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PHOTOCHEMISTRY OF HETEROCYCLIC ENAMINONES : AN ALTERNATIVE AND EFFICIENT ROUTE TO CRYPTOLEPINE ALKALOID FRAMEWORK

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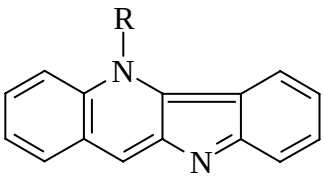
Abstract – Photochemical reactivity of heterocyclic enaminone is described in view of the synthesis of cryptolepine analogs (**5**). The reaction conditions are shown to have some influence on the regioselectivity as well as the yields of photocyclization

INTRODUCTION

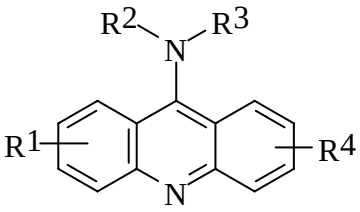
Interest in the chemistry of pyridocarbazoles and indoloquinolines has increased this last decade since these skeletons are present in a large number of alkaloids of biological interest. For example, the indoloquinoline type alkaloids quindoline (**1**) and cryptolepine (**2**) extracted from the roots of *Cryptolepis sanguinolenta*[1] have been shown to exhibit promising *in vitro* and *in vivo* antiplasmodial activities[2] (Scheme 1). However, poor works have been conducted to increase the activities of such alkaloids by slight modifications of the heterocyclic nucleus.[3] As an example of such possible modifications, it was shown, in the acridine series, that the tetrahydro derivatives possessing a carbonyl group on the C-1 position (floxacrine type compounds (**4**)) exhibited higher activities on *Plasmodium berghei* than the parent mepacrine type compounds (**3**).[4] As a part of our program concerning the elaboration of analogs of natural products,[5] we are interested in the chemistry as well as in the biological activities of such modified

heterocyles.

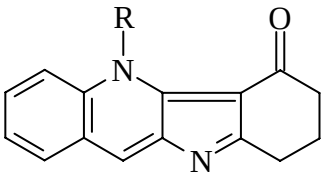
Scheme 1



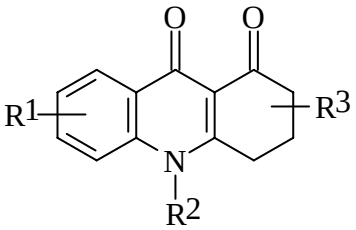
1 quindoline R = H
2 cryptolepine R=CH_3



3 "mepacrine" type



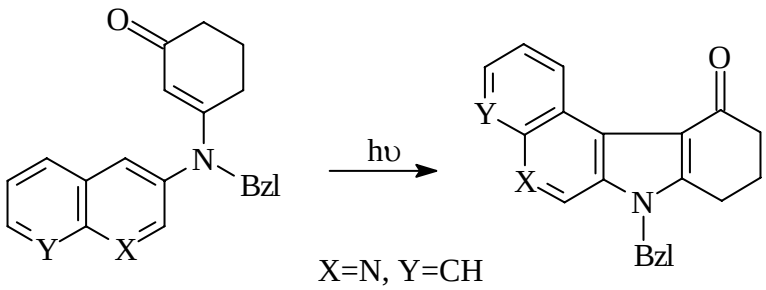
5



4 "floxacrine" type

Our synthetic methodology resides in the use of enaminones[6] derived from diverse amino-heterocyles. These compounds represent convenient tools in heterocyclic chemistry since they can be implicated in the elaboration of carbazoles,[7] β-carbolines and δ-carbolines,[8] α-carbolines,[9] pyridocarbazoles and indoloquinolines.[10] Key step of the synthesis resides in the photocyclization of enaminones to give the corresponding indolones. Two mechanisms can be implicated in such photocyclizations : a radical process with halogenated derivatives[8a] and an electrocyclization through a 6 π electron mechanism with tertiary enaminones.[8b] However, in the case of quinoline derivatives, we have shown that the tertiary enaminones (**6**) cyclized regioselectively leading exclusively to the angular tetracycles (**7**)[10] (scheme 2).

