PHOTOCYCLISATION OF KETO-LACTAMS. A NEW SYNTHESIS OF FUNCTIONALIZED 1-AZA-BICYCLO(x.y.o)ALKANES

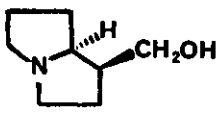
Assia Azzouzi, Monique Dufour, Jean-Claude Gramain*, and Roland Remuson

Laboratoire de Chimie et Biochimie des Substances Naturelles, U.A. C.N.R.S. 485, Université de Clermont II, B.P. 45, 63170 Aubière, France

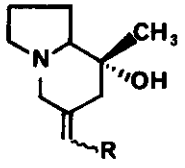
Abstract - A series of 1-azabicyclo(x.y.o)alkanes has been synthesized using an intramolecular photoreduction rea ction. The methodology consists of a regioselective abstraction of an hydrogen α to the nitrogen of an amide by the triplet $T_1(n, \pi^*)$ of a carbonyl derivative.

A lot of bicyclic alkaloids exhibit an important biological activity ; their common structure is characterized by 1-azabicyclo(x.y.o)alkane skeleton. Among these products the Senecio alkaloids (isoretronecanol 1) contain a pyrrolizidine system and possess antileukemic and antimitotic activities[1] ; there are also the indolizidine skeleton which is the common structural feature of the pumiliotoxin A and B[2], these alkaloids possess an influence on the sodium and potassium flows through the cellular membrane ; a third class of compounds are the lupin alkaloids (lupinine 2) which possess a quinolizidine motif (Scheme 1).

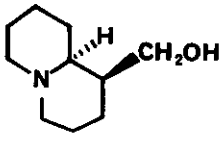
Scheme 1



Isoretronecanol(1)



Pumiliotoxins A,B



Lupinine(2)

Several methodologies were used to synthesize these alkaloids ; in our approach the second ring is created in a photochemical step based on the intramolecular photoreduction of a carbonyl group by an amide or a lactam. This reaction is equivalent to the regioselective formation of a C-C bond α to the nitrogen of an amide group (cf. Scheme 2).

Arylketones are easily photoreduced by various hydrogen donnors such as alcohols, ethers, amines...[3-9] This reaction, which possesses a very well known mechanism, has received a great attention in synthetic applications[8-10]. The most studied reaction in the intramolecular version is the NORRISH type II reaction : γ-hydrogen abstraction via a six membered transition state[11]. In the absence of hydrogen in the γ position, the hydrogens in the β[12], δ[13], even long distance position[14], are efficiently abstracted to lead to three, five or large membered rings.

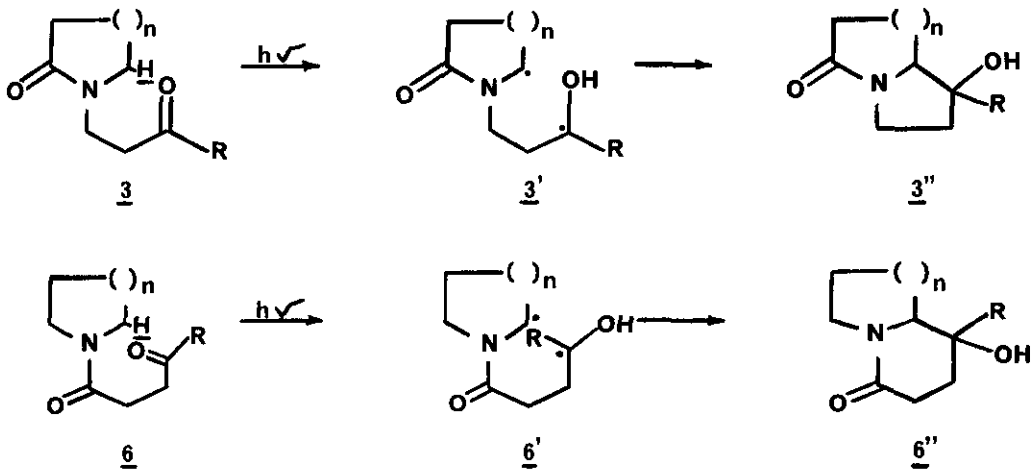
We already reported that the hydrogen α to the nitrogen of an amide group was easily abstracted by the n, π* excited triplet state of an aryl ketone in the γ position. Such a reaction was implicated in the synthesis of 1-azabicyclo(x.2.o)alkanes series [15].

In the same way, the abstraction of an hydrogen α to the nitrogen of an amide group by an α-ketoester chromophore was the key step in the total synthesis of isoretronecanol (Senecio alkaloid) [16].

We wish to report here a method to access to 1-azabicyclo(x.y.o)alkanes based on the intramolecular abstraction of the hydrogen α to the nitrogen of an amide function by a carbonyl derivative chromophore in a δ or ε position.

We studied this reaction by using models 3 (abstractable H in α position of a lactam group) and 6 (abstractable H in α position of an amide group).

Scheme 2



Irradiation of these molecules (3 and 6) would afford products 3" and 6" via a biradical intermediate (3' and 6'). This methodology allows the introduction on the created ring of a tertiary alcohol group in a β position to the nitrogen atom. This motif is present in various natural products (pumiliotoxins...) which possess important biological properties [17,18].

RESULTS AND DISCUSSION

The starting materials were easily obtained by using adapted literature procedures.

a) Formation of 5-membered rings

Irradiation (medium pressure mercury lamp, Pyrex glass vessel) of a deoxygenated solution of 1-(3-oxo-3-phenylpropyl)-2-pyrrolidone 3a in acetonitrile led to lactams 4a and 5a in 75 % yield (Table 1). Structures of 4a and 5a were elucidated by classic spectroscopic methods. Ir spectra showed absorption bands due to hydroxyl group at 3580 cm^{-1} (free OH) and to carbonyl group of five membered ring lactam at 1680 cm^{-1}. ^{1}H-Nmr spectrum of the mixture of diastereoisomers exhibited a multiplet at 3.8 ppm attributed to the three protons α to the nitrogen of the amide group.

In the same way, irradiation of the substrates 3b and 3c led to the bicyclic compounds 4b, 5b and 4c, 5c.

In each case, the photocyclisation afforded a mixture of two diastereoisomers which were separated by silica gel chromatography.

Their stereochemistry was determined in high field ^{1}H-nmr by the measurement of solvent effects on the hydrogen of the ring junction induced by the vicinal hydroxyl group of the tertiary alcohol. The most important effects are obtained for the couple of solvents chloroform - pyridine ; they are generally negative and their absolute values decrease rapidly with removing the hydroxyl group and the observed hydrogen[19].

