Reaction of α,β-Unsaturated Carbodiimides with Enamines Leading to Fused Pyridine Derivatives [1]

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The treatment of (5,5-dimethyl-3-oxo-1-cyclohexenyl)iminotriphenylphosphorane (**2**) with phenyl isocyanate (**3a**) gave *N*-(5,5-dimethyl-3-oxo-1-cyclohexenyl)-*N'*-phenylcarbodiimide (**4a**) *in situ*. The reaction of **4a** with enamines proceeded smoothly to afford the pyridine ring formation with the elimination of amine. This means that **4a** is regarded as a new class of 2-aza-1,3-butadiene. The scopes and limitation of this reaction are also discussed.

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Much attention has been paid to the [4+2] cycloaddition reaction of aza-dienes with olefins as a versatile synthetic method for heterocycles containing pyridine nuclei [2]. However, aza-dienes are less stable and reactive than carbodienes, so their application to cycloaddition reactions seems to be limited. Although an α,β-unsaturated carbodiimide, a conjugated heterocumulene, could be regarded as a 2-aza-1,3-butadiene formally, a few of its preparations [3] and reactions [4] leading to heterocycles were found. However, most of the reactions were concerned with electrocyclic ring closure involving aromatic, imino, or carbonyl π-bonds. Recently, Motoki *et al.* reported the intermolecular [4+2] cycloaddition reaction of α,β-unsaturated carbodiimide with tetracyanoethylene to give a pyridine derivative, for which a biradical mechanism was proposed [5].

In a previous paper, we reported a facile preparation of 2-alkenyl-3-azido-2-cyclohexen-1-ones and their intramolecular reactions under thermal or photochemical conditions leading to some heterocyclic systems [6]. In a continuation of our study for the synthetic usefulness of nitrene related compounds, the reaction of *N*-(5,5-dimethyl-3-oxo-1-cyclohexenyl)-*N'*-aryl(tosyl or alkyl)carbodiimides **4** with enamines are presented, in which the carbodiimides **4** are prepared *in situ* by the aza-Wittig reaction of the iminophosphorane and corresponding isocyanates.

Results and Discussion.

The treatment of 3-azido-5,5-dimethyl-2-cyclohexen-1-one (**1**) with triphenylphosphine (1.0 equivalent) in dichloromethane at room temperature gave the iminophosphorane **2** in quantitative yield. The aza-Wittig reaction of **2** with phenyl isocyanate (**3a**) in toluene under reflux gave the carbodiimide **4a** in 48% yield, which was not stable enough for column chromatography on silica gel. The reaction of **4a** with 1-(1-pyrrolidinyl)cyclohexene (**5**) in toluene under reflux gave 6-anilino-3,3-dimethyl-3,4,7,8,9,10-hexahydro-1(2*H*)-phenanthridinone (**6a**) and 5,5-dimethyl-3-{[(1-pyrrolidinyl)anilinomethylene]amino}-2-cyclohexen-1-one (**7**) in 46 and 41% yield, respectively (Scheme 1).

The structure of **6a** was established on the basis of its elemental analysis and spectral data; the ir spectrum of **6a** shows the NH absorption band at 3300 cm^{-1}, and in its cmr spectrum eight sp^3-carbon signals and eleven sp^2-carbon ones are assignable as follows: δ = 21.9 (9-C), 22.1 (8-C), 224.1 (10-C), 28.2 (CH_3), 29.1 (7-C), 32.3 (3-C), 47.7

Scheme 1

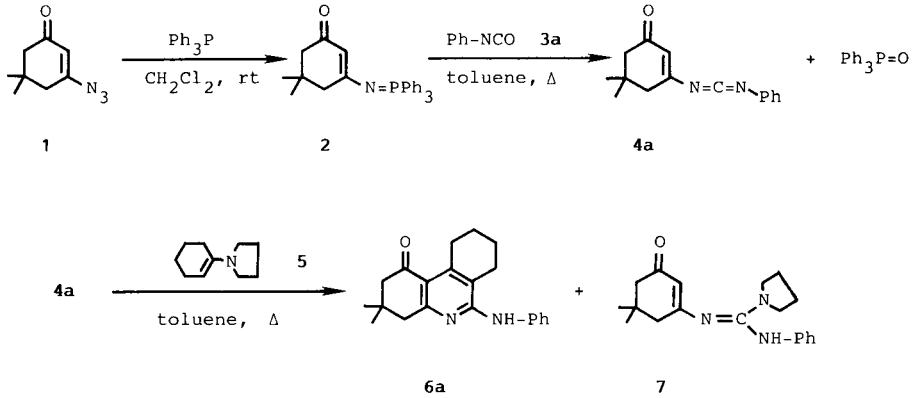
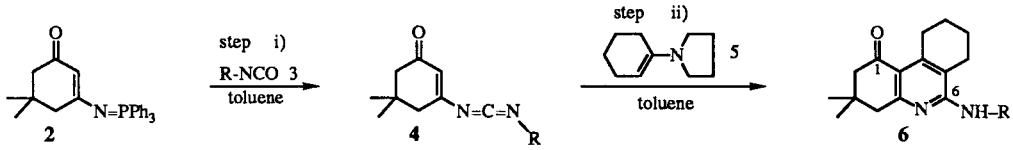