Scheme 2



6 X=N, Y=CH; X=CX,Y=N **7**

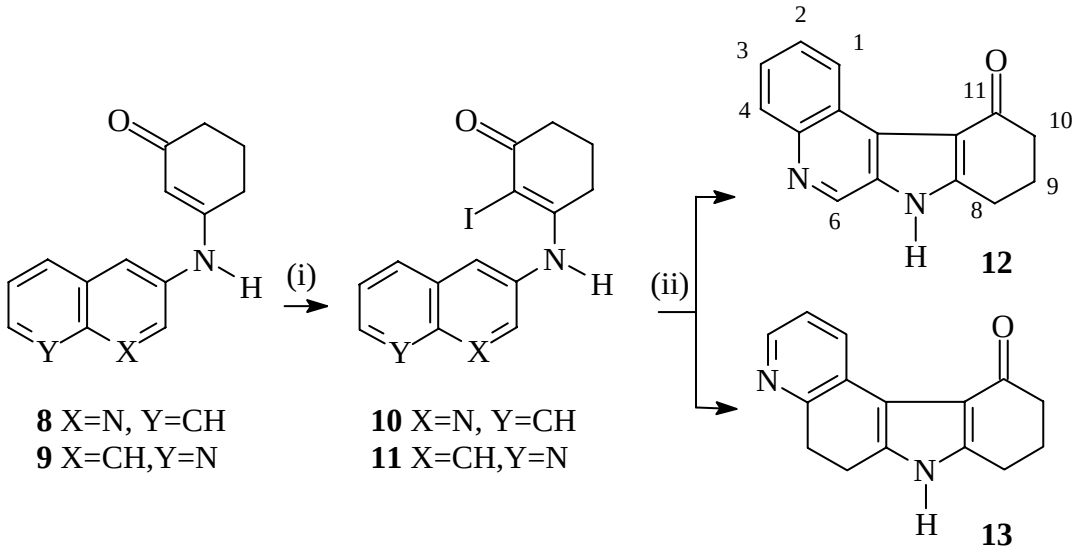
The purpose of the present work is to investigate the photochemistry of secondary halogenated enaminones in order to prepare derivatives of cryptolepine such as **5**. As the preparation of such enaminones derived from 3-amino-2-halogenoquinolines required five steps,[11] our synthetic strategy resides in the study of the

reactivity of α-halogenated enaminones derived from 3-aminoquinoline which can be obtained by a two steps process. In addition , the same investigations were performed in the 6-aminoquinoline series.

RESULTS AND DISCUSSION

Starting enaminones (**8,9**) were obtained according to published method.[10] The α-iodoenaminones (**10,11**) were synthetized by treatment of **8** and **9** with benzyltrimethylammonium dichloroiodate in 91 and 83% yields respectively. Subsequent irradiation of **10** was then performed using a Pyrex well appapatus and a medium pressure mercury UV lamp (150 W) using toluene, methanol and acetonitrile as solvent. Results are summarized in Table 1 and Scheme 3.

Scheme 3



8 X=N, Y=CH
9 X=CH,Y=N

10 X=N, Y=CH
11 X=CH,Y=N

(i) $BTMAICl_2$,CH_2Cl_2/CH_3OH (2:1), $NaHCO_3$
(ii) hυ

Table 1:Irradiation of enaminones (10, 11) under different conditions

Entry	Conditions	Substrate	Yield (%) of compd	Total yield (%) of cyclized compds from 8 and 9
1	Toluene, $(C_2H_5)_3N$, 2 h	**10**	**8** (80)	0
2	CH_3OH, $(C_2H_5)_3N$, 2 h	**10**	**8** (60) and **12** (15)	9
3	CH_3CN, $(C_2H_5)_3N$, 2 h	**10**	**12** (77)	46
4	CH_3CN, $(C_2H_5)_3N$, 2 h	**11**	**9** (37) and **13** (25)	13

