

## Photolysis of Olefinic N-Chloropyrrolidinones, N-Chlorosuccinimides and N-Chloro-oxazolidinones: Reactivity of Cyclic Carboxamidyl, Imidyl and Carbamyl Radicals in Intramolecular Reactions

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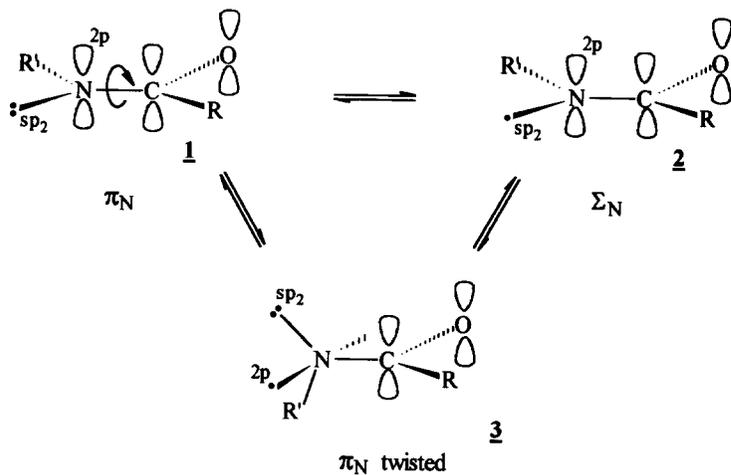
### Abstract :

N-Chloro-alkenylpyrrolidinones, an N-chloro-alkenylsuccinimide and N-chloro-alkenylloxazolidinones were prepared as precursors of olefinic cyclic carboxamidyl, imidyl and carbamyl radicals constrained to undergo intramolecular reactions uniquely via their planar or slightly twisted (30–35°)  $\Pi_N$  state (1,5-transfer of an allylic hydrogen, 5-*exo* or 6-*exo* cyclization to give bicyclo[2.2.1]azaheptane and bicyclo[3.2.1]azaoctane skeletons respectively), those intramolecular reactions being inaccessible to the planar  $\Sigma_N$  state. Their photolysis gave products arising uniquely from intermolecular reactions of those nitrogen radicals (addition to an external olefin, hydrogen abstraction from the solvent, allylic hydrogen abstraction). An intramolecular reaction leading to bicyclo[3.3.0]azaoctane derivatives via 5-*exo* cyclization was observed with an N-chloro-alkenylpyrrolidinone and an N-chloro-alkenylloxazolidinone. In these two cases, both the  $\Pi_N$  and the  $\Sigma_N$  states of the cyclic amidyl radical allow orbital overlap for 5-*exo* cyclization. © 1999 Elsevier Science Ltd. All rights reserved.

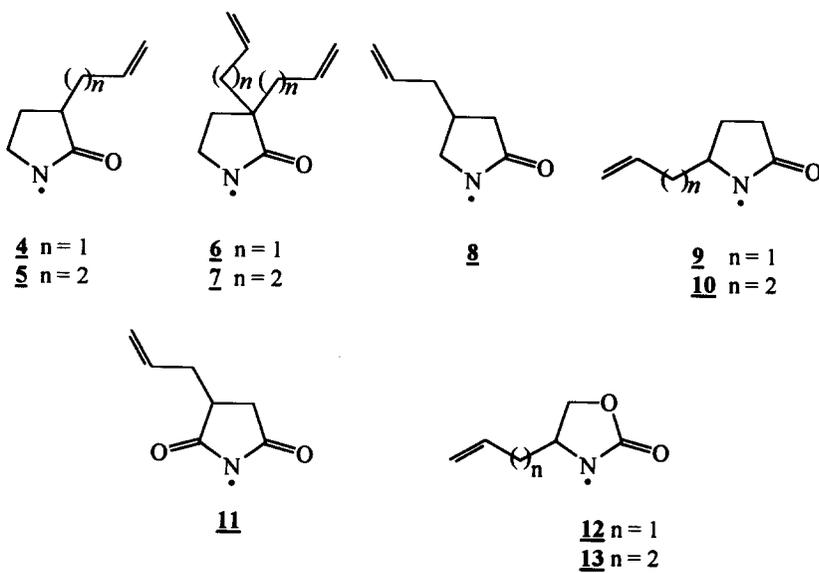
### INTRODUCTION

Amidyl radicals are known to add to olefins to form C-N bonds,<sup>1–19</sup> which shows that the unpaired spin resides mainly on the nitrogen (Scheme 1). It has been shown by EPR spectroscopy that the electronic ground state of amidyl radicals is  $\Pi_N$  (see **1**, Scheme 1).<sup>20–22</sup> However, to our knowledge, there is no example in the literature where the addition of an amidyl radical to an olefin would involve unequivocally the planar or slightly twisted (30–35°)  $\Pi_N$  ground state. On the other hand, there are cases of intramolecular addition of acyclic amidyls to a double bond (5-*exo*- and 6-*exo* cyclizations leading to bicyclic and tricyclic systems) where only the  $\Sigma_N$  state (see **2**, Scheme 2) or a highly twisted ( $\geq 70^\circ$ )  $\Pi_N$  state (**5**) (see **3**, Scheme 1) can be the reactive species.<sup>5, 12, 13</sup>

Cyclic amidyl and imidyl radicals have been shown to be more reactive towards olefins in intermolecular additions than their acyclic analogues.<sup>7</sup> In order to see if bicyclic skeletons could be constructed by cyclization of olefinic cyclic amidyls and to evaluate the reactivity of their electronic states (planar or slightly twisted  $\Pi_N$  and  $\Sigma_N$  states), we studied the olefinic cyclic amidyl radicals **4** to **13**. For the olefinic carboxamidyl radicals **4**, **5**, **6**, **7** and **8**, and the olefinic succinimidyl radical **11**, only the  $\Pi_N$  state can undergo intramolecular addition to the double bond (or intramolecular abstraction of an allylic hydrogen) according to the inspection of molecular models. In the case of the carboxamidyl radicals **9** and **10**, and of carbamyl radicals **12** and **13**, both the  $\Pi_N$  and  $\Sigma_N$  states can, in an intramolecular reaction, add to the double bond. Radicals **10** and **13** can also abstract an allylic hydrogen (1,5-transfer) via the  $\Pi_N$  or the  $\Sigma_N$  state. We report the results in this paper. The nitrogen radicals were generated by photolysis of the corresponding N-chloramides.



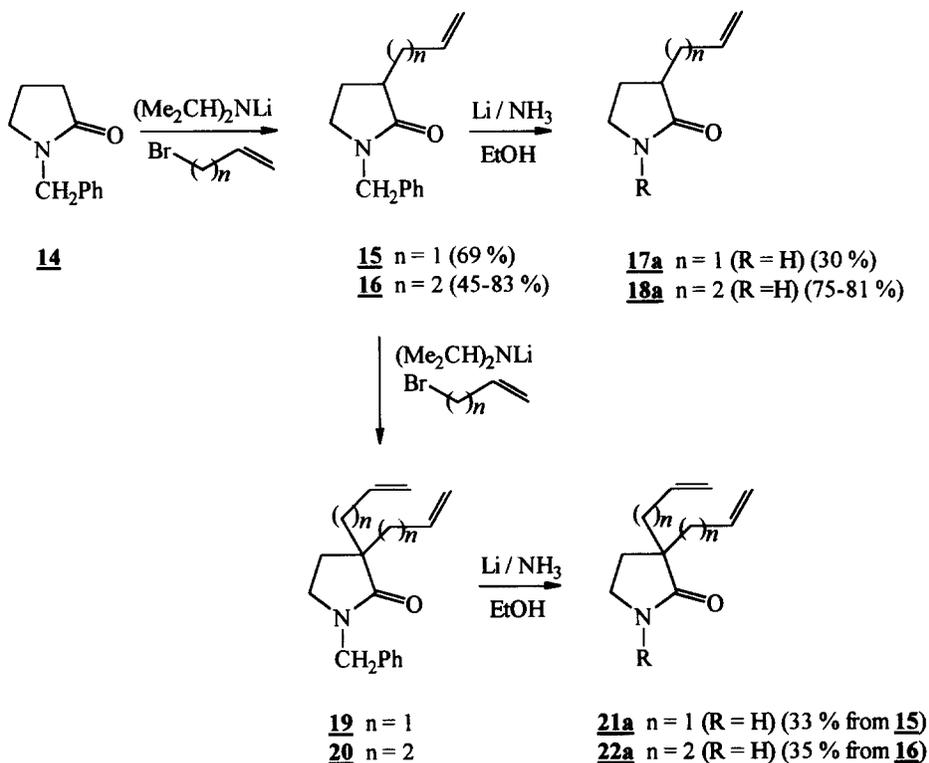
Scheme 1



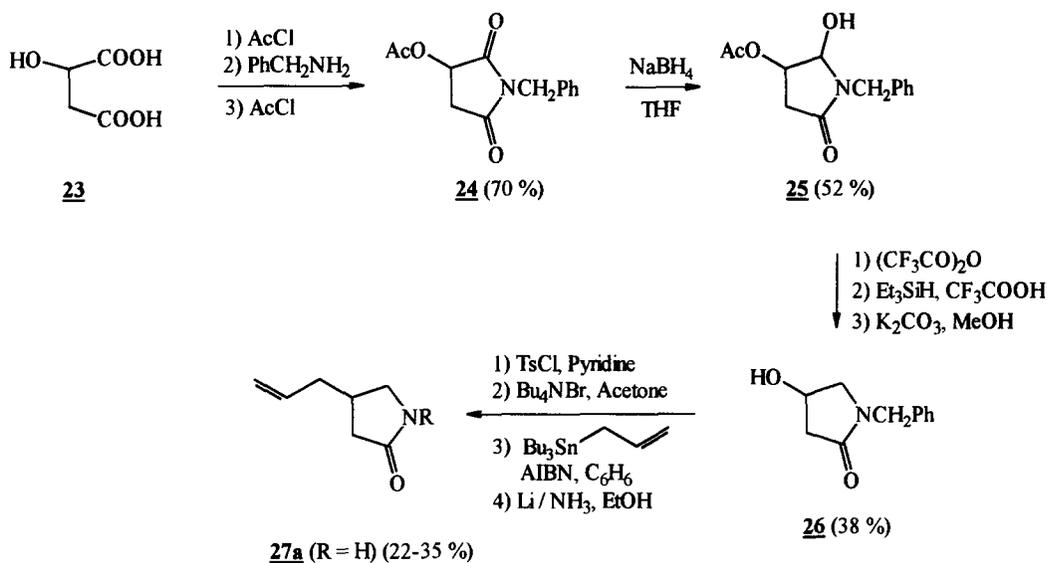
## RESULTS AND DISCUSSION

## Carboxamidyl radicals

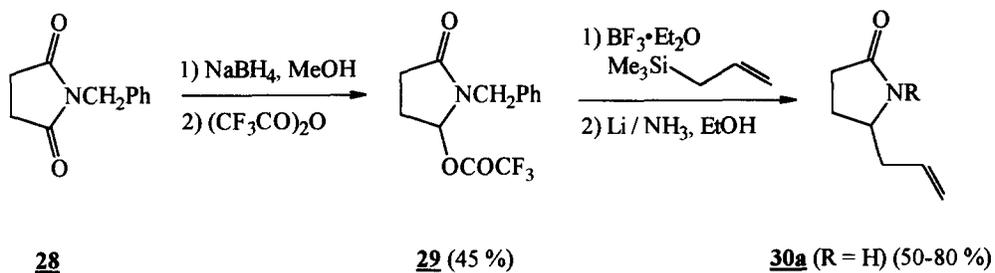
The 3-monoalkenyl- and 3,3-dialkenylpyrrolidin-2-ones **17a** (R = H) and **18a** (R = H) were prepared as shown in Scheme 2 using a procedure described by Padwa *et al.*<sup>23</sup> Preparation of 4-allylpyrrolidin-2-one (**27a**, R = H) was carried out according to a method reported by Caballero and coworkers<sup>24</sup> (Scheme 3). To prepare 5-allylpyrrolidin-2-one (**30a**, R = H), a Baker and Sifniades reduction<sup>25</sup> of N-benzylsuccinimide (**28**) was combined with a Takacs and Weidner alkenylation<sup>26</sup> of the resulting trifluoroacetate **29** (Scheme 4). Finally, 5-(but-3-enyl)pyrrolidin-2-one (**32a**, R = H) was prepared by sodium borohydride reduction of succinimide (**31**) in acid medium followed by reaction with 3-butenylmagnesium bromide (Scheme 5). Treatment of the above six pyrrolidinones with a commercial sodium hypochlorite solution<sup>27</sup> afforded the corresponding N-chloropyrrolidinones (**17b**, **18b**, **21b**, **22b**, **27b**, **30b** and **32b** (R = Cl)) in yields ranging from 53 to 100 % (95-100 % active chlorine by iodometry).



