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Reaction of 1-Pyrrolidino-1-cyclohexene with Imidoyl Chlorides and a Route to Producing Phenanthridines

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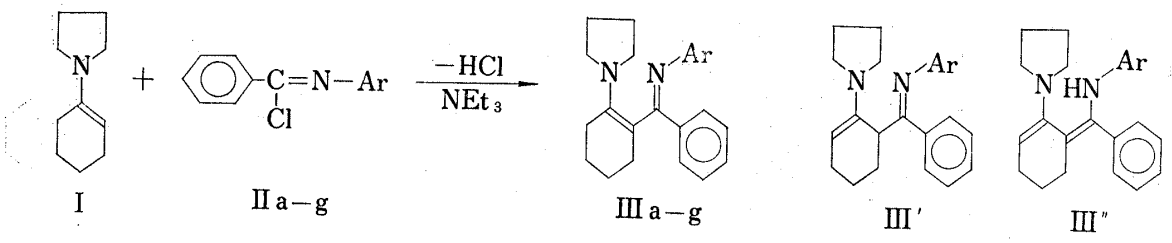
Reaction of 1-pyrrolidino-1-cyclohexene with N-arylbenzimidoyl chlorides has been successfully performed to result in introduction of benzimidoyl groupings at β-carbon of the enamine. Easy hydrolysis of enamine moiety of these products provides an effective means of preparation of mono-anils of 2-benzoylcyclohexanone, from which several phenanthridine derivatives have been newly obtained by action of polyphosphoric acid.

Literature contains many reports[2] describing the reaction of enamines with acyl halides, in which introduction of acyls at β-carbon of enamines has been realized by the production of β-diketones after acid hydrolysis of the reaction products. However, no report has appeared describing the reaction of enamine with imidoyl chloride. For the purpose of developing synthesis of phenanthridine derivatives we have initiated a reaction of an enamine, 1-pyrrolidino-1-cyclohexene (I), known to possess high nucleophilicity among the enamines from cyclohexanone, with a number of N-arylbenzimidoyl chlorides (IIa—g), which provides introduction of benzimidoyl grouping at β-carbon of the enamine. Hydrolysis of the reaction products has been shown to lead to the formation of mono-anils of β-diketones, which are capable of producing phenanthridine derivatives by acid catalyst.

1-Pyrrolidino-1-cyclohexene (I) was allowed to react with N-arylbenzimidoyl chlorides (IIa—g) in chloroform in the presence of triethylamine at room temperature. Except the runs with IIf and IIg well crystallized products were obtained in considerable yields, which were identified as 2-(N-arylbenzimidoyl)-1-pyrrolidino-1-cyclohexenes (IIIa—e). Other two possible structures (III′, III″) should be ruled out by noting the absence of vinylic proton signal at δ-value below 4.0 in their nuclear magnetic resonance (NMR) spectra.



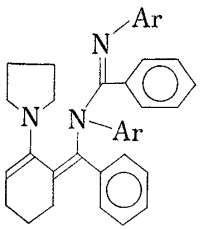
I IIa—g IIIa—g III′ III″

IIa, IIIa: Ar=C_6H_5
IIb, IIIb: Ar=p-$CH_3C_6H_4$
IIc, IIIc: Ar=p-$CH_3OC_6H_4$
IId, IIId: Ar=p-ClC_6H_4
IIe, IIIe: Ar=β-$C_{10}H_7$
IIf, IIIf: Ar=m-ClC_6H_4
IIg, IIIg: Ar=α-$C_{10}H_7$

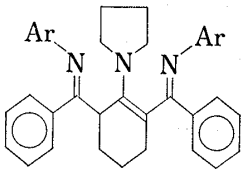
Chart 1

1) Location: *2-2-1, Oshika, Shizuoka.*
2) G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *J. Am. Chem. Soc.*, **85**, 207 (1963); S. Hünig, E. Benzing, and E. Lücke, *Chem. Ber.*, **90**, 2833 (1957); S. Hünig and M. Salzwedel, *Chem. Ber.*, **99**, 823 (1966).

Although in the use of IIf and IIg difficulties in crystallization were encountered, identities of the raw products were established by converting into 2-[α-(arylamino)benzylidene]cyclohexanones (Vf, g) by hydrolysis refluxing with aqueous ethanol as described later.



