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REACTIVITY OF HETEROCYCLIC ENAMINONES: REGIOSELECTIVE SYNTHESIS OF POLYFUSED INDOLONES

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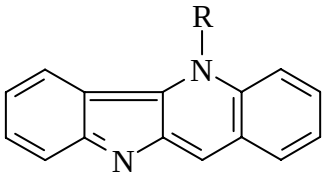
Abstract- Photocyclization of heterocyclic enaminones to give partial hydrogenated derivatives of indolo[2,3-*c*]quinoline, pyrido[2,3-*c*]carbazole, and pyrido[4,3-*a*]carbazole is described. In addition, 3-[(5'-quinolinyl)-benzylamino]cyclohex-2-en-1-one and 3-[(8'-quinolinyl)benzylamino]cyclohex-2-en-1-one undergo C-N bond cleavages and a benzyl migration on the C-6 and C-7 positions respectively.

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 interests. 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

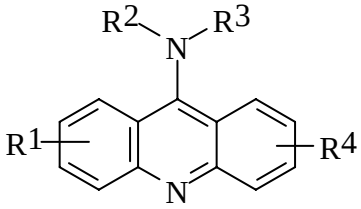
parent mepacrine type compounds (**3**).[4] As a part of our program concerning the elaboration of analogs of natural products,[5] we are interested in the chemistry as well as in the biological activities of such modified heterocyles. Our methodology resides in the photocyclizations of enaminones[6] derived from diverses amino-heterocyles to give polyfused indolones. In this context, we had previously described the reactions of enaminones respectively derived from 3-aminopyridines[7] and from 2-aminopyridines[8] to give the corresponding pyridoindolones as synthetic intermediates for the synthesis of analogs of murrayaquinones.[9] Poor regioselectivities were found in these reactions. As a continuation of these studies, we now report the regioselective synthesis of partial hydrogenated polyfused indolones which can be further implicated in the synthesis of a new class of antiplasmodial pyridocarbazoles and indoloquinolines.