In toluene, starting material **(10)** was recovered in 80% yield, while in methanol and in acetonitrile, compound **(10)** gave the 8,9,10,11-tetrahydroindolo[2,3-*c*]quinolin-11-one (**12**) by a regioselective

cyclisation on the C-4 position of the quinolinic nucleus. Structure of **12** was easily determined by ^{1}H-NMR, and by comparison with the *N*-benzyl derivative.[10] More precisely the ^{1}H-NMR spectra of **12** showed a characteristic singlet of H-6 at δ 8.76, while the signal of H-1 was shifted downfield due to the proximity of the carbonyl group and appeared as a double doublet (δ 9.67, J = 5.9 and 3.7 Hz). In a similar manner, the 5,6,8,9,10,11-hexahydropyrido[2,3-*c*]carbazol-11-one (**13**) was obtained from **11** in 25% yield, by a regioselective cyclisation on the C-7 position of the quinolinic nucleus, and no formation of the tetrahydro derivative was found. Structural determination of **13** was made on the basis of selective INEPT experiments as illustrated in Figure 1. In particular, carbon C-11b and C-4a were expected to show significant long-range coupling with both protons H-1 and H-6, while carbon C-11c would exhibit a long-range coupling with H-6 and H-2, respectively. As illustrated in Figure 1, the selective irradiation of the signal at δ 7.05 (H-2) showed the transfer of C-11c only (δ 130.8), while the selective irradiation of the signal at δ 2.96 caused a polarization transfer to C-11c and C-6a (δ 133.2) and was attribued at H-5. In a same manner, selective irradiation of the signal at δ 8.76 (H-1) showed the transfer of C-11b (116.1 ppm) and C-4a (δ 155.8), while the selective irradiation of the signal at δ 2.72 caused a polarization transfer to C-4a and C-11b and was attributed at H-6. For this compound, the signal of H-1 was not as deshielded as for compound **(12)**. A possible explanation resides in the twisted conformation of this molecule which would limit the deshielding effect of the carbonyl group on H-1.

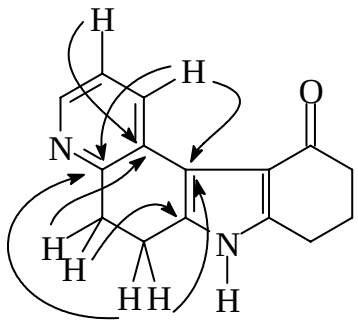


Figure 1 : Long range ^{1}H-^{13}C NMR correlations of compound **(13)** observed from INEPT spectrum

An alternative method was then investigated which consisted to generate in situ an halogenated species **(10,11)**. For this purpose, the enaminones **(8**, **9)** were irradiated with 10 equivalents of iodine in acetonitrile (method A). In these conditions, the formation of α-iodoenaminones **(10**, **11)** occurred and was controlled by thin layer chromatography and ^{1}H-NMR spectrum. After two hours, triethylamine was added, and these species finally gave **12**, **13** in 70 and 36% yields respectively (Table 2). When performing these reactions directly in presence of triethylamine (method B), the intermediary iodoenaminones **(10**,**11)** were not detected and **12**, **13** were obtained (75 and 42% yields respectively).