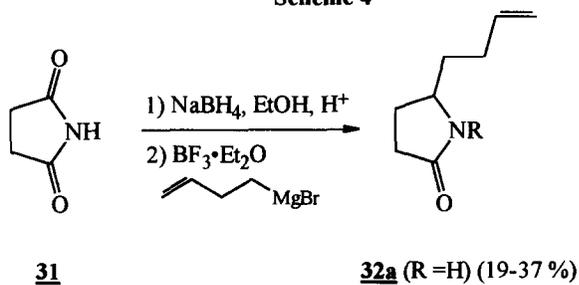
Scheme 2



Scheme 3

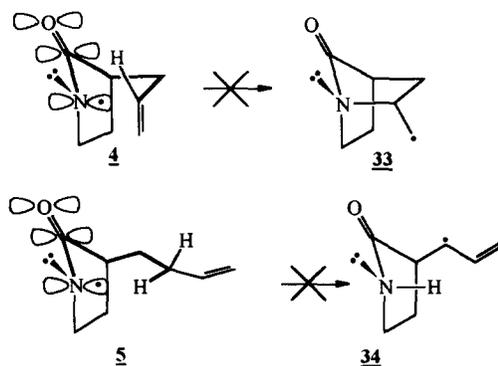


Scheme 4



Scheme 5

The results of photolysis of N-chloro-monoalkenylpyrrolidin-2-ones **17b** and **18b** (R = Cl) are presented in Table 1. It is noteworthy that the parent amides **17a** and **18a** were almost the sole products detected by gas liquid chromatography (GLC) and isolated by flash chromatography in the yields indicated. They were formed by intermolecular hydrogen abstraction from the solvent, either by the amidyl radical<sup>28</sup> or by the chlorine atom (Goldfinger type mechanism<sup>29</sup>). These intermolecular reactions were clearly faster than intramolecular reactions of amidyl radicals **4** and **5**. As illustrated in Scheme 6 for radical **4**, only the planar or a slightly twisted (30–35°)  $\Pi_N$  state allows good overlap between the p orbital on nitrogen containing the unpaired spin and the  $\pi$  orbital of the double bond and, thus, can participate in an intramolecular addition to the double bond (5-*exo* cyclization on the acyl chain in the case of **4**, 6-*exo* cyclization on the acyl chain in the case of **5**). For the planar or a slightly twisted  $\Sigma_N$  state of radicals **4** and **5**, the  $sp^2$  orbital containing the unpaired spin cannot overlap with the  $\pi$  orbital of the double bond according to molecular models. Similarly, intramolecular abstraction of an allylic hydrogen through a 1,5 transfer on the acyl chain in the case of radical **5** is possible only with the planar or slightly twisted  $\Pi_N$  state since it allows overlap (not optimum) between the p orbital on nitrogen and the  $\sigma$  orbital of the allylic C–H bond (angle of about 150° for a 35° twisted  $\Pi_N$  radical, see Scheme 6). In the case of radical **4**, such a 1,5 transfer of an allylic hydrogen through the N-alkyl chain should be slower because of the much poorer alignment of the allylic C–H bond and the  $p_N$  orbital of the twisted (35°)  $\Pi_N$  state (angle of 90°). Thus, intramolecular reactions of the  $\Pi_N$  state of cyclic amidyl radicals **4** and **5**, namely 5-*exo* cyclization of **4**, 6-*exo* cyclization of **5** and 1,5-transfer of an allylic hydrogen in **5**, are slower than intermolecular hydrogen abstraction from the solvent by the amidyl radical (through the  $\Pi_N$  or the  $\Sigma_N$  state) and/or the chlorine atom. This might be due to the inherent unreactivity of the  $\Pi_N$  state of these cyclic amidyls or to unfavorable interactions in the transition states leading to bicyclo[2.2.1]azaheptane or to bicyclo[3.2.1]azaoctane skeletons.<sup>30</sup>



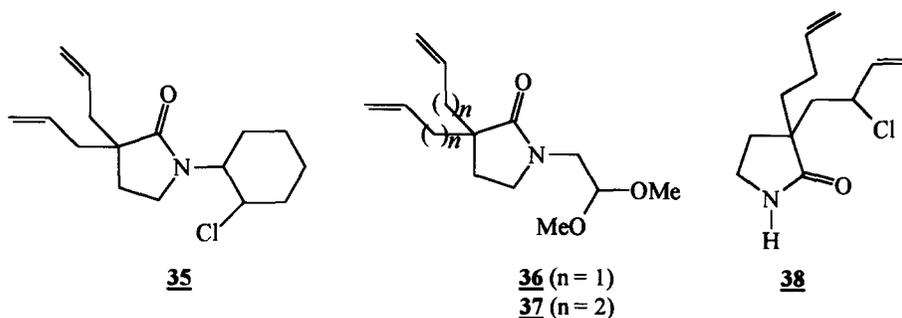
**Table 1.** Photolysis of N-Chloro-3-allylpyrrolidin-2-one (**17b**, R = Cl) and N-Chloro-3-butenylpyrrolidin-2-one (**18b**, R = Cl)

N-Chlorolactam (R = Cl)	Photolysis conditions <sup>a</sup>	Conc. (M)	Photolysis duration (h)	Yield of parent lactam (R = H) <sup>b</sup> (%)
<b>17b</b>	A	0.050	2.5	33 ( <b>17a</b> )
<b>18b</b>	B	0.020	1.5	98 ( <b>18a</b> )
<b>18b</b>	C	0.022	11	51 <sup>c</sup> ( <b>18a</b> )

<sup>a</sup> The photolyses were carried out in a Rayonet reactor using a quartz cell. Conditions A: 254 nm lamps, CH<sub>2</sub>Cl<sub>2</sub> (solvent), -78 °C ; conditions B: 254 nm, cyclohexane, 10 °C ; conditions C: 300 nm, CH<sub>2</sub>Cl<sub>2</sub>, -78 °C.

<sup>b</sup> Yield of products isolated by flash chromatography.

<sup>c</sup> The yield takes into account 2 % of unreacted N-chlorolactam **18b** (iodometric titration). A chlorinated compound identified by GC-MS only was isolated in a 4 % yield.



As shown in Table 2, entries 1, 2 and 3, the photolysis of N-chlorolactam **21b** (R = Cl), precursor of carboxamidyl radical **6**, led exclusively to the parent lactam **21a** (R = H). Under conditions A (entry 1), the yield of parent lactam (81%) was even higher than that obtained in the photolysis of N-chlorolactam **17b** (R = Cl) (Table 1, entry 1: 33%). So, despite the fact that the probability of the intramolecular process (5-*exo* cyclisation on the acyl chain) should be higher in the case of radical **6** having two propenyl chains than with radical **5** having only one propenyl chain, it remained slower than intermolecular hydrogen abstraction from the solvent. The intermolecular trapping of radical **6** by cyclohexene (entry 4, 6% of 1,2-adduct **35**) and by tertibutoxyethylene (entry 5, 33% of adduct **36** after methanolysis of the  $\alpha$ -chloroether) shows clearly that the intramolecular reactions of the  $\Pi_N$  state of such carboxamidyl radical are slower than intermolecular addition to an olefin which could involve the  $\Pi_N$  or the  $\Sigma_N$  state.<sup>30</sup>

**Table 2.** Photolysis of N-Chloro-3,3-diallylpyrrolidinone (**21b**, R = Cl)

Entry	Photolysis conditions <sup>a</sup>	Conc. (M)	Photolysis duration (h)	Yield <sup>b</sup> (%)	
				Parent lactam <b>21a</b> (R = H)	Other products
1	A	0.030	11	81	
2	B	0.015 to 0.020	2.5 to 4	99-100	
3	C	0.020	5	100	
4	B + 7eq. 	0,016	7	60	6 ( <b>35</b> , <i>trans</i> / <i>cis</i> = 1.5)
5	C + 7eq. 	0,017	9.5	65	33 ( <b>36</b> )

<sup>a</sup> See footnote a of Table 1. In entry 2, the range of values were obtained from two different experiments.

<sup>b</sup> See footnote b of Table 1.

The photolysis of N-chlorolactam **22b** (R = Cl) with two butenyl groups at position 3 did not give any bicyclic lactam (bicyclo[3.2.1]azaoctane) resulting from a 6-*exo* cyclization (on the acyl chain) of amidyl radical **7** (Table 3, entries 1 to 4) as in the case of the photolysis of N-chloro-3-butenyl-pyrrolidin-2-one (**18b**, R=Cl) (see Table 1). However, in contrast with the results of Table 1, a monochloro derivative resulting from allylic hydrogen abstraction (see **38**) was isolated in a 39 % yield along with 49 % of the parent lactam **22a** (R = H) when the photolysis of **22b** (R = Cl) was carried out under conditions C (Table 3, entry 2 : CH<sub>2</sub>Cl<sub>2</sub>, -78°C). When the photolysis of **22b** (R = Cl) was carried out under conditions B (entry 1 : cyclohexane, 10°C), the yield of parent lactam **22a** was about the same (53 %) as under conditions C but the allylic chloride **38** was not detected among the many unidentified products formed in small amounts. Concerning the mechanism of formation of allylic chloride **38**, there are three possibilities: i) intramolecular abstraction of an allylic hydrogen by the amidyl radical **7** (1,5-transfer via the acyl chain with a non optimum angle of about 150° between the p<sub>N</sub> orbital and the C–H bond as with **5**, see Scheme 6); ii) intermolecular abstraction of an allylic hydrogen by the amidyl radical **7**; iii) intermolecular abstraction of an allylic hydrogen by the chlorine atom. When the photolysis of **22b** (R = Cl) was carried out in the presence of cyclohexene oxide as HCl trap to break the chlorine-atom chain reaction (Goldfinger type mechanism<sup>29</sup>), the yields of parent lactam **22a** (R = H) and allylic chloride **38** remained the same (Table 3, entry 3). In the presence of tertibutoxyethylene which is a good trap

for both  $\text{Cl}_2$  and  $\text{HCl}$  produced in the chlorine-atom chain, the yields of parent amide **22a** and allylic chloride **38** were lower (entry 4) due to the fact that about 50 % of the reaction involved the radical chain addition of N-chlorolactam **22b** to tertibutoxyethylene, but the ratio of allylic chloride **38** to parent amide **22a** remained the same. The experiments of entries 3 and 4 of Table 3 therefore strongly suggest that a chlorine-atom chain was not involved in hydrogen abstraction from the solvent ( $\text{CH}_2\text{Cl}_2$ ) and in the formation of allylic chloride **38**. Furthermore, intramolecular hydrogen abstraction by the amidyl radical **7** for the formation of allylic chloride **38** does not seem highly probable for the following reasons: i) such a 1,5-transfer of allylic hydrogen via the N-alkyl chain was not observed in the case of radical **6**; ii) the 1,5-transfer of an allylic hydrogen in the case of radical **7** would occur via the acyl chain and it has been shown that, in the case of an acyclic carboxamidyl radical (photolysis of N-chloro-N-(1,1,3-trimethyl-butyl)-3,3-dimethylbutanamide<sup>31</sup>), 1,5-transfer of hydrogen was faster for a hydrogen on the N-alkyl chain than for a hydrogen on the N-acyl chain. Therefore, intermolecular allylic hydrogen abstraction by amidyl radical **7**, which could also abstract hydrogen from the solvent, appears the most probable mechanism for the formation of allylic chloride **38**. In agreement with this, a slight increase of the molar ratio of allylic chloride **38** to parent amide **22a**, from 0.55 to 0.80, was observed upon increasing the concentration of N-chlorolactam **22b** ( $\text{R} = \text{Cl}$ ) from 0.004 M to 0.014 M when the photolysis of **22b** was carried out in  $\text{CH}_2\text{Cl}_2$  at  $-78^\circ\text{C}$ . Such an increase of substrate concentration should indeed lead to an increase of the frequency of collisions between amidyl radical **7** and N-chlorolactam **22b** ( $\text{R} = \text{Cl}$ ) and/or parent lactam **22a** ( $\text{R} = \text{H}$ ) and, hence, lead to an increase of the **38/22a** molar ratio. Chow and coworkers<sup>31</sup> had proposed that the  $\Pi_{\text{N}}$  amidyl radical was responsible for the preference for hydrogen abstraction on the N-alkyl chain in the photolysis of N-chloro-N-(1,1,3-trimethyl-butyl)-3,3-dimethylbutanamide mentioned above but they had no unequivocal evidence of the participation of the  $\Pi_{\text{N}}$  radical since, from an inspection of molecular models, both the  $\Sigma_{\text{N}}$  and  $\Pi_{\text{N}}$  radicals appear to offer a good overlap for 1,5-transfer of an hydrogen on the N-alkyl chain (as well as on the acyl chain).

Photolysis of N-chloro-4-allylpyrrolidin-2-one (**27b**,  $\text{R} = \text{Cl}$ ) in  $\text{CH}_2\text{Cl}_2$  at  $-78^\circ\text{C}$  (conditions C) gave the parent amide **27a** ( $\text{R} = \text{H}$ ) as the sole product. Once again, hydrogen abstraction from the solvent was faster than the intramolecular reactions of amidyl radical **8** (5-*exo* cyclization on the N-alkyl chain to a bicyclo[2.2.1]azaheptane and 1, 5-transfer of an allylic hydrogen on the acyl chain) which could occur only via the  $\Pi_{\text{N}}$  state.