Table 1

Preparation of Phenanthridines 6 by tho One-pot Method from Iminophosphorane 2



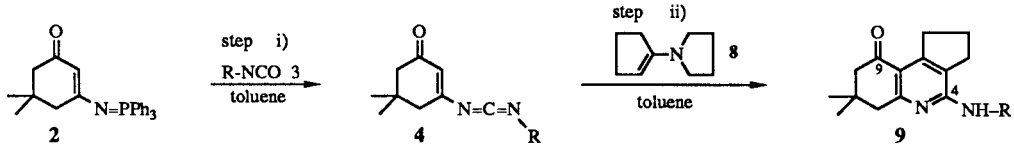
2 4 6

	R	Reaction Condidtions step i) Temperature Time (hours)	step ii) Temperature Time (hours)	Product (Yield/%) [a]
a	Phenyl	reflux (0.5)	reflux (20)	**6a** (45)
b	C_6H_4-Cl(3)	reflux (0.5)	reflux (20)	**6b** (22)
c	1-Naphthyl	reflux (0.5)	reflux (20)	**6c** (38)
d	Tosyl	rt (1.0)	reflux (2)	**6d** (36)
e	Butyl	reflux (7.0)	reflux (24)	**6e** (21)

[a] Based on isolated product.

Table 2

Preparation of Cyclopenta[*c*]quinolines 9 by the One-pot Method from Iminophosphorane 2



2 4 9

	R	Reaction Condidtions step i) Temperature Time (hours)	step ii) Temperature Time (hours)	Product (Yield/%) [a]
a	Phenyl	reflux (0.5)	reflux (20)	**9a** (84)
b	C_6H_4-Cl(3)	reflux (0.5)	reflux (20)	**9b** (54)
c	1-Naphthyl	reflux (0.5)	reflux (20)	**9c** (46)
d	Tosyl	rt (1.0)	reflux (2)	**9d** (40)
e	Butyl	reflux (7.0)	reflux (24)	**9e** (42)

[a] Based on isolated product.

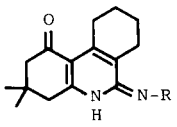
(4-C), 54.4 (2-C), 115.1 (6a-C), 118.7 (10b-C), 120.3, 122.9, 128.8, 139.8 (phenyl-C), 149.4 (10a-C), 154.7 (4a-C), 161.2 (6-C), 199.0 (1-C).

On the other hand, the pmr spectrum of the reaction mixture showed the existence of **7**, but **7** could not be isolated after the usual work-up with column chromatography on silica gel. The structural confirmation of **7** was accomplished by the comparison with the authentic sample from **4a** and pyrrolidine.

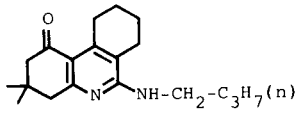
A one-pot procedure for the preparation of phenanthridine **6a** from iminophosphorane **2a** was also examined; phenanthridine **6a** was obtained in 45% yield. This means that the carbodiimide **4a** is prepared in almost quantitative yield and this one-pot method is available for this preparation. In order to elucidate the reaction profiles, the one-pot method was examined for the reaction of *N*-(5,5-dimethyl-3-oxo-1-cyclohexenyl)-*N'*-(3-chlorophenyl)- **4b**, -*N'*-(1-naphthyl)- **4c**, -*N'*-tosyl- **4d**, and -*N'*-butylcarbodiimide **4e** with enamine **5**. In these cases, phenanthridines **6b-e** were obtained in fair yields and these results are recorded in Table 1.

For the product **6**, the 3,3-dimethyl-6-(substituted imino)-3,4,5,6,7,8,9,10-octahydro-1(2*H*)-phenanthridinone structure **6'** is also possible, a tautomeric isomer of **6**. However, in the pmr spectrum of **6e**, the signal patterns of the *n*-butyl methylene proton adjacent to the nitrogen atom were observed to be complex and they were changed to triplet after the treatment with deuterium oxide. In the cmr spectrum of **6a**, the phenyl carbon signals also corresponded to those of anilino phenyl group: 120.3 (C_o), 122.9 (C_p), 128.8 (C_m), and 139.9 (C_i) [7]. The similarity of the ν NH absorption bands or chemical shift of NH pro-

tons of **6a-e** suggested that products **6a-e** had a common structure.



