Cycloaddition Reactions of Ketoimines. Part II. Synthesis of Substituted Phenanthridines and Cyclopenta[*c*]quinolines [1]

Vittorio Lucchini, Maurizio Prato*, Gianfranco Scorrano* and Paolo Tecilla

Centro C.N.R. Meccanismi di Reazioni Organiche, Dipartimento di Chimica Organica, via Marzolo 1, 35131 Padova, Italy

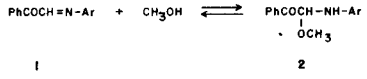
Received December 6, 1985

Substituted 4-benzoyl-3a,4,5,9b-tetrahydro-3*H*-cyclopenta[*c*]quinolines **3** and 6-benzoyl-5,6,6a,7,8,10a-hexahydrophenanthridines **10** are obtained through Lewis acid catalyzed addition of 1-phenyl-2-arylamino-2-methoxyethanones **2** to cyclopentadienes and 1,3-cyclohexadiene respectively. Compounds **3** can be converted to the aromatized analogues by reaction with 2,3-dichloro-5,6-dicyanobenzoquinone in refluxing benzene. Compounds **10** are oxidized by sulfur either in decalin or in quinoline to substituted 6-benzoylphenanthridines.

J. Heterocyclic Chem., **23**, 1135 (1986).

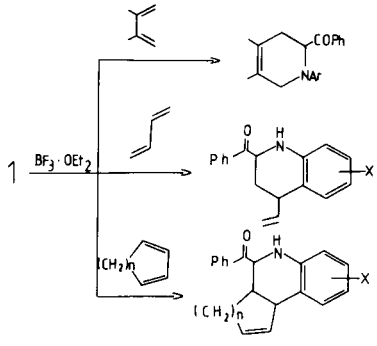
Diels-Alder reactions of azadienes are attractive routes to nitrogen heterocycles [2]. Utilization of Schiff bases in the synthesis of substituted quinolines is well known [3], and recently *N*-benzilideneanilines [4] and iminium ions [5] have been reported to react with electron-rich olefins to form tetrahydroquinolines.

We have recently reported [1,6] the behavior of phenylglyoxal anils **1** [7,8] toward conjugated double bonds.



1 2

Depending on the reaction partner and on reaction conditions, the anils **1** undergo dienic or dienophilic addition with formation of nitrogen heterocycles containing one, two, or three fused rings (Scheme 1).

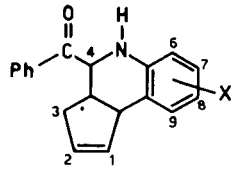


SCHEME 1

In this paper we describe the synthetic utility of the last reaction in Scheme 1 for the formation of phenanthridine (n = 2) or cyclopenta[*c*]quinoline (n = 1) skeletons. The factors which govern the different degree of electro-, regio- and stereoselectiveness of these reactions and the mechanistic rationalization thereof are described elsewhere [1].

The methanol adducts **2** can be easily synthesized and purified, while the free anils are considerably more difficult to isolate and appear to be highly hygroscopic. However, since the adducts **2** are in equilibrium with the free anils **1** in the reaction solvent (methylene chloride), they can be conveniently utilized as potential Diels-Alder reagents [7].

The reaction of the α-ketoimines **1** or their equivalents **2** with cyclopentadiene in anhydrous methylene chloride at room temperature, under boron trifluoride catalysis, affords quantitative yields of the corresponding tetrahydrocyclopenta[*c*]quinolines **3a-h**. The structure of the reaction products has been determined through nmr analysis (NOE and double resonance) and reported elsewhere [6]. The yields of the crystallized products, together with the spectroscopic and analytical data of adducts **3a-h** are reported in Table I.



3a, X = 8-Cl **c**, X = 8-OMe **e**, X = 6-COOH **g**, X = H
b, X = 8-NO_2 **d**, X = 8-Me *f*, X = 6-OMe **h**, X = 8-OH

The oxidative aromatization of tetrahydroquinolines **3** has been thoroughly investigated in the case of compounds **3a** (X = 8-Cl). Reaction with manganese dioxide (8 equivalents) in refluxing toluene gives fair yields (73%) of the dihydro derivative **4**. The compound can be isolated as such from this solvent, but undergoes a tautomeric equilibrium with the enamine isomer **5** in deuteriochloroform, which can be followed by nmr spectroscopy.

