al.¹⁷ N-Tritylation was then performed following the original procedure of Helferich et al.¹⁸ to give 16a. All
physical and spectral properties of 16a, whether obtained as the minor product in the reaction of sodium methoxide with α-lactam (4a) or by an independent synthesis, are identical.

**Scheme 10.** An independent synthesis of methyl 2-methyl-2-triphenylmethylaminopropanoate (16a).

ACKNOWLEDGEMENT

We thank Mr. Lin (Leo) Yu for excellent technical assistance.

**EXPERIMENTAL**

**General Remarks:** Melting points are uncorrected and were measured on a Thomas-Hoover® capillary melting point apparatus. Thin layer chromatography (TLC) was performed with Analtech® silica gel glass backed plates (250 microns) and recorded as a function of Rf values. All flash chromatographic separations were performed employing silica gel (JT Baker®, 40 µm) as the stationary phase. IR spectra were measured on a Perkin Elmer® Fourier Transform (FT-IR) Spectrum 1000 interferometer. NMR spectra (1H and 13C) were performed on either a 500 or 400 MHz Bruker® instrument with tetramethylsilane as the internal standard. Microanalyses were performed by Atlantic Microlab, Inc. (Norcross, Georgia). MS spectra were recorded either on a Hewlett Packard® G1800A GCD System or a Hewlett Packard 5890 gas chromatograph equipped with a 5971A mass selective detector. The ESI tandem MS spectrum was performed on a Finnigan LCQ quadrupole ion trap mass spectrometer at the Scripps Research Institute (La Jolla, California).

The reagents tert-butylamine, tritylamine, sodium methoxide, sodium tert-butoxide, thionyl chloride and adamantaneacetic acid, as well as the solvents n-octane, n-nonane, THF and ether were all obtained from Aldrich® (Milwaukee, WI). Ethyl acetate, dichloromethane, n-heptane and benzene were obtained from J. T. Baker® (Phillipsburg, NJ). n-Hexane was obtained from EM Science (Gibbstown, NJ) and both tert-butyl cyanide and 1,2-dichloroethane were purchased from Lancaster® (Pelham, NH). 3,3,3-Triphenylpropionic acid was obtained from Alfa Aesar® (Ward Hill, MA) and tert-butyl isocyanide was
purchased from Fluka® (Milwaukee, WI). Methanol was purchased from Fisher Scientific® (Fair Lawn, NJ).

**N-Triphenylmethyl-2-bromo-2-methylpropanamide (3a).**

The general procedure of Lengyel and Aaronson\(^\text{10}\) was followed. To a solution of tritylamine (5.27 g, 0.020 mol) and triethylamine (2.43 g, 0.024 mol) in 50 mL of dichloromethane at 0°C was added 2-bromo-2-methylpropanoyl bromide (4.83 g, 0.021 mol) (Aldrich) in one portion. The reaction mixture stirred overnight, slowly coming to rt, and then was diluted with dichloromethane (40 mL) and water (40 mL). The organic layer was washed with distilled water (25 mL), twice with 0.05 N HCl (20 mL), twice with saturated NaHCO\(_3\) (25 mL), and distilled water (30 mL). It was dried with Na\(_2\)SO\(_4\) and the dichloroethane was removed under reduced pressure to afford 8.20 g (100 %) of crude solid. Pure 3a was obtained by flash chromatography, using \(n\)-hexane/ethyl acetate:95/5, to give 6.73 g (82.4 %) of a white/yellow solid, mp 134-136°C. TLC (90 % \(n\)-hexane: 10 % ethyl acetate) \(R_f = 0.47\). IR (CCl\(_4\)): 3400 (N-H); 3050, 3020 (aromatic C-H); 2980, 2920 (aliphatic C-H); 1685 (C=O, amide) cm\(^{-1}\). \(^1\)H-NMR (CDCl\(_3\)): \(\delta = 1.95\) (s, CH\(_3\)-C-CH\(_3\), methyl protons, 6H), 7.28 (m, phenyl protons, 15H), and 8.01 (s, NH-proton, exchanges for deuterium in CDCl\(_3\)/CF\(_3\)COOD, 1H). \(^1\)C-NMR (CDCl\(_3\)): \(\delta = 32.56\) (CH\(_3\)-C-CH\(_3\), methyl carbons attached to C2), 63.96 (tertiary carbon attached to carbonyl carbon), 70.76 (-C(Ph)\(_3\), trityl carbon adjacent to nitrogen), 127.43 (phenyl carbons in para position), 128.24 (phenyl carbons in meta position), 128.62 (phenyl carbons in ortho position), 144.46 (phenyl carbons attached to trityl carbon), and 170.59 (C=O, carbonyl carbon). MS: m/z 328, (M-Br)+; 260, ((C\(_6\)H\(_5\))\(_3\)CNH\(_3\))^+; 243, ((C\(_6\)H\(_5\))\(_3\)C)^+; 165, (C\(_{13}\)H\(_9\)+, fluorenly cation), base peak; 104, (C\(_6\)H\(_3\)CNH)^+; 77, (C\(_6\)H\(_3\))^+; 69, (C\(_4\)H\(_5\)O)^+; 41, (C\(_3\)H\(_3\))^+. Anal. Calcd for C\(_{23}\)H\(_{22}\)NOBr: C 67.65; H 5.43; N 3.43; Br 19.57. Found: C 67.75; H 5.50; N 3.44; Br 19.45.

**Attempted synthesis of 3,3-dimethyl-1-triphenylmethylaziridin-2-one (4a).**

\(N\)-Trityl-2-bromo-2-methylpropanamide (0.50 g, 0.0012 mol) (3a) was dissolved in 25 mL of ether at 0°C. Sodium tert-butoxide (0.129 g, 0.00135 mol) was added in one portion. After 30 min of stirring the reaction mixture was filtered, \(n\)-hexane (50 mL) was added to the filtrate, and the solvent was removed under reduced pressure until approximately 25 mL remained. The remaining mixture was filtered and an
IR spectrum of the filtrate showed a strong α-lactam (4a) carbonyl band at 1835 cm⁻¹ and a small amide carbonyl band (3a) at 1680 cm⁻¹. Due to the instability of α-lactam (4a), all attempts to purify it were unsuccessful. It rearranged to N-tritylmethacrylamide (5), which was identical with N-tritylmethacrylamide synthesized by an independent method.