**Table 3.** Photolysis of N-Chloro-3,3-di(but-3-enyl)-pyrrolidin-2-one (**22b**, R = Cl)

Entry	Photolysis conditions <sup>a</sup>	Conc. (M)	Photolysis duration (h)	Yield <sup>b</sup> (%)	
				Parent lactam <b>22a</b> (R = H)	Other products
1	B	0.020	2	53	Many minor products <sup>c</sup>
2	C	0.014	9	49 <sup>d</sup>	39 <sup>d</sup> ( <b>38</b> )
3	C + 7-8 eq. 	0.018-0.019	6-6.5	48-50	35-38 ( <b>38</b> )
4	C + 3,5-7 eq. 	0.011-0.017	7-8.5	25-27	46-50 ( <b>37</b> ) 18 ( <b>38</b> )

<sup>a</sup> See footnote a of Table 1. In entries 3 and 4, the range of values correspond to two different experiments.

<sup>b</sup> See footnote b of Table 1.

<sup>c</sup> None of the minor products were identified or characterized.

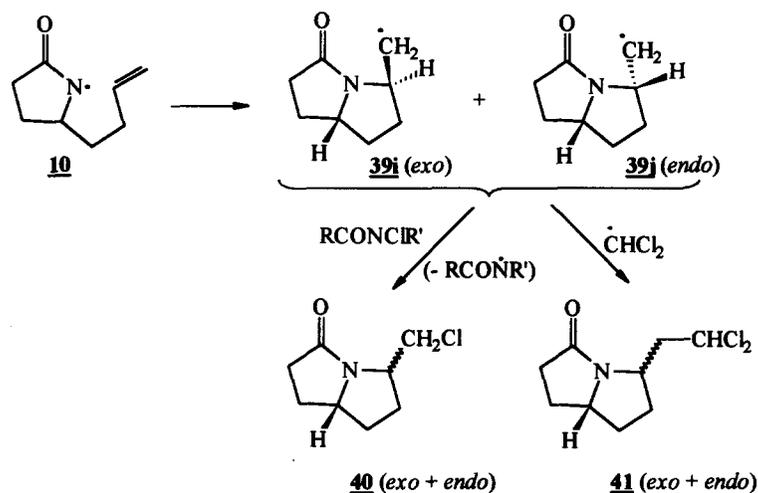
<sup>d</sup> The yield takes into account 4 % of unreacted N-chlorolactam **22b** (iodometric titration).

Photolysis of N-chloro-5-allylpyrrolidin-2-one **30b** (R = Cl), in cyclohexane at 10°C (conditions B), gave the parent lactam in a 94 % yield (Table 4, entry 1). This is not surprising since 5-*endo* cyclization of radicals is a slow process, usually not observed<sup>32</sup>.

Irradiation of N-chloro-5-butenylpyrrolidin-2-one **32b** (R = Cl), in CH<sub>2</sub>Cl<sub>2</sub> at –78°C (conditions C), gave the bicyclic lactams **40** and **41** (bicyclo[3.3.0]azaoctane skeleton, Scheme 7) via 5-*exo* cyclization of amidyl radical **10**, in a total yield of 9 to 24 % and as a 2:1 to 2.5:1 mixture of two diastereomers (Table 4, entry 2). Esker and Newcomb<sup>33</sup> have also obtained a 2:1 mixture of diastereomeric bicyclic lactams by reaction of N-thiophenyl-5-(but-2-enyl)pyrrolidin-2-one with tributyltin hydride initiated by AIBN. Since a substituent at position 2 of a *cis*-bicyclo[3.3.0]octane shows a strong preference for the *exo* orientation<sup>35</sup> (see **39i** in Scheme 7), the low stereoselectivity of the cyclization of radical **10**, a 2:1 ratio of diastereomeric bicyclic lactams (see **40** and **41**), infers that the transition state is early, as would be expected from the fact that the addition of an amidyl radical to a double bond should be exothermic. Inspection of molecular models shows: i) that both the  $\Pi_N$  (30–35° twisted) and  $\Sigma_N$  states can participate in a 5-*exo* cyclization; ii) that cyclization of the  $\Pi_N$  state of **10** should give the *exo* isomer **39i** predominantly because of stronger interactions in the transition state leading to the *endo* isomer **39j**; and iii) that interactions in the two transition states for cyclization of the

$\Sigma_N$  state appear to be similar. These observations, combined with the fact that no cyclization was observed in the examples where only the  $\Pi_N$  state could have cyclized, suggest that the  $\Sigma_N$  state, and not the  $\Pi_N$  state, would be involved in the cyclization of radical **10**. However, such conclusion is not on firm ground for the following reasons: i) the cyclization of radical **10** gives bicyclo[3.3.0]azaoctanes whereas the cyclization of amidyl radicals **4** to **8** would have given bicyclo[2.2.1]azaheptanes or bicyclo[3.2.1]azaoctanes and, therefore, less unfavourable interactions might be involved in the transition state for the cyclization of radical **10** than that of radicals **4** to **8**; and ii) in radical **10**, the overlap between the orbital containing the unpaired spin and the  $\pi$  orbital of the double bond appears to be better (more favourable orientation) with the  $\Sigma_N$  state than the  $\Pi_N$  state, again from the inspection of molecular models.

The dichlorinated bicyclic lactams **41** must have been formed by coupling of the diastereomeric radicals **39j** and **39i** with a dichloromethyl radical (Scheme 7). Their formation provides further evidence that hydrogen abstraction from the solvent did occur in the photolyses discussed above and was the reaction mainly responsible for the formation of the parent lactam in all photolyses described so far including this one (43–44 % yield of **32a**, Table 4, entry 2). We made no attempt to detect the products of solvent chlorination.



Scheme 7

**Table 4.** Photolysis of N-Chloro-5-alkenylpyrrolidin-2-ones **30b** and **32b** (R = Cl)

Entry	N-Chloro-lactam (R = Cl)	Conc. (M)	Photolysis conditions <sup>a</sup>	Photolysis duration (h)	Yield <sup>b</sup> (%)	
					Parent lactam (R = H)	Other products
1	<b>30b</b>	0.020	B	1.5	94 ( <b>30a</b> )	
2	<b>32b</b>	0.017	C	14.5-17.5	43-44 ( <b>32a</b> )	5-13 ( <b>40</b> ) <sup>c</sup> 4-11 ( <b>41</b> ) <sup>d,e</sup>

<sup>a</sup> See footnote a of Table 1. In entry 2, the range of values were obtained from three different experiments.

<sup>b</sup> See footnote b of Table 1.

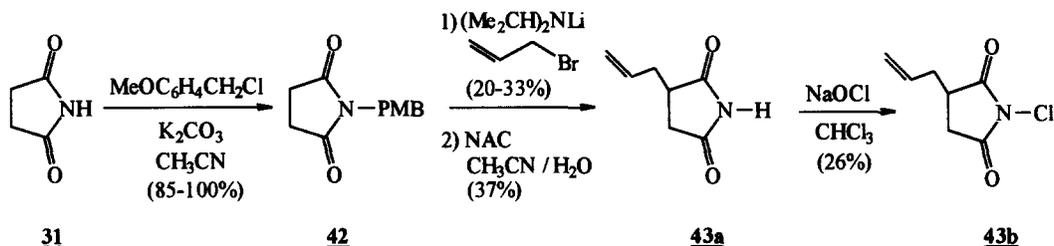
<sup>c</sup> Mixture of diastereomers in a 2 : 1 ratio as determined by HPLC.

<sup>d</sup> Mixture of diastereomers in a 2.5 : 1 ratio as determined by <sup>1</sup>H NMR.

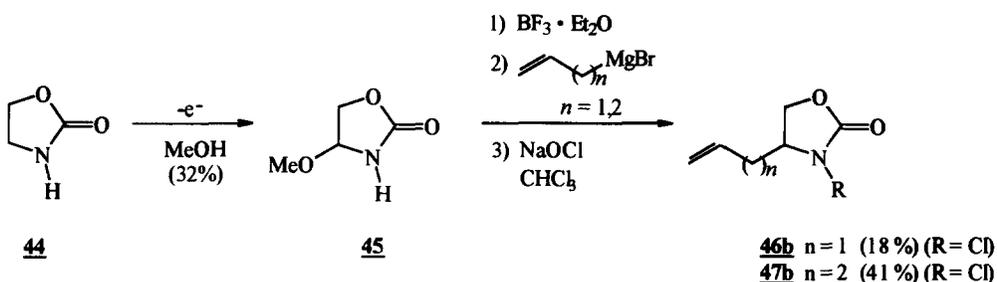
<sup>e</sup> In addition to **32a**, **40** and **41**, a dichlorinated compound (according to mass spectrometry) was isolated in a 11-22 % yield but its structure was not elucidated.

### Imidyl and carbamyl radicals

The preparation of N-chloro-3-allylsuccinimide **43b** is described in Scheme 8 and that of N-chloro-4-alkenyloxazolidinones **46b** (R = Cl) and **47b** (R = Cl) in Scheme 9.

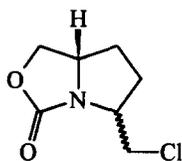


Photolysis of N-chloro-3-allylsuccinimide (**43b**, R = Cl) under conditions B and C (defined in footnote a of Table 1) gave only the parent 3-allylsuccinimide (**43a**, R = H) in a 80-85 % yield. As in the case of pyrrolidinyl radical **4** and for the same reasons, 5-*exo* cyclization of the intermediate imidyl radical **11**, which could have occurred only through the  $\Pi_N$  state, was slower than intermolecular hydrogen abstraction from the solvent. It is interesting to note that, in intermolecular radical-chain addition to olefins, N-chlorosuccinimide gave higher yields of addition than N-chloropyrrolidin-2-one.<sup>7</sup>



Scheme 9

The results of Table 5, entry 1, show that the photolysis of N-chloro-4-allyloxazolidin-2-one (**46b**, R = Cl) in  $\text{CH}_2\text{Cl}_2$  at  $-78^\circ\text{C}$  (conditions C) gave only the parent carbamate **46a** (R = H). Thus, hydrogen abstraction from the solvent was the sole process occurring as in the photolysis of the analogous N-chloro-allylpyrrolidinone **30b** (R = Cl) (Table 4, entry 1). In the photolysis of N-chloro-4-butenyloxazolidin-2-one (**47b**, R = Cl), under conditions C also (Table 5, entry 2), the intermediate carbamyl radical **13** underwent 6-*exo* cyclization to give a 2:1 diastereomeric mixture of bicyclo[3.3.0]azaoctanes (see bicyclic carbamates **48**) as did the closely analogous carboxamidyl radical **10** in the photolysis of N-chloro-5-butenylpyrrolidin-2-one (**32b**, R = Cl) (see bicyclic lactams **40** and **41**, Table 4, entry 2). However, the photolysis of **47b** (R = Cl) gave a much higher yield of cyclization (48% of **48**) than the the photolysis of **32b** (R = Cl) (average yield of **40** + **41**: 16%). This is not surprising since the intermolecular radical-chain addition of N-chlorocarbamates to olefins has been reported to give higher yields than the addition of the analogous N-chlorocarboxamides, both for cyclic<sup>7</sup> and acyclic<sup>1, 2, 6</sup> N-chloro precursors. This could reflect the higher reactivity, towards olefins, of a carbamyl radical as compared to a carboxamidyl radical.<sup>6, 7</sup>

**48** (*exo* + *endo*)

**Table 5.** Photolysis of N-Chloro-4-alkenyloxazolidin-2-ones **46b** (R = Cl) and **47b** (R = Cl) <sup>a</sup>

Entry	N-Chlorocarbamate (R = Cl)	Conc. (M)	Photolysis duration (h)	Yield <sup>b</sup> (%)	
				Parent carbamate (R = H)	Other product
1	<b>46b</b>	0.008	10	100 ( <b>46a</b> )	
2	<b>47b</b>	0.015	9	0	<b>48</b> ( <b>48</b> ) <sup>c</sup>

<sup>a</sup> Conditions C (see footnote a of Table 1).<sup>b</sup> See footnote b of Table 1.<sup>c</sup> Mixture of diastereomers in a 2:1 ratio as determined by GLC.