The resonance pattern of **4** can be easily distinguished from that of **5**. Vicinal protons 3a and 9b of **4** resonate at δ 3.92 and 4.18, exhibiting a typical vicinal coupling constant of 10.9 Hz. Proton 9b in **5** appears as a broad singlet, with small coupling with protons 1, 2, 3, and 3'. The reso-

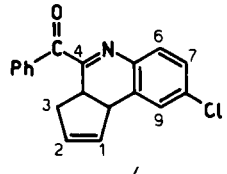
Table I

Analytical and Spectroscopic Data for Substituted 4-Benzoyl-3a,4,5,9b-tetrahydro-3*H*-cyclopenta[*c*]quinolines **3a-h**

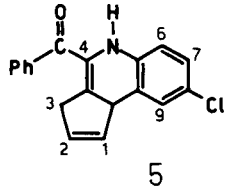
Compound	X	^{1}H-NMR [a] H_1	H_2	H_3	$H_{3'}$	H_{3a}	H_4	H_{9b}	% Yield	mp °C (solvent)	Formula	Analysis [b] C%	H%	N%
3a	8-Cl —	5.57	5.70	2.37	1.89	3.30	5.02	4.14	87	178-179 (EtOH)	$C_{19}H_{16}ClNO$	73.66 (73.69)	5.18 (5.22)	4.46 [c] (4.46)
3b	8-NO_2 —	5.81	5.59	2.31	1.90	3.38	5.20	4.23	88	189-192 (EtOH)	$C_{19}H_{16}N_2O_3$	71.31 (71.24)	4.94 (5.03)	8.74 (8.74)
3c	8-OMe 3.75	5.72	5.58	2.40	1.90	3.28	5.00	4.16	87	152-153 (EtOH)	$C_{20}H_{19}NO_2$	78.59 (78.66)	6.23 (6.27)	4.52 (4.58)
3d	8-Me 2.25	5.72	5.57	2.41	1.89	3.29	5.02	4.15	92	185-186 (EtOH)	$C_{20}H_{19}NO$	83.16 (83.01)	6.72 (6.62)	4.88 (4.84)
3e	6-COOH —	5.69	5.57	2.44	1.94	3.37	5.16	4.24	73	215-216 (EtOH)	$C_{20}H_{17}NO_3$	74.92 (74.98)	5.39 (5.35)	4.68 (4.52)
3f	6-OMe 3.83	5.73	5.55	2.45	1.89	3.31	5.02	4.19	61	37-40 (*n*-pentane)	$C_{20}H_{19}NO_2$	78.40 (78.66)	6.23 (6.27)	4.57 (4.58)
3g	H —	5.74	5.57	2.44	1.93	3.33	5.14	4.21	64	156-157 (EtOH)	$C_{19}H_{17}NO$	83.09 (82.88)	6.24 (6.22)	5.12 (5.08)
3h	8-OH —	5.70	5.59	2.40	1.91	3.29	5.00	4.13	76	184-185 (EtOH)	$C_{19}H_{17}NO_2$	78.28 (78.33)	5.82 (5.88)	4.80 (4.81)

[a] All spectra were run in deuteriochloroform solution at 200 MHz, using tetramethylsilane as internal standard. [b] Calculated values in parenthesis. [c] Cl, 11.41 (11.49).

nance of nitrogen proton 5 shows the variability in chemical shift and signal width characteristic of exchangeable protons.

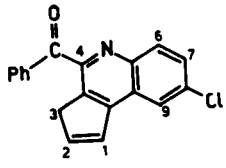


4

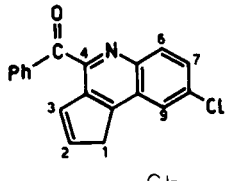


5

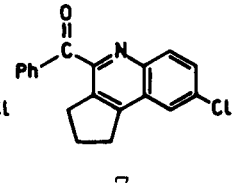
By refluxing compound **3a** in decalin in the presence of sulfur (8 equivalents) two different oxidized products, **6** and **7** are isolated in low yields (35 and 23%, respectively).