6'



6e

Similarly, the reaction of carbodiimides **4a-e** with 1-(1-pyrrolidinyl)cyclopentene (**8**) gave 4-(substituted amino)-7,7-dimethyl-1,2,3,6,7,8-hexahydro-9*H*-cyclopenta-[*c*]quinolin-9-ones **9a-e** in fair to good yields, and these results are summarized in Table 2.

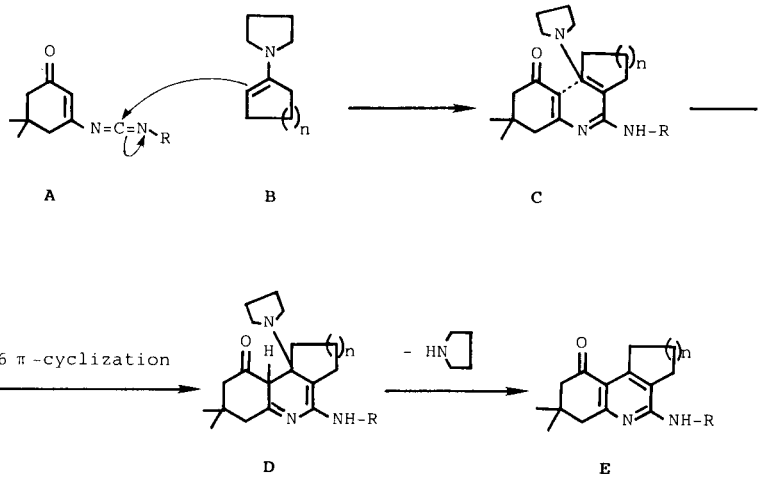
The reaction of **4a** with electron-deficient olefins or acetylene, such as *N*-methylmaleimide or dimethyl acetylenedicarboxylate, gave only a mixture of polymeric materials.

A plausible pathway for the phenanthridine **6** or cyclopenta[*c*]quinoline **9** synthesis is demonstrated in Scheme 2. The nucleophilic attack of the β-carbon atom of enamine **B** to the center carbon atom of carbodiimide **A** would take place initially to give an amidine **C**. The 6 π-electrocyclic ring closure of **C** gives a dihydropyridine derivative **D**, which is aromatized to pyridine derivative **E** with the elimination of pyrrolidine.

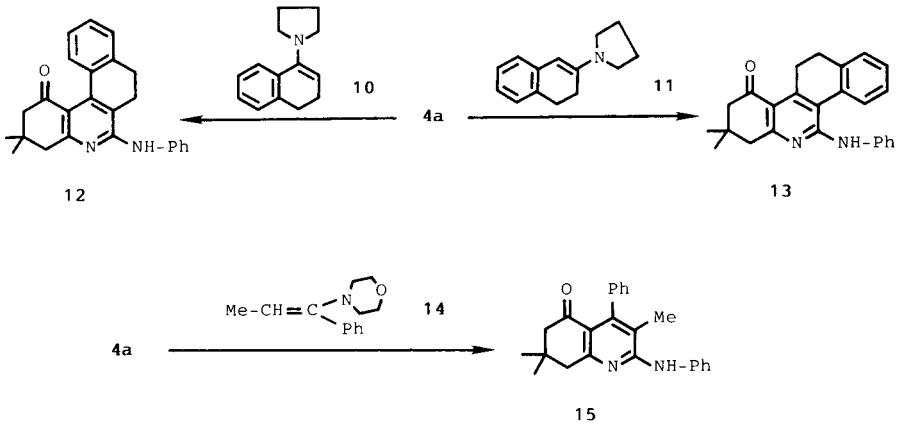
The reaction of carbodiimide **4a** with other enamines were also investigated. Carbodiimide **4a** was allowed to react with 1-(1-pyrrolidinyl)- **10** and 2-(1-pyrrolidinyl)-3,4-dihydronaphthalene (**11**) to give regio-isomeric benzophenanthridines **12** and **13**, respectively. The reaction of **4a** with acyclic enamine **14** also gave a quinoline derivative **15** (Scheme 3).

In conclusion, the reaction of α,β-unsaturated carbodiimides **4** with enamine proceeded smoothly to afford pyridine ring formation with the elimination of amine.

Scheme 2



Scheme 3



This means that the carbodiimides **4** are regarded as a new class of 2-aza-1,3-butadienes.

Further investigations on the synthetic usefulness of the carbodiimides **4** are now in progress.

EXPERIMENTAL

General.