**Independent synthesis of N-triphenylmethylmethacrylamide (5).**

The general procedure of Lengyel and Aaronson¹⁰ was followed. Tritylamine (3.00 g, 0.012 mol) and triethylamine (1.21 g, 0.012 mol) were dissolved in dichloromethane (20 mL) at 0°C. Methacryloyl chloride (1.21 g, 0.012 mol) (Aldrich) was added and stirred for 1 h at 0°C, then slowly warmed to rt overnight. It was washed with distilled water (2 x 15 mL), 5 % aqueous NaHCO₃ (2 x 10 mL), and again with distilled water (2 x 15 mL). The organic layer was dried over Na₂SO₄ and the dichloromethane removed under reduced pressure to give 3.77 g (96 %) of a colored oily residue, which solidified upon standing. The crude product was recrystallized twice from 13 mL of boiling n-heptane/ethyl acetate (10:3) to yield 2.40 g (61 %) of a white solid (5) with mp 132°C. TLC (70 % n-hexane: 30 % ethyl acetate) Rᵣ = 0.68. IR (CCl₄): 3454 (N-H); 3070, 3033 (aromatic C-H); 2930 (aliphatic C-H); 1690 (C=O, amide); 1635 cm⁻¹ (C=C). \(^1\)H-NMR (CDCl₃): \(\delta = 2.01\) (s, \(\text{H}_3\text{C}-\text{C}=\), methyl protons, 3H) \(^5\) (s, olefinic proton \textit{trans} to amide carbonyl, 1H), 5.75 (s, olefinic proton \textit{cis} to amide carbonyl), 7.02 (s, NH-proton, exchanges for deuterium in CDCl₃/CF₃COOD, 1H), and 7.28 (m, phenyl protons, 15H). \(^1\)C-NMR (CDCl₃): \(\delta = 19.06\) (\(\text{CH}_3\text{-C}=\), methyl carbon attached to olefinic carbon), 70.52 (-\(\text{C}(\text{Ph})_3\), trityl carbon adjacent to nitrogen), 119.23 (\(\text{CH}_3\text{-C}=\), olefinic carbon attached to amide carbonyl), 127.21 (phenyl carbons in \textit{para} position), 128.17 (phenyl carbons in \textit{meta} position), 128.75 (phenyl carbons in \textit{ortho} position), 141.53 (H₂\text{C}=\), 144.86 (phenyl carbons attached to trityl carbon), and 167.64 (C=O, amide carbonyl carbon). MS: m/z 327, M⁺, C₂₃H₂₁NO; 250, (M-C₆H₅)⁺; 243, ((C₆H₅)₃C)⁺; 234, (M-93); 165, (C₁₃H₉)⁺; 69, (C₄H₅O)⁺, base peak; 41, (C₃H₅)⁺. Anal. Calcd for C₂₃H₂₁NO: C 84.37; H 6.46; N 4.28. Found: C 84.09; H 6.42; N 4.33.

**Reaction of 3,3-dimethyl-1-triphenylmethylaziridin-2-one (4a) with methanol.**

Crude 3,3-dimethyl-1-triphenylmethylaziridin-2-one (4a) was generated \textit{in situ} and reacted with methanol by the following procedure: N-Trityl-2-bromo-2-methylpropanamide (3a) (0.380 g, 0.93 mmol) was
dissolved in 30 mL of anhydrous ether cooled to -20°C with an acetone/dry ice bath. Then in one portion, sodium tert-butoxide (0.353 g, 3.67 mmol) was added with stirring. After 25 min, methanol (7.87 g, 0.246 mol) was added, and the reaction mixture stirred at -20°C for 1 h. It was then allowed to stir for an additional hour at rt. The methanol was removed under reduced pressure. The residue was taken up in ethyl acetate (35 mL) and washed three times with distilled water (20 mL). The organic layer was dried with Na2SO4 and the solvent was evaporated under reduced pressure to afford 0.430 g of an oil, which crystallized upon standing. Flash chromatography, using 90:10 n-hexane/ethyl acetate as eluent, and subsequent recrystallization from boiling n-hexane yielded 0.210 g (63 %) of pure N-trityl-2-methoxy-2-methylpropanamide (15a) with mp 125-127°C. TLC (80 % n-hexane: 20 % ethyl acetate) Rf = 0.47. IR (CCl4): 3410 (N-H); 3060, 3020 (aromatic C-H); 2950, 2970 (aliphatic C-H), 1690 (C=O, amide) cm⁻¹.

¹H-NMR (CDCl₃): δ = 1.39 (s, CH₃-C-CH₃, gem. dimethyl protons, 6H), 3.37 (s, -OCH₃, methoxy protons, 3H), 7.27 (m, phenyl protons, 15H), and 8.01 (s, NH-proton, exchanges for deuterium in CDCl₃/CF₃COOD, 1H). ¹³C-NMR (CDCl₃): δ = 23.16 (CH₃-C-CH₃, methyl carbons attached to C2), 51.47 (-OCH₃, methoxy carbon), 69.78 (-C(Ph)₃, trityl carbon adjacent to nitrogen), 79.31 (tertiary carbon attached to carbonyl carbon), 127.12 (phenyl carbons in para position), 128.10 (phenyl carbons in meta position), 128.80 (phenyl carbons in ortho position), 145.10 (C1 carbons of the trityl moiety), and 174.06 (C=O, carbonyl carbon). MS: m/z 359, M⁺, C₂₄H₂₅NO₂; 327, (M-CH₃OH)⁺; 243, (C(C₆H₅))⁺; 165, (C₁₃H₀)⁺; 87, (C₄H₇O₂)⁺, base peak; 59, (C₃H₇O⁺). Anal. Calcd for C₂₄H₂₅NO₂: C 80.19; H 7.01; N 3.90. Found: C 80.01; H 7.06; N 3.89.

Reaction of 3,3-dimethyl-1-triphenylmethylaziridin-2-one (4a) with sodium methoxide.