The hydrogen of the ring junction was easily identified by ^{1}H-nmr (250 MHz) : it appeared as a quadruplet between 3.5 and 4.0 ppm. This method has already been used for the determination of structures of 1-aza bicyclo (x.2.o) alkanes[15]. The validity of the method has been confirmed in this case by RX molecular diffraction. Thus, the measured solvent effect $\Delta^{CDCl_3}_{C_5H_5N}$ is about -50 Hz for the "cis" isomer[a] and about zero for the "trans" isomer.

We observed that the isomers ratio depended on the size of the lactam ring. In the case of strained products (4a and 5a) the preponderant isomer was the most crowded compound ; a similar observation had already been done for analog molecules[15]. Most of the literature results which concern the photocyclisation of 1,4-diradicals (NORRISH type II reaction) also show that the preponderant isomer is the most crowded one[13a,20]. This observation is very difficult to rationalize, in particular, no explanation based on the stability of the formed products can be given.

The rate of the reaction depends on the size of the starting lactam ; it decreases when the size of the lactam increases (2-pyrrolidone, 2-piperidone, ε-caprolactam). A similar effect was already noted about the rate of the bimolecular photoreduction of benzophenone by lactams[21]. Simultaneously, the yields decrease with the appearance of photodegradation products which become preponderant in the case of 7-membered ring compounds[22].

Modification of chromophore was then considered ; thus, irradiations of methylketone 3d and ester 3e were studied in order to access to new intermediates in the total synthesis of bicyclic alkaloids.

Ketone 3d and ester 3e possess a photochemical behavior very different from that of arylketones 3a, 3b and 3c ; in particular their molecular extinction coefficients are very low above 300 nm, and consequently these chromophores require particular conditions of irradiation : use of a liquid filter system cutting off the radiations below 280 nm to avoid absorption of the chromophore lactam.

The methylketone 3d is inert whatever the conditions of irradiation (Pyrex glass, quartz glass or liquid filter system with a medium pressure mercury lamp used as source).

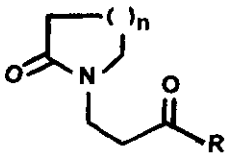
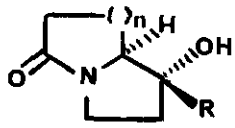
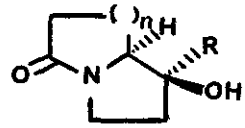
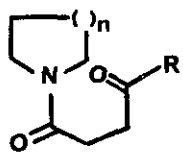
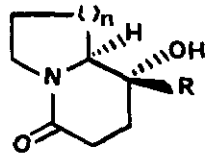
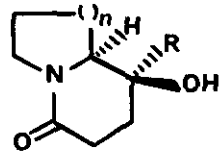
No excellent results are known concerning the abstraction of hydrogens α to the nitrogen of an amide group by a chromophore methylketone (even in the most favourable case : NORRISH type II reaction[15]). In our example, two unfavourable data are conjugated : abstractable hydrogens in δ position (seven-membered transition state) and use of a methylketone as chromophore which exhibits a low absorption around 280 nm.

The photoreduction of esters is not well documented in literature, few examples only mention the photoreaction of monofunctionalized molecules[23,24]. These molecules absorb near 200 nm.

In our case, it is not possible to irradiate the ester 3e around 200 nm which is the absorption zone of the lactam.

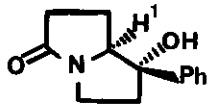
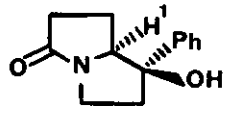
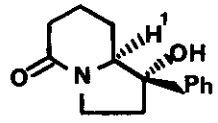
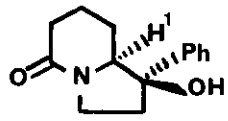
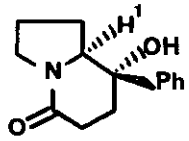
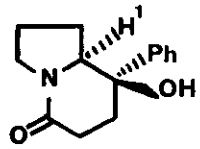
[a]The isomer in which the hydrogen of the ring junction and the hydroxyl group are "cis" is called "cis" isomer, the other being called "trans" isomer.

Table 1 : Abstraction of hydrogens in δ and ε positions by phenyl and methyl ketones.

Starting materials			Bicyclic compounds	
				
3			**4**	**5**
Compounds	n	R	Yield[a] (%)	Yield (%)
3a	1	Ph	60	15
3b	2	Ph	18	27
3c	3	Ph	8	7
3d	1	Me	0	0
3e	1	OMe	0	0
				
6			**7**	**8**
Compounds	n	R	Yield[a] (%)	Yield (%)
6a	1	Ph	31	26
6b	2	Ph	0	0
6c	3	Ph	49	28
6d	1	Me	15	10
6e	2	Me	0	0
6f	3	Me	15	10

[a] Isolated and unoptimized yields.

Table 2 - Chemical shifts (in Hz at 250 MHz) in $CDCl_3$ and C_5H_5N

Compounds	Chemical shifts of ^1H (Hz)		
	$CDCl_3$	Pyridine	Δδ(Hz)
4a 	1049.21	1096.25	- 47.04
5a 	1032.63	1031.71	+ 0.92
4b 	922.00	971.60	- 49.60
5b 	905.00	904.50	+ 0.50
7a 	955.00	1002.00	- 47.00
8a 	929.70	933.70	- 4.00

b) Formation of 6-membered rings

Substrates being required for this study have to possess a protected α position to avoid abstraction of hydrogens in this position.

We considered the compounds 6 in which the α position is protected by a carbonyl group which moreover activates the hydrogens α to the nitrogen atom.

These substrates were easily prepared by opening the corresponding lactone and oxidizing the intermediate alcohol.

Irradiation (similar conditions as in the precedent paragraph) of a deoxygenated solution of 1-(4-oxo-4-phenylbutyryl) pyrrolidine 6a in t-butylalcohol led to lactams 7a and 8a in 57 % yield. The structures of products were elucidated by spectroscopic methods : Ir spectra showed absorption bands due to the hydroxyl group at 3590 cm^{-1} (free OH) and to the carbonyl of a six-membered ring lactam at 1635 cm^{-1}. The ^{1}H-nmr spectra of diastereoisomeric mixture showed a multiplet at 3.85 ppm attributed to the hydrogen of the ring junction.

The stereochemistry of the substrates 7 and 8 had been determined by measuring the solvent effects $\Delta^{CDCl_3}_{C_5H_5N}$ in high field ^{1}H-nmr, as for the compounds 4 and 5, the preponderant isomer was the most crowded compound ("cis" isomer).

Good results were obtained concerning the irradiation of the seven-membered ring (6c) which led to the bicyclic compound (7c,8c) in a 77 % overall yield. On the other hand, the irradiation of substrates 6b and 6e did not afford the desired quinolizidine system, the starting material undergoing a photodegradation.