Table 2 : Irradiation of enaminones (8) and (9)

Entry	Conditions	Substrate	Reaction time	Yield (%) of compound					
				8	**10**	**12**	**9**	**11**	**13**
1	method A	**8**	**2 h**	50*	35*	15*	-	-	-
			$(C_2H_5)_3N$ 3 h more	0	0	70	-	-	-
2	method B	**8**	**4 h**	0	0	75	-	-	-
3	method A	**9**	**2 h**	-	-	-	70*	30*	0*
			$(C_2H_5)_3N$ 3 h more	-	-	-	60	0	36
4	method B	**9**	**4 h**	-	-	-	52	0	42

method A : hυ, I_2, CH_3CN, 2 h, then addition of $(C_2H_5)_3N$ and 3 h more

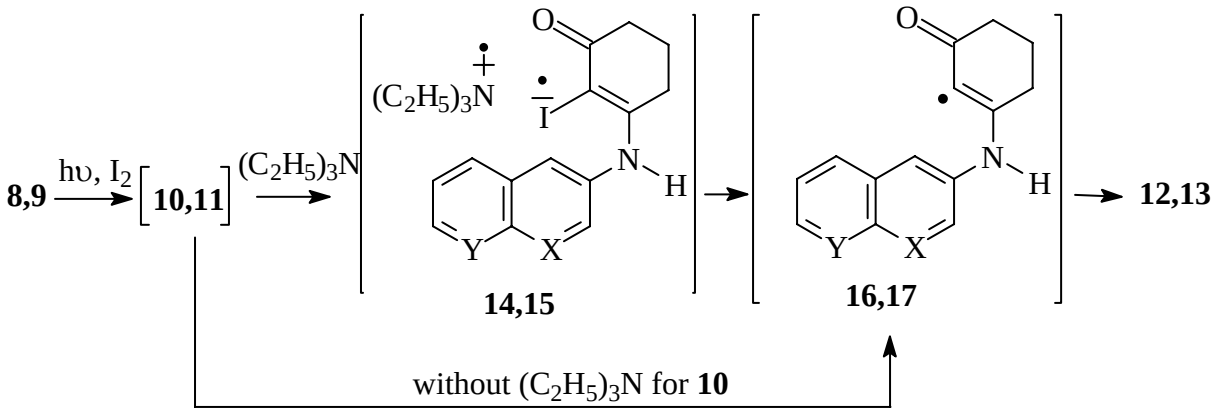
method B : hυ, I_2, $(C_2H_5)_3N$, CH_3CN, 5

*determined from ^{1}H-NMR spectra of the crude mixtures

Since triethylamine is well known to be an electrondonor in photoinduced electron transfert (PET),[12] and since α-iodoenaminones have already been described by Sha to undergo such electron transfer,[13] we can reasonably suppose that such a mechanism was implicated in the cyclization of **10**, **11** as illustrated in Scheme 4. This hypothesis is well supported when considering the reactivity of **9**, which cylization under triethylamine mediated PET conditions led to compound (**13**), while without triethylamine no cyclization occurred.

Scheme 4

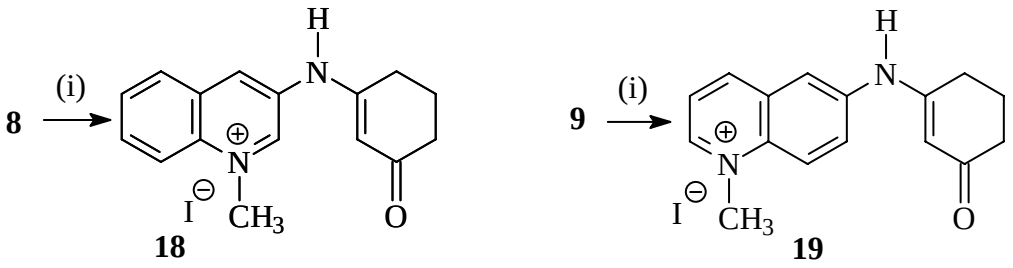
Proposed general pathway for the formation of 12,13