6a



6b

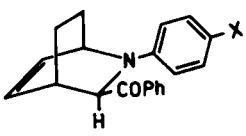


7

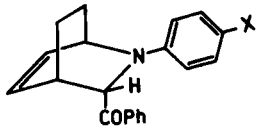
Compound **7** is the only one formed, and in even lower yield, when **3a** is refluxed in decalin in the presence of Pd/C. On the other hand, **3a** is quantitatively oxidized by 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in benzene at room temperature to compound **4**, which is further oxidized to **6** (61% yield) by refluxing with the same reagent.

In agreement with the report of Eisch *et al.* [9] concerning the unsubstituted homologue, the cyclopenta[*c*]quinolines **6a** and **6b** are in tautometric equilibrium in chloroform solution, through a probable double suprafacial [1,5]-sigmatropic shift of the proton around the cyclopentadiene ring [10]. As the attainment of equilibrium is slow, different nmr signals are observed, which have been attributed to isomers **6a**, and **6b** through a NOE investigation by means of nmr differential spectroscopy (see Experimental). The **6a:6b** ratio in deuteriochloroform is 3:1. The structure of **7** is easily inferred from the analysis of the nmr spectrum in the aliphatic region: two triplets are observed at δ 3.31 and 3.33 and a quintet at δ 2.32, which are diagnostic of an asymmetric CH_2-CH_2-CH_2 system.

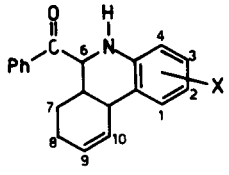
From the reaction of **1** or the corresponding methanol derivatives **2** at room temperature with cyclohexadiene in anhydrous methylene chloride with boron trifluoride etherate as catalyst, three products **8,9** and **10** were isolated in different ratios depending on the substituent X [1].

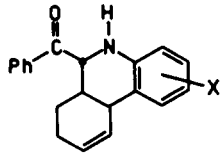


8



9





10a, X = 2-Cl
b, X = 2-NO_2
c, X = 2-OMe
d, X = 2-Me

As detailed elsewhere [1], the dienophilic addition product **8** undergoes a stereospecific amino-Claissen rearrangement to **10** under more drastic conditions (refluxing benzene for 16 hours and stoichiometric boron trifluoride etherate), while the corresponding conversion of **9** gives non specifically, both **10** and **11**.

Taking advantage of this finding, the addition of **1** or **2** to cyclohexadiene can be specifically directed by choosing the more severe conditions, yielding mixtures of **10** (always the major product) and **11**, only. In the attempted isolations by recrystallization, only the adducts **10a-d** were recovered, whose analytical and spectroscopic data are collected in Table II together with the yields of **10** and **11**. To obtain the corresponding phenanthridines, the reaction mixture can be oxidized without any need to separate the two isomers **10** and **11**. Oxidation of **10a** (X = 2-Cl) with DDQ affords the dihydrophenanthridine **12**

Table II

Analytical and Spectroscopic Data for Substituted 6-Benzoyl-5,6,6a,7,8,10a-hexahydrophenanthridines **10a-d**

Compound	X	^{1}H-NMR [a] H_6	H_{6a}	H_7	$H_{7'}$	H_8	$H_{8'}$	H_9	H_{10}	H_{10a}	% Yield [b] **10&11**	**10**	mp °C (solvent)	Formula	Analysis [c] C%	H%	N%
10a	2-Cl —	5.11	2.43	1.34	1.12	1.98	1.81	5.73	6.19	3.73	90	57	170-171 (EtOH)	$C_{20}H_{18}ClNO$	74.11 (74.18)	5.59 (5.60)	4.32 [d] (4.33)
10b	2-NO_2 —	5.19	2.55	1.28	1.13	1.95	1.95	5.77	6.27	3.75	85	49	165-166 (MeOH)	$C_{20}H_{18}N_2O_3$	71.66 (71.84)	5.41 (5.43)	8.23 (8.38)
10c	2-OMe 3.75	5.09	2.40	1.39	1.14	1.86	1.86	5.72	6.21	3.76	[e]	74	138-139 (EtOH)	$C_{21}H_{21}NO_2$	78.92 (78.97)	6.63 (6.63)	4.32 (4.38)
10d	2-Me 2.24	5.10	2.41	1.42	1.13	1.91	1.91	5.71	6.24	3.76	87	47	164-165 (EtOH)	$C_{21}H_{21}NO$	83.33 (83.13)	7.05 (6.98)	5.20 (5.27)

[a] All spectra were run in deuteriochloroform solution at 200 MHz, using tetramethylsilane as internal standard. [b] Yields of **10** are obtained from crystallization of the reaction mixture containing **10** and **11**. [c] Calculated values in parenthesis. [d] Cl, 11.07 (10.95). [e] As partial aromatization processes occur in refluxing benzene, better yields of **10** are obtained at room temperature in methylene chloride.