3,3-Dimethyl-1-triphenylmethylaziridin-2-one (4a) was generated in situ and reacted with sodium methoxide by the following procedure: to a solution of N-trityl-2-bromo-2-methylpropanamide (3a) (1.00 g, 0.0024 mol) in 50 mL of anhydrous ether cooled to 0°C, was added sodium tert-butoxide (0.254 g, 0.00264 mol) while stirring. After 30 min, a suspension of sodium methoxide (0.388 g, 0.0072 mol) and methanol (0.115 g, 0.0036 mol) in 40 mL of freshly distilled THF was added in one portion, and the reaction mixture stirred at 0°C for 30 min. It was then stirred overnight at rt. The reaction mixture was
filtered and the filtrate was evaporated under reduced pressure to yield 1.23 g of a solid residue which was flash chromatographed using 90 % n-hexane: 10 % ethyl acetate as eluent, to give 0.55 g (63.8 %) of pure N-trityl-2-methoxy-2-methylpropanamide (15a) as the major product, with mp 127-129°C. TLC (80 % n-hexane: 20 % ethyl acetate) R_f = 0.41. IR (CCl_4): 3409 (N-H); 3062, 2981 (C-H); 1694 (C=O) cm^{-1}. ^1H-NMR (CDCl_3): δ = 1.39 (s, CH_3-C-CH_3, gem. dimethyl protons, 6H), 3.37 (s, -OCH_3, methoxy protons, 3H), 7.27 (m, phenyl protons, 15H), and 8.01 (s, NH-proton, exchanges for deuterium in CDCl_3/CF_3COOD, 1H). ^13C-NMR (CDCl_3): δ = 23.16 (CH_3-C-CH_3, methyl carbons attached to C2), 51.47 (-OCH_3, methoxy carbon), 69.78 (-C(Ph)_3, trityl carbon adjacent to nitrogen), 79.31 (tertiary carbon attached to carbonyl carbon), 127.12 (phenyl carbons in para position), 128.10 (phenyl carbons in meta position), 128.80 (phenyl carbons in ortho position), 145.10 (C1 carbons of the trityl moiety), and 174.06 (C=O, carbonyl carbon). MS: m/z 359, M^+, C_{24}H_{25}NO_2; 327, (M-CH_3OH)^+; 243, (C(C_6H_5)_3)^+; 165, (C_{13}H_9)^+; 87, (C_4H_7O_2)^+, base peak; 59, (C_3H_7O)^+. Anal. Calcd for C_{24}H_{25}NO_2: C 80.19; H 7.01; N 3.90. Found: C 80.54; H 7.03; N 3.87.

The minor product eluted was methyl 2-methyl-2-triphenylmethylaminopropanoate (16a) (0.07 g, 8.1 %, mp 110-111°C). TLC (85 % n-hexane: 15 % ethyl acetate) R_f = 0.51. IR (CCl_4): 3348 (N-H); 3086, 3060, 3021 (aromatic C-H); 2997, 2950 (aliphatic C-H); 1740 (ester C=O) cm^{-1}. ^1H-NMR (CDCl_3): δ = 1.27 (s, CH_3-C-CH_3, gem. dimethyl protons, 6H), 2.98 (br s, N-H proton, 1H), 3.17 (s, -OCH_3, methoxy protons, 3H), 7.15 (t, J = 5 Hz, para protons of the trityl moiety, 3H), 7.22 (t, J = 5 Hz, meta protons of the trityl moiety, 6H), and 7.55 (d, J = 5.5 Hz, ortho protons of the trityl moiety). ^13C-NMR (CDCl_3): δ = 27.92 (CH_3-C-CH_3, methyl carbons attached to C2), 51.54 (-OCH_3, methoxy carbon), 58.08 (tertiary carbon attached to carbonyl carbon), 69.94 (-C(Ph)_3, trityl carbon adjacent to nitrogen), 126.11 (phenyl carbons in para position), 127.37 (phenyl carbons in meta position), 129.32 (phenyl carbons in ortho position), 146.82 (C1 carbons of the trityl moiety), and 177.24 (C=O, carbonyl carbon). MS: m/z no detectable molecular ion; 300, (M-COOCH_3)^+; 282, (M-C_6H_5)^+; 243 [(C_6H_5)_3C]^+, base peak; 165 (C_{13}H_9)^+; 104, (C_6H_5CNH)^+; 77, (C_6H_5)^+; 69, (C_4H_7O)^+; 41, (C_3H_7)^+. Anal. Calcd for C_{24}H_{25}NO_2: C 80.19; H 7.01; N 3.90. Found: C 80.28; H 7.10; N 3.89.
2-Bromoadamantaneacetyl chloride (2b).

The general procedure of Harpp et al. was followed. A solution of 1-adamantaneacetic acid (1b) (12.85 g, 0.066 mol) and thionyl chloride (31.50 g, 0.265 mol) in carbon tetrachloride (7 mL) was heated between 35-45°C for 30 min. After cooling to rt, finely powdered N-bromosuccinimide (14.13 g, 0.0794 mol), carbon tetrachloride (33 mL), and 4 drops of 48 % HBr were added to the reaction mixture with stirring. It was then heated for 20 min at 60-65°C, then refluxed at approximately 85°C for 30 min, and finally stirred at rt overnight. The carbon tetrachloride and excess thionyl chloride were removed under reduced pressure and the resulting residue was taken up in carbon tetrachloride (50 mL). The resulting mixture was filtered and washed three times with carbon tetrachloride to afford a solid (succinimide, mp 121°C, exhibiting an IR spectrum superimposable on that of an authentic sample). All of the carbon tetrachloride was removed from the filtrate and the resulting oil was vacuum distilled at 105-107°C/0.7 mm Hg to obtain 2b (88 %). IR (CCl₄): 2911 and 2853 (aliphatic C-H); 1800 (carbonyl of acid chloride); 1765 cm⁻¹ (weak overtone vibration). ¹H-NMR (CCl₄): δ = 1.80 (CH₂ protons of the adamantane moiety, 12H); 2.05 (CH protons of the adamantane moiety, 3H); 4.20 (s, Br-C-H proton, 1H). Crude 2b was used without further purification.

N-Triphenylmethyl-2-bromoadamantanacetamide (3b).

