

## Formation of Lactams Via Photoelectron-Transfer Catalyzed Reactions of N-Allylamines with $\alpha,\beta$ -Unsaturated Esters

Suresh Das\*, J. S. Dileep Kumar, Kalchar Shivaramayya and Manapurathu V. George

Photochemistry Research Unit, Regional Research Laboratory (CSIR), Trivandrum, India 695 019

**Abstract:** Anthraquinone photosensitized reactions of a few N-allylamines with  $\alpha,\beta$ -unsaturated esters have been investigated. These reactions led predominantly to the formation of lactams along with trace amounts of products arising out of tandem radical addition reactions. A mechanism is proposed involving the rearrangement of the  $\alpha$ -aminoalkyl radical, initially generated via anthraquinone photosensitized reactions, to  $\alpha$ -aminoalkyl radicals. Subsequent reactions of these radicals with  $\alpha,\beta$ -unsaturated esters can lead to the observed products.

### Introduction

The synthesis of nitrogen containing heterocycles using  $\alpha$ -aminoalkyl radicals has attracted considerable attention in recent years. Such radicals have been generated thermally via tributyltin hydride mediated reductive cleavage of C-X bonds (X = Se, S, and halogen)<sup>1-4</sup> and photochemically via electron transfer catalyzed reactions of  $\alpha$ -silylamines.<sup>5,6</sup> These processes are however constrained by the requirement of prior derivatization of amines. We have recently reported that  $\alpha$ -aminoalkyl radicals, which are efficiently generated via anthraquinone photosensitized reaction of amines can be effectively used for the construction of carbon-carbon bonds adjacent to nitrogen.<sup>7,8</sup> Lactam formation was observed in the reaction of  $\alpha$ -aminoalkyl radicals, thus generated from primary and secondary amines, with  $\alpha,\beta$ -unsaturated esters. However, most  $\alpha,\beta$ -unsaturated esters undergo facile Michael-type thermal addition with secondary amines to yield the corresponding N-adducts. In order to minimise the extent of thermal adduct formation the reactions were carried out at low temperatures.<sup>8</sup>

Here we report on the anthraquinone photocatalyzed reaction of some allylamines with  $\alpha,\beta$ -unsaturated esters leading, predominantly, to lactams. Since we deal with tertiary amines here, thermal Michael addition does not interfere in these cases.

### Results and Discussion

Irradiation of argon-saturated solutions containing allylamine,  $\alpha,\beta$ -unsaturated esters and catalytic amounts of anthraquinone using 'Pyrex' filtered output of a medium pressure mercury lamp (Hanovia) led predominantly to the formation of the corresponding lactams. In some cases, formation of trace amounts of complex diastereomeric mixture of products arising out of tandem radical addition reactions were observed.

Thus, for example, the photosensitized reaction of N-allylpiperidine (2) with methyl crotonate (9) gave a diastereomeric mixture (1:4) (1S,9S:1R,9S) of 1-methyl-3-indolizidone (15), along with minor amounts of a complex diastereomeric mixture of the quinolizidine derivative 6, whereas the photosensitized reaction of N-allylpiperidine (2) with methyl acrylate (20) and methyl methacrylate (24) gave 3-indolizidone (25) and a diastereomeric mixture (2:3) (2S,9S:2R,9S) of 2-methyl-3-indolizidone (26), respectively as major products. These results together with those obtained for other allylamines are summarized in Table 1.