Finally, when compared to the first method, interest of this last method resides in the efficient one pot synthesis of angular tetracyles **(12**, **13)** from the enaminones **(8**, **9)** through a radical process. In addition, when compared to the photocyclization of the corresponding tertiary enaminones, no change in the regioselectivity was observed. In an attempt to change the regioselectivity of these photocyclizations, we

investigated the reactivity of quaternary ammonium salts of the quinoline nucleus **(18**, **19)**. Their preparation was expected to be performed directly by a regioselective *N*-alkylation of **8** and **9** since the nitrogens of the enaminone part were poor nucleophilic species and needed to be firstly deprotonated before reacting with alkyl halides.[8] These two quinolinium salts were effectively obtained by treatment of **8,9** by methyl iodide in acetronitrile in 66 and 63% yields, and their structures well established by NMR spectral experiments (^{1}H COSY, HMQC, HMBC)

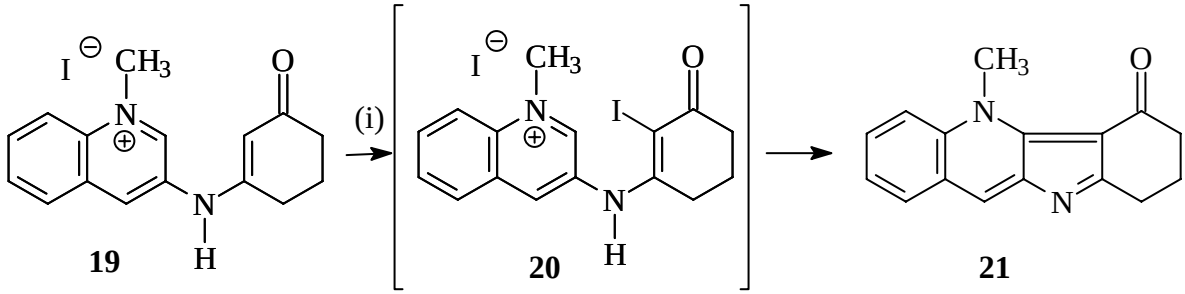
Scheme 5



(i) CH_3I, CH_3CN, reflux 2 h

Iodination of **18** and **19** was then investigated with $BTMAICl_2$. Curiously no α-iodoenaminones could be isolated in these reactions, compound **(19)** led only to a degradation mixture, while **18** gave the unexpected tetrahydro derivative of cryptolepine **(21)** in 12% yield (Scheme 6). Formation of this tetracycle was expected to be the result of a spontaneous cyclization of a highly reactive intermediary α-iodoenaminone **(20)**.

Scheme 6



(i) $BTMAICl_2$,CH_2Cl_2/CH_3OH (2:1), $NaHCO_3$

Structural determination of compound **(21)** was performed on the basis of NMR spectral data. The most important assignment informations were acquired from HMBC spectrum. The most convenient starting point for the assignment was the hydrogen H-11 (Figure 2). Connectivities were observed from H-11 (δ 8.22) to the carbons resonating at 144.9, 135.8 and 129.9. The carbon resonating at 144.9 also showed connectivities with the proton of the *N*-methyl group and was assigned as C-5a. The carbon resonating at 135.8 also exhibited connectivities with the double triplet at δ 7.70 (H-3 determined from COSY, HMQC

and HMBC spectra) and the proton of the *N*-methyl group, and was assigned as C-4a. All ^{1}H and ^{13}C signals were then unambigously assigned.

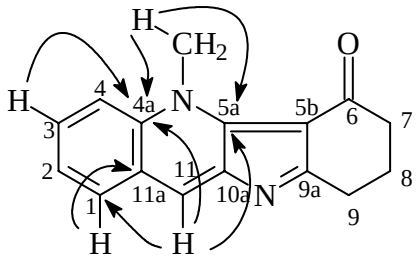


Figure 2 : Long range ^{1}H-^{13}C NMR correlations of compound **(21)** observed from HMBC spectrum.