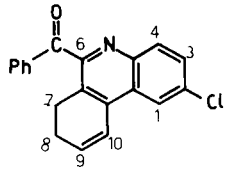
Table III

Analytical and spectroscopic data for substituted 6-benzoyl phenanthridines **13a-d**

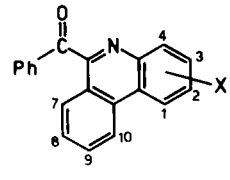
Compound	X	^{1}H-NMR [a] H_1	H_3	H_4	H_7	H_8	H_9	H_{10}	% Yield [b] in Quinoline **13**	in Decalin **13 (14)**	mp. °C (solvent)	Formula	Analysis [c] C%	H%	N%
13a	2-Cl —	8.61	8.02	8.14	8.15	7.71	7.92	8.64	71	52 (10)	186-187 (Toluene)	$C_{20}H_{12}ClNO$	75.40 (75.59)	3.81 (3.81)	4.50 [d] (4.41)
13b	2-NO_2 —	9.57	8.57	8.33	8.17	7.99	8.03	8.81	—	18 (14)	239-240 (EtOH)	$C_{20}H_{12}N_2O_3$	73.12 (73.16)	3.62 (3.68)	8.49 (8.53)
13c	2-OMe 4.07	7.97	8.05	8.13	8.19	7.67	7.87	8.65	52	71 (6)	181-182 (Toluene)	$C_{21}H_{15}NO_2$	80.27 (80.49)	4.87 (4.82)	4.67 (4.47)
13d	2-Me 2.68	8.44	8.04	8.10	8.14	7.65	7.88	8.71	68	— —	171-172 (EtOH)	$C_{21}H_{15}NO$	84.81 (84.82)	5.02 (5.08)	4.72 (4.71)

[a] All spectra were run in deuteriochloroform solution at 200 MHz, using tetramethylsilane as internal standard. [b] See text. [c] Calculated values in parenthesis. [d] Cl, 11.25 (11.02).

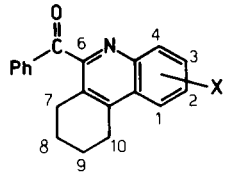
in 77% yield. Attempts to further oxidize **12** with DDQ were unsuccessful. Full aromatization of **10-d** to phenanthridines **13a-d** was achieved by refluxing with sulfur in either quinoline or decalin. The yields and analytical data for compounds **13** are reported in Table III. It must be noted that for the reaction in decalin, formation of compound **13** is accompanied by 6-14% of the tetrahydrophenanthridine derivative **14**. The structure of **12**, **13**, and **14** have been determined by analysis of nmr spectra. In particular the aliphatic region in the spectrum of **14a** exhibits two complex multiplets at δ 1.84 and 1.98 and two triplets at δ 2.83 and 3.15 which are consistent with an asymmetric CH_2-CH_2-CH_2-CH_2 chain.



12



13a, X = 2-Cl
b, X = 2-NO_2
c, X = 2-OMe
d, X = 2-Me



14a, X = 2-Cl
b, X = 2-NO_2

EXPERIMENTAL

Melting points are uncorrected. The nmr spectra were run on a Bruker WP 200 spectrometer at 200 MHz, in deuteriochloroform with tetramethylsilane as internal standard. Mass spectra were recorded on a 5970 HP mass spectrometer coupled with a 5890 HP gas-chromatograph.

Materials and Solvents.

The anils **1** and their methanol adducts were prepared according to published procedure [7]. Solvents were dried and distilled. Cyclopentadiene and 1,3-cyclohexadiene were freshly distilled.

Nuclear Overhauser Effect Measurements [11]. Determination of the Configuration of Isomers **6a** and **6b**.