Compounds 6d and 6f led to desired bicyclic compounds in low yields ; the reaction only occurred when a filter solution cutting off below 280 nm was used.

In conclusion, we adjusted a general method for acceding to heterobicyclic compounds. In our approach, the second ring had been created by an intramolecular photoreduction of a carbonyl derivative by an amide or a lactam group.

This reaction constitutes an efficient method to generate azabicyclic systems possessing a nitrogen atom in the ring junction.

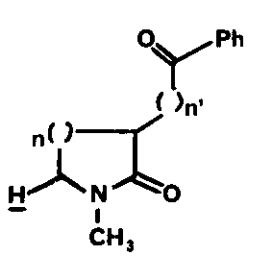
We tried to increase the applicability of this reaction by changing the arylketone chromophore with the methylketone and ester . We did not get any satisfying results because the low photoreactivity of the substrates.

However, we have to mention the excellent reactivity of the α-keto ester group, being used with success in the total synthesis of isoretronecanol[16].

c) Irradiation of 3-benzoyl and 3-phenacyl lactams.

The access to azabicyclo(x.y.z)alkanes (z≠0) has been studied using this methodology. In these examples, the chromophore arylketone has to be fixed on the lactam ring. We were interested in the substrates 9, intramolecular abstraction of the activated hydrogen α to the nitrogen atom if followed by cyclization would lead to bridged compounds of type 10 (Scheme 3).

Scheme 3



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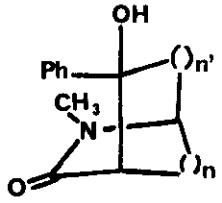


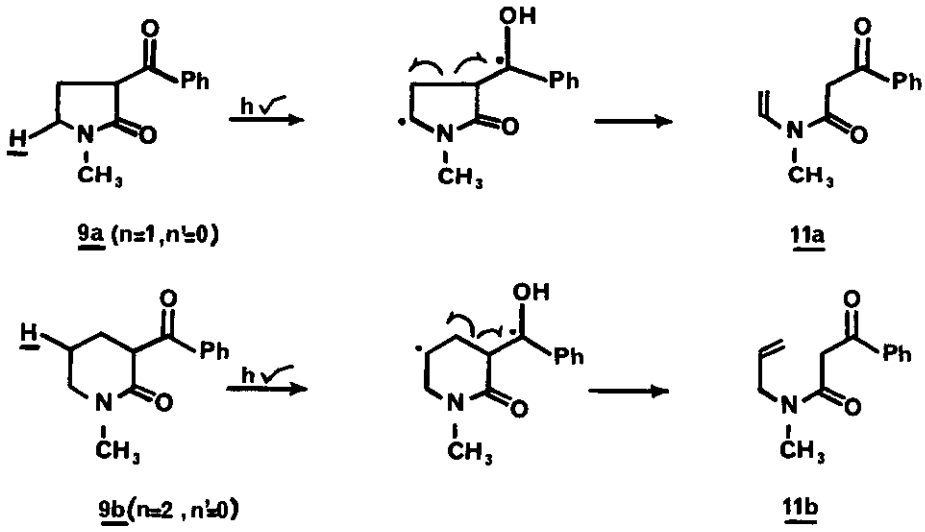
10

Examination of molecular models shows that the abstraction of hydrogen α to the nitrogen is only possible when the molecules are in particular conformations. However, there is a competition between such an abstraction and a γ abstraction implicated in a NORRISH type II reaction which is a very efficient process.

1) 3-Benzoyl lactams 9a and 9b

Irradiation (medium pressure mercury lamp, Pyrex) of a deoxygenated solution of 9a and 9b led to opening products 11a and 11b (Scheme 4).

Scheme 4



9a (n=1,n'=0) 11a

9b(n=2 ,n'=0) 11b

Structures of 11a and 11b were elucidated by the examination of spectroscopic data : Ir spectra showed absorption bands at 1675 cm^{-1} due to the aliphatic amide and at 1690 cm^{-1} attributed to the

aromatic ketone. The ^{1}H-nmr spectra exhibited broad singlets about 15.0 ppm due to the proton of the enol group and a singlet about 4.0 ppm corresponding to the protons α to the carbonyl group of the ketone form.

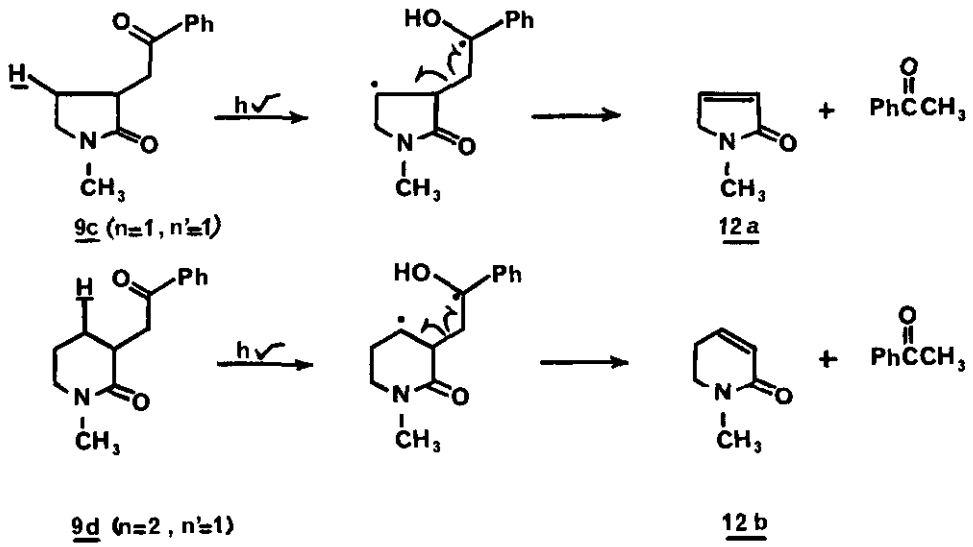
These results show that :

1 - NORRISH type II reaction occurs with efficiency and the aryl ketone group can adopt an axial conformation, allowing the H abstraction.
2 - Only scission products of the 1,4 biradical were isolated, may be due to the flexibility of the molecules which allows the overlap of the sp orbital of the radical and of the sp^3 orbitals of the central C-C bond (cf. ref. 8 p. 120).
3 - When there is competition between a NORRISH type II reaction and a δ abstraction of an hydrogen (although it is activated by an amide group, cf. 9b) priority is in favor of NORRISH type II reaction.