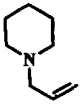
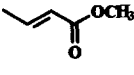
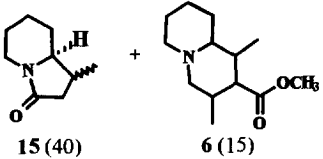
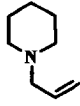
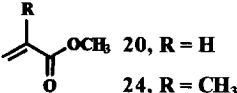
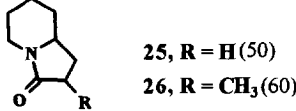
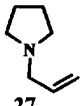
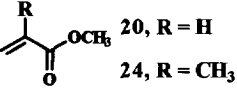
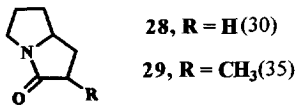
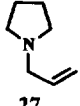
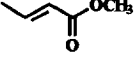
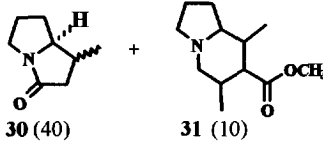
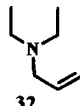
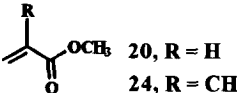
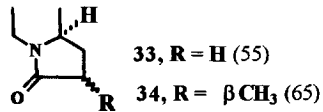
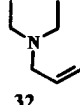
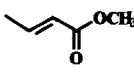
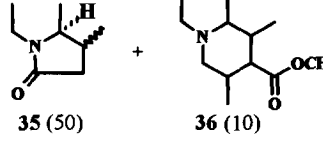
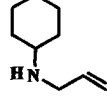
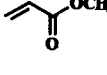
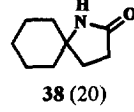
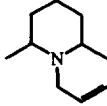
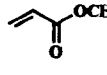
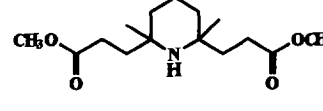
Irradiation of these solutions by 'Pyrex' filtered light will lead to selective excitation of anthraquinone, since the amine and  $\alpha,\beta$ -unsaturated esters do not have significant absorptions above 300 nm. On excitation, anthraquinone is converted to its triplet state with a quantum yield of nearly one.<sup>9</sup> Electron transfer quenching of triplet anthraquinone by the allylamine will lead to the formation of solvent caged aminium and ketyl radical ions, which can undergo proton exchange. In a recent report on the study of anthraquinone photocatalyzed reactions of several amines including allylamines by chemically induced nuclear dynamic polarization (CIDNP), Goez and Frisch observed that incage proton exchange dominates in the case of allyl substituents whereas, with methyl, ethyl and isopropyl substituents, deprotonation occurred predominantly outside the solvent cage.<sup>10,11</sup> This has been attributed to the increased driving force for deprotonation from the allyl group due to allylic stabilization. The thermodynamic as well as stereoelectronic factors connected with earlier studies<sup>10-13</sup> on deprotonation of aminium radicals strongly suggest that in anthraquinone photosensitized reactions of N-allylamines,  $\alpha$ -aminoallyl radical generation will predominate over that of  $\alpha$ -aminoalkyl radical generation.

Formation of the different products in the present study, however, indicates that the initial carbon-carbon bond forming reactions occur through  $\alpha$ -aminoalkyl radicals. It is quite likely that the initially formed  $\alpha$ -aminoallyl radicals, undergo transformation to  $\alpha$ -aminoalkyl radicals, which then participate in the addition reactions. A reasonable pathway for the formation of different products in the reaction of N-allylpiperidine (2) with methyl crotonate (9) is shown in Scheme 1.

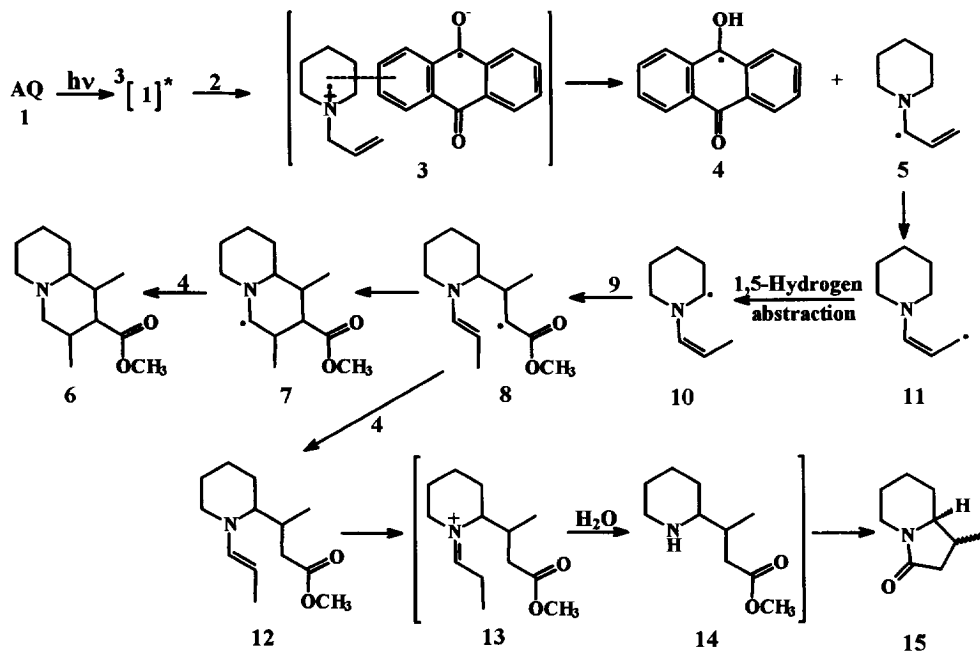
The  $\alpha$ -aminoallyl radical 5, formed initially can isomerise to give the radical 11, which can undergo a 1,5-hydrogen abstraction to yield the  $\alpha$ -aminoalkyl radical 10. Intramolecular 1,5-hydrogen atom abstractions in amines leading to the formation of  $\alpha$ -aminoalkyl radicals is well documented.<sup>7,14,15</sup> Addition of 10 to methyl crotonate (9) would give the adduct radical 8. The formation of the quinolizidine derivative 6 is attributed to the tandem intramolecular addition of the adduct radical 8 to give 7 which can subsequently be quenched by the anthraquinone ketyl radical (4). Alternatively, the adduct radical 8 can be quenched by 4 to yield an enamine derivative 12. Anthraquinone used in these reactions is recovered quantitatively. The enamine can undergo dealkylation under work-up with adventitious water to give 14, presumably through the iminium intermediate 13. Lactonization of 14 will result in the formation of the indolizidone 15 (Scheme 1). Pathways similar to those shown in Scheme 1 may be operating in the formation of the observed products in the reaction of the various N-allylamines with  $\alpha,\beta$ -unsaturated esters shown in Table 1.