Scheme 1

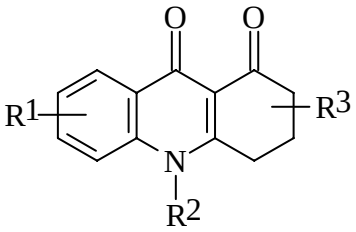


1 quindoline R = H

2 cryptolepine R= CH_3



3 "mepacrine" type

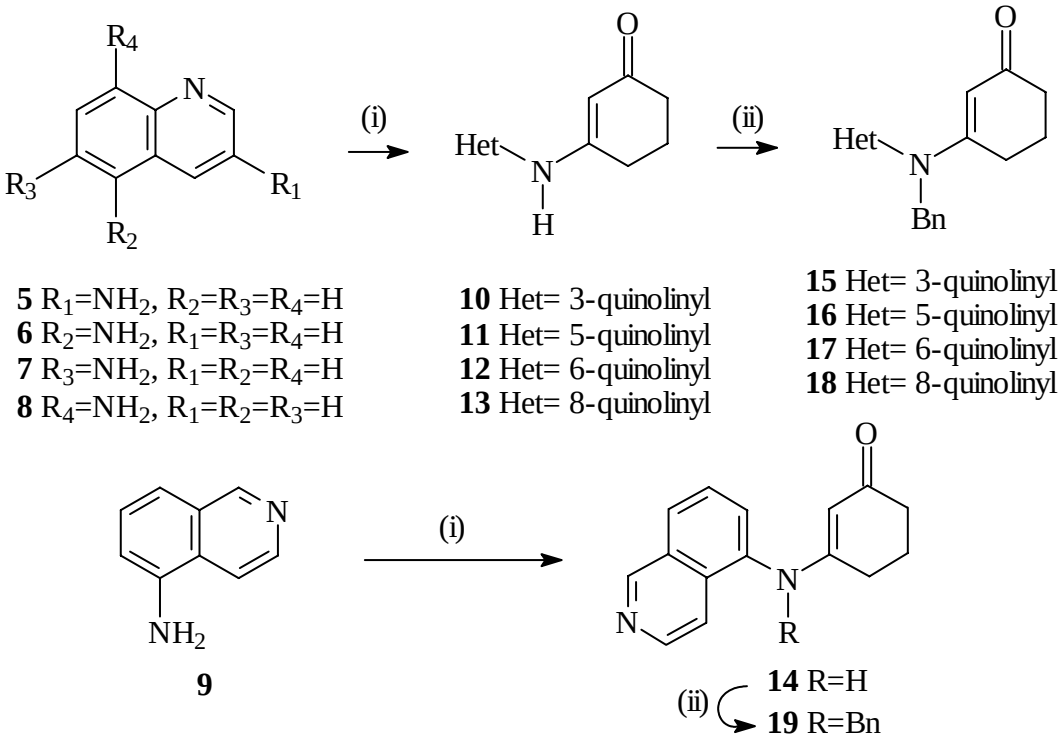


4 "floxacrine" type

Results and discussion

The required *N*-[quinolinyl]enaminones (**10, 11, 12,** and **13**)and *N*-[isoquinolinyl]enaminone (**14),** were obtained with good yields from the corresponding 3-amino-, 5-amino-, 6-amino-, 8-aminoquinolines, and 5-aminoisoquinoline (**5, 6, 7, 8** and **9**) respectively by condensation with 1,3-cyclohexanedione in refluxing toluene according to our previous methodology.[7,8] Subsequent protection of the nitrogen atom was achieved by treatment of the secondary enaminones with sodium hydride in refluxing toluene followed by addition of 1.1 equivalent of benzyl chloride to give **15, 16, 17, 18,** and **19** (Scheme 2).

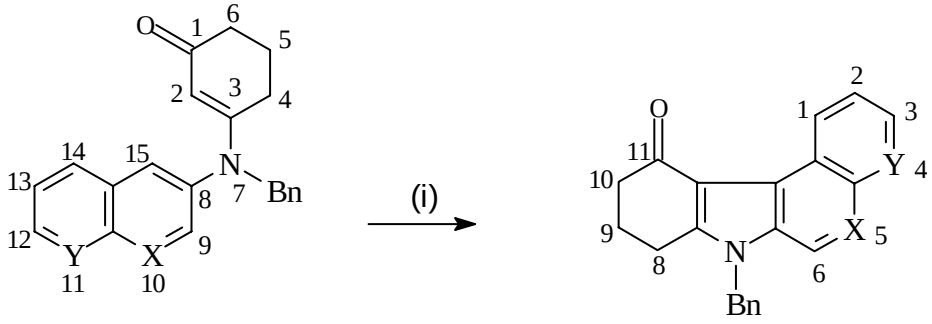
Scheme 2



(i) 1,3-cyclohexanedione, toluene, p-TSA, reflux
(ii) a: NaH, toluene b: $C_6H_5CH_2Cl$

Photochemical studies: **Irradiation of tertiary enaminones** (**15 and 17).** The reactions were conducted by irradiating with "black light" (see experimental section) in a Pyrex immersion well apparatus. Optimal conditions were obtained with methanol as a solvent. Under these conditions, compounds (**15** and **17**) led to regioselectives reactions on the C-15 positions giving respectively **20** and **21** with 75 and 60% yields (Scheme 3).

Scheme 3

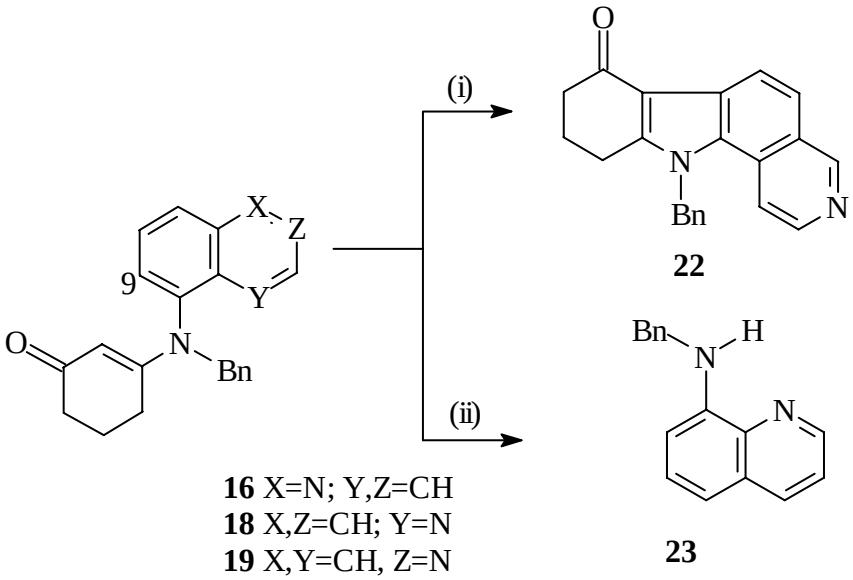


reagents and conditions : hυ ("black light", Pyrex), MeOH -10 h for **15**
-14 h for **17**

Position of cyclization on the C-15 position of **15** to give **20** was easily determined by ^{1}H-NMR which showed a characteristic singlet of H-6 at δ 8.86, while the signal of H-1 was shifted downfield (δ 9.92, multiplet) by the proximity of the carbonyl group. In the case of compound (**21**), a similar deshielding effect was observed on H-1 which appeared as a doublet at δ 10.44 (J = 8.5 Hz).