Synthesis of **21** was then investigated directly from **18** by photochemical process in presence of iodine (Table 3). The first condition tested was without $(C_2H_5)_3N$ in order to isolate the presumaly intermediary iodo derivative **(20)**. In contrast with the results observed with **8** and **9**, compound **(20)** was not isolated and **21** was obtained in 32% yield. This yield was optimized at 61% performing the reaction with $(C_2H_5)_3N$. Finally when irradiating **18** without iodine, no reaction occurred indicating that the cyclization probably occurred through the iodo species **(20)**.

Table 3: Irradiation of enaminone (18)

Conditions	Yield (%)of compds
I_2/CH_3CN/ 2 h	**18** (43) and **21** (32)
$I_2/CH_3CN/(C_2H_5)_3N$/45 min	**21** (61)
$CH_3CN/(C_2H_5)_3N$/2 h	**18** (100)

CONCLUSION

In this paper, we have reported the application of heterocyclic enaminones derived from quinolines in the synthesis of indoloquinolines and pyridocarbazoles derivatives. By this methodology the cryptolepine alkaloid analog **(21)** was prepared as an interesting synthon for the preparation of compounds of biological interest.

EXPERIMENTAL

Melting points were determined on a Büchi capillary melting point apparatus and are not corrected. Elemental analysis was perfomed by Microanalytical Center, ENSCM, Montpellier. Spectral measurements were taken

using the following instruments: ^{1}H-NMR spectra were taken on Brüker AC 100 or WM 360 or EM 400WB; ^{13}C-NMR spectra were obtained at 26°C with proton noise decoupling at 25 MHz with a Brüker AC 100 instrument. Chemical shifts are expressed relative to residual chloroform. MS spectra were recorded on a LKB 2091 spectrometer at 15eV [θ(source)=180°C]. Dichloromethane was dried over activated alumina and distilled from calcium hydride.

Typical procedure for iodination of enaminones with $BTMAICl_2$: 9.0 Mmol of the appropriate enaminone **(8,9)**, 3 g (9.0 mmol) of $BTMAICl_2$, and 5 g (56 mmol) of $NaHCO_3$ were added to an anhydrous solution of CH_3OH-CH_2Cl_2 (60 mL-120 mL), and the mixture was stirred under a nitrogen stream for 30 min at rt. The resulting mixture was filtered and the solvents were evaporated to give the crude 2-halogenoenaminones **(10,11)** which were then purified by chromatography on alumine eluted with dichloromethane.

Typical procedure for irradiation of enaminones. A medium pressure mercury lamp was used (150W, TQ 150) with a Pyrex reactor, allowing emissions lower than 290 nm. A solution of the appropriate enaminone (1.6 mmol) in 400 mL of freshly distilled and degased appropriate solvent with or without 10 equivalents of triethylamine was irradiated. The solvents were then evaporated under reduced pressure. Purifications were performed by flash chromatography of the residual oils on silica gel using a CH_2Cl_2/CH_3OH mixture as eluent (95/5).

2-Iodo-3-[3-Quinolinylamino]cyclohex-2-en-1-one (10) : this compound was obtained in 91% yield from **8;** mp 140-142°C (recrystallization solvent: CH_2Cl_2); ^{1}H-NMR ($CDCl_3$, 100 MHz) δ 1.96 (m, 2H, H-5), 2.58 (m, 4H, H-4 and H-5), 7.42 (br s, NH)7.45-8.10 (m, 5H), 8.72 (d, *J* = 2.0 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 25 MHz) δ 21.7, 28.4, 36.2, 80.4, 127.3, 127.5, 127.6, 129.1, 129.6, 130.7, 131.1, 146.1, 148.2, 162.5, 190.1. Anal. Calcd for $C_{15}H_{13}N_2OI$: C 49.47, H 3.59, N 7.69. Found : C 49.31, H 3.61, N 7.56.