All melting points are uncorrected. The ir spectra were measured on a JASCO IR-Report-100 spectrophotometer as potassium bromide pellets unless otherwise stated. The pmr spectra were obtained on JEOL GSX-270 and/or JMN-MH-100 spectrometers for deuteriochloroform solution; the chemical shifts are expressed in parts per million downfield from internal tetramethylsilane. Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad signal; and ov, overlapping each other. The cmr spectra were obtained on a JEOL GSX-270 spectrometer for deuteriochloroform solution. The mass spectra were determined with a JEOL JMS-012G-2 or JMS-D spectrometer at an ionization energy of 75 eV. Elemental analyses were performed on a Hitachi 026 CHN analyzer. All nonaqueous reactions were run under a positive pressure of argon. All solvents were dried by standard methods before use. The progress of most reactions was monitored by thin-layer chromatography (Silica Gel 60F-254, Merck). Visualization was made with ultraviolet light (254 and 365 nm). Chromatographic purification was performed with Wakogel C-200 (100-200 mesh, Wako Pure Chemical Industries LTD) and/or Silica Gel 60 (230-400 mesh, Merck).

Preparation of *N*-(5,5-Dimethyl-3-oxo-1-cyclohexenyl)-*N'*-phenylcarbodiimide (**4a**).

Methanesulfonyl chloride (3.78 g, 33 mmoles) in tetrahydrofuran (THF) (10 ml) was added dropwise to a solution of 5,5-dimethyl-1,3-cyclohexanedione (4.21 g, 30 mmoles) and triethylamine (5.1 ml, 36 mmoles) in THF at 0°. The reaction mixture was stirred for 2 hours at the same temperature, and the resultant precipitates were filtered off and the filtrate was evaporated. The residue was subjected to column chromatography on silica gel to give 5,5-dimethyl-3-methanesulfonyloxy-2-cyclohexen-1-one (6.54 g, in quantitative yield) as an eluate of hexane/ethyl acetate = 2/1. The sulfone ester was used for the next reaction without further purifications. Sodium azide (2.93 g, 45 mmoles) in water (10 ml) was added dropwise to the sulfone ester (6.54 g, 30 mmoles) in methanol (50 ml) at -5°. The reaction mixture was stirred at the same temperature for 34 hours and extracted with dichloromethane (6 x 30 ml). The organic layer was washed with water and dried over anhydrous magnesium sulfate. The dichloromethane was removed under reduced pressure to give 3-azido-5,5-dimethyl-2-cyclohexen-1-one (**1**) (4.89 g, in quantitative yield). Azido **1** was used in the next reaction without further purifications. Triphenylphosphine (3.93 g, 15.1 mmoles) in dichloromethane (15 ml) was added dropwise to a solution of **1** (2.49 g, 15.1 mmoles) in dichloromethane (35 ml) at room temperature. The reaction mixture was stirred at the temperature for 2 hours, and evaporated to give a residue. The residue was subjected to column chromatography on silica gel to give **2** (4.11 g, 68%) as an eluate of hexane/ethyl acetate = 1/4.

Phenyl isocyanate (**3a**) (55 μl, 0.50 mmole) was added to a solution of iminophosphorane **2** (200 mg, 0.50 mmole) in toluene (5 ml). The reaction mixture was heated under reflux for 5 minutes and the solvent was evaporated to dryness. The resultant triphenylphosphine oxide was crystallized with ether and filtered off. The filtrate was evaporated to give a residue, which was subjected to short column chromatography on silica gel to give **4a** (57 mg, 48%) as an eluate of hexane/ethyl acetate = 3/1.

5,5-Dimethyl-3-methanesulfonyloxy-2-cyclohexen-1-one.

This compound was obtained as pale yellow oil; ir (sodium chloride): 1670 (CO), 1360, 1170 (SO_2) cm^{-1}; pmr: 1.10 (s, 6H, $-CH_3$), 2.32 (br s, 2H, 6-H), 2.52 (br s, 2H, 4-H), 3.28 (s, 3H, $-CH_3$), 6.10 (br s, 2H, 2-H).

3-Azido-5,5-dimethyl-2-cyclohexen-1-one (**1**).

This compound was obtained as a yellow oil; ir (neat): 2080 (N_3), 1650 (CO) cm^{-1}; pmr: 1.08 (s, 6H, $-CH_3$), 2.30 (ov, total 4H, 4-and 6-H), 5.82 (br s, 1H, 2-H).

Azide **1** is known [8], but our method afforded an improved yield and was more easily facilitated.

N-(5,5-Dimethyl-3-oxo-1-cyclohexenyl)iminotriphenylphosphorane (**2**).

This compound was obtained as colorless prisms (hexane), mp 168-169°; ir: 1605 (CO), 1430 (N=P) cm^{-1}; pmr: 1.08 (s, 6H, $-CH_3$), 2.18 (br s, 2H, 6-H), 2.52 (br s, 2H, 4-H), 5.15 (br s, 1H, 2-H), 7.4-8.0 (ov, total 15H, phenyl).

Anal. Calcd. for $C_{26}H_{26}NOP$: C, 78.17; H, 6.56; N, 3.51. Found: C, 78.43; H, 6.39; N, 3.44.