Irradiation of enaminones (16, 18 and 19): In order to appreciate the influence of the position of the intracyclic nitrogen atom on such reactions, we were interested in the reactivity of the enaminones (**16, 18** and **19**)**.** While **16** and **18** were recovered unchanged under irradiation in a Pyrex reactor, compound (**19**) led to the formation of the pyridocarbazole (**22**) (best result obtained in acetonitrile by irradiating in the range 290-350 nm (maximum at 313 nm)). Change of the solvents and wavelenght was no more effective for **16**, while in the case of **18,** irradiation in methanol in the range 290-350 nm led to a reductive cleavage of the C-N bond to give **23** [13] (scheme 4).

Scheme 4



16 X=N; Y,Z=CH
18 X,Z=CH; Y=N
19 X,Y=CH, Z=N

(i) Z= N, hυ, MeOH, 10 h, 365 nm, ("black light,Pyrex)
(ii) Y= N, hυ, MeOH, 2 h, 313 nm (Pyrex)

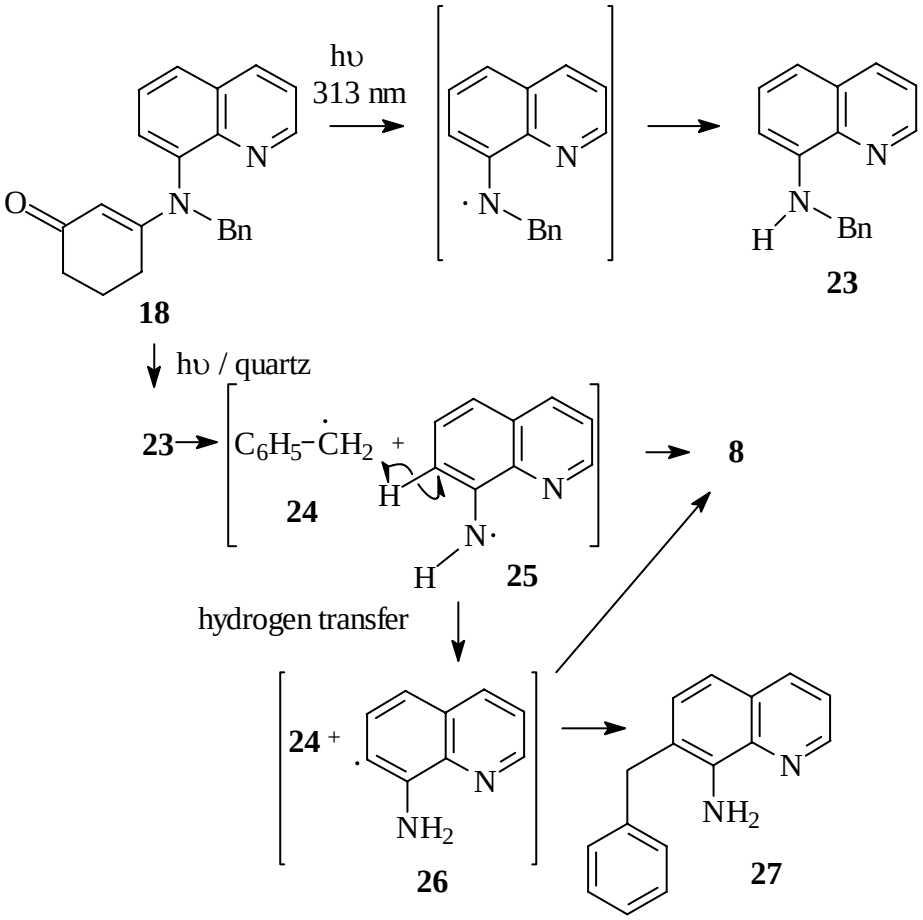
These results clearly indicate the dramatic effect of the presence of a nitrogen atom adjacent to the benzene ring, while in the case of the isoquinoline ring, the cyclization occurred in a satisfactory manner (yield 65%). Such differences of reactivity are not surprising since it has been demonstrated in the benzene series itself, that yields of photocyclizations can be greatly dependant of the nature, and the position of substituents on the aromatic ring.[14] An interesting problem arised with the differences of reactivity observed for **16** and **18** and with the unexpected formation of compound (**23**) through a $C_{(enaminone)}$-N bond cleavage. With respect to the general pathways described for the photolysis of tertiary

amines,[15] we can reasonably suppose that such cleavage occurred through a radical process. In the case of **16**, no reaction was found at 313 nm, while in the case of **18**, photoinduced homolysis of $C_{(enaminone)}$-N bond occurred, indicating that the strengh of such bond is greatly affected by the position of the intracyclic nitrogen atom. In a last attempt, reactions of **16** and **18** were investigated at 254 nm. When compound (**18**) was irradiated for 30 min at 254 nm, 8-aminoquinoline (**8**) was isolated admixed with **23** and 8-amino-7-benzylquinoline (**27**) (Scheme 5).