The general procedure of Schlesinger and Prill was followed. Dropwise, to a solution of triphenylmethylamine (11.41 g, 0.044 mol) and triethylamine (4.45 g, 0.044 mol) in dichloromethane (300 mL), was added a solution of 2-bromoadamantaneacetyl chloride (2b) (11.66 g, 0.04 mol) in dichloromethane (50 mL). After stirring overnight, the reaction mixture was washed three times with distilled water (100 mL). The organic layer was then dried with Na₂SO₄ and the solvent was removed under reduced pressure. The resulting yellow oil, crude 3b, was purified by flash chromatography using 90:10 n-hexane:ethyl acetate as eluent, to obtain pure 3b (48.9 %, mp 183-184°C). TLC (90 % hexane: 10 % ethyl acetate) Rₜ = 0.55. IR (CCl₄): 3416 (N-H); 3064, 3030 (aromatic C-H); 2915, 2854 (aliphatic C-H); 1685 (carbonyl of amide) cm⁻¹. ¹H-NMR (CDCl₃): δ = 1.59-1.66 (m, the three methylene groups of the adamantane moiety farther away from the bromine, 6H), 1.75-1.78 (m, the three methylene groups
closer to the bromine, 6H), 1.97 (s, methine protons of the adamantane moiety, 3H), 3.99 (s, proton on brominated carbon adjacent to carbonyl group, 1H) and 7.31-7.32 (m, protons on the trityl moiety, 15H).

$^{13}$C-NMR (CDCl$_3$): $\delta = 28.51$ (methine carbons of the adamantane moiety), 36.66 (methylene carbons of the adamantane moiety), 39.98 (quaternary carbon of the adamantyl moiety), 67.00 (brominated carbon adjacent to carbonyl carbon), 70.94 (trityl carbon adjacent to nitrogen), 127.25 (phenyl carbons in para position), 128.17 (phenyl carbons in meta position), 128.65 (phenyl carbons in ortho position), 144.37 (C1 carbons of the trityl moiety) and 165.88 (carbonyl carbon of amide). Anal. Calcd for C$_{31}$H$_{32}$NOBr: C 72.37; H 6.27; N 2.72; Br 15.53. Found: C 72.46; H 6.37; N 2.69; Br 15.46.

3-(1-Adamantyl)-1-triphenylmethylaziridin-2-one (4b).

The general procedure of Sheehan and Lengyel$^3$ was followed. Sodium tert-butoxide (0.267 g, 0.00278 mol) was directly added to a solution of N-triphenylmethyl-2-bromoadamantane-acetamide (3b) (1.30 g, 0.00253 mol) in ether (60 mL) and THF (5 mL) at 0°C. After stirring for 1 h, the reaction mixture was washed three times with distilled water (20 mL). The organic layer was then dried with Na$_2$SO$_4$ and the solvent was removed under reduced pressure to afford a quantitative yield of crude 3-(1-adamantyl)-1-triphenylmethylaziridin-2-one (4b). Crude 4b was recrystallized from n-hexane to yield 0.81 g of pure (4b) (74 %, mp 131–133°C). TLC (90 % n-hexane: 10 % ethyl acetate) $R_f = 0.38$. IR (CCl$_4$): 3055 and 3020 (aromatic C-H); 2920 and 2850 (aliphatic C-H); 1837 (carbonyl of $\alpha$-lactam) cm$^{-1}$. $^1$H-NMR (CDCl$_3$) $\delta = 1.46 – 1.71$ (m, methylene protons of the adamantane moiety, 12H), 1.96 (s, proton on the methine carbon of the adamantane moiety, 3H), 2.03 (s, proton on C-2 of aziridinone ring, 1H) and 7.27 – 7.47 (m, phenyl protons of the trityl moiety, 15H). $^{13}$C-NMR (CDCl$_3$): $\delta = 26.24$ (methylene carbons of the adamantane moiety), 33.35 (methine carbons of the adamantane moiety), 36.77 (quaternary carbon of the adamantane moiety), 40.10 (methine carbon in aziridinone ring), 56.27 (quaternary carbon of the trityl moiety), 127.69 (phenyl carbons in para position), 128.22 (phenyl carbons meta positions), 129.02 (phenyl carbons in ortho position), 142.74 (C1 carbons of the trityl moiety) and 161.72 (carbonyl carbon). Anal. Calcd for C$_{31}$H$_{31}$NO: C 85.87; H 7.21; N 3.23. Found: C 85.97; H 7.29; N 3.12.
Thermal decomposition of 3-(1-adamantyl)-1-triphenylmethylaziridin-2-one (4b).

α-Lactam (4b) (0.200 g, 0.46 mmol) was refluxed in 5 mL of n-octane for 1 h. TLC (100 % chloroform) Rf = 0.61 and 0.79 (two spots). IR (CCl4): 3070 (aromatic C-H); 2966 and 2922 (aliphatic C-H); 2856 and 2701 (H-C stretches from aldehyde); 2125 (NC stretch); 1727 (carbonyl of aldehyde) cm⁻¹. GC shows two peaks on the chromatogram (of relatively equal area) corresponding to adamantyl aldehyde (6) and trityl isonitrile (7) (as verified by MS spectrum), respectively. A sample of trityl isonitrile synthesized by an independent method for comparison showed a similar retention time and MS spectrum. MS (7): m/z 269, M⁺, C20H15N; 192 (M – C₆H₅)+; 165, (C13H9⁺, fluorenyl cation) base peak; 77 (C₆H₅)+; 51 (C₄H₃)+. MS (6): m/z 164, M⁺, C11H16O; 135, (M – CHO)+, base peak; 93, (base peak – C₃H₆); 79, (base peak – C₄H₈).

Reaction of 3-(1-adamantyl)-1-triphenylmethylaziridin-2-one (4b) with methanol.