## CONCLUSION

We have shown that whenever a carboxamidyl, imidyl or carbamyl radical is constrained to react in its  $\Pi_N$  configuration to form bicyclo[2.2.1]azaheptane or bicyclo[3.2.1]azaoctane skeletons, intermolecular reactions (hydrogen abstraction from the solvent, allylic hydrogen abstraction from the substrate, addition to an external olefin) are faster than intramolecular reactions even if these intramolecular reactions are normally favored processes such as 5-*exo* cyclization (radicals **4**, **6,8** and **11**), 6-*exo* cyclization (radicals **5** and **7**) and 1,5-transfer of an allylic hydrogen (radicals **5** and **7**). The most probable mechanism of formation of allylic chloride **38** in the photolysis of N-chlorobutenylpyrrolidinone **22b** (R = Cl) appears to be intermolecular allylic hydrogen abstraction by the amidyl radical. On the other hand, radicals **10** and **13** did cyclize (5-*exo* cyclization) to 2:1 diastereomeric mixtures of bicyclo[3.3.0]azaoctanes (see **40**, **41** and **48**). No firm conclusion could be drawn concerning the electronic state,  $\Pi_N$  or  $\Sigma_N$ , of carboxamidyl radical **10** and carbamyl radical **13** involved in the latter cyclizations. Computational studies might shed light on the reactivity of the electronic states of the radicals generated in this study.<sup>30</sup>

## EXPERIMENTAL SECTION

Infrared spectra were taken on a Perkin-Elmer 1600 Series FTIR spectrophotometer. Routine <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AC-300 spectrophotometer. Mass spectra were taken from a Hewlett Packard 5971 mass selective detector coupled with a HP 5890 Series II gas chromatograph. High resolution mass spectra were recorded on a ZAB-2F model VG apparatus. Flash chromatography was carried out on E. M. Merck F-254 silica gel (220–400 mesh). HPLC separations were carried out with a Hewlett-Packard chromatograph, model 1050, equipped with an UV detector ( $\lambda = 260$  nm) using a semi preparative inverted phase C<sub>18</sub> Vydac column. Melting points were taken on a Buchi apparatus and are uncorrected.

### 3-Allyl-N-benzylpyrrolidin-2-one (**15**)

In a 100 mL three-neck round bottomed flask, a solution of 1.7 mL (1.3 g, 13 mmol) of dry diisopropylamine in 40 mL of anhydrous THF was cooled to 0°C under argon, then 8 mL (12.8 mmol) of a hexane solution of nBuLi 1.6 M was added dropwise. After cooling to -78°C, 2 g (11.4 mmol) of N-benzylpyrrolidin-2-one (**14**) dissolved in 7 mL of anhydrous Et<sub>2</sub>O was added. After stirring for 15 minutes, 1 mL (1.4 g, 11.6 mmol) of allyl

bromide was added. The solution was allowed to warm up to ambient temperature and stirred overnight. A saturated solution of  $\text{NH}_4\text{Cl}$  was then added. Extraction with ethyl ether followed by flash chromatography of the crude product ( $\text{Et}_2\text{O}$ ) afforded 1.69 g (7.8 mmol, 69 %) of oily **15**; IR ( $\text{cm}^{-1}$ ,  $\text{CHCl}_3$ ): 3009 (=C-H), 2925 (aliphatic C-H), 1675 (C=O);  $^1\text{H}$  NMR,  $\delta$  (ppm,  $\text{CDCl}_3$ ): 1.55–1.65 (1H, m,  $\text{H}_\alpha$  of  $\text{CH}_2\text{-CH-CO}$ ), 2.05–2.55 (2H, m), 2.5–2.7 (2H, m), 3.17 (2H, m,  $\text{CH}_2\text{-CH}_2\text{-N}$ ), 4.45 (2H, m, N- $\text{CH}_2\text{-Ph}$ ), 5.03–5.14 (2H, m,  $\text{CH}_2\text{=CH-}$ ), 5.73–5.86 (1H, m,  $\text{CH}_2\text{=CH-}$ ), 7.22–7.36 (5H, m, aromatic H);  $^{13}\text{C}$  NMR,  $\delta$  (ppm,  $\text{CDCl}_3$ ): 23.9 (N- $\text{CH}_2\text{-CH}_2$ ), 35.5 ( $\text{CH}_2\text{-CH=CH}_2$ ), 41.4 ( $\text{CH-CO}$ ), 44.8 (N- $\text{CH}_2\text{-CH}_2$ ), 46.8 (N- $\text{CH}_2\text{-Ph}$ ), 116.9 ( $\text{CH}_2\text{=CH-}$ ), 127.5, 128.1, 128.6 (tertiary aromatic C), 135.5 ( $\text{CH}_2\text{=CH-}$ ), 136.6 (quaternary aromatic C), 178.4 (C=O); MS (m/e): 215 ( $\text{M}^+$ ), 174 ( $\text{M}^+$  - allyl); HRMS: calc. for  $\text{C}_{14}\text{H}_{17}\text{NO}$ : 215.2944; found: 215.2950.

### 3-Allylpyrrolidin-2-one (**17a**, R = H)

In a 100 mL three-neck round bottomed flask, 40 mL of  $\text{NH}_3$  were condensed and 0.30 g (43 mmol) of metallic lithium was added. A solution of 1.58 g (73 mmol) of **15** in 10 mL of anhydrous  $\text{Et}_2\text{O}$  and 1 mL (0.78 g, 17 mmol) of freshly distilled dry EtOH was added. After 18 h, ethyl acetate and a saturated solution of  $\text{NH}_4\text{Cl}$  were added. The aqueous solution was extracted with ethyl acetate and dried with  $\text{Na}_2\text{SO}_4$ . Removal of the solvent left 288 mg (2.3 mmol, 32 %) of **17a** (yellow oil); IR ( $\text{cm}^{-1}$ ,  $\text{CHCl}_3$ ): 3220 (NH), 3005 (=C-H), 2950 (aliphatic C-H), 1690 (C=O);  $^1\text{H}$  NMR,  $\delta$  (ppm,  $\text{CDCl}_3$ ): 1.73–1.86 (1H, m,  $\text{CH-CO}$ ), 2.09–2.26 (2H, m), 2.38–2.57 (2H, m), 3.26–3.31 (2H, m,  $\text{CH}_2\text{-CH}_2\text{-N}$ ), 5.01–5.10 (2H, m,  $\text{CH}_2\text{=CH-}$ ), 5.70–5.83 (1H, m,  $\text{CH}_2\text{=CH-}$ ), 7.07 (1H, m, NH);  $^{13}\text{C}$  NMR,  $\delta$  (ppm,  $\text{CDCl}_3$ ): 26.5 ( $\text{CH}_2\text{-CH}_2\text{-CH}$ ), 34.9 ( $\text{CH}_2\text{-CH=CH}_2$ ), 40.4, 40.5 ( $\text{CH}_2\text{-N}$  and  $\text{CH-CO}$ ), 116.7 ( $\text{CH}_2\text{=CH-}$ ), 135.5 ( $\text{CH}_2\text{=CH-}$ ); MS (m/e): 125 ( $\text{M}^+$ ), 96 ( $\text{M}^+$  - allyl); HRMS: calc. For  $\text{C}_7\text{H}_{11}\text{NO}$ : 125.1700; found: 125.1711.

### 3-(But-3-enyl)-N-benzylpyrrolidin-2-one (**16**)

The same procedure as that described above for the preparation of **15** using 4-bromobut-1-ene afforded **16** as an oil (6.47 g, 28 mmol, 83 %); IR ( $\text{cm}^{-1}$ ,  $\text{CHCl}_3$ ): 3009 (=C-H), 2923 (aliphatic C-H), 1672 (C=O), 1260 (C-O);  $^1\text{H}$  NMR,  $\delta$  (ppm,  $\text{CDCl}_3$ ): 1.43–1.69 (2H, m,  $\text{CH}_2\text{-CH}_2\text{-CH=CH}_2$ ), 2.02–2.22 (4H, m,  $\text{CH}_2\text{-CH=CH}_2$  and  $\text{CH}_2\text{-CH}_2\text{-CH-CO}$ ), 2.44–2.47 (1H, m,  $\text{CH-CO}$ ), 3.15–3.18 (2H, m,  $\text{CH}_2\text{-CH}_2\text{-N}$ ), 4.39–4.50 (2H, m, N- $\text{CH}_2\text{-Ph}$ ), 4.96–5.08 (2H, m,  $\text{CH}_2\text{=CH-}$ ), 5.78 (1H, m,  $\text{CH}_2\text{=CH-}$ ), 7.20–7.34 (5H, m, aromatic H);  $^{13}\text{C}$  NMR,  $\delta$  (ppm,  $\text{CDCl}_3$ ): 24.4, 30.2, 30.9 ( $\text{CH}_2\text{-CH}_2\text{-CH=CH}_2$  and N- $\text{CH}_2\text{-CH}_2$ ), 40.8 ( $\text{CH-CO}$ ), 44.4 (N- $\text{CH}_2\text{-CH}_2$ ), 46.2 (N- $\text{CH}_2\text{-Ph}$ ), 114.7 ( $\text{CH}_2\text{=CH-}$ ), 127.1, 127.6, 128.2 (tertiary aromatic C), 136.3 (quaternary aromatic C), 137.6 ( $\text{CH}_2\text{=CH-}$ ), 176.1 (C=O); MS (m/e): 229 ( $\text{M}^+$ ), 175 ( $\text{M}^+$  -  $\text{CH}_2\text{CH}_2\text{CH=CH}_2$ ); HRMS: calc. for  $\text{C}_{15}\text{H}_{19}\text{NO}$ : 229.3212; found: 229.3220.

### 3-(But-3-enyl)pyrrolidin-2-one (**18a**, R = H)

The same procedure as that described for the conversion of **15** into **17a** was used to convert **16** into **18a** which was obtained as an oil (483 mg, 3.5 mmol, 81 %); IR ( $\text{cm}^{-1}$ ,  $\text{CHCl}_3$ ): 3441 (N-H free), 3224 (N-H bonded), 3007 (=C-H), 2889 (aliphatic C-H), 1687 (C=O);  $^1\text{H}$  NMR,  $\delta$  (ppm,  $\text{CDCl}_3$ ): 1.35–1.50 (1H, m), 1.67–1.80 (1H, m), 1.89–2.40 (5H, m), 3.22–3.37 (2H, m,  $\text{CH}_2\text{-CH}_2\text{-N}$ ), 4.92–5.06 (2H, m,  $\text{CH}_2\text{=CH-}$ ), 5.71–5.86 (1H, m,  $\text{CH}_2\text{=CH-}$ ), 6.92 (1H, m, NH);  $^{13}\text{C}$  NMR,  $\delta$  (ppm,  $\text{CDCl}_3$ ): 27.5, 30.0, 31.3 ( $\text{CH}_2\text{-CH}_2\text{-CH=CH}_2$  and N- $\text{CH}_2\text{-CH}_2$ ), 40.3 ( $\text{CH}_2\text{-NH}$  and  $\text{CH-CO}$ ), 115.0 ( $\text{CH}_2\text{=CH-}$ ), 137.8 ( $\text{CH}_2\text{=CH-}$ ), 180.6 (C=O); MS (m/e): 139 ( $\text{M}^+$ ), 85 ( $\text{M}^+$  -  $\text{CH}_2\text{CH}_2\text{CH=CH}_2$ ); HRMS: calc. for  $\text{C}_8\text{H}_{13}\text{NO}$ : 139.1968; found: 139.1962.

### 3,3-Diallylpyrrolidin-2-one (**21a**)

3-Allyl-N-benzylpyrrolidin-2-one (**15**) was alkylated with allylbromide as described above for the allylation of N-benzylpyrrolidin-2-one (**14**). Debenzylation of the crude product was carried out with lithium in ammonia using the same procedure as above for the debenzylation of **15**. The diallylpyrrolidinone **21a** was obtained as an oil (358 mg, 1.85 mmol, 55 %); IR ( $\text{cm}^{-1}$ ,  $\text{CHCl}_3$ ): 3437 (N-H free), 3222 (N-H bonded), 3006 (=C-H), 2902 (aliphatic C-H), 1688 (C=O);  $^1\text{H}$  NMR,  $\delta$  (ppm,  $\text{CDCl}_3$ ), J (Hz): 2.04 (2H, t, J = 7.1,  $\text{CH}_2\text{-CH}_2\text{-N}$ ), 2.20 (2H, dd, J = 8.3 and 13.7,  $\text{CH}_2\text{-CH=CH}_2$ ), 2.35 (2H, dd, J = 6.2 and 13.8,  $\text{CH}_2\text{-CH=CH}_2$ ), 3.23 (2H, t, J = 7.1,  $\text{CH}_2\text{-CH}_2\text{-N}$ ), 5.09–5.14 (4H, m,  $\text{CH}_2\text{=CH-}$ ), 5.71–5.85 (2H, m,  $\text{CH}_2\text{=CH-}$ ), 5.94 (1H, m, NH);  $^{13}\text{C}$  NMR,  $\delta$  (ppm,  $\text{CDCl}_3$ ): 35.0 (NH- $\text{CH}_2\text{-CH}_2$ ), 36.1 ( $\text{CH}_2\text{-CH=CH}_2$ ), 46.2 (NH- $\text{CH}_2\text{-CH}_2$ ), 48.8 (C-CO), 117.1 ( $\text{CH}_2\text{=CH-}$ ), 131.2 ( $\text{CH}_2\text{=CH-}$ ), 181.2 (C=O); MS (m/e): 165 ( $\text{M}^+$ ), 123 ( $\text{M}^+$  - allyl); HRMS: calc. for  $\text{C}_{10}\text{H}_{15}\text{NO}$ : 165.2346; found: 165.2350.