2-Iodo-3-[6-Quinolinylamino]cyclohex-2-en-1-one (11) : This compound was obtained in 91% yield from **8;** brown oil; ^{1}H-NMR ($CDCl_3$, 100 MHz) δ 2.10 (m, 2H, H-5), 2.58 (m, 4H, H-4 and H-6), 7.40-7.58 (m, 4H), 8.03-8.18 (m, 2H), 8.87 (d, *J* = 3.7 Hz); ^{13}C-NMR ($CDCl_3$, 25 MHz) δ 21.4, 28.2, 35.9, 79.2, 121.5, 122.4, 127.3, 127.6, 129.5, 134.9, 135.7, 145.1, 149.6, 162.8, 189.9. Anal. Calcd for $C_{15}H_{13}N_2OI$: C 49.47, H 3.59, N 7.69. Found : C 49.52, H 3.61, N 7.71

(*7H*)-8,9,10,11-tetrahydroindolo[2,3-*c*]quinolin-11-one (12) : This compound was obtained from **10** according to the typical procedure; mp 144-146 °C (recrystallization solvent: ethyl acetate); ^{1}H-NMR (DMSO-d_6, 100 MHz) δ 2.13 (m, H-9), 2.60, t, *J* = 6.2 Hz, H-10), 2.90 (t, *J* = 5.8 Hz, H-8), 7.56 (m, 2H), 8.76 (s, H-6), 9.67 (dd, *J* = 5.9 and 3,7 Hz, H-1); ^{13}C-NMR ($CDCl_3$, 25 MHz) δ 22.9, 23.3, 38.9, 114.3, 123.2, 125.0, 125.3, 126.5, 127.6, 129.1, 129.3, 137.7, 143.8, 153.3, 192.9. Anal. Calcd for $C_{15}H_{12}N_2O$: C 76.25, H 5.12, N 11.85. Found : C 76.19, H 5.23, N 11.79.

This compound was also obtained following the alternative procedure as follow: a solution of enaminone **(8)** (500 mg, 2 mmol), iodine (500 mg, 2 mmol), triethylamine (4 mL) in 400 mL of acetonitrile was irradiated for 5 h in a pyrex filtered reactor. After evaporation of the solvent, the residue was neutralized with a 10% solution of $Na_2S_2O_3$, and then extracted with dichloromethane. Organic layers wered dried over sodium sulfate, evaporated under vacuo and the crude mixture was purified by by flash chromatography on silica gel using a CH_2Cl_2/CH_3OH mixture as eluent (95/5).

5,6,8,9,10,11-hexahydropyrido[2,3-*c*]carbazol-11-one (13): This compound was obtained from **11** according to the typical procedure; mp 264-266°C (recrystallization solvent: ethyl acetate); ^{1}H-NMR (CD_3OD, 400MHz) δ 2.00, (q, 2H, *J* = 6.2 Hz, H-9), 2.38 (t, 2H, *J* = 6.2 Hz, H-10), 2.72 (m, 4H, H- 6 and H-8), 2.96 (t, 2H, *J* = 8.3 Hz, H-5), 7.05 (dd, 1H, *J* = 7.8 and 4.9 Hz, H-2), 7.94 (dd, *J* = 4.9 and 1.3 Hz, H-3), 8.76 (dd, *J* = 7.8 and 1.3 Hz, H-1); ^{13}C-NMR (CD_3OD, 100 MHz) δ 21.9, 24.3, 25.2, 32.9, 40.2, 116.1, 118.1, 123.6, 130.8, 133.2, 134.8, 145.0, 148.3, 155.8, 197.0. Anal. Calcd for $C_{15}H_{14}N_2O$: C 75.60, H 5.92, N 6.71. Found : C 75.56, H 5.87, N 6.72.