2) 3-Phenacyl lactams 9c and 9d

Irradiation (similar conditions as precedent) of a deoxygenated solution of 9c and 9d in t-butylalcohol afforded similarly compounds 12a and 12b accompanied with acetophenone (Scheme 5).

Scheme 5



Structures of 12a and 12b were elucidated by comparison with literature spectroscopic data.
12a and 12b resulted from a NORRISH type II reaction. So, when γ abstraction is possible, it occurs even if several other conformations of starting materials would facilitate δ or ε abstraction of the hydrogen activated by the lactam group.
As for precedent products 11a and 11b, NORRISH type II reaction occurs with the scission of the intermediate 1,4 biradical.

EXPERIMENTAL

Melting points were determined using a Reichert hot stage apparatus and are uncorrected. Proton nuclear magnetic resonance spectra were recorded on Jeol C60H and Cameca 250 spectrometers. Carbon-13 nuclear magnetic resonance spectra were run on a Jeol FX60 spectrometer. Chemical shifts are recorded as δ-values (parts per million) relative to tetramethyl silane as the internal reference standard. A Perkin-Elmer 377 instrument was used to determine ir spectra. Uv spectra were recorded using a Cary 15 spectrometer. Analyses were performed by the Microanalysis Central Service of the CNRS. Merck Kieselgel $60PF_{254}$ coated on glass plates was used for analytical chromatography. Irradiations were performed in a Pyrex or quartz glass vessel using a medium pressure mercury lamp (PHILIPS 250 W). The reaction mixture was flushed with a stream of dry nitrogen to remove oxygen.

1-(3-Oxo-3-phenylpropyl)lactams (3a), (3b) and (3c) were prepared according to the literature procedure[25].

1-(3-Oxo-3-methylpropyl)-2-pyrrolidone (3d)

A mixture of 1-(diethylmethyl)ammonium-3-butanone (5.7 g, 0.02 mol), 2-pyrrolidone(1.7 g, 0.02 mol) and p-toluenesulfonic acid (0.05 g) was refluxed in dry xylene (10 ml) for 4 h. The solvent was evaporated to give a residue which was leached with methylene chloride, washed with water and dried over Na_2SO_4. Evaporation of the solvent afforded 3d (1.1 g, 35 %) ; ir (cm^{-1}) 1720 and 1680 ; ^{1}H-nmr ($CDCl_3$) δ 2.2 (s, 3H, CH_3CO), 2.7 (m, 2H, CH_2-CON), 3.5 (m, 4H, CH_2-NCO).

1-(2-Carbomethoxyethyl)-2-pyrrolidone (3e)

To a stirred solution of 2-pyrrolidone (15.5 g, 0.18 mol) and Triton B (1.05 ml) in dioxan (60 ml) was added dropwise methyl acrylate (15 g, 0.17 mol). The resulting solution was stirred at room temperature for 72 h and acidified. Evaporation of volatiles gave the crude product which was distilled under vacuo to give 3e (22 g, 72 %) ; $bp_{0.5}$ 90°C, ir (cm^{-1}) 1740 and 1702 ; ^{1}H-nmr ($CDCl_3$) δ 3.6 (m, 4H, CH_2-NCO), 3.75 (s, 3H, CO_2Me).

Irradiation of 1-(3-Oxo-3-phenylpropyl)-2-pyrrolidone 3a

A deoxygenated solution of 3a (1 g) in acetonitrile (150 ml) was irradiated for 6 h in a Pyrex glass vessel using a medium pressure mercury lamp (PHILIPS 250 W). The solvent was evaporated and the residue chromatographed on a silica gel column. Elution with CH_2Cl_2/MeOH (95-5) gave :

- 1-aza-2-oxo-6-hydroxy-6-phenyl bicyclo (3.3.0) octane 4a (0.6 g, 60 %) ; mp 162°C (acetone); ir (cm^{-1}) 3580, 3340 and 1680 ; ^{1}H-nmr (250 MHz, $CDCl_3$) δ 7.2 (5H, m, arom.), 3.9 (broad s, 1H, OH, exch. with D_2O), 3.8 (1H, dd, CH-C(OH)Ph) ; ^{1}H-nmr (250 MHz, C_5H_5N) δ 7.5 (5H, m, arom.), 4.0 (1H, broad s, OH), 3.8 (1H, dd, CH-C(OH)Ph) ; ^{13}C-nmr ($CDCl_3$) δ 177.4, 142.9, 80.2, 70.7, 40.5 (d), 32.8, 22.35.

Anal. Calcd. for $C_{13}H_{15}NO_2$: C, 71.86 ; H, 6.96 ; N, 6.45. Found : C, 71.80 ; H, 7.05 ; N, 6.38.

- 1-aza-2-oxo-6-hydroxy-6-phenyl bicyclo (3.3.0) octane 5a (0.15 g, 15 %) ; mp 196°C (acetone); ir (cm^{-1}) 3580, 3340 and 1680 ; ^{1}H-nmr (250 MHz, $CDCl_3$) δ 7.2 (5H, m, arom.), 3.8 (1H, broad s, OH, exch. with D_2O), 4.13 (1H, dd, CH-C(OH)Ph) ; ^{1}H-nmr (250 MHz, C_5H_5N) δ 7.5 (5H, m, arom.), 3.9 (1H, broad s, OH, exch. with D_2O), 4.13 (1H, dd, CH-C(OH)Ph) ; ^{13}C-nmr ($CDCl_3$) δ 176.1, 142.35, 77.8, 70.9, 41.45 (d), 33.9, 17.35.

Anal. Calcd. for $C_{13}H_{15}NO_2$: C, 71.86 ; H, 6.96 ; N, 6.45. Found : C, 71.82 ; H, 7.00 ; N, 6.40.

Irradiation of 1-(3-Oxo-3-phenylpropyl)-2-piperidone 3b

A deoxygenated solution of 3d (1 g) in acetonitrile (150 ml) was irradiated for 29 h. The solvent was evaporated and the residue chromatographed on a silica gel column. Elution with CH_2Cl_2/MeOH (95-5) afforded :

- 1-aza-2-oxo-7-hydroxy-7-phenyl bicyclo (4.3.0) nonane 4b (0.17 g, 18 %) ; mp 185-186°C (acetone) ; ir (cm^{-1}) 3580 and 1628 ; ^{1}H-nmr (250 MHz, $CDCl_3$) δ 7.2 (5H, m, arom.), 5.7 (1H, broad s, OH, exch. with D_2O), 3.6 (3H, m), 2.0 (8H, m) ; ^{1}H-nmr (250 MHz, C_5H_5N) δ 7.3 (5H, m, arom.), 5.8 (1H, s, OH), 3.9 (1H, dd, CH-C(OH)Ph) ; ^{13}C-nmr ($CDCl_3$) δ 171.4, 143.8, 81.6, 68.3, 44.6, 38.4, 31.4, 24.95, 20.6.