N-(5,5-Dimethyl-3-oxo-1-cyclohexenyl)-*N'*-phenylcarbodiimide (**4a**).

This compound was obtained as pale yellow oil; ir: 2110 (-N=C=N-), 1660 (CO) cm^{-1}: pmr: 1.10 (s, 6H, $-CH_3$), 2.28 (br s, 2H, 6-H), 2.42 (br s, 2H, 4-H), 5.88 (br s, 1H, 2-H), 7.1-7.5 (ov, 5H, phenyl); ms: m/z 240 (M^+).

This compound did not give satisfactory analytical results because of its instability.

Reaction of **4a** with Enamines. General Procedure.

A solution of carbodiimide **4a** (57 mg, 0.24 mmole) and 1-(1-pyrrolidinyl)cyclohexene (**5**) (39 μl, 0.24 mmole) in toluene (3 ml) was heated under reflux for 30 minutes. The reaction mixture was evaporated to dryness, which was subjected to column chromatography on silica gel to give **6a** (35 mg, 46%) as an eluate of hexane/ethyl acetate = 3/1.

One-pot Method.

Phenyl isocyanate (**3a**) (55 μl, 0.50 mmole) was added to a solution of iminophosphorane **2** (0.20 g, 0.50 mmole) in toluene (5 ml). The reaction mixture was heated under reflux for 30 minutes. To the reaction mixture enamine **5** (0.12 ml, 0.75 mmole) was added and the mixture was heated under reflux for 20 hours.

A similar chromatographic purification gave **6a** (0.72 g, 45%).

6-Anilino-3,3-dimethyl-3,4,7,8,9,10-hexahydro-1(2*H*)-phenanthridinone (**6a**).

This compound was obtained as colorless needles (hexane-benzene), mp 183-185°; ir: 3330 (NH), 1640 (CO) cm^{-1}; pmr: 1.08 (s, 6H, $-CH_3$), 1.7-1.9 (ov, total 4H, 8- and 9-H), 2.45 (br s, 2H, 2-H), 2.50 (t, 2H, 7-H, J = 6.4 Hz), 2.89 (br s, 2H, 4-H), 3.18 (t, 2H,

10-H, J = 6.3 Hz), 6.52 (br s, 1H, NH), 7.1, 7.3, 7.7 (3m, total 5H, phenyl); ms: m/z (relative intensity) 321 (23), 320 (M^+, base peak), 319 (79), 305 (M^+ -Me, 11), 291 (4), 229 (11), 160.0 (M^+/2, 5).

Anal. Calcd. for $C_{21}H_{24}N_2O$: C, 78.72; H, 7.55; N, 8.74; M, 320. Found: C, 79.01; H, 7.65; N, 8.81.

Pyrrolidine (15 mg, 0.21 mmole) was added to a solution of carbodiimide **4a** (48 mg, 0.20 mmole) in THF (5 ml) at room temperature. The reaction mixture was stirred for 10 minutes and evaporated to give a crystalline **7** (62 mg, in quantitative yield). The yield of **7** (41%) in the reaction of **4a** with **5** was determined by pmr spectrum of the reaction mixture (**6a**/**7** = 10/9).

5,5-Dimethyl-3-{[(1-pyrrolidinyl)anilinomethylene]amino}-2-cyclohexen-1-one (**7**).

This compound was obtained as pale yellow prisms (hexane/ethyl acetate), mp 174-175°; ir: 1620 (CO) cm^{-1}; pmr: 0.92 (s, 6H, $-CH_3$), 1.8-2.1 (ov, total 4H, pyrrolidinyl-3'- and -4'-H), 2.08, 2.17 (2s, each 2H, 4- and 6-H), 3.4-3.7 (ov, total 4H, pyrrolidinyl-2'- and -5'-H), 5.10 (br s, 1H, 2-H), 7.0-7.6 (m, 5H, phenyl); ms: m/z (relative intensity) 311 (M^+, 35), 296 (M^+-CH_3, 20), 259 (40), 240 (**4a**$^+$, 9) 227 (Ph-CNH^+, base peak).

Anal. Calcd. for $C_{19}H_{25}N_3O$: C, 73.28; H, 8.09; N, 13.46; M, 311. Found: C, 73.50; H, 8.33; N, 13.18.

6-(3-Chloroanilino)-3,3-dimethyl-3,4,7,8,9,10-hexahydro-1(2*H*)-phenanthridinone (**6b**).