The measurement tubes were deoxygenated by repeated freeze-thaw cycles and then sealed under vacuum. The usual routine for differential NOE experiments was adopted [12]; as the only modification, a multiplet was saturated with the least decoupling power by an 8 seconds cyclic perturbation of all multiplet lines [13]. The percentage enhancements were obtained from the coefficients of the reference spectrum, which resulted in exact matching with the perturbed spectrum in the region of interest. Errors were estimated at about 0.5%.

Methylenic resonances of the cyclopentadiene ring in both isomers **6a** and **6b** are in the form of triplets. Decoupling experiments show that vicinal and allylic coupling constants with the vinylic protons are similar, at the same time allowing detection of the vinylic resonances.

Irradiation of the methylenic resonance of the minor isomer at δ 3.81 brings about a 9.8% enhancement of the vinylic resonance at δ 6.83 and of an aromatic doublet at δ 7.98, assigned to proton 9 which shows a typical *meta* coupling constant. Therefore the minor isomer has the structure **6b**.

Irradiation of the methylenic triplet at δ 4.00 results only in a 10.3% enhancement of the vinylic resonance at δ 7.13. From saturation of the other vinylic resonance at δ 7.46, the doublet pertaining to aromatic proton 9 can be singled out from the resonance multiplet of the *ortho* benzoylic protons at about δ 8.17, with an associated 8.8% enhancement. Irradiation in this region causes a 8.5% enhancement of the vinylic proton. The major isomer has therefore the structure **6a**.

Synthesis of Substituted 4-Benzoyl-3a,4,5,9b-tetrahydro-3*H*-cyclopenta[*c*]quinolines **3a-h**. General Procedure.

Freshly distilled cyclopentadiene (10 mmoles) was added to a solution of anils **1** or their equivalents **2** (6.5 mmoles) and boron trifluoride etherate (0.6 mmoles) in 40 ml of anhydrous methylene chloride. After disappearance of substrate the solution was poured into water, the organic layer extracted, washed with dilute sodium hydrogen carbonate, dried and evaporated under reduced pressure. The solid obtained was recrystallized from an appropriate solvent (see Table I). Analytical and spectroscopic data of compounds **3a-h** are reported in Table I. The compounds **3a-h** exhibit characteristic mass spectra with m/e relative to M^+, M^+-105 (100%), 105, 77.

Oxidation of Compound **3a** with Magnanese Dioxide.

Manganese dioxide (6.82 g, 78.4 mmoles) was added to a solution of **3a** (3.1 g, 10 mmoles) in 100 ml of toluene. After refluxing for two hours, the hot reaction mixture was filtered and the solvent removed. Chromatography on a silica gel column using chloroform as eluting solvent and crystallization from ethanol afforded 2.25 g (73%) of 8-chloro-4-benzoyl-3a,9b-dihydro-3*H*-cyclopenta[*c*]quinoline **4**, mp 124-125°; nmr: δ 2.38 (ddq, H_3, $J_{3,3'}$ = 16.6, $J_{3,3a}$ = 6.8, $J_{1,3}$ = $J_{2,3}$ = $J_{3,9a}$ = 2.1), 3.01 (ddq, $H_{3'}$, $J_{3',3a}$ = 9.2, $J_{1,3'}$ = $J_{2,3'}$ = $J_{3',9a}$ = 1.9), 3.92 (ddd, H_{3a}, $J_{3a,9a}$ = 10.9), 4.18 (broad d, H_{9a}), 5.94 (dq, H_2, $J_{1,2}$ = 5.8, $J_{2,9a}$ = 2.0), 5.98 (dq, H_1, $J_{1,9a}$ = 2.0), 7.22 (complex m, H_7 and H_9), 7.40 (d, H_6, $J_{6,7}$ = 9.2), 7.48 (m, COPh, H_m), 7.61 (m, COPh, H_p), 8.12 (m, COPh, H_o); ms: 307 (M^+, 75), 306 (M-1,100).

Anal. Calcd. for $C_{19}H_{14}ClNO$: C, 74.14; H, 4.58; N, 4.55; Cl, 11.52. Found: C, 74.15; H, 4.59; N, 4.55; Cl, 11.49.