Anal. Calcd. for $C_{14}H_{17}NO_2$: C, 72.70 ; H, 7.41 ; N, 6.06. Found : C, 72.78 ; H, 7.51 ; N, 6.09.

- 1-aza-2-oxo-7-hydroxy-7-phenyl bicyclo (4.3.0) nonane 5b (0.275 g, 27 %) ; mp 205°C (acetone) ; ir (cm^{-1}) 3580 and 1629 ; ^{1}H-nmr (250 MH , $CDCl_3$) δ 7.4 (5H, m, arom.), 5.3 (1H, broad s, OH), 3.7 (3H, m), 2.0 (8H, m) ; ^{1}H-nmr (250 MHz, C_5N_5N) δ 7.5 (5H, m, arom.), 5.4 (1H, s, OH), 3.7 (3H, m), 2.0 (8H, m) ; ^{13}C-nmr ($CDCl_3$) δ 171.8, 142.7, 80.6, 69.1, 44.2, 38.2, 31.3, 21.5, 20.85.

Anal. Calcd. for $C_{14}H_{17}NO_2$: C, 72.70 ; H, 7.41 ; N, 6.06. Found : C; 72.84 ; H, 7.12 ; N, 6.23.

Irradiation of 1-(3-Oxo-3-phenylpropyl) ε-Caprolactam 3c

A deoxygenated solution of 3c (1 g) in acetonitrile (150 ml) was irradiated for 12 h using a medium pressure mercury lamp (PHILIPS 400 W). The solvent was evaporated and the residue chromatographed on a silica gel column. Elution with CH_2Cl_2/MeOH (95-5) gave :

- 1-aza-2-oxo-8-hydroxy-8-phenyl bicyclo (5.3.0) decane 5c (0.07 g, 7 %) ;mp 134°C(acetone); ir (cm^{-1}) 3580 and 1614 ; ^{1}H-nmr (250 MHz, $CDCl_3$) δ 7.4 (5H, m, arom.), 4.5 (1H, broad s, OH, exch. with D_2O), 2.7 (3H with 1H, dd, CH-C(OH)Ph), 1.7 (6H, m) ; ^{1}H-nmr (250 MHz, C_5H_5N) δ 7.5 (5H, m, arom.), 4.6 (1H, s, OH), 2.9 (1H, dd, CH-C(OH)Ph), 1.8 (6H, m) ; ^{13}C-nmr ($CDCl_3$) δ 174.6, 143.6, 82.5, 69.2, 44.3, 39.8, 38.0, 29.4, 27.9, 23.2.

Anal. Calcd. for $C_{15}H_{19}NO_2$: C, 73.44 ; H, 7.81 ; N, 5.71. Found : C, 73.56 ; H, 7.70 ; N, 5.81.

- 1-aza-2-oxo-8-hydroxy-8-phenyl bicyclo (5.3.0) decane 4c (0.08 g, 8 %) ;mp 155-156°C(acetone); ir (cm^{-1}) 3580 and 1622 ; ^{1}H-nmr (250 MHz, $CDCl_3$) δ 7.5 (5H, m, arom.), 3.8 (3H with 1H, dd, CH-C(OH)Ph), 3.5 (1H, broad s, OH, exch. with D_2O), 2.3 (4H, m), 1.8 (6H, m) ; ^{1}H-nmr (250 MHz, C_5H_5N) δ 7.6 (5H, m, arom.), 4.0 (1H, dd, CH-C(OH)Ph), 4.2 (1H, m), 3.7 (1H, s, OH), 2.3 (4H, m), 1.8 (6H, m) ; ^{13}C-nmr ($CDCl_3$) δ 174.5, 143.1, 83.1, 69.0, 45.4, 39.3, 38.2, 29.0, 27.5, 23.0.

Anal. Calcd. for $C_{15}H_{19}NO_2$: C, 73.44 ; H, 7.81 ; N, 5.71. Found : C, 73.51 ; H, 7.75 ; N, 5.79.

1-(4-Hydroxy-4-phenylbutyryl)amine

According to the literature procedure[26], a solution of γ-phenyl γ-butyrolactone (one equivalent) and amine (one equivalent) in water (80 % solution) was refluxed for 4 h. Then, the mixture was chilled and extracted with methylene chloride. Organic layers were combinated, washed with water and dried over Na_2SO_4. Evaporation of the solvent afforded the desired compound and purification by chromatography column (silica gel) afforded pure product isolated as an oil.

1-(4-Hydroxy-4-phenylbutyryl)pyrrolidine (6a')

90 % yield ; ir (cm^{-1}) 3300 and 1615 ; ^{1}H-nmr ($CDCl_3$) δ 7.2 (5H, m, arom.), 5.0 (1H, s, OH, exch. with D_2O), 4.7 (1H, t, CH(OH)Ph), 3.2 (4H, m, CH_2N), 2.1 (8H, m, pyrrolidine ring). ^{1}H-nmr ($CDCl_3$)

δ 7.2 (5H, m, arom.), 5.0 (1H, s, OH, exch. with D_2O), 4.7 (1H, t, C<u>H</u>(OH)Ph), 3.2 (4H, m, CH_2N), 2.1 (8H, m, pyrrolidine ring).

<u>1-(4-Hydroxy-4-phenylbutyryl)piperidine (6b')</u>

90 % yield ; ir (cm^{-1}) 3350 and 1615 ; ^{1}H-nmr ($CDCl_3$) δ 7.3 (5H, m, arom.), 4.7 (1H, t, C<u>H</u>-OH), 4.0 (1H, s, OH, exch. with D_2O), 3.45 (4H, m, CH_2N), 2.3 (4H, m), 1.58 (6H, m, piperidine ring). ^{1}H-nmr ($CDCl_3$) δ 7.3 (5H, m, arom.), 4.7 (1H, t, C<u>H</u>(OH)Ph), 4.0 (1H, s, OH, exch. with D_2O), 3.45 (4H, m, CH_2N), 2.3 (4H, m), 1.58 (6H, m, piperidine ring).

<u>1-(4-Hydroxy-4-phenylbutyryl)hexamethyleneimine (6c')</u>

95 % yield ; ir (cm^{-1}) 3300 and 1610 ; ^{1}H-nmr ($CDCl_3$) δ 7.35 (5H, m, arom.), 4.8 (1H, t, C<u>H</u>(OH)Ph), 4.7 (1H, s, OH, exch. with D_2O), 3.5 (4H, m, CH_2N), 2.3 (4H, m), 1.55 (8H, m, amine ring).