### 3,3-Di-(but-3-enyl)pyrrolidin-2-one (**22a**)

It was prepared from 3-(but-3-enyl)-N-benzylpyrrolidin-2-one (**16**) exactly as above using 4-bromobut-1-ene as alkylating agent and was obtained as a yellow oil (1.09 g, 5.6 mmol, 100 %); IR ( $\text{cm}^{-1}$ ,  $\text{CHCl}_3$ ): 3218 (N-H), 3005 (aliphatic C-H), 2940 (=C-H), 1690 (C=O);  $^1\text{H}$  NMR,  $\delta$  (ppm,  $\text{CDCl}_3$ ), J (Hz): 1.61 (4H, m,  $\text{CH}_2\text{-CH}_2\text{-CH=CH}_2$ ), 1.67 (1H, m, N-H), 1.99–2.16 (6H, m), 3.30 (2H, t, J = 7.1,  $\text{CH}_2\text{-CH}_2\text{-N}$ ), 4.93–5.06 (4H, m,

$\text{CH}_2=\text{CH}-$ ), 5.76–5.85 (2H, m,  $\text{CH}_2=\text{CH}-$ );  $^{13}\text{C}$  NMR,  $\delta$  (ppm,  $\text{CDCl}_3$ ): 28.6 ( $\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}_2$ ), 33.3 ( $\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}_2$ ), 35.4 ( $\text{NH}-\text{CH}_2$ ), 45.7 ( $\text{NH}-\text{CH}_2-\text{CH}_2$ ), 50.4 ( $\text{C}-\text{CO}$ ), 114.6 ( $\text{CH}_2=\text{CH}-$ ), 135.8 ( $\text{CH}_2=\text{CH}-$ ), 182.7 ( $\text{C}=\text{O}$ ); MS (m/e): 193 ( $\text{M}^+$ ), 139 ( $\text{M}^+ - \text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}_2$ ); HRMS: calc. for  $\text{C}_{12}\text{H}_{19}\text{NO}$ : 193.2882; found: 193.2876.

### 3-Acetoxy-N-benzylsuccinimide (24)

The preparation was carried out according to procedure described by Caballero and coworkers.<sup>24</sup> In a 500 mL round-bottomed flask, a solution of 40 g (0.298 mol) of malic acid (**23**) and 150 mL (165.6 g, 2.1 mol) of acetyl chloride was heated to reflux for 2.5 h. After removal of excess acetyl chloride in vacuo, the residue was dissolved in  $\text{CH}_2\text{Cl}_2$ , cooled to  $0^\circ\text{C}$ , then was added 32.8 mL (32.2 g, 0.3 mol) of benzylamine dissolved in 300 mL of  $\text{CH}_2\text{Cl}_2$ . Dichloromethane was distilled off and 90 mL (99.4 g, 1.3 mol) of acetyl chloride was added. After refluxing for 3 h, acetyl chloride and acetic acid were removed in vacuo. The pH was then adjusted to 7 with aqueous  $\text{Na}_2\text{CO}_3$ . The aqueous mixture was extracted with  $\text{CH}_2\text{Cl}_2$  (3x) and dried over  $\text{MgSO}_4$ . After flash chromatography, 51.7 g (0.209 mol, 70 %) of imide **24** (oil) was isolated; IR ( $\text{cm}^{-1}$ ,  $\text{CHCl}_3$ ): 3027 ( $=\text{C}-\text{H}$ ), 2949 (aliphatic C-H), 1750 ( $\text{C}=\text{O}$  very wide band);  $^1\text{H}$  NMR,  $\delta$  (ppm,  $\text{CDCl}_3$ ), J (Hz): 2.15 (3H, s,  $\text{CH}_3-\text{CO}$ ), 2.67 (1H, dd, J = 4.9 and 18.4,  $\text{H}_a$  of  $\text{N}-\text{CO}-\text{CH}_2$ ), 3.16 (1H, dd, J = 8.7 and 18.4,  $\text{H}_b$  of  $\text{N}-\text{CO}-\text{CH}_2$ ), 4.70 (2H, m,  $\text{N}-\text{CH}_2-\text{Ph}$ ), 5.45 (1H, dd, J = 4.9 and 8.7,  $\text{AcO}-\text{CH}-\text{CO}$ ), 7.29–7.41 (5H, m, aromatic H);  $^{13}\text{C}$  NMR,  $\delta$  (ppm,  $\text{CDCl}_3$ ): 20.4 ( $\text{CH}_3-\text{CO}$ ), 35.6 ( $\text{N}-\text{CO}-\text{CH}_2$ ), 42.6 ( $\text{N}-\text{CH}_2-\text{Ph}$ ), 67.4 ( $\text{AcO}-\text{CH}-\text{CO}$ ), 128.0, 128.6, 128.8 (tertiary aromatic C), 135.0 (quaternary aromatic C), 169.6, 172.8, 173.1 ( $\text{C}=\text{O}$ ); MS (m/e): 247 ( $\text{M}^+$ ), 187 ( $\text{M}^+ - \text{OAc}$ ); HRMS: calc. for  $\text{C}_{13}\text{H}_{13}\text{NO}_4$ : 247.2500; found: 247.2495.

### 4-Acetoxy-5-hydroxy-N-benzylpyrrolidin-2-one (25)

In a 250 mL round-bottomed flask, a solution of 12.7 g (51 mmol) of imide **24**, 100 mL of THF and 5 mL of  $\text{H}_2\text{O}$  was cooled to  $-20^\circ\text{C}$ , then 2.2 g (58 mmol) of  $\text{NaBH}_4$  was added in small portions. After stirring for 10 min,  $\text{HCl}$  2 M was added to bring the pH to 5. The solvent was removed in vacuo then water and chloroform were added. The residue was extracted with chloroform and the organic phase was washed with brine then dried with  $\text{Na}_2\text{SO}_4$ . Evaporation of the solvent in vacuo gave 10.38 g (42 mmol, 82 %) of a white solid. Recrystallisation in hexanes /  $\text{AcOEt}$  afforded 6.6 g (26 mmol, 52 %) of **25** (mixture of diastereoisomers) as white crystals: m. p.:  $102\text{--}108^\circ\text{C}$ ; IR ( $\text{cm}^{-1}$ ,  $\text{CHCl}_3$ ): 3568 ( $\text{O}-\text{H}$  free), 3365 ( $\text{O}-\text{H}$  bonded), 3026 ( $=\text{C}-\text{H}$ ), 2936 (aliphatic C-H), 1740, 1700 ( $\text{C}=\text{O}$ ), 1239 ( $\text{C}-\text{O}$ );  $^1\text{H}$  NMR,  $\delta$  (ppm,  $\text{CDCl}_3$ ), J (Hz): 2.13 (3H, s,  $\text{COCH}_3$  of one isomer), 2.16 (3H, s,  $\text{COCH}_3$  of one isomer), 2.32 (1H, m,  $\text{O}-\text{H}$  of one isomer), 2.36 (1H, m,  $\text{O}-\text{H}$  of one isomer), 2.61 (1H, dd, J = 5.3 and 16.8,  $\text{H}_a$  of  $\text{CH}_2-\text{CH}-\text{OAc}$  of both isomers), 2.76 (1H, dd, J = 7.3 and 16.8,  $\text{H}_b$  of  $\text{CH}_2-\text{CH}-\text{OAc}$  of both isomers), 4.32–4.60 (2H, m,  $\text{N}-\text{CH}_2-\text{Ph}$  of both isomers), 5.30 (1H, dt, J = 5.3 and 7.3,  $\text{CH}_2-\text{CH}-\text{OAc}$  of both isomers), 5.36 (1H, dd, J = 5.3,  $\text{CH}-\text{OH}$  of both isomers), 7.25–7.40 (5H, m, aromatic H of both isomers);  $^{13}\text{C}$  NMR,  $\delta$  (ppm,  $\text{CDCl}_3$ ): 20.8 ( $\text{COCH}_3$ ), 34.4 ( $\text{CH}-\text{CH}_2-\text{CO}$ ), 49.0 ( $\text{N}-\text{CH}_2-\text{Ph}$ ), 72.6 ( $\text{CH}_2-\text{CH}-\text{OAc}$ ), 87.7 ( $\text{CH}-\text{OH}$ ), 127.4, 128.7, 128.9 (tertiary aromatic C), 136.9 (quaternary aromatic C), 164.1 ( $\text{C}=\text{O}$  of  $\text{OAc}$ ), 172.2 ( $\text{C}=\text{O}$  of the amide); MS (m/e): 249 ( $\text{M}^+$ ); HRMS: calc. for  $\text{C}_{13}\text{H}_{15}\text{NO}_4$ : 249.2658; found: 249.2660.

### 4-Hydroxy-N-benzylpyrrolidin-2-one (26)

To a solution of 5 g (20 mmol) of **25** in 60 mL of chloroform were added 3.4 mL (5.06 g, 24 mmol) of trifluoroacetic anhydride. After stirring for 30 min, chloroform was removed in vacuo. The residue was dissolved in 20 mL of trifluoroacetic acid and 4 mL (2.9 g, 25.2 mmol) of triethylsilane were added. After stirring for 1 h, the solution was concentrated under vacuum and a saturated  $\text{NaHCO}_3$  solution was added. The aqueous mixture was extracted with chloroform and the organic phase washed with a saturated  $\text{NaHCO}_3$  solution then with water and dried over  $\text{Na}_2\text{SO}_4$ . The oily crude product (6.6 g) was purified by flash chromatography ( $\text{Et}_2\text{O}-\text{AcOEt}$  4:1 as eluent) to give 3.1 g (13.3 mmol, 67 %) of 4-acetoxy-N-benzylpyrrolidin-2-one. Hydrolysis of 2 g (8.57 mmol) of this lactam was carried out by two successive treatments with  $\text{K}_2\text{CO}_3$  in  $\text{MeOH}$  (1.8 g, 13 mmol, in 125 mL then 1.2 g, 8.7 mmol, in 80 mL). The usual work up gave 0.91 g (4.8 mmol, 57 %) of hydroxylactam **26** as a brownish oil; IR ( $\text{cm}^{-1}$ ,  $\text{CHCl}_3$ ): 3448 ( $\text{O}-\text{H}$  free), 3368 ( $\text{O}-\text{H}$  bonded), 3011 ( $=\text{C}-\text{H}$ ), 2876 (aliphatic C-H), 1676 ( $\text{C}=\text{O}$ );  $^1\text{H}$  NMR,  $\delta$  (ppm,  $\text{CDCl}_3$ ), J (Hz): 2.29 (1H, m,  $\text{OH}$ ), 2.44 (1H, dd, J = 2.5 and 17.9,  $\text{H}_a$  of  $\text{CH}_2-\text{CO}$ ), 2.75 (1H, dd, J = 6.6 and 17.4,  $\text{H}_b$  of  $\text{CH}_2-\text{CO}$ ), 3.20 (1H, dd, J = 2.1 and 10.9,  $\text{H}_a$  of  $\text{HOCH}-\text{CH}_2-\text{N}$ ), 3.51 (1H, dd, J = 5.6 and 10.9,  $\text{H}_b$  of  $\text{HOCH}-\text{CH}_2-\text{N}$ ), 4.48 (3H, m,  $\text{N}-\text{CH}_2-\text{Ph}$  and  $\text{HO}-\text{CH}$ ), 7.23–7.37 (5H, m, aromatic H);  $^{13}\text{C}$  NMR,  $\delta$  (ppm,  $\text{CDCl}_3$ ): 41.0 ( $\text{CH}_2-\text{CO}$ ), 46.3 ( $\text{CH}-\text{CH}_2-\text{N}$ ), 55.7 ( $\text{N}-\text{CH}_2-\text{Ph}$ ), 63.9 ( $\text{HO}-\text{CH}$ ), 127.5, 127.9, 128.6 (tertiary aromatic C), 135.9 (quaternary aromatic C), 173.3 ( $\text{C}=\text{O}$ ); MS (m/e): 191 ( $\text{M}^+$ ); HRMS: calc. for  $\text{C}_{11}\text{H}_{13}\text{NO}_2$ : 191.2292; found: 191.2300.