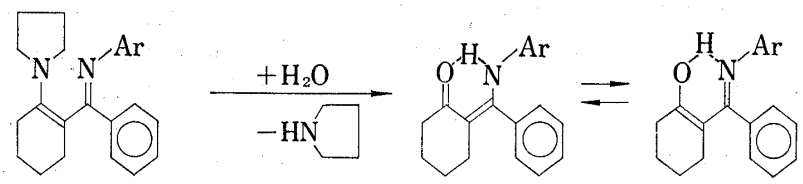
IV



IV'

It was also observed in the runs with IIa, d, e, f that the products (III) suffered further attack of imidoyl chlorides to give the diimidoyl-substituted compounds (IVa, d, e, f) as by-products. Between the two possible structures, IV and IV', for these products the structure IV appears proper, because their NMR spectra of these exhibited vinylic proton signals as triplet at δ-value around 4.3 which should be absent in the structure IV'. An analogy has been known in the formation of dibenzoyl-substituted enamines in the reaction of enamines with acyl halides.[3] The structures of these products have been defined to be similar to that of the above diimidoyl-substituted products.

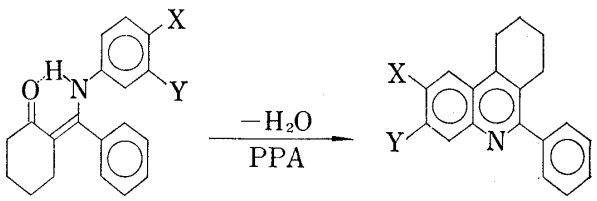
The foresaid 2-(N-arylbenzimidoyl)-1-pyrrolidino-1-cyclohexenes (IIIa—e) were shown easily to suffer hydrolysis of enamine moiety by refluxing with aqueous ethanol to give the corresponding 2-[α-(arylamino)benzylidene]cyclohexanones (Va—e). Analogues, Vf, g, were obtained from the foregoing unpurified IIIf, g. Except Va, these anils of 2-benzoylcyclohexanone obtained have not appeared in literature. Their NMR, infrared (IR), and ultraviolet (UV) spectra were interpreted to be indicative of the two tautomeric



III a—g Va—g V'

Chart 2

forms, keto-enamine (V) and enol-imine (V') forms, although evidence for defining the two structures did not appear in these spectra. On inspection of literature there has appeared only Va[4] as diaryl-substituted ketoenamine, but the assignment of keto-enamine structure described in this previous paper does not seem to be sufficient.



Va, b, c, f VIa, b, c, f

Va, VIa: X=H, Y=H
Vb, VIb: X=CH_3, Y=H
Vc, VIc: X=CH_3O, Y=H
Vf, VIf: X=H, Y=Cl

Chart 3

Anils of β-diketones have been known to be capable of the formation of quinolines by influence of acid catalyst. Then Va—g were subjected to the quinoline ring-closure in expectation of production of phenanthridine derivatives. This was succesfully performed by heating along with polyphosphoric acid at 120—130° to give the corresponding phenanthridine derivatives in fair yields in most runs, although no reaction occurred with Vd

3) R. Helmers, *Tetrahedron Letters*, **1966**; 1905, *idem*, *Acta Chem. Scand.*, **19**, 2139 (1965).
4) H. George and H.J. Roth, *Tetrahedron Letters*, **1970**, 3361.