This compound was also obtained from **9** following the same alternative procedure used for the preparation of **12**

3-(3-ketocyclohexen-1-yl)amino-1-methylquinolinium iodide (18) : To a stirred solution of enaminone **8** (500 mg, 2 mmol) in acetonitrile (50 mL) was 1.42 g (10 mmol) of methyl iodide. The resulting mixture was stirred for 12 h. The precipitate which appeared was then filtered and washed with cold acetonitrile to give **18** (66%); mp 210-220°C (recrystallization solvent: methanol); ^{1}H-NMR (CD_3OD, 400 MHz) δ 1.97 (m, 2H, H-5), 2.25 (t, 2H, *J* = 6.8 Hz, H-6), 2.62 (t, *J* = 6.0 Hz, H-4), 4.62 (s, 3H, N(CH_3)), 5.60 (s, H-2), 8.00 (t, *J* = 7.9 Hz, H-13), 8.15 (dt, *J* = 7.9 and 1.4 Hz, H-12), 8.44 (m, 2H, H-11 and H-14), 8.93, (d, *J* = 1.9 Hz, H-15), 9.48 (d, *J* = 1.9 Hz, H-9); ^{13}C-NMR (CD_3OD, 100 MHz) δ 21.3, 28.1, 36.5, 45.6, 100.5, 118.9, 129.5, 130.1 (2C), 133.6, 133.7, 135.4, 136.04, 146.9, 160.8, 196.6.

6-(3-ketocyclohexen-1-yl)amino-1-methylquinolinium iodide (19) ; This compound was obtained in 63% yield by the same procedure used for the preparation of **18**; mp 220-222°C (recrystallization solvent: methanol); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.96 (m, 2H, H-5), 2.26 (t, 2H, *J* = 6.4 Hz, H-6), 2.63 (t, 2H, *J* = 5;7 Hz, H-4), 4,59 (s, 3H, N(CH_3)), 5.77 (s, H-2), 8.07 (m, 2H, H-9 and H-13), 8.13 (d, *J* = 13.0 Hz, H-10), 9.21 (d, *J* = 8.42 Hz, H-14), 9.33 (d, *J* = 5.5 Hz, H-12), 9.42 (s, NH); ^{13}C-NMR (DMSO-d_6, 100 MHz) δ 21.3, 28.6, 36.5, 45.2, 101.1, 117.1, 120.5, 122.4, 130.5 (2C), 134.7, 140.6, 145.7, 159.7, 196.8.

5-Methyl-6,7,8,9-tetrahydroindolo[3,2-*b*]quinolin-6-one (21); A solution of enaminone **(18)** (500 mg, 1.27 mmol), iodine (500 mg, 2 mmol), triethylamine (4 mL) in 400mL of acetonitrile was irradiated for 45 min in a pyrex filtered reactor. After evaporation of the solvent, the residu was neutralized with a 10% solution of $Na_2S_2O_3$, and then extracted with dichloromethane. Organic layers were dried over sodium sulfate, evaporated under vacuo and the crude mixture was purified by by flash chromatography on neutral alumina using a $(C_2H_5)_2$/CH_3OH mixture as eluent (95/5). mp 206-208°C (recrystallization solvent: methanol); ^{1}H-NMR ($CDCl_3$, 400MHz) δ 2.09 (m, 2H, H-8), 2.60 (t, 2H, *J* = 6.8 Hz, H-7), 3.07 (t, 2H, *J* = 6.4 Hz, H-9), 4.91 (s, 3H, N(CH_3)), 7.47 (t, *J* = 7.2 Hz, H-2) 7.70 (dt, *J* = 7.2 and 1.4 Hz, H-3), 7.85 (d, *J* = 7.2 Hz, H-4), 7.91 (dd, *J* = 7.2 and 1.4 Hz, H-1), 8.22 (s, H-11); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 22.6, 29.5, 41.9, 107.2, 115.7, 123.9, 124.1, 126.4, 129.9, 130.1, 135.8, 144.9, 145.3, 176.8, 192.6. Anal. Calcd for $C_{16}H_{14}N_2O$: C 76.77, H 5.63, N 11.19. Found : C 76.68, H 5.71, N 11.02.

REFERENCES AND NOTES

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