### 4-Allylpyrrolidin-2-one (27a)

In a 50 mL round-bottomed flask, 0.85 g (4.4 mmol) of hydroxylactam **26** was dissolved in 20 mL of pyridine. The solution was cooled to 0°C and 1.8 g (9.4 mmol) of tosyl chloride were added. The solution was stirred for 2 h and kept overnight in the refrigerator. The mixture was extracted with methylene chloride. The organic layer was washed 10 times with water then twice with HCl 3 %. The solution was dried over Na<sub>2</sub>SO<sub>4</sub>. Removal of the solvent in vacuo gave 0.86 g (2.5 mmol, 57 %) of 4-tosyl-N-benzylpyrrolidin-2-one as a brownish oil. In a 25 mL round-bottomed flask, 205 mg (0.6 mmol) of this tosylate and 1.2 g (3.7 mmol) of tetrabutylammonium bromide were dissolved in 10 mL of acetone. After stirring for 4 days at room temperature, water was added and the solution concentrated under vacuum. The usual work up gave 120 mg (0.47 mmol, 79 %) of 4-bromo-N-benzylpyrrolidin-2-one. In a 10 mL round-bottomed flask, 175 mg (0.69 mmol) of 4-bromo-N-benzylpyrrolidin-2-one, 25 mg (0.15 mmol) of AIBN and 525 mg (1.6 mmol) of allyltributyltin were dissolved in 4 mL of dry benzene. After refluxing for 5.5 h (in the dark), the solution was kept in the refrigerator overnight. Benzene was evaporated and the residue was purified by flash chromatography (Et<sub>2</sub>O) to afford 4-allyl-N-benzylpyrrolidin-2-one (114 mg, 0.53 mmol, 77 %). Debenzylation was carried out with Li/NH<sub>3</sub> as described above for the debenzilation of **15** to give lactam **27a** as an oil (226 mg, 1.8 mmol, 100 %); IR (cm<sup>-1</sup>, CHCl<sub>3</sub>): 3220 (N-H), 3005 (=C-H), 2950 (aliphatic C-H), 1691 (C=O); <sup>1</sup>H NMR, δ (ppm, CDCl<sub>3</sub>), J (Hz): 2.02 (1H, dd, J = 6.7 and 16.4, H<sub>a</sub> of CH<sub>2</sub>-CO), 2.20 (2H, t, J = 6.9, CH<sub>2</sub>-CH=CH<sub>2</sub>), 2.38-2.57 (2H, m, H<sub>b</sub> of CH<sub>2</sub>-CO and CH-CH<sub>2</sub>-CO), 3.04 (1H, dd, J = 5.8 and 9.7, H<sub>c</sub> of CH<sub>2</sub>-NH), 3.46 (1H, dd, J = 7.6 and 9.7, H<sub>d</sub> of CH<sub>2</sub>-NH), 5.02-5.09 (2H, m, CH<sub>2</sub>=CH-), 5.65-5.79 (1H, m, CH<sub>2</sub>=CH-), 6.73 (1H, m, NH); <sup>13</sup>C NMR, δ (ppm, CDCl<sub>3</sub>): 30.6 (CH<sub>2</sub>-CH=CH<sub>2</sub>), 37.1 (N-CH<sub>2</sub>-CH), 38.6 (CH<sub>2</sub>-CO), 52.1 (N-CH<sub>2</sub>-CH), 118.0 (CH<sub>2</sub>=CH-), 136.1 (CH<sub>2</sub>=CH-), 183.4 (C=O); MS (m/e): 125 (M<sup>+</sup>); HRMS: calc. for C<sub>7</sub>H<sub>11</sub>NO: 125.1700; found: 125.1702.

#### 5-Allylpyrrolidin-2-one (**30a**)

In a 250 mL round-bottomed flask, 5 g (26 mmol) of N-benzylsuccinimide (**28**) was dissolved in 150 mL of methanol. The solution was cooled to 0°C and 5.2 g (137 mmol) of NaBH<sub>4</sub> were added in small portions. After stirring for 30 min, CH<sub>2</sub>Cl<sub>2</sub> and a saturated solution of NaHCO<sub>3</sub> were added. The pH was brought to 7 with a 2 M HCl solution. The residue obtained after extraction with CH<sub>2</sub>Cl<sub>2</sub> (5x) and the usual work up was dissolved in 200 mL of CHCl<sub>3</sub> and 5.2 mL (7.7 g, 37 mmol) of trifluoroacetic anhydride were added. After stirring at room temperature for 75 min, the solution was cooled to 0°C. A solution of 11 mL (8.0 g, 79 mmol) of triethylamine in 100 mL of CH<sub>2</sub>Cl<sub>2</sub> was then added dropwise. The organic layer was washed with a NH<sub>4</sub>Cl solution. After evaporation of the solvent, 3.37 g (12 mmol, 46 %) of crude ester **29** was obtained and was immediately used for the next step. In a 250 mL round-bottomed flask, 2.2 g (7.7 mmol) of crude ester **29** was dissolved in 150 mL of CH<sub>2</sub>Cl<sub>2</sub>. After cooling to -78°C, 2.5 mL (2.8 g, 20 mmol) of BF<sub>3</sub>·Et<sub>2</sub>O dissolved in 25 mL of anhydrous THF were added. After stirring for 1 h at -78°C, a solution of 3 mL (2.16 g, 19 mmol) of allyltrimethylsilane in 25 mL of anhydrous THF were added. The solution was allowed to warm up to room temperature and stirred overnight. After addition of a saturated NaHCO<sub>3</sub> solution, extraction with CH<sub>2</sub>Cl<sub>2</sub> (3x) and usual work up, the crude product, an orange oil, was separated by flash chromatography (Et<sub>2</sub>O) to give 5-allyl-N-benzylpyrrolidin-2-one as an oil. Debenzylation was carried out with Li/NH<sub>3</sub> as described for the debenzilation of **15** to afford lactam **30a** as an oil (413 mg, 3.3 mmol, 87 %); IR (cm<sup>-1</sup>, CHCl<sub>3</sub>): 3432 (N-H free), 3221 (N-H bonded), 3018 (=C-H), 2992 (aliphatic C-H), 1676 (C=O), 1423 (C=C), 1264 (C-N); <sup>1</sup>H NMR, δ (ppm, CDCl<sub>3</sub>), J (Hz): 1.72-1.83 (1H, m, H<sub>a</sub> of CH<sub>2</sub>-CH<sub>2</sub>-CO), 2.14-2.37 (5H, m, H<sub>b</sub> of CH<sub>2</sub>-CH<sub>2</sub>-CO, CH<sub>2</sub>-CO, CH<sub>2</sub>-CH=CH<sub>2</sub>), 3.71 (1H, qt, J = 6.5, CH-NH), 5.11-5.17 (2H, m, CH<sub>2</sub>=CH-), 5.68-5.80 (2H, m, CH<sub>2</sub>=CH- et NH); <sup>13</sup>C NMR, δ (ppm, CDCl<sub>3</sub>): 29.0 (CH<sub>2</sub>-CO), 31.1 (NH-CH-CH<sub>2</sub>), 37.0 (CH<sub>2</sub>-CH=CH<sub>2</sub>), 52.3 (NH-CH), 118.1 (CH<sub>2</sub>=CH-), 128.5 (CH<sub>2</sub>=CH-), 184.2 (C=O); MS (m/e): 125 (M<sup>+</sup>), 84 (M<sup>+</sup> - allyl); HRMS: calc. for C<sub>7</sub>H<sub>11</sub>NO: 125.1700; found: 125.1692.

#### 5-(But-3-enyl)pyrrolidin-2-one (**32a**)

In a 100 mL round-bottomed flask, 0.7 g (7.1 mmol) of succinimide (**31**) was dissolved in 50 mL of EtOH. After cooling the solution to 0°C, 0.4 g (10.6 mmol) of NaBH<sub>4</sub> was added. Every 15 min, 1 to 2 drops of HCl 2 M were added until the pH reached 3.5 (5 h). The mixture was stirred at 0°C for 1 h then the pH was brought to 7 with an ethanolic solution of KOH. The solvent was removed in vacuo. Chloroform was added to the residue and the solids removed by filtration. Evaporation of the filtrate under vacuum gave 5-ethoxypyrrrolidin-2-one (911 mg, 7.1 mmol, 100 %) as an oil. A solution of butenylmagnesium bromide prepared from 4-bromo-1-butene (2.0 g, 14.7 mmol) and magnesium (400 mg, 16.5 mmol) in anhydrous THF (20 mL) was added along with 1.3 mL (10.6 mmol) of BF<sub>3</sub>·Et<sub>2</sub>O to a solution of 0.47 g (3.6 mmol) of 5-ethoxypyrrrolidin-2-one in 50 mL of anhydrous THF pre-cooled to -30°C. The reaction mixture was allowed to warm up to room temperature and stirred overnight. Addition of aqueous NH<sub>4</sub>Cl, extraction with ethyl acetate followed by the usual work up and separation of the crude oil (582 mg) by flash chromatography (Et<sub>2</sub>O-AcOEt 1:1) afforded 188 mg (1.35 mmol, 37%) of the desired lactam **32a**; IR (cm<sup>-1</sup>, CHCl<sub>3</sub>): 3433 (N-H free), 3226 (N-H bonded),

3016 (=C-H), 2935 (aliphatic C-H), 1692 (C=O);  $^1\text{H NMR}$ ,  $\delta$  (ppm,  $\text{CDCl}_3$ ), J (Hz): 1.52-1.75 (3H, m), 2.10 (2H, qt, J = 1.2 and 7.3,  $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2$ ), 2.18-2.35 (3H, m), 3.64 (1H, qt, J = 6.7,  $\text{CH}-\text{NH}$ ), 4.95-5.08 (2H, m,  $\text{CH}_2=\text{CH}-$ ), 5.72-5.85 (1H, m,  $\text{CH}_2=\text{CH}-$ ), 6.82 (1H, m,  $\text{NH}$ );  $^{13}\text{C NMR}$ ,  $\delta$  (ppm,  $\text{CDCl}_3$ ): 27.8, 28.5, 29.6, 30.1 ( $\text{CH}_2-\text{CH}_2-\text{CO}$ ,  $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2$ ), 50.4 ( $\text{CH}-\text{NH}$ ), 114.3 ( $\text{CH}_2=\text{CH}-$ ), 137.8 ( $\text{CH}_2=\text{CH}-$ ), 178.8 (C=O); MS (m/e): 139 ( $\text{M}^+$ ), 84 ( $\text{M}^+ - \text{CH}_2=\text{CHCH}_2\text{CH}_2$ ); HRMS: calc. for  $\text{C}_8\text{H}_{13}\text{NO}$ : 139.1968; found: 139.1975.

#### General procedure for the N-chlorination of lactams **17a**, **18a**, **21a**, **22a**, **30a** and **32a**

The method of N-chlorination is based on a previously described procedure.<sup>27</sup> The lactam (0.50 to 0.70 mmol) was dissolved in chloroform (3-4 mL). The solution was cooled to 0°C, protected from light and a commercial solution of NaOCl (5-6 %) was added. The resulting mixture was allowed to warm up to room temperature. The reaction was followed by TLC. After completion of the reaction (4 to 168 h depending on the lactam), the organic phase was separated and extracted with  $\text{CH}_2\text{Cl}_2$  (5x). The amount of active chlorine of the N-chlorolactam isolated after the usual work up was 95-100 % as determined by iodometry. The yields of N-chlorination varied between 53 and 100 %. The N-chlorolactam was used immediately.

#### Typical procedure for the photolysis of N-chlorolactams

In a 25 mL quartz photolytic cell, 0.2 mmol to 1.25 mmol of N-chlorolactam was dissolved in 25 mL of dry  $\text{CH}_2\text{Cl}_2$  or dry cyclohexane (freshly distilled over CaH<sub>2</sub>). Oxygen-free nitrogen was bubbled through the solution for 5 minutes and the solution was irradiated in a Rayonet RPR 100 reactor equipped with 16 external irradiation lamps (253.7 or 300.0 nm lamps). Irradiation was carried out at 10°C in cyclohexane and at -78°C in  $\text{CH}_2\text{Cl}_2$ . After complete disappearance of the N-chlorolactam (by TLC or starch-iodide paper test), the reaction mixture was allowed to warm up to room temperature and the solvent removed under vacuum. The products were isolated by flash chromatography. In footnote a of Table 1, the photolysis conditions have been identified as conditions A (254 nm,  $\text{CH}_2\text{Cl}_2$ , -78°C), conditions B (254 nm, cyclohexane, 10°C) and conditions C (300 nm,  $\text{CH}_2\text{Cl}_2$ , -78°C). Some typical procedures are described below.