Interestingly, we have not observed lactam formation in the anthraquinone photocatalyzed reactions of N-butenylpiperidine and N-butenylpyrrolidine with  $\alpha,\beta$ -unsaturated esters. In these cases multiple olefin addition products were formed, which were similar to those obtained in an earlier study on anthraquinone

Table 1. Anthraquinone ( $10^{-4}$  M) photosensitized reaction of N-allylamines (15 mmol) with  $\alpha,\beta$ -unsaturated esters (15 mmol) in degassed acetonitrile solutions (350 mL) using a 450 W medium pressure Hanovia lamp (Time of irradiation 2 h).

| Amine   | Ester   | % Conversion of ester | Product (%)  |
|---|---|-----------------------|--|
| <br>2    | <br>9                                      | 15                    | <br>15 (40) + 6 (15)   |
| <br>2    | <br>20, R = H<br>24, R = CH <sub>3</sub>   | 22<br>20              | <br>25, R = H (50)<br>26, R = CH <sub>3</sub> (60)           |
| <br>27   | <br>20, R = H<br>24, R = CH <sub>3</sub>   | 18<br>20              | <br>28, R = H (30)<br>29, R = CH <sub>3</sub> (35)           |
| <br>27  | <br>9                                     | 15                    | <br>30 (40) + 31 (10)                                       |
| <br>32 | <br>20, R = H<br>24, R = CH <sub>3</sub> | 20<br>20              | <br>33, R = H (55)<br>34, R = $\beta$ CH <sub>3</sub> (65) |
| <br>32 | <br>9                                    | 15                    | <br>35 (50) + 36 (10)                                      |
| <br>37 | <br>20                                   | 15                    | <br>38 (20)   |
| <br>39 | <br>20                                   | 18                    | <br>23 (30)  |

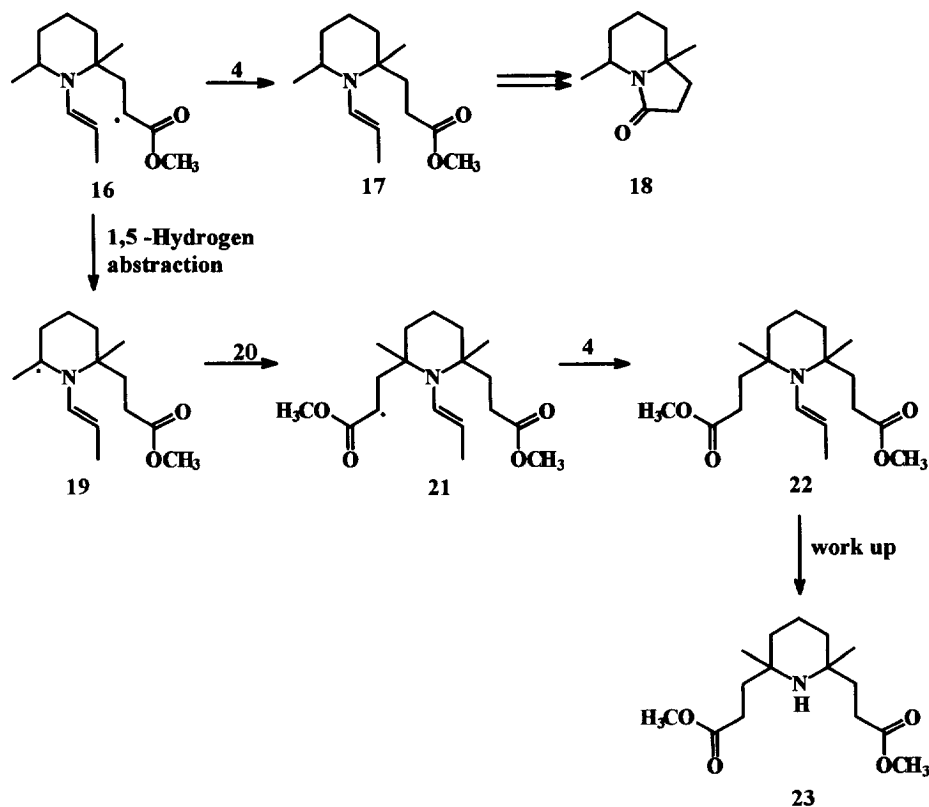
photocatalyzed reactions of triethylamine with olefinic substrates.<sup>7</sup> This indicates that the deallylation pathway suggested in Scheme 1 for N-allylamines is necessary for formation of the corresponding lactams.