This compound was obtained as colorless needles (hexane-benzene), mp 164-165°; ir: 3325 (NH), 1640 (CO) cm^{-1}; pmr: 1.06 (s, 6H, $-CH_3$), 1.6-2.0 (ov, total 4H, 8- and 9-H), 2.3-2.6 (ov, total 4H, 2- and 7-H), 2.86 (br s, 2H, 4-H), 3.10 (br t, 2H, 10-H, J = 5 Hz), 6.45 (br s, 1H, NH), 6.89 (br d, 1H, phenyl-6'-H, J = 8 Hz), 7.12 (br t, 1H, phenyl-5'-H, J = 8 Hz), 7.40 (br d, 1H, phenyl-4'-H, J = 8 Hz), 7.80 (br s, 1H, phenyl-2'-H); ms: m/z (relative intensity) 356 (M^+, 35), 355 (41), 354 (M^+, base peak), 353 (73), 351, 349 (M^+ -Me), 229 (M^+ -Ar, 11).

Anal. Calcd. for $C_{21}H_{23}N_2OCl$: C, 71.08; H, 6.53; N, 7.89; M, 354.5. Found: C, 71.38; H, 6.66; N, 8.09.

6-[(1-Naphthyl)amino]-3,3-dimethyl-3,4,7,8,9,10-hexahydro-1(2*H*)-phenanthridinone (**6c**).

This compound was obtained as colorless needles (hexane-benzene), mp 180-181°; ir: 3340 (NH), 1650 (CO) cm^{-1}; pmr: 0.95 (s, 6H, $-CH_3$), 1.5-2.0 (ov, total 4H, 8- and 9-H), 2.32 (br s, 2H, 4-H), 2.5 (br t, 2H, 7-H, J = 8 Hz), 2.7 (br s, 2H, 2-H), 3.1 (br t, 2H, 10-H, J = 8 Hz), 6.75 (br s, 1H, NH), 7.3-8.1 (ov, total 7H, aromatic); ms: m/z 370 (M^+).

Anal. Calcd. for $C_{25}H_{26}N_2O$: C, 81.04; H, 7.07; N, 7.56; M, 370. Found: C, 81.18; H, 7.06; N, 7.51.

3,3-Dimethyl-3,4,7,8,9,10-hexahydro-6-(tosylamino)-1(2*H*)-phenanthridinone (**6d**).

This compound was obtained as colorless needles (hexane-benzene), mp 182-183°; ir: 3180 (NH), 1675 (CO), 1310, 1130 (SO_2) cm^{-1}; pmr: 1.10 (s, 6H, $-CH_3$), 1.5-1.9 (ov, total 4H, 8- and 9-H), 2.37 (s, 3H, $-CH_3$), 2.4-2.6 (ov, total 4H, 2- and 7-H), 2.76 (br s, 2H, 4-H), 3.05 (br t, 2H, 10-H, J = 7 Hz), 7.20 (br d, 2H, phenyl, J = 8 Hz), 7.77 (br d, 2H, phenyl, J = 8 Hz), 11.6-12.6 (br, 1H, NH); ms: m/z (relative intensity) 398 (M^+, 25), 334 (M^+ -SO_2, 50), 333 (52), 243 (M^+ -Ts, base peak).

This compound **6d** did not give satisfactory analytical data, since it contained the recrystallizing solvents indefinitely.

6-(Butylamino)-3,3-dimethyl-3,4,7,8,9,10-hexahydro-1(2*H*)-phenanthridinone (**6e**).

This compound was obtained as colorless needles (hexane), mp 168-169°; ir: 3330 (NH), 1635 (CO) cm^{-1}; pmr: 0.96 (t, 3H, $-CH_2-CH_3$, J = 7 Hz), 1.05 (s, 6H, $-CH_3$), 1.3-2.0 (ov, total 6H, 8- and 9-H and $-CH_2-CH_2-$), 2.20 (br t, 2H, 7-H, J = 6 Hz), 2.34, 2.73 (2s, each 2H, 4- and 7-H), 3.05 (br t, 2H, 10-H), 3.48 (br q, 2H, N-CH_2-), 4.46 (br, 1H, NH); ms: m/z (relative intensity) 300 (M^+, 63), 285 (M^+ -Me, 6), 271 (M^+ -C_2H_5, 67), 258 (M^+ -C_3H_6, 47), 244 (M^+ -C_4H_8, base peak).

Anal. Calcd. for $C_{19}H_{28}N_2O$: C, 75.95; H, 9.39; N, 9.33; M, 300. Found: C, 76.25; H, 9.34; N, 9.35.

4-Anilino-7,7-dimethyl-1,2,3,6,7,8-hexahydro-9*H*-cyclopenta[*c*]-quinolin-9-one (**9a**).