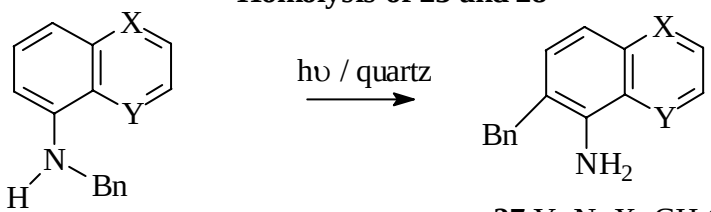
Scheme 5

General reaction pathways for homolysis of *N*-benzyl derivatives

Homolysis of 18



Homolysis of 23 and 28



23 Y=N, X=CH
28 X=N, Y=CH

27 Y=N, X=CH (32%)
(admixed with **8** (9%))
29 Y=N, X=CH (6%)
(admixed with **6** (26%))

Formation of **27** occurred through homolysis of the $C_{(benzyl)}$-N bond to give the intermediary species (**24**) and (**25**). Radical species (**25**) could further undergo a photoinduced 1,3-hydrogen transfer to give the radical species (**26**) which, by coupling with **24**, gave compound (**27**). In this pathway, 8-aminoquinoline could be produced either through **25** and **26**. This result was confirmed by studying the homolysis of **23** (obtained by *N*-benzylation of **8**) which led to a mixture of **27** (major product) and **8**. These results are in good agreement with those obtained recently by Siskos and co-workers[16] and earlier by Ogata and co-workers[17] who described the photoinduced homolysis of *N*-benzylaniline at 254 nm to give such an *ortho* (or *para*) benzyl migration. In the case of **16** such photolysis did not occurred, and starting material was recovered unchanged, while in the same conditions, the *N*-benzyl derivative (**28**)[18] (obtained from **6** by *N*-benzylation) underwent a $C_{(benzyl)}$-N bond cleavage to give **6** as the major compound. In this case, benzyl migration occurred on C-6 position to give **29** as the minor compound. These results indicate that the strengh of the $C_{(benzyl)}$-N bond is greatly increased by the presence the enaminone moiety.

Conclusion

Formation of fused indolones from 3, 6-aminoquinolines and 5-aminoisoquinoline heterocycles by means of photocyclization of enaminones is a remarkable process occuring with a total regioselectivity in the crucial step. In addition, when the electrocyclic ring closure did not occur, a photoinduced homolysis of $C_{(enaminone)}$-N bond was observed, and the strengh of such bond is found to be dependent of the nature of the heterocycle. Furthermore, the strengh of $C_{(benzyl)}$-N bond is greatly increased by the presence of the enaminone moiety, and photoinduced homolysis of such bond is only permitted after an initial $C_{(enaminone)}$-N bond cleavage.

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.

3-[3'-Quinolinylamino]cyclohex-2-en-1-one (10) : A solution of 3-aminoquinoline (**5**) (1 g, 7.7 mmol), 1,3-cyclohexanedione (0.95 g, 8.46 mmol), and *p*-toluenesulfonic acid monohydrate (70 mg, 0.39 mmol) in 100 mL of anhydrous toluene was refluxed with a Dean-Stark for 3 h. After cooling, the solution was

basified (10% Na_2CO_3) and extracted with dichloromethane. Organic layers were dried over sodium sulfate and evaporated *in vacuo*. Recrystallisation of the yellow paste from ethanol gave 1.28 g (77%) of **10** ; mp 171-173°C ; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.92 (m, 2 H), 2.28 (t, 2 H, *J* = 6.4 Hz), 2.53 (t, 2 H, *J* = 6.0 Hz), 5.65 (s, 1 H), 7.41 (t, 1 H, *J* = 7.3 Hz), 7.56 (m, 2 H), 7.83 (d, 1 H, *J* = 1.9 Hz), 7.93 (d, 1 H, *J* = 8.4 Hz), 8.66 (d, 1 H, *J* = 1.9 Hz), 8.80 (s, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.6, 29.2, 36.5, 99.6, 127.2, 127.3, 127.5, 127.7, 128.8 (2 carbons), 132.2, 145.1, 147.2, 163.3, 198.8. Anal. Calcd for $C_{15}H_{14}N_2O$: C 75.60, H 5.93, N 11.76. Found : C 75.53, H 5.99, N 11.71.