α-Lactam (4b) (0.44 g, 1.01 mmol) was dissolved in methanol (15 mL) and refluxed for 24 h. Solvent was removed under reduced pressure to afford a light yellow oil. Crystallization from hot hexane (3 mL) yielded 0.42 g (89.4 %) of a white solid, N-triphenylmethyl-2-(1-adamantyl)-2-methoxyacetamide (15b), mp 131–133°C. TLC (80 % n-hexane: 20 % ethyl acetate) Rf = 0.58. IR (CCl4): 3409 (N-H); 3062 and 3025 (aromatic C-H); 2915 and 2848 (aliphatic C-H); 1694 (carbonyl band of amide) cm⁻¹. ¹H-NMR (CDCl₃): δ = 1.61 and 1.69 (m, methylene protons of the adamantane moiety, 12H), 1.96 (s, methine protons of the adamantane moiety, 3H), 3.03 (s, proton on carbon adjacent to the carbonyl carbon, 1H), 3.41 (s, protons of the methoxy group, 3H), 7.30 (s, phenyl protons, 15H) and 7.64 (s, NH proton, exchanges for deuterium in CDCl₃/CF₃COOD, 1H). ¹³C-NMR (CDCl₃): δ = 28.47 (methine carbons of the adamantane moiety), 37.20 (methylene carbons of the adamantane moiety), 38.57 (quaternary carbon of the adamantane moiety), 59.87 (carbon adjacent to the carbonyl carbon), 70.14 (-C(C₆H₅)₃, trityl carbon adjacent to nitrogen), 91.92 (carbon of the methoxy group), 127.14 (phenyl carbons in para position), 128.08 (phenyl carbons in meta position), 128.82 (phenyl carbons in ortho position), 144.96 (C1 carbons of the trityl moiety) and 170.00 (carbonyl carbon of amide). Anal. Calcd for C₃₂H₃₅NO₂: C 82.54; H 7.58; N 3.01. Found: C 82.57; H 7.58; N 3.01.
Reaction of 3-(1-adamantyl)-1-triphenylmethylaziridin-2-one (4b) with sodium methoxide.

A solution of sodium methoxide (0.15 g, 2.76 mmol) in methanol (20 mL) was added to a solution of α-lactam (4b) (0.20 g, 0.46 mmol) in THF (5 mL). After stirring at rt for 16 h, the methanol and THF were removed under reduced pressure and the remaining residue was dissolved in 1,2-dichloroethane. The solution was washed three times with distilled water (35 mL), dried with Na₂SO₄, and the solvent was removed under reduced pressure to afford crude methyl 2-(1-adamantyl)-2-triphenylmethylaminoacetate (16b). Crude 16b was recrystallized from a hot n-hexane/ethyl acetate (50/50) solution to afford pure 16b (0.17 g, 81 %, mp 188–189°C). TLC (90 % n-hexane: 10 % ethyl acetate) Rₜ = 0.62. IR (CCl₄): 3324 (N-H); 3060 and 3033 (aromatic C-H); 2907 and 2851 (aliphatic C-H); 1734 (carbonyl band of ester) cm⁻¹.

¹H-NMR (CDCl₃): δ = 1.51 (t, J = 11.8 Hz, methylene protons at the 4, 6, 9 and 10 positions on the adamantane moiety, 8H), 1.68 (q, J = 12.1 Hz, methylene protons at the 2 and 8 positions on the adamantane moiety, 4H), 1.87 (d, J = 12.0 Hz, methine protons on the adamantane moiety, 3H), 2.53 (d, J = 14.5 Hz, NH proton, exchanges for deuterium in CDCl₃/CF₃COOD, 1H), 3.07 (s, protons on the methoxy group, 3H), 3.10 (s, proton of the carbon adjacent to the carbonyl carbon, 1H), 7.16 (t, J = 7.11 Hz, phenyl protons in para position, 3H), 7.25 (t, J = 7.13 Hz, phenyl protons in meta position, 6H) and 7.53 (d, J = 7.28 Hz, phenyl protons in ortho position, 6H). ¹³C-NMR (CDCl₃): δ = 28.86 (methine carbons of the adamantane moiety), 37.23 (methylene carbons at the 4, 6, 9 and 10 positions of the adamantane moiety), 37.77 (methylene carbons at the 2 and 8 positions of the adamantane moiety), 39.53 (quaternary carbon of the adamantyl moiety), 50.77 (carbon of the methoxy group), 64.87 (carbon adjacent to the carbonyl carbon), 70.65 (trityl carbon adjacent to nitrogen), 126.47 (phenyl carbons in para position), 127.76 (phenyl carbons in meta position), 129.48 (phenyl carbons in ortho position), 146.31 (C1 carbons of the trityl moiety) and 173.59 (carbonyl carbon of the ester). Anal. Calcd for C₃₂H₃₅NO₂: C 82.54; H 7.58; N 3.01. Found: C 82.52, H 7.78, N 2.91.

Pure crystalline α-methoxy amide (15b) was collected as a minor product, 0.04 g (19 %), which had the same melting point (131-133°C), Rₜ value on TLC (0.58) and IR (carbonyl band at 1694 cm⁻¹) as that of amide (15b) obtained from the reaction of α-lactam (4b) with methanol.
2-Bromo-3,3,3-triphenylpropanoyl chloride (2c).

The general procedure of Harpp et al.\textsuperscript{8} was followed. A solution of 3,3,3-triphenylpropionic acid (1c) (20.00 g, 0.066 mol) and thionyl chloride (31.5 g, 0.265 mol) in carbon tetrachloride (7 mL) was refluxed at 65°C for 30 min. Finely powered \textit{N}-bromosuccinimide (14.13 g, 0.079 mol), carbon tetrachloride (33 mL) and 4 drops of 48 % HBr were then added to the reaction mixture and stirred for 30 min between 70-85°C and then stirred overnight. Carbon tetrachloride and thionyl chloride were removed from the reaction mixture under reduced pressure and carbon tetrachloride was added to the residue. The mixture was vacuum filtered to yield a solid (succinimide, mp 121°C, exhibiting an IR spectrum superimposable on that of an authentic sample), which was washed three times with 15 mL of carbon tetrachloride. Carbon tetrachloride was removed from the filtrate under reduced pressure until approximately 20 mL remained. Solid precipitated and was filtered to obtain crude 2c (14.52 g, 54.9 %, mp 126-130°C). The carbon tetrachloride of the filtrate was removed under reduced pressure and replaced with 20 mL of \textit{n}-hexane. Filtration of the resulting mixture yielded a second crop of crude 2c (5.27 g, 19.9 %, total yield of 2c was 74.8 %). IR (CCl₄): 3092, 3062, 3037 (aromatic C-H); 1805 (carbonyl of acid chloride); 1745 cm\textsuperscript{-1} (weak overtone vibration). 60 MHz \textsuperscript{1}H-NMR: \(\delta = 6.00\) (s, Br-C-H proton, 1H) and 7.20 (m, phenyl protons, 15H). Crude 2c was used without further purification.