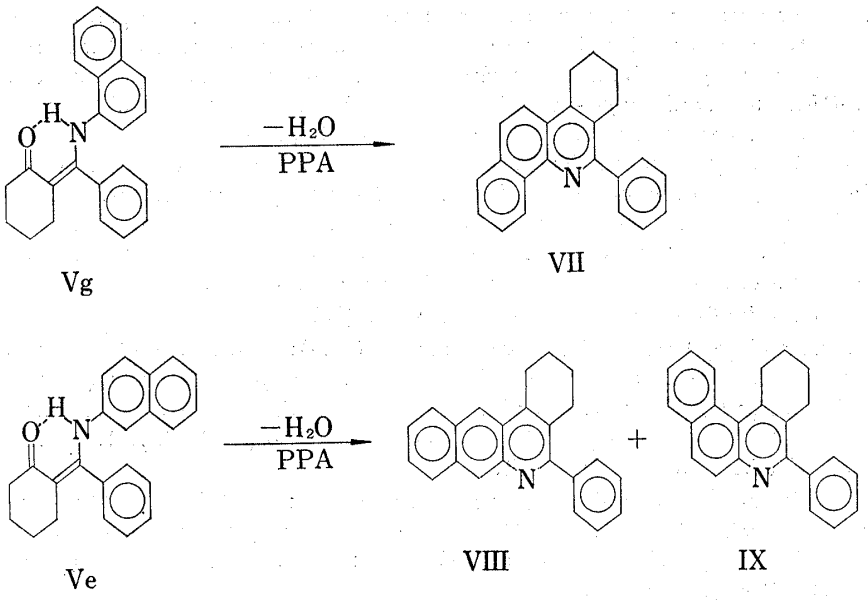


Chart 4

probably owing to its low reactivity. The compounds, Va, b, c, f gave the corresponding 7,8, 9,10-tetrahydro-6-phenylphenanthridines (VIa, b, c, f), among which VIa has been known.[5] These products exhibited UV spectra characteristic of their quinoline rings and IR and NMR spectra consistent with their structures. In identification of VIf a possibility of quinoline ring-closure at ortho position against chloro-substituent of Vf was ruled out by noting that in its NMR spectrum the coupling constant of the 4-proton as doublet at δ 8.15 was 2.1 Hz suggesting no coupling with 3-proton but with 2-proton.

By the polyphosphoric acid reaction Vg and Ve gave the corresponding benzo[*c*]phenanthridine (VII) and benzo[*b*]phenanthridine (VIII) in 90% and 80% yields, respectively. In the latter the corresponding benzo[*a*]phenanthridine (IX) was additionally obtained in 9% yield. The compound, Ve, therefore favours the ring-closure at 3-position of its naphthyl ring more than at 1-position, presumably because of increasing steric hindrance between 8-position of naphthyl and 6-position of cyclohexanone ring, expected in the latter ring-closure. Among the three benzophenanthridine products IX was identical with an authentic specimen prepared according to the previously known method[6] and the others have been unknown. The three materials exhibited UV spectra characteristic of the benzoquinoline skeletons in their structures and their NMR and IR spectra consistent with their structures.

Experimental[7]

General Procedure for Reaction of 1-Pyrrolidino-1-cyclohexene (I) with N-Arylbenzimidoyl Chlorides (IIa—g)——There were used seven N-arylbenzimidoyl chlorides, prepared by the reaction of N-arylbenzamides with phosphorus pentachloride, in which Ar=C_6H_5 (IIa), *p*-$CH_3C_6H_4$ (IIb), *p*-$CH_3OC_6H_4$ (IIc), *p*-ClC_6H_4 (IId), β-$C_{10}H_7$ (IIe), *m*-ClC_6H_4 (IIf), and α-$C_{10}H_7$ (IIg). To a stirred solution of 0.06 mole of I and 0.08 mole of triethylamine in dry chloroform (40 ml) was slowly added at 15—20° a solution of each 0.04 mole of IIa-g in dry chlo-

5) *a*) D.A. Denton, R.K. Smalley, and H. Suschitzky, *J. Chem. Soc.*, **1964**, 2421; *b*) L.S. Povarov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1966**, 337 [*C.A.*, **64**, 17539 *e* (1966)].

6) N.S. Kozlov, G.V. Vorob'eva, and G.S. Bychkova, *Vestsi Akad. Navuk Belarus. SSR, Ser. Khim. Navuk*, **1969**, 80 [*C.A.*, **72**, 43395 *m* (1970)].

7) All melting and boiling points are uncorrected. IR and UV spectra were recorded on a Hitachi EPI-G2 grating spectrophotometer and a Hitachi EPS-3T spectrophotometer, respectively. NMR spectra were taken with a JEOL JNM-C-60H spectrometer using tetramethylsilane as an internal standard. The following abbreviations are used: s=singlet, d=doublet, t=triplet, m=multiplet, br=broad, sh=shoulder, and ar=aromatic.