This compound was obtained as colorless needles (hexane-benzene), mp 174-175°; ir 3360 (NH), 1640 (CO) cm^{-1}; pmr: 1.09 (s, 6H, $-CH_3$), 2.15 (m, 2H, 2-H), 2.44 (br s, 2H, 8-H), 2.71 (t, 2H, 3-H, J = 7.5 Hz), 2.92 (br s, 2H, 6-H), 3.34 (t, 2H, 1-H, J = 7.7 Hz), 6.40 (br s, 1H, NH), 7.05 (br t, 1H, phenyl-4'-H, J = 7.4 Hz), 7.33 (br t, 2H, phenyl-3'-H, J = 7.9 Hz), 7.70 (d, 2H, phenyl-2'-H, J = 7.7 Hz); cmr: 24.2 (2-C), 28.3 (CH_3), 28.4 (7-C), 32.7 (3-C), 24.7 (1-C), 46.9 (6-C), 53.0 (8-C), 118.1 (9a-C), 119.8 (3a-C and phenyl-C_o), 122.8 (phenyl-C_p), 128.9 (phenyl-C_m), 139.8 (phenyl-C_i), 153.5 (9b-C), 156.0 (5a-C), 162.2 (4-C), 198.2 (9-C); ms: m/z 306 (M^+, base peak), 305 (78), 291 (M^+ -Me, 7), 250 (5), 244 (7), 153.0 (M^+/2, 5).

Anal. Calcd. for $C_{20}H_{22}N_2O$: C, 78.40; H, 7.24; N, 9.14; M, 306. Found: C, 78.69; H, 7.32; N, 9.04.

4-(3-Chloroanilino)-7,7-dimethyl-1,2,3,6,7,8-hexahydro-9*H*-cyclopenta[*c*]quinolin-9-one (**9b**).

This compound was obtained as colorless prisms (hexane-benzene), mp 165-166°; ir: 3290 (NH), 1630 (CO) cm^{-1}; pmr: 1.08 (s, 6H, $-CH_3$), 2.2 (m, 2H, 2-H), 2.42 (br s, 2H, 8-H), 2.65 (t, 2H, 3-H, J = 8 Hz), 2.90 (br s, 2H, 6-H), 3.34 (t, 2H, 1-H, J = 8 Hz), 6.40 (br s, 1H, NH), 6.95 (br d, 1H, phenyl-6'-H, J = 8 Hz), 7.16 (br t, 1H, phenyl-5'-H, J = 8 Hz), 7.48 (br d, 1H, phenyl-4'-H, J = 8 Hz), 7.85 (br s, 1H, phenyl-2'-H); ms: m/z (relative intensity) 342 (M^+, 36), 341 (36), 342 (M^+, base peak), 339 (50), 286 (14), 257 (18).

Anal. Calcd. for $C_{20}H_{21}N_2OCl$: C, 70.48; H, 6.21; N, 8.22; M, 340.5. Found: C, 70.46; H, 6.33; N, 8.27.

7,7-Dimethyl-1,2,3,6,7,8-hexahydro-4-[(1-naphthyl)amino]-9*H*-cyclopenta[*c*]quinolin-9-one (**9c**).

This compound was obtained as yellow prisms (hexane), mp 145-146°; ir: 3460 (NH), 1650 (CO) cm^{-1}; pmr: 1.02 (s, 6H, $-CH_3$), 2.1 (m, 2H, 2-H), 2.38 (br s, 2H, 8-H), 2.48 (br t, 2H, 3-H, J = 8 Hz), 2.76 (br s, 2H, 6-H), 3.26 (t, 2H, 1-H, J = 8 Hz), 7.0 (br, 1H, NH), 7.3-8.0 (ov, total 7H, aromatic); ms: m/z (relative intensity) 356 (M^+, base peak), 341 (M^+ -Me, 33), 300 (12), 272 (15), 229 (M^+ -naphthyl, 6), 178.0 (M^+/2, 12).

Anal. Calcd. for $C_{24}H_{24}N_2O$: C, 80.87; H, 6.79; N, 7.86; M, 356. Found: C, 80.62; H, 6.96; N, 7.64.

7,7-Dimethyl-1,2,3,6,7,8-hexahydro-4-(tosylamino)-9*H*-cyclopenta-[*c*]quinolin-9-one (**9d**).

This compound was obtained as pale yellow prisms (hexane-benzene), mp 205-206°; ir: 3160 (NH), 1660 (CO), 1330, 1120 (SO_2) cm^{-1}; pmr: 1.10 (s, 6H, $-CH_3$), 2.05 (m, 2H, 2-H), 2.36 (s, 3H, $-CH_3$), 2.40 (br s, 2H, 8-H), 2.70 (t, 2H, 3-H, J = 7 Hz), 2.79 (br s, 2H, 6-H), 3.25 (t, 2H, 1-H, J = 7 Hz), 7.20 (d, 2H, phenyl, J = 8

Hz), 7.81 (t, 2H, phenyl, J = 8 Hz), 11.5-12.3 (br, 1H, NH); ms: m/z (relative intensity) 384 (M^+, 23), 320 (M^+ -SO_2, 77), 319 (base peak), 229 (M^+-Ts, 96), 155 (Ts^+, 13), 91 (38).

Anal. Calcd. for $C_{21}H_{24}N_2O_3S$: C, 65.61; H, 6.29; N, 7.29; M, 384. Found: C, 65.86; H, 6.38; N, 7.16.