\textit{N}-(\textit{tert}-Butyl)-2-bromo-3,3,3-triphenylpropanamide (3c).

The general procedure of Lengyel and Aaronson\textsuperscript{10} was followed. To a solution of \textit{tert}-butylamine (3.22 g, 0.044 mol) in dichloromethane (200 mL) was dropwise added a solution of crude 2-bromo-3,3,3-triphenylpropanoyl chloride (2c) (8.00 g, 0.02 mol) dissolved in dichloromethane (50 mL). The reaction mixture stirred for 3 h, was washed three times with distilled water (100 mL), and then the organic layer was dried with Na\textsubscript{2}SO\textsubscript{4}. The dichloromethane and excess \textit{tert}-butylamine were removed under reduced pressure to obtain crude 3c (8.42 g, 96 %). After recrystallization from an \textit{n}-heptane/ethyl acetate solvent system (55/45), analytically pure 3c (7.21 g, 82.6 %, mp 224-225°C) was obtained. TLC (90 % \textit{n}-hexane: 10 % ethyl acetate) \(R_f = 0.47\). IR (CCl₄): 3410 (N-H); 3050, 3030 (aromatic C-H); 1805 (carbonyl of acid chloride); 1745 cm\textsuperscript{-1} (weak overtone vibration). 60 MHz \textsuperscript{1}H-NMR (CDCl₃): \(\delta = 1.02\) (s, protons on the \textit{tert}-butyl moiety, 1H).
9H), 4.89 (s, NH proton, exchanges for deuterium in CDCl₃/CF₃COOD, 1H), 5.88 (s, proton attached to the brominated carbon) and 7.29 – 7.45 (m, protons on the the trityl moiety, 15H). ¹³C-NMR (CDCl₃): δ = 27.98 (methyl carbons of the tert-butyl group), 51.37 (tertiary carbon of the tert-butyl group attached to the nitrogen), 60.27 (brominated carbon adjacent to the carbonyl carbon), 61.54 (quaternary carbon of the trityl moiety), 126.99 (phenyl carbons in para position), 127.92 (phenyl carbons in meta position), 130.37 (phenyl carbons in ortho position), 144.24 (C1 carbons of the trityl moiety) and 166.96 (carbonyl carbon of the amide). Anal. Calcd for C₂₅H₂₆NOBr: C 68.81; H 6.01; N 3.21; Br 18.31. Found: C 69.08; H 6.13; N 3.15; Br 18.06.

1-tert-Butyl-3-triphenylmethylaziridin-2-one (4c).

The general procedure of Sheehan and Lengyel³ was followed. N-tert-Butyl-2-bromo-3,3,3-triphenylmethylpropanamide (3c) (1.00 g, 2.29 mmol) was dissolved in dry THF (25 mL) at rt. Sodium tert-butoxide (0.51 g, 5.27 mmol) was added and the reaction mixture stirred for 0.5 h. The solvent was removed under reduced pressure and the residue was dissolved in dichloromethane (25 mL). The solution was transferred to a separatory funnel and washed three times with 35 mL of distilled water. The organic layer was dried over Na₂SO₄ and the solvent was removed under reduced pressure to afford 0.78 g (96.3 %) of a yellow oil. Crude 4c was crystallized from a mixture of n-hexane (10 mL) and ethyl acetate (6 mL) to afford 0.38 g (46.9 %) of pure crystalline 4c, mp 172–174°C, with sintering from 160°C. TLC (80 % n-hexane: 20 % ethyl acetate) R_f = 0.59. IR (CCl₄): 3062 and 3033 (aromatic C-H); 2981 and 2929 (aliphatic C-H); 1848 (carbonyl of α-lactam) cm⁻¹. ¹H-NMR (CDCl₃) δ = 1.16 (s, tert-butyl protons, 9H), 4.07 (s, proton on C-3 of the aziridinone ring, 1H) and 7.15 – 7.31 (m, phenyl protons of the trityl moiety, 15H). ¹³C-NMR (CDCl₃): δ = 27.80 (methyl carbons of the tert-butyl group), 52.79 (tertiary carbon of the tert-butyl group adjacent to the nitrogen), 57.64 (quaternary carbon of the trityl moiety), 57.81 (methine carbon in the aziridinone ring), 126.87 (phenyl carbons in para position), 127.84 (phenyl carbons in meta position), 130.21 (phenyl carbons in ortho position), 144.12 (C1 carbons of the trityl moiety) and 157.51 (carbonyl carbon). Anal. Calcd for C₂₅H₂₅NO: C 84.31; H 6.97; N 3.94. Found: C 84.31; H 6.97; N 4.03
Thermal decomposition of 1-tert-butyl-3-triphenylmethylaziridin-2-one (4c).

α-Lactam (4c) (0.100 g, 0.28 mmol) was refluxed in 5 mL of n-nonane for 75 min. IR (n-nonane): 2257 (C≡N); 2132 (N≡C); 1734 (carbonyl of aldehyde) cm⁻¹. n-Nonane, tert-butyl nitrile (11), and tert-butyl isocyanide (9) were removed under reduced pressure to give crude triphenylethanal (8). TLC (90 % n-hexane: 10 % ethyl acetate), 3 spots, Rf = 0.64 (major component), 0.29 (minor component) and 0.23 (minor component). IR (CCl₄) of aldehyde (8): 3063 and 3031 (aromatic C-H); 2960 and 2929 (aliphatic C-H); 2855 and 2729 (hydrogen stretch of carbonyl); 1735 cm⁻¹ (carbonyl of aldehyde). The GC retention time and MS spectrum of 9 were identical to an authentic sample of tert-butyl isocyanide (Fluka). MS (9): m/z 83, M⁺, C₅H₉N; 68 (M – CH₃)+; 57 (M – CN)+; 41 (C₃H₅)+.

For NMR spectral data and elemental analysis of 8 see the thermal decomposition of 4d.

Reaction of 1-tert-butyl-3-triphenylmethylaziridin-2-one (4c) with sodium methoxide.