roform (20 ml). The reaction mixture was allowed to stand at room temperature over night. After evaporation of the solvent under reduced pressure the residual solid was extracted with hot isopropyl ether or benzene several times, leaving triethylamine hydrochloride. From the corresponding extract there was obtained each of 2-(N-arylbenzimidoyl)-1-pyrrolidino-1-cyclohexenes, IIIa—e, and in the runs with IIa,d,e,f additionally each of the diimidoyl-substituted products, IVa,d,e,f, as sparingly soluble materials. The former, IIIa—e, were isolated by concentration of the extracts as orange crystals which were recrystallized from dry acetone. The latter, IVa,d,e,f, crystallized in ethanol as pale yellow crystals. In the runs with IIf and IIg, since difficulties were encountered in crystallization of the corresponding products, IIIf,g, the raw products were directly subjected to the succeeding hydrolysis as decribed later. Yields, based on the starting imidoyl chlorides, and identities of the products are described as follows.

i) 2-(N-Arylbenzimidoyl)-1-pyrrolidino-1-cyclohexenes (IIIa—e)

2-(N-Phenylbenzimidoyl)-1-pyrrolidino-1-cyclohexene (IIIa): Obtained by the reaction of IIa, bp 131—133° (0.35 mmHg), mp 38—39°, with I. Yield, 71%. Orange yellow prisms (acetone), mp 121—122°. *Anal.* Calcd. for $C_{23}H_{26}N_2$: C, 83.59; H, 7.93; N, 8.48. Found: C, 83.69; H, 7.93; N, 8.47. IR (KBr) cm^{-1}: 1605, 1552. UV $\lambda_{max}^{Cyclohexane}$ mμ (ε): 250 (23800), 343 (3400). NMR δ (in $CDCl_3$): 1.2—3.5 (16H, m, $8\times CH_2$), 6.65—7.6 (8H, m, ar H), 7.7—8.0 (2H, m, ar H).

2-(N-*p*-Tolylbenzimidoyl)-1-pyrrolidino-1-cyclohexene (IIIb): Obtained by the reaction of IIb, bp 148° (1.5 mmHg), mp 50—51.5°, with I. Yield, 41%. Yellow prisms (acetone), mp 102—103°. *Anal.* Calcd. for $C_{24}H_{28}N_2$: C, 83,67; H, 8.19; N, 8.13. Found: C, 83.47; H, 8.23; N, 8.08. IR (KBr) cm^{-1}: 1608, 1549. UV $\lambda_{max}^{Cyclohexane}$ mμ (ε): 250 sh (23200), 256 (23300), 347 (4120).

2-(N-*p*-Methoxyphenylbenzimidoyl)-1-pyrrolidino-1-cyclohexene (IIIc): Obtained by the reaction of IIc, bp 172—173° (1.7 mmHg), mp 58.5—59.5°, with I. Yield, 47%. Orange yellow prisms (acetone), mp 108—109°. *Anal.* Calcd. for $C_{24}H_{28}ON_2$: C, 79.96; H, 7.83; N, 7.77. Found: C, 80.11; H, 7.79; N, 7.79. IR (KBr) cm^{-1}: 1606, 1548. UV $\lambda_{max}^{cyclohexane}$ mμ (ε): 248 (22200), 256 sh (21700), 353 (4730).

2-(N-*p*-Chlorophenylbenzimidoyl)-1-pyrrolidino-1-cyclohexene (IIId): Obtained by the reaction of IId, bp 161—162° (1.7 mmHg), mp 61—62°, with I. Yield, 70%. Orange yellow needles (acetone), mp 138—140°. *Anal.* Calcd. for $C_{23}H_{25}N_2Cl$: C, 75.70; H, 6.91; N, 7.68. Found: C, 75.74; H, 6.97; N, 7.94. IR (KBr) cm^{-1}: 1601, 1540. UV $\lambda_{max}^{cyclohexane}$ mμ (ε): 256 (26900), 342 (4380).

2-(N-2-Naphthylbenzimidoyl)-1-pyrrolidino-1-cyclohexene (IIIe): Obtained by the reaction of IIe, mp 67—68°, with I. Yield, 53%. Red prisms (acetone), mp 143—145°. *Anal.* Calcd. for $C_{27}H_{28}N_2$: C, 85.22; H, 7.42; N, 7.36. Found: C, 85.20; H, 7.43; N, 7.66. IR (KBr) cm^{-1}: 1600, 1550. UV $\lambda_{max}^{Cyclohexane}$ mμ (ε): 229 (38300), 249 (39100), 255 sh (38300), 336 (7140), 350 sh (5950).

ii) Diimidoyl-substituted Products (IVa,d,e,f)