Compound **4** undergoes partial tautomerization in deuteriochloroform to 8-chloro-4-benzoyl-5,9b-dihydro-3*H*-cyclopenta[*c*]quinoline **5**; nmr: δ 2.69 (dt, H_3, $J_{3,3'}$ = 22.7, $J_{1,3}$ = $J_{2,3}$ = 2.1), 2.93 (dtd, $H_{3'}$, $J_{1,3'}$ = $J_{2,3'}$ = 2.4, $J_{3',9a}$ = 1.2), 4.50 (broad s, H_{9a}), 5.85 (dq, H_2, $J_{1,2}$ = 5.59, $J_{2,9a}$ = 2.4), 6.28 (dq, H_1, $J_{1,9a}$ = 2.4), 6.81 (broad s, H_5), 6.85 (d, H_6, $J_{6,7}$ = 8.2), 7.10 (dd, H_7, $J_{7,9}$ = 2.4), 7.13 (complex m, H_9), 7.47 (m, COPh, H_m), 7.54 (m, COPh, H_p), 7.66 (m, COPh, H_o).

Oxidation of **3a** with Sulfur in Decalin.

A solution of **3a** (0.31 g, 1.0 mmoles) and sulfur (0.26 g, 8 mmoles) in 50 ml of decalin was refluxed for two hours. Evaporation of the solvent under reduced pressure and chromatography on a silica gel column (toluene as eluting solvent) afforded the 8-chloro-4-benzoyl-1*H* and 3*H*-cyclopenta[*c*]quinoline **6** and 8-chloro-4-benzoyl-1,2-dihydro-3*H*-cyclopenta[*c*]quinoline **7**. Compound **6** was obtained in 35% yield (0.107 g) mp 173-174° (ethanol); nmr: isomer **6a**, δ 4.00 (t, H_3, $J_{2,3}$ = $J_{1,3}$ = 1.7), 7.13 (dt, H_2, $J_{1,2}$ = 5.8), 7.46 (dt, H_1), 7.51 (m, COPh, H_m), 7.63 (m, COPh, H_p), 7.67 (H_7, $J_{6,7}$ = 9.1, $J_{7,9}$ = 2.4), 8.14 (d, H_9), 8.17 (d, H_6), 8.17 (m, COPh, H_o); isomer **6b**, δ 3.81 (t, H_1, $J_{1,2}$ = $J_{1,3}$ = 1.8), 6.83 (dt, H_2, $J_{2,3}$ = 5.5), 7.42 (dt, H_3), 7.51 (m, COPh, H_m), 7.60 (dd, H_7, $J_{6,7}$ = 9.1, $J_{7,9}$ = 2.4), 7.63 (m, COPh, H_p), 7.99 (d, H_9), 8.17 (d, H_6), 8.17 (m, COPh, H_o).

Anal. Calcd. for $C_{19}H_{12}ClNO$: C, 74.64; H, 3.96; N, 4.59; Cl, 11.59. Found: C, 74.54; H, 3.92; N, 4.52; Cl, 11.51.

Compound **7** was obtained in a yield of 23% (0.071 g) mp 150-151° (ethanol); nmr: δ 2.32 (quintet, H_2, $J_{1,2} = J_{2,3} = 7.6$), 3.31 (t, H_1), 3.33 (t, H_3), 7.49 (m, COPh, H_m), 7.59 (m, COPh, H_p), 7.64 (dd, H_7, $J_{6,7} = 9.0$, $J_{7,9} = 2.4$), 7.84 (d, H_9), 8.07 (m, COPh, H_o), 8.11 (d, H_6).

Anal. Calcd. for $C_{19}H_{14}ClNO$: C, 74.15; H, 4.58; N, 4.55; Cl, 11.52. Found: C, 73.92; H, 4.50; N, 4.54; Cl, 11.56.

Oxidation of **3a** in Decalin with Pd/C as Catalyst.

A solution of 0.31 g (1.0 mmole) of **3a** and 0.010 g of 10% Pd/C in 20 ml of decalin is refluxed for one hour. Filtration followed by evaporation of the solvent under reduced pressure and chromatography on a silica gel column (toluene as eluting solvent) afforded 0.081 g (27%) of compound **7**.

Oxidation of **3a** with DDQ: Formation of 8-Chloro-4-benzoyl-1*H* and 3*H*-cyclopenta[*c*]quinoline **6**.