α-Lactam (4c) (0.08 g, 0.230 mmol) was dissolved in THF (5 mL) and sodium methoxide (0.049 g, 0.92 mmol) dissolved in methanol (10 mL) was added. The reaction was stirred at rt for 16 h. Solvent was removed under reduced pressure and redissolved in 1,2-dichloroethane. The solution was washed three times with 35 mL of distilled water. The organic layer was dried over Na₂SO₄ and the solvent was removed under reduced pressure to afford 0.08 g (88.9 %) of a clear oil (16c). Crude 16c was flash chromatographed under nitrogen using 80:20 n-hexane:ethyl acetate as eluent to afford 0.07 g (78 %) of pure methyl ester, methyl 2-tert-butylamino-3,3,3,-triphenylpropanoate (16c), mp 116–118°C. TLC (95 % n-hexane: 5 % ethyl acetate) Rf = 0.45. IR (CCl₄): 3350 (N-H); 3062 and 3033 (aromatic C-H); 2966 and 2907 (aliphatic C-H); 1741 (carbonyl of ester) cm⁻¹. ¹H-NMR (CDCl₃): δ = 1.06 (s, protons on the tert-butyl group, 9H), 1.44 (br s, NH proton, exchanges for deuterium in CDCl₃/CF₃COOD, 1H), 3.30 (s, protons on the methoxy group, 3H), 4.91 (s, proton on the carbon adjacent to the carbonyl carbon, 1H) and 7.13 – 7.46 (m, phenyl protons, 15H). ¹³C-NMR (CDCl₃): δ = 29.67 (methyl carbons of the tert-butyl group), 51.02 (carbon of the methoxy group), 51.36 (tertiary carbon of the tert-butyl group adjacent to the nitrogen), 61.72 (quaternary carbon of the trityl moiety), 62.93 (methine carbon adjacent to the carbonyl carbon), 126.22 (phenyl carbons in para position), 127.15 (phenyl carbons in meta position), 130.63
(phenyl carbons in ortho position), 144.94 (C1 carbons of the trityl moiety) and 176.06 (carbonyl carbon of the ester). Anal. Calcd for C_{26}H_{29}NO_{2}: C 80.59; H 7.54; N 3.61. Found: C 80.69; H 7.45; N 3.58.

**N-(1-Adamantyl)-2-bromo-3,3,3-triphenylpropanamide (3d).**

The general procedure of Lengyel and Aaronson\textsuperscript{10} was followed. To a suspension of adamantylamine (2.50 g, 0.0165 mol) and triethylamine (1.67 g, 0.0165 mol) in dichloromethane (200 mL) was dropwise added a solution of crude 2-bromo-3,3,3-triphenylpropanoyl chloride (2c) (6.00 g, 0.015 mol) dissolved in dichloromethane (40 mL). The reaction mixture stirred for 1 h, was washed three times with distilled water (100 mL), once with 1M HCl (100 mL), twice with distilled water (100 mL), and the organic layer was then dried with Na$_2$SO$_4$. The dichloromethane was removed under reduced pressure to obtain crude 3d (7.13 g, 92 %). After recrystallization from an n-heptane/ethyl acetate solvent system (50/50), analytically pure 3d (5.38 g, 70 %, mp 188-190°C) was obtained. TLC (80 % n-hexane: 20 % ethyl acetate) $R_f = 0.71$. IR (CCl$_4$): 3408 (N-H); 3061 (aromatic C-H); 2911, 2851 (aliphatic C-H); 1670 (carbonyl of amide) cm$^{-1}$. $^1$H-NMR (CDCl$_3$): $\delta = 1.52-1.67$ (m, methylene protons of the adamantyl moiety, 12H), 1.94 (s, methine protons of adamantyl moiety, 3H), 4.78 (s, NH proton, exchanges for deuterium in CDCl$_3$/CF$_3$COOD, 1H), 5.84 (s, proton attached to the brominated carbon), and 7.23 – 7.45 (m, phenyl protons, 15H). $^{13}$C-NMR (CDCl$_3$): $\delta = 29.22$ (methine carbons of the adamantyl moiety), 36.20 and 40.45 (methylene carbons of the adamantyl moiety), 51.92 (C1 carbon of the adamantyl moiety), 60.19 (brominated carbon adjacent to the carbonyl carbon), 61.37 (quaternary carbon of the trityl moiety), 127.21 (phenyl carbons in para position), 128.13 (phenyl carbons in meta position), 129.81 (phenyl carbons in ortho position), 144.24 (C1 carbons of the trityl moiety) and 166.96 (carbonyl carbon of the amide). Anal. Calcd for C$_{31}$H$_{32}$NOBr: C 72.37; H 6.27; N 2.72; Br 15.53. Found: C 72.54; H 6.29; N 2.70; Br 15.64.

**1-(1-Adamantyl)-3-triphenylmethylaziridine-2-one (4d).**

The general procedure of Sheehan and Lengyel\textsuperscript{3} was followed. Sodium tert-butoxide (0.37 g, 0.0039 mol) was directly added to a solution of $N$-(1-adamantyl)-2-bromo-3,3,3-triphenylpropanamide (3d) (0.51 g, 0.001 mol) in THF (10 mL). After stirring for 2 min at 25°C, ether (100 mL) and distilled water (25
mL) were added to the reaction mixture. The aqueous layer was removed and the organic layer was washed twice more with distilled water (25 mL). The organic layer was then dried with Na₂SO₄ and the solvent was removed under reduced pressure to afford an oil (0.51 g), which contained crude 4d. Flash chromatography of this oil, using a mobile phase of 95/5:hexane/ethyl acetate, yielded pure 4d (0.24 g, 56 %, mp 155–156°C). TLC (95 % n-hexane: 5 % ethyl acetate) Rₓ = 0.24. IR (CCl₄): 3062 (aromatic C-H); 2915 and 2854 (aliphatic C-H); 1850 (carbonyl of α-lactam) cm⁻¹. ¹H-NMR (CDCl₃) δ = 1.54 – 1.83 (m, methylene protons of the adamantane moiety, 12H), 2.03 (s, methine protons of the adamantane moiety, 3H), 4.14 (s, proton on C₃ of aziridinone ring, 1H) and 7.14 – 7.29 (m, phenyl protons, 15H). ¹³C-NMR (CDCl₃): δ = 29.32 (methine carbons of the adamantane moiety), 33.91 and 40.99 (methylene carbons of the adamantane moiety), 51.98 (C1 carbon of the adamantane moiety), 57.68 (methine carbon in aziridinone ring), 58.28 (quaternary carbon of the trityl moiety), 126.83 (phenyl carbons in para position), 127.78 and 127.92 (phenyl carbons in meta position), 130.28 (phenyl carbons in ortho position), 144.12 (C₁ carbons of the trityl moiety) and 157.12 (carbonyl carbon). Anal. Calcd for C₃₁H₃₁NO: C 85.87; H 7.21; N 3.23. Found: C 85.86; H 7.37; N 3.16