Scheme 1

The major product isolated from the reaction of N-allyl-2,6-dimethylpiperidine (39) with methyl acrylate (20) was the 2:1 ester-amine adduct 23. The formation of 23 in this reaction can be rationalized in terms of the pathways shown in Scheme 2.

The photosensitized addition of 39 to 20 in presence of anthraquinone can lead to the adduct radical 16 in a manner similar to that shown in Scheme 1 for N-allylpiperidine. One of the possible modes of transformation of 16 is to undergo hydrogen atom abstraction from anthraquinone ketyl radical (4) to give 17, which ultimately can lead to the indolizidone 18. We have not been able to isolate 18 from the product mixture. However, the GC-MS data showed a peak at  $m/z$  167, which could be due to 18 ( $M^+$ ). An intramolecular hydrogen abstraction in 16 could result in the formation of a new radical 19, which could then add on another methyl acrylate molecule to give the bis-adduct radical 21. Subsequent hydrogen abstraction of 21 from the ketyl radical, 4 would give the bis-adduct 22, which during work-up could give 23, by the pathway shown in Scheme 2. The intramolecular hydrogen atom abstraction in 16 is facilitated by the presence of the methyl substituents which will make the  $\alpha$ -hydrogen more labile.



Scheme 2

### Experimental Section

The IR spectra were recorded on a Perkin-Elmer model 882 Infrared Spectrophotometer. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a JEOL EX-90 FT NMR Spectrometer, using tetramethylsilane (TMS) as internal standard and the  $^{13}\text{C}$  signals were assigned by using QUART and DEPT programmes. The mass spectra were recorded either on a Finnigan MAT model 8430 or JEOL JMS AX 505 HA mass spectrometer or 5890 Series 2 Hewlett-Packard GC-MS. The GC analyses were carried out on a Hewlett-Packard 5890 Series II gas chromatograph and the HPLC analyses were carried out using a Shimadzu LC-8A liquid chromatograph. All steady state photoreactions were carried out using a 450 W medium pressure mercury lamp with a Pyrex filter ( $\lambda > 290 \text{ nm}$ ) under argon or nitrogen atmosphere. The allylamines were prepared by known procedures. Anthraquinone was purified by sublimation. All other reagents and solvents reagents were purified and distilled before use.

In a typical run, the photolysis mixture, consisting of 15 mmol (or 10 mmol) of allylamine and 15 mmol of  $\alpha,\beta$ -unsaturated ester in acetonitrile (350 mL) containing ( $10^{-4} \text{ M}$ ) anthraquinone was purged with argon or

nitrogen before irradiation. After irradiation (2 h), the solvent and the unchanged reactants were removed under reduced pressure and the product mixture was chromatographed using either a flash column or Chromatotron. Quantitative recovery of anthraquinone was observed in each case. The yields reported are based on the olefinic substrate consumed, which was estimated by HPLC. The reported product distribution was based on GC and GC-MS analyses of the product mixtures.