IVa (Ar=C_6H_5): Yellow prisms (AcOEt), mp 203—206°. *Anal.* Calcd. for $C_{36}H_{35}N_3$: C, 84.83; H, 6.92; N, 8.25. Found: C, 84.64; H, 6.91; N, 8.30. IR (KBr) cm^{-1}: 1608, 1590, 1578. NMR δ (in $CDCl_3$): 1.25—3.0 (12H, m, $6\times CH_2$), 3.2—4.05 (2H, m, CH_2), 4.23 (1H, t, J=4.0 Hz, -CH=), 5.97—6.17, 6.7—7.9 (2H, 18H, m, ar H). IVd (Ar=*p*-ClC_6H_4): Yellow prisms (AcOEt), mp 196—199°. *Anal.* Calcd. for $C_{36}H_{33}N_3Cl_2$: C, 74.73; H, 5.75; N, 7.26. Found: C, 74.85; H, 5.68; N, 7.11. IR (KBr) cm^{-1}: 1610, 1587, 1574. NMR δ (in $CDCl_3$): 1.4—3.1 (12H, m, $6\times CH_2$), 3.1—3.9 (2H, m, CH_2), 4.27 (1H, t, J=4.0 Hz, -CH=), 5.80—6.00, 6.7—7.8 (2H, 16H, m, ar H). IVe (Ar=β-$C_{10}H_7$): Yellow prisms (AcOEt), mp 209—211°. *Anal.* Calcd. for $C_{44}H_{39}N_3$: C, 86.66; H, 6.43; N, 6.89. Found: C, 86.46; H, 6.53; N, 6.98. IR (KBr) cm^{-1}: 1610, 1592, 1580. NMR δ (in $CDCl_3$: 1.2—3.0 (12H, m, $6\times CH_2$), 3.2—3.9 (2H, m, CH_2), 4.07 (1H, t, J=4.0 Hz, -CH=), 6.10—6.30, 6.40—6.50, 6.7—6.95 (1H, 1H, 22H, m, ar H). IVf (Ar=*m*-ClC_6H_4): Yellow prisms (AcOEt), mp 210—213°. *Anal.* Calcd. for $C_{36}H_{33}N_3Cl_2$: C, 74.73; H, 5.75; N, 7.26. Found: C, 74.61; H, 5.68; N, 7.81. IR (KBr) cm^{-1}: 1609, 1584, 1572. NMR δ (in $CDCl_3$): 1.4—3.1 (12H, m, $6\times CH_2$), 3.1—3.9 (2H, m, CH_2), 4,31 (1H, t, J=4.0 Hz, -CH=), 5.60—5.85, 6.08—6.20, 6.65—7.85 (1H, 1H, 16H, m, arH).

General Procedure for Hydrolysis of 2-(N-Arylbenzimidoyl)-1-pyrrolidino-1-cyclohexenes (IIIa—g)—IIIa-e was easily hydrolysed by refluxing its 80% aq. EtOH soution for 0.5 hr into the corresponding 2-[α-(arylamino)benzylidene]cyclohexanone (Va—e). Evaporation of the solvent gave the corresponding product in almost pure form, which was recrystallized from appropriate solvent. Yield was almost quantitative in every run. As shown in the foregoing the raw materials obtained as IIIf, g were hydrolysed similarly.

2-[α-(Phenylamino)benzylidene]cyclohexanone (Va): Obtained from IIIa. Yellow needles (aq. EtOH), mp 135—136°. *Anal.* Calcd. for $C_{19}H_{19}ON$: C, 82.28; H, 6.91; N, 5.05. Found: C, 82.14; H, 6.89; N, 5.16. IR (KBr) cm^{-1}: 1566, 1582. UV λ_{max}^{EtOH}mμ (ε): 241 (9400), 365 (18800). NMR δ (in $CDCl_3$): 1.3—2.1 (4H, m, 4- and 5-H), 2.15 (2H, br t, J=5.3 Hz, 3-H), 2.50 (2H, br t, J=6.4 Hz, 6-H), 13.90 (1H, br, NH).