3-[5'-Quinolinylamino]cyclohex-2-en-1-one (11): This compound was obtained in 61% yield from 5-aminoquinoline (**6**) according to the general procedure used for the synthesis of **10**; mp 118-120°C; ^{1}H NMR ($CDCl_3$, 100 MHz) δ 1.94 (m, 2 H) 2.19 (t, 2 H, *J* = 6.2 Hz), 2.56 (t, 2 H, *J* = 4.65 Hz), 4.85 (s, 1 H), 7.27 (m, 2 H), 7.51 (t, 1 H, *J* = 7.9 Hz), 7.88 (d, 1 H, *J* = 8.3 Hz), 8.14 (d, 1 H, *J* = 8.3 Hz), 8.75 (m, 2 H); ^{13}C NMR ($CDCl_3$, 25 MHz) δ 21.6, 24.1, 35.9, 99.0, 121.1, 124.4, 124.7, 127.8, 128.9, 131.6, 134.1, 148.1, 150.2, 166.1, 198.3. Anal. Calcd for $C_{15}H_{14}N_2O$: C 75.60, H 5.93, N 11.76. Found: C 75.67, H 6.01, N 11.63.

3-[6'-Quinolinylamino]cyclohex-2-en-1-one (12): This compound was obtained in 80% yield from 6-aminoquinoline (**7**) according to the general procedure used for the synthesis of **10**; brown paste; ^{1}H NMR ($CDCl_3$, 100 MHz) δ 1.89 (m, 2 H), 2.27 (t, 2 H, *J* = 5.8 Hz), 2.51 (t, 2 H, *J* = 5.4 Hz), 5.60 (s, 1 H), 7.10-7.38 (m, 3 H), 7.87 (m, 2 H), 8.65 (d, 1 H, *J* = 5.0 Hz), 8.94 (s, 1 H); ^{13}C NMR ($CDCl_3$, 25 MHz) δ 21.3, 28.8, 35.9, 98.8, 119.3, 121.3, 126.1, 128.2, 129.3, 135.6, 136.6, 144.7, 149.0, 163.5, 199.0. Anal. Calcd for $C_{15}H_{14}N_2O$: C 75.60, H 5.93, N 11.76. Found C 75.81, H 5.85, N 11.82.

3-[8'-Quinolinylamino]cyclohex-2-en-1-one (13): This compound was obtained in 59% yield from 8-aminoquinoline (**8**) according to the general procedure used for the synthesis of **10**; mp 115-117°C; ^{1}H NMR ($CDCl_3$, 100 MHz) δ 1.90 (m, 2 H), 2.33 (t, 2 H, *J* = 5.7 Hz), 2.53 (t, 2 H, *J* = 5.2 Hz), 5.91 (s, 1 H), 7.25 (m, 3H), 7.45 (m, 1 H), 7.95 (d, 1 H, *J* = 8.3 Hz), 8.62 (d, 1 H, *J* = 3.7 Hz), 8.72 (s,1 H); ^{13}C NMR ($CDCl_3$, 25 MHz) δ 20.7, 25.7, 35.5, 100.9, 115.7, 120.4, 120.7, 125.3, 127.2, 134.2, 135.2, 138.3, 147.2, 158.2, 197.2. Anal. Calcd for $C_{15}H_{14}N_2O$: C 75.60, H 5.93, N 11.76. Found : C 75.71, H 5.79, N 11.70.

3-[5'-Isoquinolinylamino]cyclohex-2-en-1-one (14): This compound was obtained in 78% yield from 5-aminoisoquinoline (**9**) according to the general procedure used for the synthesis of **10**; mp 219-221°C; ^{1}H NMR ($CDCl_3$, 100 MHz) δ: 1.95 (m, 2 H), 2.22 (t, 2 H, *J* = 5.7 Hz), 2.59 (t, 2 H, *J* = 5.4 Hz), 4.88 (s, 1

H), 7.39-7.45 (m, 2 H), 7.60 (d, 1 H, *J* = 5.9 Hz), 7.78 (dd, 1 H, *J* = 6.0 and 3.2 Hz), 8.39 (d, 1 H, *J* = 5.9 Hz), 8.74 (br s, 1 H), 9.16 (s, 1 H); ^{13}C NMR ($CDCl_3$, 25 MHz) δ 21.7, 28.6, 36.2, 99.2, 115.6, 126.3, 126.8, 128.0, 128.9, 131.7, 133.3, 152.4, 165.3, 198.0. Anal. Calcd for $C_{15}H_{14}N_2O$: C 75.60, H 5.93, N 11.76. Found : C 75.51, H 5.79, N 11.71.