<u>1-(4-Hydroxy-4-methylbutyryl)pyrrolidine (6d')</u>

85 % yield ; ir (cm^{-1}) 3400 and 1630 ; ^{1}H-nmr ($CDCl_3$) δ 4.0 (1H, m, OH, exch. with D_2O), 3.8 (1H, m, $CH(OH)CH_3$), 3.45 (4H, m, CH_2N), 2.45 (2H, t), 1.9 (6H, m, pyrrolidine ring), 1.65 (3H, d, CH_3).

<u>1-(4-Hydroxy-4-methylbutyryl)piperidine (6e')</u>

89 % yield ; ir (cm^{-1}) 3400 and 1635 ; ^{1}H-nmr ($CDCl_3$) δ 3.8 (1H, m, C<u>H</u>(OH)CH_3), 3.5 (5H, m, CH_2N and OH exch. with D_2O), 2.45 (2H, t), 1.8 (2H, m), 1.6 (6H, m, piperidine ring), 1.2 (3H, d, CH_3) .

<u>1-(4-Hydroxy-4-methylbutyryl)hexamethyleneimine (6f')</u>

91 % yield ; ir (cm^{-1})3400 and 1630 ; ^{1}H-nmr ($CDCl_3$) δ 3.7 (1H, m, C<u>H</u>-C(OH)CH_3), 3.5 (5H, m, CH_2N and OH exch. with D_2O), 2.5 (2H, t), 1.6 (10H, m, amine ring), 1.2 (3H, d, CH_3).

<u>1-(4-Oxo-4-phenylbutyryl)amine</u>

Compounds <u>6a</u>, <u>6b</u>, <u>6c</u>, <u>6d</u>, <u>6e</u> and <u>6f</u> were obtained in good yields (75 to 85 %) as oils using Jones reagent (chromic acid/sulfuric acid)[27] from corresponding alcohols,respectively.

<u>1-(4-Oxo-4-phenylbutyryl)pyrrolidine (6a)</u>

mp 84-85°C (ether) ; ir (cm^{-1})1690 and 1630 ; uv (EtOH) λ_{max} (nm) 240, 278 ; ^{1}H-nmr ($CDCl_3$) δ 7.7 (5H, m, arom.), 3.4 (6H, m), 2.7 (2H, t), 1.9 (4H, m, CH_2 pyrrolidine ring).

<u>1-(4-Oxo-4-phenylbutyryl)piperidine (6b)</u>

mp 50-51°C (ether) ; ir (cm^{-1}) 1690 and 1640 ; Uv(EtOH) λ_{max} (nm) 240, 278 ; ^{1}H-nmr ($CDCl_3$) δ 7.8 (5H, m, arom.), 3.5 (6H, m), 2.80 (2H, m), 1.65 (6H, m, piperidine ring).

<u>1-(4-Oxo-4-phenylbutyryl)hexamethyleneimine (6c)</u>

ir (cm^{-1}) 1685 and 1625 ; uv (EtOH) λ_{max} (nm) 240, 278 ; ^{1}H-nmr ($CDCl_3$) δ 7.75 (5H, m, arom.), 3.45 (6H, m), 2.8 (2H, m), 1.65 (8H, m, amine ring) .

1-(4-Oxo-4-methylbutyryl)pyrrolidine (6d)

ir (cm^{-1}) 1725 and 1645 ; uv (EtOH) ε_{260} = 21, ε_{313} = 1.3 ; ^{1}H-nmr ($CDCl_3$) δ 2.65 (4H, m, CH_2N), 2.2 (3H, s, CH_3), 1.9 (4H, m, pyrrolidine ring), .

1-(4-Oxo-4-methylbutyryl)piperidine (6e)

ir (cm^{-1}) 1725 and 1645 ; uv (EtOH) ε_{260} = 21, ε_{313} = 0.6 ; ^{1}H-nmr ($CDCl_3$) δ 3.5 (4H, m, CH_2N), 2.7 (4H, m), 2.2 (3H, s, CH_3), 1.6 (6H, m, piperidine ring).

1-(4-Oxo-4-methylbutyryl)hexamethyleneimine (6f)

ir (cm^{-1}) 1725 and 1645 ; uv (EtOH) ε_{260} = 26, ε_{313} = 3 ; ^{1}H-nmr ($CDCl_3$) δ 3.45 (4H, m, CH_2N), 2.65 (4H, m), 2.2 (3H, s, CH_3), 1.6 (8H, m, amine ring), .

Irradiation of 1-(4-Oxo-4-methylbutyryl)pyrrolidine 6a

A deoxygenated solution of 6a (2 g) in t-butylalcohol (500 ml) was irradiated for 24 h (Philips 400 W). The solvent was evaporated and the residue chromatograph ed on a silica gel column. Elution with ethyl acetate afforded:

- 1-aza-2-oxo-5-hydroxy-5-phenyl bicyclo (4.3.0) nonane 7a (0.62 g, 31 %);mp 173°C (CH_2Cl_2-hexane) ; ir (cm^{-1}) 3420 and 1635 ; ^{1}H-nmr (60 MHz, $CDCl_3$) 7.4 (5H, s, arom.), 4.2 (1H, s, OH, exch. with D_2O), 3.85 (1H, t, CH-N), 3.5 (2H, m, CH_2-N), 2.3 (4H, m), 1.7 (4H, m, pyrrolidine ring) ; ^{1}H-nmr (250 MHz), δ ($CDCl_3$) 3.82 (1H, q, C_6-H) ; δ (C_5H_5N) 4.01 (1H, q, C_6-H) ; ^{13}C-nmr ($CDCl_3$) δ 169.7, 144.0, 128.25, 127.5, 125.8, 73.55, 66.9, 45.2, 37.05, 30.15, 27.55, 22.2.
Anal. Calcd for $C_{14}H_{17}NO_2$: C, 72.7 ; H, 7.41 ; N, 6.06. Found : C, 72.51 ; H, 7.56 ; N, 6.27.
- 1-aza-2-oxo-5-hydroxy-5-phenyl bicyclo (4.3.0) nonane 8a (0.51 g, 26 %); mp 168-170°C (CH_2Cl_2-hexane) ; ir (cm^{-1}) 3420 and 1670 ; ^{1}H-nmr (60 MHz, $CDCl_3$) δ 7.55 (5H, m, arom.), 4.4 (1H, s, OH, exch. with D_2O), 3.8 (1H, m, CH-N), 3.6 (2H, m, CH_2N), 2.55 (2H, m), 2.25 (2H, m), 1.7 (4H, m, pyrrolidine ring) ; ^{1}H-nmr (250 MHz) δ ($CDCl_3$) 3.72 (1H, q, C_6-H) ; δ (C_5H_5N) 3.73 (1H, q, C_6-H); ^{13}C-nmr ($CDCl_3$) δ 169.3, 144.65, 128.4, 127.2, 124.9, 71.35, 67.05, 46.15, 34.8, 28.45, 26.25, 21.85.
Anal. Calcd for $C_{14}H_{17}NO_2$: C,72.70 ; H, 7.41 ; N, 6.06. Found : C, 72.34 ; H, 7.44 ; N, 6.12.