#### Photolysis of N-chloro-3,3-diallylpyrrolidin-2-one (**21b**, R = Cl) in the presence of cyclohexene : obtention of N-(2-chlorocyclohexyl)-3,3-diallylpyrrolidin-2-one (**35**)

Conditions B were used. Flash chromatographic separation (hexanes-Et<sub>2</sub>O 1 : 1) gave the parent lactam **21a** (R = H) (39 mg, 0.24 mmol, 60 %) and the adduct **35** (7mg, 0.025 mmol, 6 %) as an oil consisting of a 3 : 2 mixture of *trans* and *cis* isomers according to the  $^1\text{H NMR}$  spectrum (see below); IR ( $\text{cm}^{-1}$ ,  $\text{CHCl}_3$ ): 3007 (=C-H), 2915 (aliphatic C-H), 1678 (C=O);  $^1\text{H NMR}$ ,  $\delta$  (ppm,  $\text{CDCl}_3$ ), J (Hz): 1.25-2.54 (13H, m), 3.16-3.28 (1H, m), 3.35-3.56 (1H, m), 3.61-3.78 (1H, m), 3.83-4.00 (2H of the *trans* isomer, m,  $\text{CHCl}-\text{CH}$ ), 4.11 (1H of the *cis* isomer, dt, J = 4.0 and 12.5,  $\text{CHCl}-\text{CH}$ ), 4.65 (1H of the *cis* isomer, m,  $\text{CHCl}-\text{CH}$ ), 5.05-5.20 (4H, m,  $\text{CH}_2=\text{CH}-$  of both isomers), 5.64-5.95 (2H, m,  $\text{CH}_2=\text{CH}-$  of both isomers);  $^{13}\text{C NMR}$ ,  $\delta$  (ppm,  $\text{CDCl}_3$ ): 22.7, 23.9, 24.6, 25.0, 25.4, 25.6, 26.8, 27.4, 30.0, 31.6, 33.3, 36.6, 40.7, 41.4, 41.5, 41.7, 42.4, 45.7, 54.0, 59.4, 63.5, 118.2, 118.3, 119.4, 132.7, 134.0, 134.3, 173.9; MS (m/e): 283 ( $\text{M}^+ + 2$ ), 281 ( $\text{M}^+$ ), 239 ( $\text{M}^+ - \text{allyl}$ ); HRMS: calc. for  $\text{C}_{16}\text{H}_{24}\text{NOCl}$ : 281.0717; found: 281.0710.

#### Photolysis of N-chloro-3,3-diallylpyrrolidin-2-one (**21b**, R = Cl) in the presence of tertibutoxyethylene : obtention of N-(2,2-dimethoxyethyl)-3,3-diallylpyrrolidin-2-one (**36**)

Conditions C were used. Excess methanol was added at -78°C at the end of the photolysis. Flash chromatographic separation (hexanes-Et<sub>2</sub>O 1 : 1 → Et<sub>2</sub>O → AcOEt) gave the parent lactam **21a** (R = H) (53 mg, 0.32 mmol, 65 %) and the adduct **36** as an oil (35 mg, 0.14 mmol, 33 %); IR ( $\text{cm}^{-1}$ ,  $\text{CHCl}_3$ ): 3007 (=C-H), 2934 (aliphatic C-H), 1680 (C=O);  $^1\text{H NMR}$ ,  $\delta$  (ppm,  $\text{CDCl}_3$ ), J (Hz): 1.91 (2H, t,  $\text{CH}_2-\text{CH}_2-\text{N}$ ), 2.17 (2H, dd, J = 8.4 and 13.7,  $\text{CH}_2=\text{CH}-\text{CH}_2$ ), 2.34 (2H, dd, J = 6.4 and 13.5,  $\text{CH}_2=\text{CH}-\text{CH}_2$ ), 3.30 (2H, t, J = 7.2,  $\text{CH}_2-\text{CH}_2-\text{N}$ ), 3.37-3.39 (8H, m,  $2\text{CH}_3\text{O}$  and  $\text{N}-\text{CH}_2-\text{CH}$ ), 4.47 (1H, t, J = 5.5,  $\text{N}-\text{CH}_2-\text{CH}$ ), 5.06-5.11 (4H, m,  $\text{CH}_2=\text{CH}-$ ), 5.66-5.80 (2H, m,  $\text{CH}_2=\text{CH}-$ );  $^{13}\text{C NMR}$ ,  $\delta$  (ppm,  $\text{CDCl}_3$ ): 27.1 ( $\text{CH}_2=\text{CH}-\text{CH}_2$ ), 41.5 ( $\text{N}-\text{CH}_2-\text{CH}$ ), 44.4 ( $\text{CH}_2-\text{CH}_2-\text{N}$ ), 45.7 ( $\text{CH}_2-\text{CH}_2-\text{N}$ ), 47.4 (C-CO), 53.9 ( $2\text{CH}_3\text{O}$ ), 102.0 ( $\text{N}-\text{CH}_2-\text{CH}$ ), 118.3 ( $\text{CH}_2=\text{CH}-$ ), 133.9 ( $\text{CH}_2=\text{CH}-$ ), 177.4 (C=O); MS (m/e): 253 ( $\text{M}^+$ ), 238 ( $\text{M}^+ - \text{CH}_3$ ), 222 ( $\text{M}^+ - \text{OCH}_3$ ); HRMS: calc. for  $\text{C}_{14}\text{H}_{23}\text{NO}_3$ : 253.1678; found: 253.1667.

#### Photolysis of N-chloro-3,3-di(but-3-enyl)-pyrrolidin-2-one (**22b**, R = Cl) : obtention of 3-(2-chlorobut-3-enyl)-3-(but-3-enyl)-pyrrolidin-2-one (**38**)

Conditions C were used. Flash chromatographic separation (hexanes-Et<sub>2</sub>O 1 : 1 → Et<sub>2</sub>O) allowed the recovery of unreacted N-chlorolactam **22b** (3 mg, 0.013 mmol, 4 %), the isolation of parent lactam **22a** (31 mg, 0.16 mmol, 46 %) and the isolation of allylic chloride **38** (29 mg, 0.13 mmol, 37 %) as an oil; IR ( $\text{cm}^{-1}$ ,  $\text{CHCl}_3$ ): 3067 (=C-H), 2930 (aliphatic C-H), 1681 (C=O);  $^1\text{H NMR}$ ,  $\delta$  (ppm,  $\text{CDCl}_3$ ), J (Hz) : 1.78-1.89 (2H, m), 1.95-

2.24 (7H, m), 3.85-3.98 (3H, m, CH<sub>2</sub>-CH<sub>2</sub>-N and ClCH-CH=CH<sub>2</sub>), 4.97-5.12 (4H, m, CH<sub>2</sub>=CH-), 5.76-5.90 (2H, m, CH<sub>2</sub>=CH-); <sup>13</sup>C NMR, δ (ppm, CDCl<sub>3</sub>): 27.8, 28.1, 36.1, 37.1, 46.8, 48.1, 53.4, 115.1, 115.2, 137.4, 180.6; MS (chemical ionisation with NH<sub>3</sub>): 247 (MNH<sub>4</sub><sup>+</sup> + 2), 245 (MNH<sub>4</sub><sup>+</sup>), 230 (MH<sup>+</sup> + 2), 228 (MH<sup>+</sup>).

**Photolysis of N-chloro-3,3-di(but-3-enyl)-pyrrolidin-2-one (22b, R = Cl) in the presence of tert-butoxyethylene : obtention of N-(2,2-dimethoxyethyl)-3,3-di(but-3-enyl)-pyrrolidin-2-one (37)**

Conditions C were used. Flash chromatographic separation (hexanes-Et<sub>2</sub>O 1 : 1 → Et<sub>2</sub>O) gave the parent lactam **22a** (R = H) (22 mg, 0.11 mmol, 27 %) and the adduct **37** (60 mg, 0.21 mmol, 50 %) as an oil; IR (cm<sup>-1</sup>, CHCl<sub>3</sub>): 2980 (aliphatic C-H), 1680 (C=O); <sup>1</sup>H NMR, δ (ppm, CDCl<sub>3</sub>), J (Hz): 1.61 (4H, m, CH<sub>2</sub>-CH<sub>2</sub>-CH=CH<sub>2</sub>), 1.99-2.16 (6H, m), 3.30 (2H, t, J = 7.1, CH<sub>2</sub>-CH<sub>2</sub>-N), 3.37-3.40 (8H, m, 2CH<sub>2</sub>O and N-CH<sub>2</sub>-CH), 4.50 (1H, t, J = 5.7, N-CH<sub>2</sub>-CH), 4.93-5.06 (4H, m, CH<sub>2</sub>=CH-), 5.76-5.85 (2H, m, CH<sub>2</sub>=CH-); <sup>13</sup>C NMR, δ (ppm, CDCl<sub>3</sub>): 28.6 (CH<sub>2</sub>-CH<sub>2</sub>-CH=CH<sub>2</sub>), 33.3 (CH<sub>2</sub>-CH<sub>2</sub>-CH=CH<sub>2</sub>), 35.4 (NH-CH<sub>2</sub>), 40.9 (N-CH<sub>2</sub>-CH), 45.7 (NH-CH<sub>2</sub>-CH<sub>2</sub>), 50.4 (C-CO), 53.5 (2CH<sub>2</sub>O), 103.1 (N-CH<sub>2</sub>-CH), 114.6 (CH<sub>2</sub>=CH-), 135.8 (CH<sub>2</sub>=CH-), 182.7 (C=O); MS (m/e): 281 (M<sup>+</sup>); HRMS: calc. for C<sub>16</sub>H<sub>27</sub>NO<sub>3</sub>: 281.3942; found: 281.3940.

**Photolysis of N-chloro-5-(but-3-enyl)-pyrrolidin-2-one (32b) : obtention of 8-(chloromethyl)-pyrrolizidin-2-ones (40) and 8-(2,2-dichloroethyl)-pyrrolizidin-2-ones (41)**

Conditions C were used. The crude product was separated by HPLC to give the parent lactam **32a** (R = H) (27 mg, 0.20 mmol, 43 %), a dichlorinated product (10 mg, 0.047 mmol, 11 %) according to GC-MS, a mixture (2 : 1 by HPLC) of diastereoisomeric bicyclic lactams **40** as an oil (4 mg, 0.023 mmol, 5 %), and a mixture (2.5 : 1 by integration of the CHCl<sub>2</sub> <sup>1</sup>H NMR signal) of diastereoisomeric bicyclic lactams **41** as an oil (4 mg, 0.018 mmol, 4 %).

**Bicyclic lactams 40** : IR (cm<sup>-1</sup>, CHCl<sub>3</sub>): 2980 (aliphatic C-H), 1676 (C=O); <sup>1</sup>H NMR, δ (ppm, CDCl<sub>3</sub>): 1.58-1.73 (1H, m, H<sub>a</sub> of C<sub>6</sub> of both isomers), 1.76-1.84 (1H, m, H<sub>a</sub> of C<sub>4</sub> of both isomers), 1.87-1.96 (1H, m, H<sub>b</sub> of C<sub>6</sub> of both isomers), 2.18-2.28 (2H, m, H<sub>b</sub> of C<sub>4</sub> and H<sub>a</sub> of C<sub>7</sub> of both isomers), 2.31-2.37 (1H, m, H<sub>b</sub> of C<sub>7</sub> of both isomers), 2.54-2.62 (1H, m, H<sub>a</sub> of C<sub>3</sub> of both isomers), 2.70-2.82 (1H, m, H<sub>b</sub> of C<sub>3</sub> of both isomers), 3.68-3.85 (2H, m, H of C<sub>8</sub> and H<sub>a</sub> of CH<sub>2</sub>Cl of both isomers), 3.97-4.06 (1H, m, H of C<sub>5</sub> of both isomers), 4.10-4.15 (1H, m, H<sub>b</sub> of CH<sub>2</sub>Cl of both isomers); <sup>13</sup>C NMR, δ (ppm, CDCl<sub>3</sub>): 27.9, 29.8, 33.3, 37.3 (C<sub>3</sub>, C<sub>4</sub>, C<sub>6</sub>, C<sub>7</sub> of both isomers), 43.6 (CH-CH<sub>2</sub>Cl of both isomers), 53.6 (CH-CH<sub>2</sub>Cl of both isomers), 64.6 (C<sub>4</sub> of both isomers), 172.0 (C=O of both isomers); MS (m/e): 175 (M<sup>+</sup> + 2), 173 (M<sup>+</sup>), 138 (M<sup>+</sup> - Cl), 124 (M<sup>+</sup> - CH<sub>2</sub>Cl); HRMS: calc. for C<sub>8</sub>H<sub>12</sub>NOCl: 173.0607; found: 173.0604.

**Bicyclic lactams 41** : IR (cm<sup>-1</sup>, CHCl<sub>3</sub>): 2978 (aliphatic C-H), 1680 (C=O); <sup>1</sup>H NMR, δ (ppm, CDCl<sub>3</sub>), J (Hz): 1.21-2.78 (8H, m), 3.16 (1H, dt, J = 5.6 and 14.5), 3.54-3.68 (1H, m), 3.78-3.83 (1H, m), 3.90-4.04 (1H, m), 6.03 (1H, dd, J = 4.9 and 8.1, CHCl<sub>2</sub> of isomer B (major isomer)), 6.21 (1H, dd, J = 4.9 and 8.1, CHCl<sub>2</sub> of isomer A (minor isomer)); <sup>13</sup>C NMR, δ (ppm, CDCl<sub>3</sub>): 28.5, 28.7, 29.0, 29.4, 29.6, 30.0, 32.3, 32.5 (C<sub>3</sub>, C<sub>4</sub>, C<sub>6</sub>, C<sub>7</sub> of both isomers), 46.4, 46.8 (CH<sub>2</sub>-CHCl<sub>2</sub> of both isomers), 54.2 (C<sub>8</sub> of both isomers), 63.9, 64.3 (C<sub>5</sub> of both isomers), 68.1, 68.5 (CH<sub>2</sub>-CHCl<sub>2</sub> of both isomers), 170.6 (C=O of both isomers); MS (m/e): 225 (M<sup>+</sup> + 4), 223 (M<sup>+</sup> + 2), 221 (M<sup>+</sup>), 188 (M<sup>+</sup> + 2 - Cl), 186 (M<sup>+</sup> - Cl), 124 (M<sup>+</sup> - CH<sub>2</sub>-CHCl<sub>2</sub>); HRMS: calc. for C<sub>9</sub>H<sub>13</sub>NOCl<sub>2</sub>: 221.0374; found: 221.0384.