A solution of DDQ in benzene (13.0 mmoles in 50 ml) was added to a solution of **3a** in benzene (6.5 mmoles in 50 ml). Immediate precipitation of the hydroquinone occurred. If the reaction was run in hexadeuteriobenzene the spectrum registered after filtration of hydroquinone was identical with that of compound **4**. Further oxidation was achieved by refluxing the solution for 3 hours. The reaction mixture was filtered and the solvent removed under reduced pressure. Crystallization from ethanol gave compound **6** in 61% yield.

Substituted 6-Benzoyl-5,6,6a,7,8,10a-hexahydrophenanthridines **10a-d**. General Procedure.

A solution of anils **1** or their equivalents **2** (6.5 mmoles), cyclohexadiene (20 mmoles), and boron trifluoride etherate (0.6 mmoles) was refluxed in anhydrous benzene for 6-15 hours. After cooling, the solution was poured in water (50 ml). Separation of the organic phase, removal of the solvent under reduced pressure and crystallization from ethanol afforded the hexahydrophenanthridines **10a-d**. In the case of **10c** (X = 2-OMe) better yields (74%) were obtained using anhydrous methylene chloride as solvent at room temperature. Yields along with analytical and spectroscopic data are reported in Table II. The compounds **10a-d** exhibit characteristic mass spectra with m/e relative to M^+, M-105 (100%), 105, 77.

Oxidation of Compound **10a** with DDQ: Formation of 2-Chloro-6-benzoyl-7,8-dihydrophenanthridine **12**.

A solution of DDQ in benzene (2.73 mmoles in 20 ml) was added to a solution of **10a** in benzene (0.91 mmoles in 50 ml). After refluxing the mixture for 3 hours, the hydroquinone was filtered off and the solvent removed under reduced pressure. Crystallization from ethanol afforded 0.22 g of **12** (77%), mp 184-185°; nmr: δ 2.40 (tdd, H_8, $J_{7,8} = 8.8$, $J_{8,9} = 4.6$, $J_{8,10} = 1.8$), 2.92 (t, H_7), 6.58 (dt, H_9, $J_{9,10} = 9.8$), 7.21 (dt, H_{10}), 7.48 (m, COPh, H_m), 7.62 (dd, H_3, $J_{3,4} = 9.1$, $J_{1,3} = 2.4$), 7.63 (m, COPh, H_p), 7.96 (m, COPh, H_o), 8.01 (d, H_4), 8.08 (d, H_1).

Anal. Calcd. for $C_{20}H_{14}ClNO$: C, 75.12; H, 4.41; N, 4.38; Cl, 11.09. Found: C, 75.04; H, 4.38; N, 4.37; Cl, 11.03.

Oxidation of Compound **10** with Sulfur in Decalin: Formation of 2-Substituted-6-benzoyl-7,8,9,10-tetrahydrophenanthridine **14** and 2-Substituted-6-benzoylphenanthridine **13**.

A solution of 2.3 mmoles of **10** and 1.77 g (55.3 mmoles) of sulfur in 50 ml of decalin was refluxed for 3 hours. The solvent was removed and the residue chromatographed on a silica gel column using toluene as eluant.

Compound **14a** was obtained in 10% yield (0.075 g) from **10a** mp 208-209°; nmr: δ 1.84 (m, H_9), 1.98 (m, H_8), 2.83 (t, H_{10}, $J_{9,10} = 6.3$), 3.40 (t, H_7, $J_{7,8} = 6.3$), 7.47 (m, PhCO, H_m), 7.62 (dd, H_3, $J_{3,4} = 8.8$, $J_{1,3} = 2.4$), 7.62 (m, PhCO, H_p), 7.91 (m, PhCO, H_o), 7.98 (d, H_1), 8.00 (d, H_4).

Anal. Calcd. for $C_{20}H_{16}ClNO$: C, 74.75; H, 5.02; N, 4.36; Cl, 11.02. Found: C, 74.64; H, 5.05; N, 4.34; Cl, 11.08.

Compound **13a** was obtained in 52% yield (0.51 g); see Table III for analytical and spectroscopic data.