*Photosensitized addition of N-allylpiperidine (2) to methyl crotonate (9).* Irradiation of an argon-bubbled solution of a mixture of **2** (1.85 g, 15 mmol) and **9** (1.5 g, 15 mmol) in acetonitrile (350 mL) containing  $10^{-4}$  M of **1** for 2 h and separation of the reaction mixture by column chromatography using a solvent mixture (3:2) of petroleum ether and ethyl acetate gave a diastereomeric mixture (1:4) (1S,9S:1R,9S) (110 mg, 40 %) of 1-methyl-3-indolizidone (**15**), as determined by capillary GC and  $^1\text{H}$  NMR data and 20 mg (15 %) of the quinolizidine **6**. The yields of the products were based on 15 % conversion of **9**.

**6** : IR spectrum  $\nu_{\text{max}}$  (neat): 2970, 2860 (CH) and 1738 (ester)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) :  $\delta$  0.9-1.15 (6 H, 2 d, m, 2  $\text{CH}_3$ ), 1.4-2.0 (6 H, m, 3  $\text{CH}_2$ ), 2.4-3.3 (7 H, m, 2  $\text{CH}_2$  and 3 CH) and 3.6-3.8 (3 H, s,  $\text{OCH}_3$ );  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  15.03, 16.82, 24.40, 24.69, 24.93, 25.38, 25.89, 29.65, 30.01, 47.10, 50.17, 54.53, 56.92, 59.18 and 174.12, 175.68 (C=O, ester); Mass spectrum,  $m/z$  (relative intensity) : 225 ( $\text{M}^+$ , 30), 210 (30), 196 (20), 166 (25), 150 (15), 124 (40), 98 (100), 83 (35) and 55 (15); Molecular weight calculated for  $\text{C}_{13}\text{H}_{23}\text{NO}_2$  : 225.1788. Found : 225.1728 (high resolution mass spectrometry, FAB).

**15** : IR spectrum  $\nu_{\text{max}}$  (neat) : 2980, 2865 (CH) and 1690 (C=O)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) :  $\delta$  0.96-1.04 (3 H, d,  $\text{CH}_3$ ,  $J = 7$  Hz for 1S,9S), 1.08-1.14 (3 H, d,  $\text{CH}_3$ ,  $J = 6$  Hz for 1R,9S), 1.4-2.2 (6 H, m, 3  $\text{CH}_2$ ), 2.3-2.8 (2 H, m,  $\text{CH}_2$ ) and 3.2-3.8 (3 H,  $\text{CH}_2$  and CH);  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  14.73, 17.89 ( $\text{CH}_3$ ), 23.20, 24.01, 24.37, 24.75, 26.25, 28.54, 31.50, 34.18, 38.39, 39.76 ( $\text{CH}_2$ ), 41.33, 46.53, 60.38, 63.96 (CH) and 173.09, 173.27 (C=O, lactam); Mass spectrum,  $m/z$  (relative intensity) : 153 ( $\text{M}^+$ , 69), 152 (100), 138 (20), 124 (15), 112 (18), 96 (10), 83 (35) and 55 (10); Molecular weight calculated for  $\text{C}_9\text{H}_{15}\text{NO}$  : 153.1188. Found : 153.1233 (high resolution mass spectrum, FAB).

*Photosensitized addition of N-allylpiperidine (2) to methyl acrylate (20).* An argon-bubbled solution of a mixture of **2** (1.85 g, 15 mmol) and **20** (1.3 g, 15 mmol) in acetonitrile (350 mL) containing  $10^{-4}$  M of **1** was irradiated for 2 h and separation of the photoproduct mixture by column chromatography using a mixture (3:1) of petroleum ether and ethyl acetate gave 150 mg (50 %) of 3-indolizidone (**25**). The yield of **25** was based on **20**, that reacted (22% conversion). The spectral data and analytical results were found to be identical to those of previously reported 3-indolizidone.<sup>8</sup>

*Photosensitized addition of N-allylpiperidine (2) to methyl methacrylate (24).* Irradiation of an argon-purged solution of a mixture of **2** (1.85 g, 15 mmol), **24** (1.5 g, 15 mmol) and **1** ( $10^{-4}$  M) in acetonitrile (350 mL) for 2 h and analysis of the product mixture on a GC-MS indicated a 60 % yield of a diastereomeric mixture (2:3) (2S,9S:2R,9S) of **26**. The yield of **26** was based on **24**, that reacted (20 % conversion). The photoproduct **26** was isolated by column chromatography and its analytical results and spectral data were in good agreement with those of 2-methyl-3-indolizidone reported earlier.<sup>7</sup>

*Photosensitized addition of N-allylpyrrolidine (27) to methyl acrylate (20).* Irradiation of an argon-bubbled solution of a mixture of **27** (1.65 g, 15 mmol) and **20** (1.3 g, 15 mmol) in acetonitrile (350 mL) containing  $10^{-4}$  M of **1** for 2 h and separation of the product mixture by column chromatography using a solvent mixture (3:1) of petroleum ether and ethyl acetate gave 80 mg (30 %) of 3-pyrrolizidone (**28**). The spectral and analytical data of **28** were found to be identical to those of 3-pyrrolizidone reported earlier.<sup>8</sup> The yield of **28** was based on **20**, that reacted (18 % conversion).