Irradiation of 1-(4-Oxo-4-phenylbutyryl)hexamethyleneimine 6c

A deoxygenated solution of 6c (2 g) in t-butyl alcohol (500 ml) was irradiated for 28 h. The solvent was evaporated and the residue chromatograph ed on a silica gel column. Elution with ethyl acetate afforded :

- 1-aza-8-hydroxy-8-phenyl-11-oxo bicyclo (5.4.0) undecane 8c (0.56 g, 28 %), mp 159-161°C (CH_2Cl_2-hexane) ; ir (cm^{-1}) 3380 and 1620 ; ^{1}H-nmr (60 MHz, $CDCl_3$) δ 7.4 (5H, m, arom.), 3.85 (2H, m, CH-N and OH, exch. with D_2O), 2.25 (4H, m), 1.65 (8H, m, amine ring) ; ^{1}H nmr (250 MHz) δ ($CDCl_3$) 3.79 (1H, t, C_7-H), δ (C_5H_5N) 3.97 (1H, t, C_7-H). ^{13}C-nmr ($CDCl_3$) δ 170.45, 146.1, 128.65, 127.45, 125.45, 74.4, 65.75, 46.05, 33.7, 29.45, 28.95, 27.55, 25.9.
Anal. Calcd for $C_{16}H_{21}NO_2$: C, 74.10 ; H, 8.16 ; N, 5.40. Found C, 74.15 ; H, 8.26 ; N, 5.48
- 1-aza-8-hydroxy-8-phenyl-11-oxo bicyclo (5.4.0) undecane 7c (0.98 g, 49 %), mp 171-172°C (CH_2Cl_2-hexane) ; ir (cm^{-1}) 3350 and 1620 ; ^{1}H-nmr (60 MHz, $CDCl_3$) δ 7.4 (5H, m, arom.), 4.25 (2H, m, CH-N

and OH, exch. with D_2O), 3.5 (1H, m, CH-N), 2.5 (5H, m), 1.4 (8H, m, amine ring); ^{1}H-nmr (250 MHz) δ($CDCl_3$) 3.5 (1H, q, C_7-H) ; δ(C_5H_5N) 3.77 (1H, q, C_7-H). ^{13}C-nmr ($CDCl_3$) δ 170.2, 145.25, 128.5, 127.8, 126.1, 73.2, 68.75, 48.05, 34.0, 28.05, 27.0, 26.35, 26.15, 25.9.
Anal. Calcd for $C_{16}H_{21}NO_2$: C, 74.10 ; H, 8.16 ; N, 5.40. Found : C, 74.04 ; H, 8.11 ; N, 5.44.

Irradiation of 1-(4-Oxo-4-methylbutyryl)pyrrolidine 6d

A deoxygenated solution of 6d (2 g) in t-butyl alcohol (500 ml) was irradiated for 12 h in a quartz glass vessel using a medium pressure mercury lamp filtered by a solution of NaBr, $2H_2O$ (400 g) and Ag_2SO_4 (1.2 g) in distilled water (1l). The solvent was then evaporated and the residue chromatograph ed on a silica gel column. Elution with ethyl acetate afforded :
- 1-aza-2-oxo-5-methyl-5-hydroxy bicyclo(4.3.0)nonane 7d (0.3 g, 15 %), mp 122-124°C (AcOEt-hexane) ; ir (cm^{-1}) 3400, 1625 ; ^{1}H-nmr (60 MHz, $CDCl_3$) δ 3.5 (4H, m, 3H α of N and OH, exch. with D_2O), 2.4 (6H, m), 1.15 (3H, s, Me), ^{13}C-nmr ($CDCl_3$) δ 168.5, 69.6, 66.6, 45.9, 36.9, 30.2, 27.3, 22.4, 19.7.
Anal. Calcd for $C_9H_{15}NO_2$: C, 63.88 ; H, 8.94 ; N, 8.28. Found: C, 63.89 ; H, 8.98 ; N, 8.31.

- 1-aza-2-oxo-5-methyl-5-hydroxy bicyclo(4.3.0)nonane 8d (0.2 g, 10 %), mp 134-136°C (AcOEt-hexane) ; ir (cm^{-1}) 3400 and 1625 ; ^{1}H-nmr (60 MHz, $CDCl_3$) δ 3.5 (4H, m, CH_2N and OH, exch. with D_2O), 2.4 (2H, m), 1.9 (6H, m), 1.3 (3H, s, Me), ^{13}C nmr ($CDCl_3$) δ 169.4, 67.2, 66.3, 45.8, 35.0, 28.1, 26.4, 26.2, 22.0.
Anal. Calcd for $C_9H_{15}NO_2$: C, 63.88 ; H, 8.94 ; N, 8.28. Found: C, 63.89 ; H, 8.99 ; N, 8.30.

Irradiation of 1-(4-Oxo-4-methylbutyryl)hexamethyleneimine 6f

A deoxygenated solution of 6f (2 g) in t-butyl alcohol (500 ml) was irradiated for 8 h (similar conditions as precedent). The solvent was evaporated and the residue chromatograph ed on a silica gel column. Elution with ethyl acetate afforded :
- 1-aza-8-methyl-8-hydroxy-11-oxo bicyclo (5.4.0) undecane 8f (0.2 g, 10 %), mp 83-85°C (AcOEt-hexane) ; ir (cm^{-1}) 3400 and 1625 ; ^{1}H-nmr (60 MHz, $CDCl_3$) δ 4.2 (1H, m, CH-N), 3.3 (2H, m, CH-N and OH, exch. with D_2O), 2.5 (3H, m), 1.7 (10H, m), 1.35 (3H, s, Me). ^{13}C-nmr ($CDCl_3$) δ 169.5, 69.4, 67.0, 47.2, 31.1, 30.9, 29.0, 27.2, 27.0, 26.7, 25.9.
Anal. Calcd for $C_{11}H_{19}NO_2$: C, 66.97 ; H, 9.71 ; N, 7.10. Found : C, 67.01 ; H, 9.75 ; N, 7.12