3-[(3'-Quinolinyl)benzylamino]cyclohex-2-en-1-one (15): Compound (**10**) (0.5 g, 2.1 mmol) was added to a suspension of sodium hydride (85 mg, 2.1 mmol, 60% in mineral oil) in anhydrous toluene (50 mL). The mixture was refluxed for 2 h and cooled to rt. Benzyl chloride (265 mg, 2.1 mmol) was then added and the mixture was refluxed for 2 h. Solvent was removed and the residue washed with water. After extraction with dichloromethane, the organic layers were dried over sodium sulfate and evaporated *in vacuo*. The crude product was chromatographed on silica gel using an ether/methanol mixture (85/15) as eluent to give 0.62 g (90%) of **15** as a yellow oil ; ^{1}H NMR ($CDCl_3$, 100 MHz) δ 2.00 (m, 2 H), 2.36 (m, 4 H), 4.97 (s, 2 H), 5.49 (s, 1 H), 7.30 (m, 5 H), 7.57-7.82 (m, 3 H), 7.96 (d, 1 H, *J* = 2.2 Hz), 8.13 (d, 1 H, *J* = 8.4 Hz), 8.75 (d, 1 H, *J* = 2.2 Hz); ^{13}C NMR ($CDCl_3$, 25 MHz) δ 21.6, 27.8, 35.3, 55.8, 102.0, 126.1 (2 carbons), 126.7, 126.8, 127.0 (2 carbons), 128.0 (2 carbons), 128.4, 129.2, 132.6, 135.2, 136.8, 145.7, 149.4, 163.8, 196.6. Anal. Calcd for $C_{22}H_{20}N_2O$: C 80.45, H 6.14, N 8.53. Found : C 80.29, H 6.01, N 8.39.

3-[(5'-Quinolinyl)benzylamino]cyclohex-2-en-1-one (16): This compound was obtained in 82% yield from **11** according the general procedure used for the synthesis of **15** ; (brown paste); ^{1}H NMR ($CDCl_3$, 100 MHz) δ 1.94 (m, 2 H), 2.34 (m, 4 H), 4.63 (d, 1 H, *J* = 15.7 Hz), 5.19 (d, 1 H, *J* = 15.7 Hz), 5.57 (s, 1 H), 7.17-7.70 (m, 8 H), 7.93 (m, 3 H), 8.97 (d, 1 H, *J* = 3.0 Hz); ^{13}C NMR ($CDCl_3$, 25 MHz) δ 21.9, 27.5, 35.6, 56.1, 100.9, 121.9, 125.4, 126.7, 127.3 (2 carbons), 128.3 (3 carbons), 128.7, 129.6, 130.6, 135.4, 139.7, 148.7, 150.6, 165.2, 197.5. Anal. Calcd for $C_{22}H_{20}N_2O$: C 80.45, H 6.14, N 8.53. Found : C 80.54, H 6.11, N 8.63.

3-[(6'-Quinolinyl)benzylamino]cyclohex-2-en-1-one (17): This compound was obtained in 84% yield from **12** according to the general procedure used for the synthesis of **15** ; (brown oil); ^{1}H NMR ($CDCl_3$, 100 MHz) δ 1.91 (m, 2 H), 2.32, (m, 4 H), 4.91 (s, 2 H), 5.41 (s, 1 H), 7.22-7.59 (m, 8 H), 8.07 (d, 2 H, *J* = 8.5 Hz), 8.85 (d, 1 H, *J* = 3.7 Hz); ^{13}C NMR ($CDCl_3$, 25 MHz) δ 22.2, 28.3, 35.7, 56.4, 101.9, 121.5, 125.5, 126.5 (2 carbons), 127.2, 128.0, 128.4 (2 carbons), 129.0, 130.7, 135.6, 135.7, 141.8, 146.3, 150.6, 164.5, 197.5. Anal. Calcd for $C_{22}H_{20}N_2O$: C 80.45, H 6.14, N 8.53. Found : C 80.48, H 6.22, N 8.38.

3-[(8'-Quinolinyl)benzylamino]cyclohex-2-en-1-one (18): this compound was obtained in 72% yield from **13** according to the general procedure used for the synthesis of **15** ; (brown oil); ^{1}H NMR ($CDCl_3$,

100 MHz) δ 1.89 (m, 2 H), 2.29 (m, 4 H), 5.06 (s, 2 H), 5.60 (s,1 H), 7.31 (m, 5 H), 7.40 (m, 3 H), 7.87 (dd, 1 H, *J* = 6.8 and 2.2 Hz), 8.27 (d, 1 H, *J* = 8.3 Hz), 9.04 (d, 1 H, *J* = 3.2 Hz); ^{13}C NMR ($CDCl_3$, 25 MHz) δ 21.6, 27.4, 35.5, 56.1, 100.1, 121.3, 125.5, 126.5 (3 carbons), 127.8 (3 carbons), 129.0, 129.21, 135.9, 136.1, 140.4, 143.6, 150.2, 165.8, 196.7. Anal. Calcd for $C_{22}H_{20}N_2O$: C 80.45, H 6.14, N 8.53. Found : C 80.61, H 5.99, N 8.51.