**3-Allylsuccinimide (43a)**

N-(*p*-Methoxybenzyl)-3-allylsuccinimide **42** was prepared from succinimide (**31**) by the same procedure as that used to transform **14** into **15**. In a 100 mL round-bottomed flask, 865 mg (3.3 mmol) of freshly prepared N-(*p*-methoxybenzyl)-3-allylsuccinimide was dissolved in 50 mL of CH<sub>3</sub>CN-H<sub>2</sub>O 9 : 1. After the addition of 4.5 g of ceric ammonium nitrate, the solution was refluxed for 36 h. The solution was cooled to room temperature and CH<sub>2</sub>Cl<sub>2</sub> was added. The organic layer was successively washed with water, 20% aqueous NaHSO<sub>3</sub>, aqueous saturated NaHCO<sub>3</sub> and water again. Flash chromatography (hexanes-Et<sub>2</sub>O 1 : 2) of the crude product after the usual work up gave the allyl imide **43a** as an oil (172 mg, 1.24 mmol, 37 %); IR (cm<sup>-1</sup>, CHCl<sub>3</sub>): 3405 (N-H free), 3214 (N-H bonded), 3018 (=C-H), 2934 (aliphatic C-H), 1785, 1723 (C=O); <sup>1</sup>H NMR, δ (ppm, CDCl<sub>3</sub>), J (Hz): 2.30-2.47 (1H, m), 2.51 (1H, dd, J = 4.7 and 18.0), 2.64-2.68 (1H, m), 2.82 (1H, dd, J = 9.5 and 18.0), 2.88-2.95 (1H, m), 5.08-5.13 (2H, m, CH<sub>2</sub>=CH-), 5.58-5.71 (1H, m, CH<sub>2</sub>=CH-), 7.81 (1H, m, NH); <sup>13</sup>C NMR, δ (ppm, CDCl<sub>3</sub>): 35.0, 35.9 (CH<sub>2</sub>=CH-CH<sub>2</sub> and CH<sub>2</sub>-CO), 41.3 (CH-CO), 117.7 (CH<sub>2</sub>=CH-), 134.8 (CH<sub>2</sub>=CH-), 174.9, 176.1 (2C=O); MS (m/e): 139 (M<sup>+</sup>); HRMS: calc. for C<sub>7</sub>H<sub>9</sub>NO<sub>2</sub>: 139.0633; found: 139.0630.

**N-Chloro-3-allylsuccinimide (43b)**

N-Chlorination of imide **43a** was carried out by the same method used above to prepare the N-chlorolactams to give N-chloroimide **43b** as an oil (32 mg, 0.18 mmol, 26 %, 100% active chlorine).

**4-Methoxyoxazolidin-2-one (45)**

Anodic oxidation of oxazolidin-2-one (**44**) was carried out in a two-compartment glass H-cell with a Nafion-324 (E. I. du Pont de Nemours & Co) membrane as separator at a constant current of 55 mA using a ESC 640 potentiostat and an 2830 BK Precision ammeter. The electrodes were made of reticulated graphite (ESC SG-132). Each compartment was filled with 100 mL of MeOH containing Et<sub>4</sub>NOTs 0.17 M as supporting electrolyte. Oxazolidinone **44** (5 g, 57 mmol) was dissolved in the anodic compartment and the current applied. The electrolysis was stopped after the consumption of 2 F / mol (theoretical amount). The anodic compartment was recovered and aqueous saturated NaHCO<sub>3</sub> was added to the reaction mixture. Extraction with ethyl acetate followed by the usual work up and flash chromatography (Et<sub>2</sub>O-AcOEt 3 : 7) of the crude yellow oil (3.18 g) afforded the methoxyoxazolidinone **45** as an oil (2.15 g, 18 mmol, 32 %); IR (cm<sup>-1</sup>, CHCl<sub>3</sub>): 3464 (N-H free), 3282 (N-H bonded), 2919 (aliphatic C-H), 1762 (C=O), 1091 (C-O); <sup>1</sup>H NMR, δ (ppm, CDCl<sub>3</sub>), J (Hz): 3.34 (3H, s, OCH<sub>3</sub>), 4.28 (1H, dd, J = 1.7 and 10.0, H<sub>a</sub> of CH<sub>2</sub>), 4.45 (1H, dd, J = 6.0 and 10.0, H<sub>b</sub> of CH<sub>2</sub>), 5.06 (1H, dt, J = 1.4 and 6.0, CH), 7.59 (1H, m, NH); <sup>13</sup>C NMR, δ (ppm, CDCl<sub>3</sub>): 54.0 (OCH<sub>3</sub>), 71.0 (N-CH-CH<sub>2</sub>), 83.8 (N-CH-CH<sub>2</sub>), 159.8 (C=O); MS (m/e): 117 (M<sup>+</sup>); HRMS: calc. for C<sub>4</sub>H<sub>7</sub>NO<sub>3</sub>: 117.0426; found: 117.0421.

**4-Allyloxazolidin-2-one (46a, R = H)**

In a dry 100 mL round-bottomed flask, 250 mg (2.1 mmol) of 4-methoxy-oxazolidin-2-one (**45**) were dissolved in 50 mL of anhydrous THF under argon. After cooling to -30°C, 10 mL of 1 M allylmagnesium bromide in Et<sub>2</sub>O was added (10 mmol, 5 eq.) along with 1 mL (1.15 g, 8.1 mmol) of BF<sub>3</sub>·Et<sub>2</sub>O. The reaction solution was allowed to warm up to room temperature and stirred overnight. A saturated solution of NH<sub>4</sub>Cl was added and the mixture was extracted with Et<sub>2</sub>O. Usual work up followed by flash chromatography (Et<sub>2</sub>O-AcOEt 3 : 2) of the residue afforded 134 mg (1.05 mmol, 50 %) of oily allyloxazolidinone **46a** (R = H); IR (cm<sup>-1</sup>, CHCl<sub>3</sub>): 3460 (N-H free), 3280 (N-H bonded), 2980 (aliphatic C-H), 1760 (C=O), 1080 (C-O); <sup>1</sup>H NMR, δ (ppm, CDCl<sub>3</sub>), J (Hz): 2.34 (2H, t, J = 6.9, CH<sub>2</sub>-CH=CH<sub>2</sub>), 3.89-3.98 (1H, m, H<sub>a</sub> of COOCH<sub>2</sub>), 4.08 (1H, dd, J = 5.6 and 8.6, H<sub>b</sub> of COOCH<sub>2</sub>), 4.48 (1H, t, J = 8.4, NH-CH), 5.14-5.21 (2H, m, CH<sub>2</sub>=CH-), 5.66-5.79 (1H, m, CH<sub>2</sub>=CH-), 7.65 (1H, m, NH); <sup>13</sup>C NMR, δ (ppm, CDCl<sub>3</sub>): 35.3 (CH<sub>2</sub>-CH=CH<sub>2</sub>), 56.7 (N-CH), 73.7 (COOCH<sub>2</sub>), 119.2 (CH<sub>2</sub>=CH-), 128.4 (CH<sub>2</sub>=CH-), 160.0 (C=O); MS (m/e): 127 (M<sup>+</sup>), 86 (M<sup>+</sup> - allyl); HRMS: calc. for C<sub>6</sub>H<sub>9</sub>NO<sub>2</sub>: 127.0633; found: 127.0628.

**4-(But-3-enyl)-oxazolidin-2-one (47a, R = H)**

The same procedure as above was used with but-3-enylmagnesium bromide. The preparation of the latter has already been described (see preparation of **16**). Flash chromatography (Et<sub>2</sub>O-AcOEt 3 : 2) of the crude product afforded 307 mg (2.2 mmol, 61 %) of oily butenylloxazolidinone **47a** (R = H); IR (cm<sup>-1</sup>, CHCl<sub>3</sub>): 3465 (N-H free), 3283 (N-H bonded), 2990 (aliphatic C-H), 1765 (C=O), 1095 (C-O); <sup>1</sup>H NMR, δ (ppm, CDCl<sub>3</sub>), J (Hz): 1.63-1.79 (2H, m, CH<sub>2</sub>-CH<sub>2</sub>-CH=CH<sub>2</sub>), 2.13 (2H, q, J = 7.4, CH<sub>2</sub>-CH<sub>2</sub>-CH=CH<sub>2</sub>), 3.89 (1H, qt, J = 6.9, NH-CH), 4.03 (1H, dd, J = 6.5 and 8.8, H<sub>a</sub> of COOCH<sub>2</sub>), 4.49 (1H, t, J = 8.2, H<sub>b</sub> of COOCH<sub>2</sub>), 4.98-5.11 (2H, m, CH<sub>2</sub>=CH-), 5.71-5.83 (1H, m, CH<sub>2</sub>=CH-), 5.83-5.97 (1H, m, NH); <sup>13</sup>C NMR, δ (ppm, CDCl<sub>3</sub>): 28.6, 33.7 (CH<sub>2</sub>-CH<sub>2</sub>-CH=CH<sub>2</sub>), 51.6 (NH-CH), 69.7 (COOCH<sub>2</sub>), 114.8 (CH<sub>2</sub>=CH-), 136.4 (CH<sub>2</sub>=CH-), 160.1 (C=O); MS (m/e): 141 (M<sup>+</sup>), 86 (M<sup>+</sup> - CH<sub>2</sub>CH<sub>2</sub>CH=CH<sub>2</sub>); HRMS: calc. for C<sub>7</sub>H<sub>11</sub>NO<sub>2</sub>: 141.0790; found: 141.0792.

**N-Chloro-7-allyloxazolidin-2-one (46b, R = Cl)** and **N-chloro-4-(but-3-enyl)oxazolidin-2-one (47b, R = Cl)** They were prepared from the corresponding carbamates **46a** (R = H) and **47a** (R = H) using the same method as that described above for the chlorination of the lactams.

**46b**: colorless oil, 30 mg (0.19 mmol, 36 %, 92 % active chlorine)

**47b**: colorless oil, 73 mg (0.42 mmol, 68 %, 98 % active chlorine)

**Photolysis of N-chloro-4-(but-3-enyl)oxazolidin-2-one (47b, R = Cl): obtention of 8-(chloromethyl)-3-oxopyrrolizidin-2-one (48)**

Conditions C were used. Flash chromatography (CH<sub>2</sub>Cl<sub>2</sub>-AcOEt 4 : 1) of the crude product afforded only one fraction consisting of an oily 2 : 1 mixture (by GLC) of diastereoisomeric pyrrolizidinones **48** (31 mg, 0.18 mmol, 48 %); IR (cm<sup>-1</sup>, CHCl<sub>3</sub>): 2975, 2905 (aliphatic C-H), 1748 (C=O); <sup>1</sup>H NMR, δ (ppm, CDCl<sub>3</sub>), J (Hz): 1.76-1.90 (1H, m, H<sub>a</sub> of C<sub>7</sub> of both isomers), 1.93-2.02 (1H, m, H<sub>b</sub> of C<sub>7</sub> of both isomers), 2.23-2.44 (2H, m, 2H of C<sub>6</sub> of both isomers), 3.84 (1H, dd, J = 2.6 and 11.3, H<sub>a</sub> of C<sub>4</sub> of both isomers), 3.91-3.94 (1H, m, H of C<sub>5</sub> of both isomers), 4.08 (1H, t, J = 8.5, H<sub>a</sub> of CH<sub>2</sub>Cl of both isomers), 4.18-4.24 (2H, m, H<sub>b</sub> of C<sub>4</sub> and H of C<sub>8</sub> of both isomers), 4.49 (1H, t, J = 8.1, H<sub>b</sub> of CH<sub>2</sub>Cl of both isomers); <sup>13</sup>C NMR, δ (ppm, CDCl<sub>3</sub>): 29.3 (both isomers), 33.3 (both isomers), 43.5 (both isomers), 55.3 (both isomers), 60.8 (both isomers), 69.6 (both isomers), 158.3 (one isomer), 158.5 (one isomer); MS (m/e): 177 (M<sup>+</sup> + 2), 175 (M<sup>+</sup>), 140 (M<sup>+</sup> - Cl), 126 (M<sup>+</sup> - CH<sub>2</sub>Cl); HRMS: calc. for C<sub>7</sub>H<sub>10</sub>NO<sub>2</sub>Cl: 175.0400; found: 175.0406.

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