1-aza-8-methyl-8-hydroxy-11-oxo bicyclo (5.4.0) undecane 7f (0.3 g, 15 %), mp 141-143°C (AcOEt-hexane); ir (cm^{-1}) 3350 and 1620 ; ^{1}H-nmr (60 MHz, $CDCl_3$) δ 4.3 (1H, m, CH-N), 3.9 (1H, s, OH, exch. with D_2O), 3.3 (1H, m, CH-N), 2.5 (3H, m), 1.7 (10H, m), 1.25 (3H, s, Me) ; ^{13}C-nmr ($CDCl_3$) δ 169.8, 69.9, 69.1, 48.1, 33.3, 30.2, 28.1, 26.7, 26.5, 26.2, 26.0.
Anal. Calcd for $C_{11}H_{19}NO_2$: C, 66.97 ; H, 9.71 ; N, 7.10. Found : C, 66.99 ; H, 9.73 ; N, 7.13

3-Benzoyl-4-methyl-2-pyrrolidone (9a)

To a solution of lithium diisopropylamide (LDA) (10 mmol) in dry THF (40 ml) was added at -78°C, under a nitrogen atmosphere a solution of 1-methyl-2-pyrrolidone (1 g, 10 mmol) in dry THF (10 ml). The mixture was stirred for 1 h at -78°C then a solution of benzoyl chloride (1.7 g, 12 mmol) in dry THF (10 ml) was added dropwise. The reaction mixture was then stirred for 30 min at -78°C. Usual work up gave 9a (0.74 g, 36 %) as an oil ; ir (cm^{-1}) 1705 and 1690 ; ^{1}H-nmr ($CDCl_3$) δ 7.4-

8.5 (5H, m, arom.), 4.45 (1H, m), 2.75 (3H, s, Me), 2.3 (2H, m) ; ^{13}C-nmr ($CDCl_3$) δ 197.0, 170.6, 136.5, 50.3, 47.9, 29.8, 21.9.

3-Benzoyl-1-methyl-2-piperidone (9b)

9b was prepared by the same procedure used for 11a . 9b was obtained in 28 % yield as an oil ; ir (cm^{-1}) 1650, 1630, ^{1}H-nmr ($CDCl_3$) δ 7.3-8.2 (5H, m, arom.), 4.5 (1H, m), 3.35 (2H, m, CH_2N), 3.0 (3H, s, Me), 2.0 (4H, m) ; ^{13}C-nmr ($CDCl_3$) δ 198.5, 170.8, 167.0, 136.4, 97.1, 49.9, 49.7, 34.8, 34.6, 25.5, 25.3, 22.8, 20.7.

1-Methyl-3-phenacyl-2-pyrrolidone (9c)

9c was prepared according to the literature procedure[28].

1-Methyl-3-phenacyl-2-piperidone (9d)

9d was prepared according to the same procedure as 9c[28] in 97 % yield and isolated as an oil ; ir (cm^{-1}) 1690 and 1655 ; ^{1}H-nmr ($CDCl_3$) δ 8.2-7.3 (5H, m, arom.), 3.9-3.06 (5H, m), 2.9 (3H, s, N-Me), 2.3-1.5 (4H, m) ; ^{13}C-nmr ($CDCl_3$) δ 199.7, 169.6, 138.1, 57.2, 41.9, 39.6, 36.1, 28.5, 23.5 ; ms m/z (%) 231 ($M^{+\cdot}$ 60), 154 (5), 126 (50), 112 (10), 111 (11), 105 (90), 83 (15), 77 (25) ; exact mass Calcd for $C_{14}H_{17}NO_2$: 231.1255. Found : 231.1256.

Irradiation of 3-Benzoyl-1-methyl-2-pyrrolidone 9a

A deoxygenated solution of 9a (1.32 g) in t-butyl alcohol (500 ml) was irradiated for 4 h. The solvent was evaporated and the residue chromatograph ed by flash chromatography. Elution with AcOEt/hexane (2-8) afforded:
- N-Vinyl-3-oxo-3-phenyl propionic amide 11a (0.63 g, 48 %) as an oil ; ir (cm^{-1}) 1670 ; ^{1}H-nmr ($CDCl_3$) δ 15.0 (1H, m, OH, exch. with D_2O), 6.5-8.4 (5H, m, arom.), 5.9 (1H, s), 3.8-4.8 (4H, m), 3.05 and 3.2 (3H, s, N-Me), 2.8-3.0 (1H, m) ; ^{13}C-nmr ($CDCl_3$) δ 193.1, 171.0, 166.0, 136.0, 126.0, 94.6, 94.0, 84.8, 45.8.

Irradiation of 3-Benzoyl-1-methyl-2-piperidone 9b

A deoxygenated solution of 9b (0.5 g) in t-butyl alcohol (70 ml) was irradiated for 5 h. The solvent was evaporated and the residue chromatograph ed by flash chromatography. Elution with AcOEt/hexane (1-1) afforded :
- *N-Allyl-3-oxo-3-phenyl propionic amide* 11b (0.2 g, 40 %) isolated as an oil ; ir (cm^{-1}) 1635 and 1690; ^{1}H-nmr ($CDCl_3$) δ 7.5-8.0 (5H, m, arom.), 5.0-6.0 (1H, m), 4.1 (4H, m), 3.0 and 2.9 (3H, s, N-Me) ; ^{13}C-nmr ($CDCl_3$) δ 194.0, 171.5, 166.9, 136.2, 135.0, 133.6, 132.4, 130.7, 128.7, 128.4, 125.9, 117.4, 117.1, 117.0, 84.7, 79.2, 78.5, 78.4, 77.1, 76.4, 75.5, 74.9, 52.9, 50.2, 46.0, 45.6, 35.5, 33.7.

Irradiation of 1-Methyl-3-phenacyl-2-pyrrolidone 9c

A deoxygenated solution of9c (0.54 g) in t-butyl alcohol (70 ml) was irradiated for 7 h. The solvent was evaporated and the residue chromatographed by flash chromatography. Elution with ethyl acetate afforded:

- acetophenone (0.16g, 83 %) and 1-methyl-3-pyrrolin-2-one 12a(0.09 g, 36 %). Spectroscopic data are in agreement with literature[29].

Irradiation of 1-Methyl-3-phenacyl-2-piperidone 9d

A deoxygenated solution of 9d (0.37 g) in t-butyl alcohol (70 ml) was irradiated for 7 h. The solvent was evaporated and the residue chromatographed by flash chromatography. Elution with ethyl acetate-hexane (6-4) afforded :
- acetophenone (0.1 g, 50 %) and 1-methyl-5,6-dihydro-2-pyridone 12b (0.06 g, 33 %) isolated as an oil; ir (cm^{-1}) 1620 and 1670 ; ^{1}H-nmr ($CDCl_3$) δ 6.3-6.8 (1H, m), 5.7-6 (1H, m), 3.45 (2H, t, CH_2-N), 3.0 (3H, s, N-Me), 2.1-2.7 (2H, m).

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