4-(Butylamino)-7,7-dimethyl-1,2,3,6,7,8-hexahydro-9*H*-cyclopenta-[*c*]quinolin-9-one (**9e**).

This compound was obtained as colorless needles (hexane), mp 126-127°; ir: 3460 (NH), 1650 (CO) cm^{-1}; pmr: 0.95 (t, 3H, -CH_2-CH_3, J = 7 Hz), 1.06 (s, 6H, -CH_3), 1.1-1.8 (ov, 4H, -CH_2-CH_2-), 2.1 (m, 2H, 2-H), 2.36 (br s, 2H, 8-H), 2.52 (t, 2H, 3-H, J = 7 Hz), 2.78 (br s, 2H, 6-H), 3.22 (t, 2H, 1-H, J = 7 Hz), 3.50 (q, 2H, N-CH_2-, J = 6 Hz), 4.4 (br, 1H, NH); ms: m/z 286 (M^+, 43), 257 (M^+, -C_2H_5, 11), 243 (M^+ -C_3H_7, 36), 230 (64), 43 (base peak).

Anal. Calcd. for $C_{18}H_{26}N_2O$: C, 75.48; H, 9.15; N, 9.78; M, 286. Found: C, 75.74; H, 9.19; N, 9.91.

A similar one-pot reaction of carbodiimide **4a** with 1-(1-pyrrolidinyl)-3,4-dihydronaphthalene (**10**) and 2-(1-pyrrolidinyl)-3,4-dihydronaphthalene (**11**) gave benzophenanthridine derivatives **12** and **13** in 22 and 42% yield, respectively. Reaction of **4a** with enamine **14** gave also a quinoline derivative **15** in 20% yield.

6-Anilino-3,3-dimethyl-3,4,7,8-tetrahydrobenzo[*k*]phenanthridin-1(2*H*)-one (**12**).

This compound was obtained yellow needles (benzene-ethanol), mp 201-202°; ir: 3380 (NH), 1650 (CO) cm^{-1}; pmr: 1.10 (s, 6H, -CH_3), 2.4 (br t, 2H, 8-H, J = 7 Hz), 2.55 (br s, 2H, 2-H), 2.88 (br t, 2H, 7-H, J = 7 Hz), 2.92 (br s, 2H, 4-H), 6.70 (br s, 1H, NH), 6.9-7.7 (ov, total 9H, aromatic); ms: m/z (relative intensity) 368 (M^+, base peak), 367 (67), 352 (9), 291 (M^+ -Ph, 4), 283 (14), 184.0 (M^+ /2, 13).

Anal. Calcd. for $C_{25}H_{24}N_2O$: C, 81.49; H, 6.56; N, 7.60; M, 368. Found: C, 81.17; H, 6.72; N, 7.46.

5-Anilino-8,8-dimethyl-7,8,9,12-tetrahydrobenzo[*k*]phenanthridin-10(11*H*)-one (**13**).

This compound was obtained as yellow prisms (hexane-ethyl acetate), mp 189-190°; ir: 3340 (NH), 1650 (CO) cm^{-1}; pmr: 1.08 (s, 6H, -CH_3), 2.48 (br s, 2H, 9-H), 2.65 (br t, 2H, 12-H, J = 7 Hz), 2.90 (br s, 2H, 7-H), 3.30 (br t, 2H, 11-H, J = 7 Hz), 6.9-7.9 (m, total 9H, aromatic); ms: m/z (relative intensity) 368 (M^+, base peak), 367 (92), 311 (6), 291 (M^+ -Ph, 6), 283 (13), 184.0 (M^+/2, 9).

Anal. Calcd. for $C_{25}H_{24}N_2O$: C, 81.49; H, 6.56; N, 7.60; M, 368. Found: C, 81.47; H, 6.64; N, 7.58.

2-Anilino-3,7,7-trimethyl-4-phenyl-7,8-dihydro-5(6*H*)-quinolinone (**15**).

This compound was obtained as colorless needles (hexane-ethyl acetate), mp 180-181°C; ir: 3350 (NH), 1650 (CO) cm^{-1}; pmr: 1.02 (s, 6H, -CH_3), 1.96 (br s, 3H, 3-CH_3), 2.43 (br, s, 2H, 6-H), 3.10 (br s, 2H, 8-H), 6.9 (br, 1H, NH), 7.2-8.1 (ov, total 10H, phenyl); ms: m/z (relative intensity) 358 (41), 357 (85), 356 (M^+, base peak), 300 (5), 271 (23), 178.0 (M^+/2, 23).

Anal. Calcd. for $C_{24}H_{24}N_2O$: C, 80.86; H, 6.79; N, 7.86; M, 356. Found: C, 80.99; H, 6.89; N, 7.88.

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