2-[α-(*p*-Tolylamino)benzylidene]cyclohexanone (Vb): Obtained from IIIb. Yellow prisms (aq. EtOH), mp 121—122°. *Anal.* Calcd. for $C_{20}H_{21}ON$: C, 82.44; H, 7.26; N, 4.81. Found: C, 82.21; H, 7.36; N, 4.80. IR (KBr) cm^{-1}: 1562, 1585. UV λ_{max}^{EtOH} mμ (ε): 243 (9830), 259 sh (5480), 366 (18700). NMR δ (in $CDCl_3$): 1.3—2.1 (4H, m, 4- and 5-H), 2.14 (2H, br t, J=5.3 Hz, 3-H), 2.18 (3H, s, CH_3), 2.50 (2H, br t, J=6.4 Hz, 6-H), 13.85 (1H, br, NH).

2-[α-(*p*-Methoxyphenylamino)benzylidene]cyclohexanone (Vc): Obtained from IIIc. Yellow needles (aq. EtOH), mp 101—102°. *Anal.* Calcd. for $C_{20}H_{21}O_2N$: C, 78.14; H, 6.89; N, 4.56. Found: C, 78.37; H, 6.82; N, 4.72. IR (KBr) cm^{-1}: 1564, 1596. UV λ_{max}^{EtOH} mμ (ε): 224 sh (9640), 240 sh (8620), 267 (4820), 366 (16400). NMR δ (in $CDCl_3$): 1.3—2.1 (4H, m, 4- and 5-H), 2.12 (2H, br t, J=5.3 Hz, 3-H), 2.49 (2H, br t, J=6.4 Hz, 6-H), 5.67 (3H, s, CH_3), 13.86 (1H, br, NH).

2-[α-(*p*-Chlorophenylamino)benzylidene]cyclohexanone (Vd): Obtained from IIId. Yellow needles (EtOH), mp 153—154°. *Anal.* Calcd. for $C_{19}H_{18}ONCl$: C, 73.19; H, 5.82; N, 4.49. Found: C, 73.62; H, 5.88; N, 4.49. IR (KBr) cm^{-1}: 1566, 1583, 1607. UV λ_{max}^{EtOH} mμ (ε): 248 (9210), 367 (19900). NMR δ (in $CDCl_3$): 1.3—2.1 (4H, m, 4- and 5-H), 2.17 (2H, br t, J=5.3 Hz, 3-H), 2.50 (2H, br t, J=6.4 Hz, 6-H), 13.84 (1H, br, NH).

2-[α-(2-Naphthylamino)benzylidene]cyclohexanone (Ve): Obtained from IIIe. Orange yellow leaflets (aq. EtOH), mp 116—117°. *Anal.* Calcd. for $C_{23}H_{21}ON$: C, 84.37; H, 6.47; N, 4.28. Found: C, 84.16; H, 6.46; N, 4.26. IR (KBr) cm^{-1}: 1563, 1585. UV λ_{max}^{EtOH} mμ (ε): 215 (37400), 237 (24600), 285 (7830), 297 (6740), 378 (22300). NMR δ (in $CDCl_3$): 1.2—2.1 (4H, m, 4- and 5-H), 2.17 (2H, br t, J=5.3 Hz, 3-H), 2.51 (2H, br t, J=6.4 Hz, 6-H), 13.71 (1H, br, NH).

2-[α-(*m*-Chlorophenylamino)benzylidene]cyclohexanone (Vf): Obtained from raw IIIf. Its yield was 41%, when calculated from IIf. Yellow needles (aq. EtOH), mp 93—94°. *Anal.* Calcd. for $C_{19}H_{18}ONCl$: C, 73.19; H, 5.82; N, 4.49. Found: C, 73.07; H, 5.73; N, 4.36. IR (KBr) cm^{-1}: 1562, 1586, 1610. UV λ_{max}^{EtOH} mμ (ε): 248 (9300), 366 (20000). NMR δ (in $CDCl_3$): 1.2—2.1 (4H, m, 4- and 5-H), 2.15 (2H, br t, J=5.3 Hz, 3-H), 2.48 (2H, br t, J=6.4 Hz, 6-H), 13.67 (1H, br, NH).

2-[α-(1-Naphthylamino)benzylidene]cyclohexanone (Vg): Obtained from raw IIIg. Its yield was 35%, when calculated from IIg. Yellow prisms (AcOEt), mp 171—172°. *Anal.* Calcd. for $C_{23}H_{21}ON$: C, 84.37; H, 6.47; N, 4.28. Found: C, 84.05; H, 6.38; N, 4.12. IR (KBr) cm^{-1}: 1538, 1585. UV λ_{max}^{EtOH} mμ (ε): 215 (49300), 240 sh (14700), 367 (14500). NMR δ (in $CDCl_3$): 1.4—2.1 (4H, m, 4- and 5-H), 2.20 (2H, br t, J=5.3 Hz, 3-H), 2.55 (2H, br t, J=6.4 Hz, 6-H), 14.28 (1H, br, NH).