*Photosensitized addition of N-allylpyrrolidine (27) to methyl methacrylate (24).* An argon-purged solution of a mixture of **27** (1.65 g, 15 mmol) and **24** (1.5 g, 15 mmol) in acetonitrile (350 mL) containing  $10^{-4}$  M of **1** was irradiated for 2 h and the product mixture on GC-MS analysis indicated a 35 % yield of a diastereomeric mixture (3:2) (2S,8S:2R,8S) of **29**. The photoproduct was isolated using column chromatography and its spectral data were found to be identical to those of the previously characterized 2-methyl-3-pyrrolizidone.<sup>7</sup> The yield of **29** was based on **24**, that reacted (20% conversion).

*Photosensitized addition of N-allylpyrrolidine (27) to methyl crotonate (9).* An argon-bubbled solution of a mixture of **27** (1.65 g, 15 mmol) and **9** (1.5 g, 15 mmol) in acetonitrile (350 mL) containing  $10^{-4}$  M of **1** was irradiated for 2 h and separation of the product mixture by column chromatography using a mixture (3:2) of petroleum ether and ethyl acetate gave 80 mg (40 %) of a diastereomeric mixture 3:7 (1S,8S:1R, 8S) of 1-methyl-3-pyrrolizidone (**30**) as determined by capillary GC and <sup>1</sup>H NMR data and 30 mg (10 %) of the indolizidine **31**. These yields were based on percentage conversion of **9** (15 %). The spectral data of **30** were found to be identical to those of the previously reported 1-methyl-3-pyrrolizidones.<sup>8</sup>

**31** : IR spectrum  $\nu_{\max}$  (neat): 2980, 2860 (CH) and 1738 (ester)  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR spectrum ( $\text{CDCl}_3$ ) :  $\delta$  0.9-1.25 (6 H, m, 2  $\text{CH}_3$ ), 1.5-2.2 (4 H, m, 2  $\text{CH}_2$ ), 2.4-3.2 (6 H, m, 2  $\text{CH}_2$  and 2 CH), 3.2-3.5 (2 H, m, 2 CH) and 3.6-3.8 (3 H, m,  $\text{OCH}_3$ ); <sup>13</sup>C NMR spectrum ( $\text{CDCl}_3$ ) :  $\delta$  16.50, 16.80, 17.50, 21.56, 24.52, 25.08, 25.62, 26.86, 28.80, 29.72, 34.50, 38.15, 38.86, 43.22, 43.88, 55.10, 51.66, 53.78, 57.50, 58.62, 59.40 and 175.54-176.60 (C=O, ester); Mass spectrum, m/z (relative intensity) : 211 ( $\text{M}^+$ , 15), 196 (25), 180 (10), 152 (28), 110 (100), 96 (30), 83 (90), 70 (50) and 55 (40); Molecular weight calculated for  $\text{C}_{12}\text{H}_{21}\text{NO}_2$  : 211.1831. Found : 211.1928 (high resolution mass spectrometry, FAB).

*Photosensitized addition of N-allyldiethylamine (32) to methyl acrylate (20).* Irradiation of an argon-purged solution of a mixture of **32** (1.8 g, 15 mmol) and **20** (1.3 g, 15 mmol) in acetonitrile (350 mL) containing  $10^{-4}$  M of **1** for 4 h, and separation of the product mixture by column chromatography using a solvent mixture (3:1) of petroleum ether and ethyl acetate gave 130 mg (55 %) of 1-ethyl-5-methyl-2-pyrrolidone (**33**). The yield reported was based on **20** that reacted (20 % conversion), as estimated by HPLC.