3-[(5'-Isoquinolinyl)benzylamino]cyclohex-2-en-1-one (19): This compound was obtained in 86% yield from **14** according to the general procedure used for the synthesis of **15** ; (brown oil); ^{1}H NMR ($CDCl_3$, 100 MHz) δ 1.98 (m, 2 H), 2.35 (t, 1 H, *J* = 5.8 Hz), 4.69 (d, 1 H, *J* = 15.2 Hz), 5.21 (d, 1 H, *J* = 15.2 Hz), 5.30 (s, 1 H), 7.27-7.72 (m, 11 H), 8.59 (d, 1 H, *J* = 8.5 Hz); ^{13}C NMR ($CDCl_3$, 25 MHz) δ 21.7, 27.2, 35.4, 55.5, 100.7, 114.6, 126.6, 126.9 (2 carbons), 127.0, 127.5, 128.0 (2 carbons), 129.0, 130.3, 132.6, 135.3, 143.7, 152.5, 164.8, 196.9. Anal. Calcd for $C_{22}H_{20}N_2O$: C 80.45, H 6.14, N 8.53. Found: C 80.54, H 6.09, N 8.67.

General methods for photochemical reactions: Three different devices were used to irradiate solutions in UV light. One of them used for tertiary enaminones (**15**) and (**17**) consists in 3 "black light" lamps Philips HPW 125W surrounded by a cylindrical mirror, the reactor in Pyrex with a cooling jacket being located along the axis of the device. The active part of the lamp is a medium pressure mercury lamp; Its emission if filtered by the black bulb. About 85% of transmitted photons correspond to the line 365 nm. Only a few percents of photons are emitted at 334 and 313 nm. In the second device 6 fluorescent low pressure lamps DUKE GL 20 (20 W) are surrounded by a cylindrical mirror, the reactor being on the axis. With a reactor in quartz, solutions are irradiated in the range 275-350 nm, the maximum being located at 313 nm. With a reactor in Pyrex, wavelengths shorter than 290 nm are cut off. In the third device, a medium pressure mercury lamp was used (150W, TQ 150) with a quartz reactor, allowing the emissions lower than 290 nm.

7-Benzyl-8,9,10,11-tetrahydroindolo[2,3-*c*]quinolin-11-one (20): A solution of enaminone (**15**) (208 mg, 0.63 mmol) in 100 mL of methanol was irradiated under nitrogen for 10 h in a Pyrex reactor with Philips HPW lamps (main emission at 365 nm). After evaporation of the solvents, the resulting precipitate was recrystallized in ether to give 144 mg (70%) of **20**; mp 197-199°C. IR (KBr) : υ_{CO} = 1650 cm^{-1}. MS; *m/z* (relative intensity) : 326 (10), 298 (5), 235 (3), 91 (100). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.26 (m, 2 H), 2.74 (t, 2 H, *J* = 6.4 Hz), 2.81 (t, 2 H, *J* = 6.1 Hz), 5.27 (s, 2 H), 6.97 (m, 1 H), 7.31 (m, 4 H), 7.47 (m, 2 H), 8.23 (m, 1 H), 8.86 (s, 1 H,), 9.92 (m, 1 H). ^{13}C NMR ($CDCl_3$, 25 MHz) δ 22.6 (2 carbons), 34.6, 47.2, 115.4, 123.4, 125.9, 126.3, 127.3, 128.2, 128.4, 129.2, 129.3, 129.9, 135.2, 135.7,

144.5, 152.5, 193.2. Anal. Calcd for $C_{22}H_{18}N_2O$: C 80.96, H 5.56, N 8.58. Found : C 80.81, H 5.49, N 8.47.

7-Benzyl-8,9,10,11-tetrahydropyrido[2,3-*c*]carbazol-11-one (21): A solution of enaminone (**17**) (95 mg, 0.29 mmol) in 140 mL of methanol was irradiated under nitrogen for 14.5 h in a Pyrex reactor with Philips HPW lamps (main emission at 365 nm). After evaporation of the solvent, the resulting precipitate was recrystallized in ether to give 46 mg (60%) of **21**; mp 174-176°C. IR (KBr) : υ_{CO} = 1650 cm^{-1}. MS ; *m/z* (relative intensity) : 326 (12), 298 (2), 235 (3), 207 (7), 179 (8), 91 (100). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.30 (m, 2 H), 2.76 (t, 2 H, *J* = 6.2 Hz), 2.98 (t, 2 H, *J* = 6.0 Hz), 5.46 (s, 2 H), 7.03 (d, 1 H, *J* = 7.0 Hz), 7.33 (m, 4 H), 7.59 (dd, 1 H, *J* = 8.5 and 4.2 Hz), 7.67 (d, 1 H, *J* = 9.0 Hz), 8.00 (d, 1 H, *J* = 9.0 Hz), 8.93 (d, 1 H, *J* = 4.2 Hz), 10.44 (d, 1 H, J= 8.5 Hz). ^{13}C NMR ($CDCl_3$, 25 MHz) δ 22.9, 23.0, 39.2, 47.2, 114.0, 120.4, 120.8, 124.2, 125.9, 126.1, 128.1, 129.3, 133.7, 135.6, 137.0, 146.0, 148.2, 151.1, 193.5. Anal. Calcd for $C_{22}H_{18}N_2O$: C 80.96, H 5.56, N 8.58. Found : C 81.05, H 5.56, N 8.61.