Compound **14b** was obtained in 14% yield (0.107 g) from **10b** mp 214-215° (ethanol): nmr: δ 1.87 (m, H_9), 2.03 (m, H_8), 2.86 (t, H_{10}, $J_{9,10} = 6.4$), 3.30 (t, H_7, $J_{7,8} = 6.4$), 7.46 (m, PhCO, H_m), 7.61 (m, PhCO, H_p), 8.18 (d, H_4, $J_{3,4} = 9.2$), 8.43 (dd, H_3, $J_{1,3} = 2.4$), 8.98 (d, H_1).

Anal. Calcd. for $C_{20}H_{16}N_2O_3$: C, 72.28; H, 4.85; N, 8.43. Found: C, 72.36; H, 4.83; N, 8.39.

Compound **14b** was obtained in 18% yield (0.135 g); see Table III for analytical and spectroscopic data.

Oxidation of Compounds **10a-d** with Sulfur in Quinoline: Synthesis of Substituted 6-Benzoylphenanthridines **13a-d**.

A solution of 2.3 mmoles of compounds **10a-d** and 6.9 mmoles (0.22 g) of sulfur in 50 ml of quinoline was refluxed for 10-60 minutes. The solvent was removed under reduced pressure and the residue chromatographed on a silica gel column using toluene as eluting solvent. Yields, spectroscopic and analytical data of compounds **13a-d** are reported in Table III. The fused ring system of one of these compounds (**13b**, X = 2-NO_2) was fully analyzed, giving the following magnetic parameters: nmr: δ 7.51 (m, PhCO, H_m), 7.67 (m, PhCO, H_p), 7.79 (ddd, H_8, $J_{7,8} = 8.2$, $J_{8,9} = 7.1$, $J_{8,10} = 1.1$), 8.02 (m, PhCO, H_o), 8.04 (ddd, H_9, $J_{7,9} = 1.3$, $J_{9,10} = 8.5$), 8.17 (ddd, H_7, $J_{7,10} = 0.7$), 8.33 (dd, H_4, $J_{3,4} = 9.0$, $J_{1,4} = 0.5$), 8.57 (dd, H_3, $J_{1,3} = 2.4$), 8.80 (dddd, H_{10}, $J_{1,10} = 0.5$), 9.57 (dt, H_1). The compounds **13a-d** exhibit characteristic mass spectra with m/e relative to M^+, 105, 77 (100%).

REFERENCES AND NOTES

[1] Part 1: V. Lucchini, M. Prato, and G. Scorrano, *J. Org. Chem.*, submitted.

[2] For an extensive review on Diels-Alder reactions of azadienes see: D. L. Boger, *Tetrahedron*, **39**, 2869 (1983).

[3] L. S. Povarov, *Russ. Chem. Rev.*, **36**, 656 (1967); E. F. Elslager and D. F. Worth, *J. Heterocyclic Chem.*, **6**, 597 (1969); S. C. Perricone, D. F. Worth and E. F. Elslager, *ibid.*, **7**, 1353 (1970).

[4] Y. Nomura, M. Kimara, Y. Takeuchi and S. Tomoda, *Chem. Letters*, 267 (1978).

[5] T. Shono, Y. Matsumara, K. Inoue, H. Ohmizu and S. Kashimura, *J. Am. Chem. Soc.*, **104**, 5753 (1982).

[6] V. Lucchini, M. Prato, U. Quintily and G. Scorrano, *J. Chem. Soc., Chem. Commun.*, 48 (1984).

[7] M. Prato, U. Quintily and G. Scorrano, *Gazz. Chim. Ital.*, **114**, 405 (1984).

[8] B. Alcaide, G. Escobar, R. Perez-Ossorio, J. Plumet, and D. Sanz, *J. Chem. Res. (M)*, 1466 (1984).

[9] J. Eisch, H. Gopal and C. T. Kuo, *J. Org. Chem.*, **43**, 2190 (1978).

[10] F. Fleming, "Frontier Orbitals and Organic Chemical Reactions", John Wiley and Sons, London, 1976.

[11] J. H. Noggle and R. E. Schirmer, "The Nuclear Overhauser Effect", Academic Press, New York, N.Y., 1970.

[12] Bruker Analytische Messtechnik GmbH "Aspect 2000 Pulse Programmer", Rheinstetten, West Germany, 1981, Program 12.4.

[13] M. Kinns and J. K. M. Sanders, *J. Magn. Reson.*, **56**, 518 (1984).