**33**: IR spectrum  $\nu_{\max}$  (neat) : 2980, 2875 (CH) and 1685 (C=O)  $\text{cm}^{-1}$ ; UV spectrum  $\lambda_{\max}$  ( $\text{CH}_3\text{CN}$ ) : 205 nm ( $\epsilon$ , 2880) and 255 (450); <sup>1</sup>H NMR spectrum ( $\text{CDCl}_3$ ) :  $\delta$  1.0-1.2 (6 H, m, 2  $\text{CH}_3$ ), 1.6-2.4 (4 H, m, 2  $\text{CH}_2$ ), 3.0-3.8 (3 H, m,  $\text{CH}_2$  and CH); <sup>13</sup>C NMR spectrum ( $\text{CDCl}_3$ ) :  $\delta$  12.31, 19.44 ( $\text{CH}_3$ ), 26.37, 29.92, 34.42 ( $\text{CH}_2$ ), 52.83 (CH) and 174.44 (C=O, lactam); Mass spectrum, m/z (relative intensity) : 127 ( $\text{M}^+$ , 30), 112 (100), 84 (40), 70 (6) and 56 (15); Molecular weight calculated for  $\text{C}_7\text{H}_{13}\text{NO}$  : 127.0997. Found : 127.0998. (high resolution mass spectrometry, FAB).

*Photosensitized addition of N-allyldiethylamine (32) to methyl methacrylate (24).* Irradiation of an argon-purged solution of **32** (1.8 g, 15 mmol) and **24** (1.5 g, 15 mmol) in acetonitrile (350 mL), containing  $10^{-4}$  M of **1** for 4 h and separation of the photolysate by column chromatography using a mixture (3:1) of petroleum ether and ethyl acetate gave 140 mg (65 %) of (3R,5S) 1-ethyl-3,5-dimethyl-2-pyrrolidone (**34**) as a single diastereomer.<sup>16</sup> The yield was based on **24** that reacted (20 %), as estimated by HPLC.

**34:** IR spectrum  $\nu_{\max}$  (neat) : 2980, 2875 (CH) and 1685 (C=O)  $\text{cm}^{-1}$ ; UV spectrum  $\lambda_{\max}$  ( $\text{CH}_3\text{CN}$ ) : 205 nm ( $\epsilon$ , 2880) and 255 (450);  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) :  $\delta$  0.99-1.06 (3 H, d,  $\text{CH}_3$ , 7Hz,  $\beta$ -methyl), 1.1-1.2 (6 H, m, 2  $\text{CH}_3$ ), 1.8-2.1 (2 H, m,  $\text{CH}_2$ ), 2.3-2.6 (2 H, t,  $\text{CH}_2$ ), 2.9-3.3 (1 H, m, CH) and 3.5-3.8 (1 H, m, CH);  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ) :  $\delta$  12.61, 16.52, 20.28 ( $\text{CH}_3$ ), 34.72, 36.54 ( $\text{CH}_2$ ), 36.69, 51.07 (CH) and 172.42 (C=O, lactam); Mass spectrum,  $m/z$  (relative intensity) : 141 ( $\text{M}^+$ , 10), 126 (40), 112 (100), 98 (6), 84 (30), 76 (6) and 56 (15); Molecular weight calculated for  $\text{C}_8\text{H}_{15}\text{NO}$  : 141.1154. Found : 141.1153 (high resolution mass spectrometry, FAB).

*Photosensitized addition of N-allyldiethylamine (32) to methyl crotonate (9).* An argon-purged solution of a mixture of **32** (1.8 g, 15 mmol) and **9** (1.5 g, 15 mmol) in acetonitrile (350 mL), containing  $10^{-4}$  M of **1** was irradiated for 4 h and separation of the photoproducts by column chromatography using a mixture (2:3) of petroleum ether and ethyl acetate gave 90 mg (50 %) of a diastereomeric mixture (2:3) (4S,5S: 4R,5S) of 1-ethyl-4,5-dimethyl-2-pyrrolidone (**35**), as determined by capillary GC data and 30 mg (10 %) of a 4-carbomethoxy-1-ethyl-2,3,5-trimethylpiperidine (**36**), based on **9** that reacted (15 % conversion).

**35:** IR spectrum  $\nu_{\max}$  (neat) : 2970, 2882 (CH) and 1688 (C=O)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) :  $\delta$  0.95-1.2 (9 H, m, 3  $\text{CH}_3$ ), 1.8-2.7 (3 H, m,  $\text{CH}_2$  and CH) and 2.8-3.9 (3 H, m,  $\text{CH}_2$  and CH);  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ) :  $\delta$  12.58, 12.79, 13.33, 14.58, 18.31, 18.46 ( $\text{CH}_3$ ), 29.64, 30.96, 38.12, 39.69 ( $\text{CH}_2$ ), 34.69, 34.93, 56.11, 60.41 (CH) and 174.26, 175.50 (C=O, lactam); Mass spectrum,  $m/z$  (relative intensity) : 141 ( $\text{M}^+$ , 35), 126 (100), 98 (10), 78 (20) and 55 (18); Molecular weight calculated for  $\text{C}_8\text{H}_{15}\text{NO}$  : 141.1232. Found : 141.1238 (high resolution mass spectrometry, FAB).