**Thermal decomposition of 1-(1-adamantyl)-3-triphenylmethylaziridin-2-one (4d).**

α-Lactam (4d) (0.200 g, 0.46 mmol) was refluxed in 5 mL of n-decane for 1 h. IR (n-decane): 2129 (N≡C) and 1734 cm⁻¹ (C=O); no band at 1850 cm⁻¹ (C=O of α-lactam) remained. n-Decane was removed under reduced pressure and the resulting solid was flash chromatographed using a mobile phase of 95/5: n-hexane/ethyl acetate to obtain a near quantitative mixture of adamantyl isonitrile (10) and triphenylethanal (8). Analytical samples of aldehyde (8) and isonitrile (10) were obtained by separation of the adamantyl isonitrile (10) by sublimation at 70°C/15 mm.

Triphenylethanal (8): mp 98–99°C. TLC (95 % n-hexane: 5 % ethyl acetate) Rₓ = 0.54. IR (CCl₄): 3088, 3063, 3034 (aromatic C-H); 2836, 2729 (aldehyde C-H); 1733 (carbonyl of aldehyde) cm⁻¹. ¹H-NMR (CDCl₃) δ = 7.05 – 7.40 (m, phenyl protons, 15H) and 10.29 (s, aldehyde proton, 1H). ¹³C-NMR (CDCl₃): δ = 69.92 (quaternary carbon of the trityl moiety), 127.40 (phenyl carbons in para position), 128.37 (phenyl carbons in meta position), 130.39 (phenyl carbons in ortho position), 140.42 (C1 carbons
of the trityl moiety) and 198.21 (carbonyl carbon). GCMS: no detected molecular ion, m/z 243, base peak, (M – CHO)$^+$, 165 (fluorenyl ion). Anal. Calcd for C$_{20}$H$_{16}$O·¼H$_2$O: C 86.77; H 6.01; O 7.22. Found: C 86.70; H 5.94.

Adamantyl isonitrile (10).$^{19}$ mp 185-186°C (lit., 185-186°C). TLC (95 % n-hexane: 5 % ethyl acetate) R$_f$ = 0.54. IR (CCl$_4$): 2906 and 2858 (aliphatic C-H); 2129 cm$^{-1}$ (N≡C). $^1$H-NMR (CDCl$_3$): $\delta$ = 1.67 (s, the three methylene groups in β position from the isonitrile moiety, 6H), 2.03 (d, J = 2.7 Hz, the three methylene groups adjacent to the isonitrile moiety, 6H), and 2.10 (s, methine protons, 3H). $^{13}$C-NMR (CDCl$_3$): $\delta$ = 29.01 (methine carbons), 35.47 and 43.55 (methylene carbons), 54.01 (C1 of the adamantyl moiety), and 151.32 (isonitrile carbon). GCMS: m/z 161, M$^+$, (C$_{11}$H$_{15}$N)$^+$; 135, base peak, (M – NC)$^+$.

**Reaction of 1-(1-adamantyl)-3-triphenylmethylaziridin-2-one (4d) with sodium methoxide.**

$\alpha$-Lactam (4d) (0.10 g, 0.231 mmol) was dissolved in THF (2.5 mL) and sodium methoxide (0.075 g, 1.39 mmol) dissolved in methanol (10 mL) was added. The reaction was stirred at rt for 20 h. The solvent was removed under reduced pressure and the remaining residue was dissolved in dichloromethane (25 mL). The solution was washed three times with 20 mL of distilled water. The organic layer was dried over Na$_2$SO$_4$ and the solvent was removed under reduced pressure to afford near quantitative yield of a clear oil, crude 16d. Crude 16d was flash chromatographed using 95:5 n-hexane:ethyl acetate as eluent to afford 0.070 g (70 %) of pure methyl 2-(1-adamantylamino)-3,3,3,-triphenylpropanoate (16d), mp 164-166°C. TLC (95 % n-hexane: 5 % ethyl acetate) R$_f$ = 0.53. IR (CCl$_4$): 3346 (N-H); 3059 and 3035 (aromatic C-H); 2906 and 2851 (aliphatic C-H); 1739 (carbonyl of ester) cm$^{-1}$. $^1$H-NMR (CDCl$_3$): $\delta$ = 1.29 (s, NH proton, exchanges in D$_2$O, 1H), 1.60 (m, methylene protons of the adamantyl moiety, 12H), 2.00 (s, methine protons of the adamantyl moiety, 3H), 3.29 (s, methoxide protons, 3H), 5.01 (s, proton on the carbon adjacent to the carbonyl carbon, 1H), and 7.08 – 7.42 (m, phenyl protons, 15H). $^{13}$C-NMR (CDCl$_3$): $\delta$ = 29.92 (methylene carbons of the adamantyl moiety), 36.79 and 43.40 (methylene carbons of the adamantyl moiety), 51.19 (carbon of the methoxy group), 51.74 (C1 carbon of the adamantyl moiety), 60.87 (methine carbon adjacent to the carbonyl carbon), 62.00 (quaternary carbon of the trityl moiety), 126.35 (phenyl carbons in para position), 127.31 (phenyl carbons in meta position), 130.87 (phenyl
carbons in ortho position), 145.01 (C1 carbons of the trityl moiety) and 176.40 (carbonyl carbon of the ester). Anal. Calcd for C_{32}H_{35}NO_{2}: C 82.54; H 7.58; N 3.01. Found: C 82.28; H 7.53; N 3.11.

REFERENCES AND NOTES

18. B. Helferich, I. Moog, and A. Junger, Ber., 1925, 58, 872.