5-Benzyl-6,7,8,9-tetrahydropyrido[4,3-*a*]carbazol-9-one (22): A solution of enaminone (**19**) (20 mg, 0.06 mmol) in 100 mL of acetonitrile was irradiated under nitrogen for 25 min in the range 290-350 nm in a Pyrex reactor. After evaporation of the solvent, the resulting precipitate was purified by chromatography on neutral alumina eluted with dichloromethane to give 13 mg (65%) of **22** ; mp 225-227°C. IR (KBr) : υ_{CO} = 1648 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.36 (m, 2 H), 2.72 (t, 2 H, *J* = 8.0 Hz), 3.04 (t, 2 H, *J* = 7.4 Hz), 5.84 (s, 2 H), 7.09 (d, 2 H, *J* = 4.0 Hz), 7.38 (m, 3 H), 7.78 (d, 1 H, *J* = 4.0 Hz), 7.87 (d, 1 H, *J*= 8.0 Hz), 8.42 (d, 1 H, *J*= 8.0 Hz), 8.68 (d, 1 H, *J* = 8.0 Hz), 9.33 (s, 1 H). ^{13}C NMR ($CDCl_3$, 25 MHz) δ 22.4, 23.3, 38.1, 49.7, 113.3, 114.0, 122.4, 122.6, 123.3, 124.5, 125.4, 125.8, 128.2, 129.5, 135.3, 143.1, 151.9, 152.8, 194.6. Anal. Calcd for $C_{22}H_{18}N_2O$: C 80.96, H 5.56, N 8.58; Found : C 80.92, H 5.71, N 8.63.

8-Benzylaminoquinoline (23) [13]**:** A solution of enaminone (**18**) (101 mg, 0.3 mmol) in 220 mL of methanol was irradiated under nitrogen for 2 h in the range 275-350 nm in a quartz reactor. After evaporation of the solvent, the resulting precipitate was chromatographed on neutral alumina eluted with dichloromethane to give 15 mg (21%) of **23** as a viscous oil.

8-amino-7-benzylquinoline (27): A solution of enaminone (**18**) (200 mg, 0.6 mmol) in 300 mL of methanol was irradiated under nitrogen for 0.5 h with a medium mercury pressure in a quartz reactor (emission at 254 nm). After evaporation of the solvent, the resulting mixture was chromatographed on silica gel eluted with dichloromethane, to give 35 mg (25%) of **27** as a brown oil. MS; *m/z* (relative intensity) 234 (100), 157 (40); ^{1}H NMR ($CDCl_3$, 100 MHz) δ 4.10 (s, 2 H), 4.50 (br s, 1 H), 7.19-7.39 (m, 8 H), 8.06, (dd, 1 H, *J* = 8.3 and 1.8 Hz), 8.74 (dd, 1 H, *J* = 4.3 and 1.8 Hz). ^{13}C NMR ($CDCl_3$, 25 MHz)

δ (CH and CH_2) 38.2, 115.8, 120.8, 126.4, 128.6 (2 carbons), 128.7 (2 carbons), 130.1, 136.0, 147.5. Anal. Calcd for $C_{16}H_{14}N_2$: C 82.02, H 6.02, N 11.96. Found : C 81.95, H 6.03, N 12.02. Further elution gave **8** (8%).

5-Amino-6-benzylquinoline (29): This compound was obtained from **28**[18] in 6% yield using the same method employed for the synthesis of **27**; brown paste; MS; *m/z* (relative intensity) 234 (100), 157 (46); ^{1}H NMR ($CDCl_3$, 100 MHz) δ 4.10 (s, 1 H), 7.24-7.60 (m, 10 H), 8.17 (d, 1 H, *J* = 7.9 Hz), 8.85 (d, 1 H, *J* = 2.9 Hz). Anal. Calcd for $C_{16}H_{14}N_2$: C 82.02, H 6.02, N 11.96. Found : C 82.13, H 5.95, N 11.92. Further elution gave **6** (26%).

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