**36:** IR spectrum  $\nu_{\max}$  (neat) : 2976, 2860 (CH) and 1740 (ester)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) :  $\delta$  0.85-1.2 (12 H, m, 4  $\text{CH}_3$ ), 1.9-3.2 (8 H, m, 2  $\text{CH}_2$  and 4 CH) and 3.6-3.8 (3 H, s,  $\text{OCH}_3$ );  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ) :  $\delta$  14.00-20.00 ( $\text{CH}_3$ ), 32-36, 44.32-46.82, 50.85-55.28 and 172-175 (C=O, ester); Mass spectrum,  $m/z$  (relative intensity) : 213 ( $\text{M}^+$ , 15), 198 (100), 180 (12), 152 (10), 138 (25), 126 (30), 112 (28), 98 (20), 78 (50) and 56 (30); Molecular weight calculated for  $\text{C}_{12}\text{H}_{23}\text{NO}_2$  : 213.1728. Found : 213.1725 (high resolution mass spectrometry, FAB).

*Photosensitized addition of N-allylcyclohexylamine (37) to methyl acrylate (20).* Irradiation of an argon-purged solution of a mixture of **37** (1.4 g, 10 mmol), **20** (1.3 g, 15 mmol) and **1** ( $10^{-4}$  M) in acetonitrile (350 mL) for 2 h and the product mixture upon GC-MS analysis indicated a 20 % yield of the spiro lactam **38** and 75 % of unchanged **37**. The GC and GC-MS data of **38** were found to be identical to those of the same spiro lactam reported earlier.<sup>7</sup>



*Photosensitized addition of 1-allyl-2,6-dimethylpiperidine (39) to methyl acrylate (20).* An argon-purged solution of a mixture of 39 (1.53 g, 10 mmol) and 20 (1.3 g, 15 mmol) in acetonitrile (350 mL) containing  $10^{-4}$  M of 1 was irradiated for 2 h and separation of the product mixture by column chromatography using a mixture (3:1) of petroleum ether and ethyl acetate gave 70 mg (30 %) of the bis- adduct 23. The yield of 23 was based on 20, that reacted (18 % conversion).

23: IR spectrum  $\nu_{\max}$  (neat) : 3300 (NH), 2985, 2860 (CH) and 1744 (ester)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR spectrum  $\text{CDCl}_3$  :  $\delta$  1.0-1.15 (6 H, 2 s, 2  $\text{CH}_3$ ), 1.2-1.4 (4 H, m, 2  $\text{CH}_2$ ), 1.5-2.0 (6 H, m, 3  $\text{CH}_2$ ), 2.2-2.6 (4 H, m, 2  $\text{CH}_2$ ) and 3.6-3.75 (6 H, s, 2  $\text{OCH}_3$ );  $^{13}\text{C}$  NMR spectrum  $\text{CDCl}_3$  :  $\delta$  28.07, 28.63 ( $\text{CH}_3$ ), 37.32, 37.61, 39.94 ( $\text{CH}_2$ ), 50.77 (C), 51.22 ( $\text{OCH}_3$ ) and 174.73 (C=O, ester); Mass spectrum, m/z (relative intensity): 286 ( $\text{MH}^+$ , 70), 270 (20), 254 (10), 198 (100), 154 (25), 130 (10), 115 (15), 85 (30), 70 (38) and 55 (15). Molecular weight calculated for  $\text{C}_{15}\text{H}_{27}\text{NO}_4$  : 286.2018 ( $\text{MH}^+$ ). Found ( $\text{MH}^+$ ) : 286.2011 (high resolution mass spectrometry, FAB).

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16. The configuration of **34** has been tentatively assigned as (3R,5S) 1-ethyl-3,5-dimethyl-2-pyrrolidone ( $J = 7$  Hz for 3-methyl protons) on the basis of analogy to the configurational assignment of (2R,9S) for 2-methyl-3-indolizidone,<sup>7</sup> when a  $J$  value of 7.2 Hz has been observed for the  $\beta$ -methyl protons. In contrast a  $J$  value of 6.5 Hz has been observed for the  $\alpha$ -methyl protons of (2S,9S) 2-methyl-3-indolizidone.

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