General Procedure for Phenanthridine Ring-formation from 2-[α-(Arylamino)benzylidene]cyclohexanones (Va—g)——Except Vd, six Va-c, e-g were successfully converted into the corresponding phenanthridines, VIa-c,f, and benzophenanthridines, VII and VIII together with IX, by action of polyphosphoric acid. Formally the reaction was carried out by heating the substrate in 10-fold of polyphosphoric acid (83% as P_2O_5) at 120—130° with constant stirring for 1 hr. Because of its low solubility Vg particularly required higher reaction temperature, 140—150°. The mixture was poured into ice-water and basified with conc. KOH. The liberated material was extracted with ether and ethereal solution was dried over $MgSO_4$, and evaporated, leaving a solid or oily residue. Trituration in petr. ether made the oily residue crystalline form in most cases. This was usually recrystallized from petr. ether. Thus the products, VIa—c, VII, were obtained. Since the runs with Vf and Ve gave hardly crystallized residures from the ethereal extracts, they were converted into perchlorates. The crystallized perchlorate obtained from Ve was shown to be composed of VIII as major and IX, which were separated by fractional recrystallization from acetonitrile. All the perchlorates were converted into free bases by treating with aq. ammonia.

7,8,9,10-Tetrahydro-6-phenylphenathridine (VIa): Obtained from Va. Yield, 88%. Prisms (petr. ether), mp 77—78° (lit.[5a] mp 79°). *Anal.* Calcd, for $C_{19}H_{17}N$: C, 87.99; H, 6.61; N, 5.40. Found: C, 88.05; H, 6.67; N, 5.42. IR (KBr) cm^{-1}: 763, 758, 716, 702. UV λ_{max}^{EtOH} mμ (ε): 230 (43200), 242 sh (26600), 281 (5710), 307 (4620), 320 (4630). NMR δ (in $CDCl_3$): 1.5—2.2 (4H, m, 8- and 9-H), 2.73 (2H, br t, J=5.3 Hz, 7-H), 3.17 (2H, br t, J=5.3 Hz, 10-H), 7.3—8.2 (9H, m, ar H). Picrate: Yellow needles (EtOH), mp 206—207° (decomp.) (lit.[5a] mp 211°, lit.[5b] mp 201—202°).

7,8,9,10-Tetrahydro-2-methyl-6-phenylphenanthridine (VIb): Obtained from Vb. Yield, 93%. Prisms (petr. ether), mp 83°. *Anal.* Calcd. for $C_{20}H_{19}N$: C, 87.87; H, 7.01; N, 5.12. Found: C, 87.73; H, 7.01; N, 5.02. IR (KBr) cm^{-1}: 836, 763, 715, 701. UV λ_{max}^{EtOH} mμ (ε): 234 (41300), 287 (5800), 310 (5070), 324 (5150). NMR δ (in $CDCl_3$): 1.5—2.2 (4H, m, 8- and 9-H), 2.54 (3H, s, CH_3), 2.72 (2H, br t, J=5.3 Hz, 7-H), 3.14 (2H, br t, J=5.3 Hz, 10-H), 7.3—7.7 (7H, m, 1- and 3-H and C_6H_5), 8.01 (1H, d, J=8.3 Hz, 4-H). Picrate: Yellow needles (EtOH), mp 174—176°. Perchlorate: Amorphous powder (EtOH), mp 209—210°.

7,8,9,10-Tetrahydro-2-methoxy-6-phenylphenanthridine (VIc): Obtained from Vc. Yield, 48%. Prisms (isopropyl ether-hexane), mp 81.5—82°. *Anal.* Calcd. for $C_{20}H_{19}ON$: C, 83.01; H, 6.62; N, 4.84. Found: C, 83.12; H, 6.60; N, 4.80. IR (KBr) cm^{-1}: 837, 763, 708. UV λ_{max}^{EtOH} mμ (ε): 234 (40200), 247 (37300), 282 sh (6200), 324 (6070), 335 (6750). NMR δ (in $CDCl_3$): 1.5—2.25 (4H, m, 8- and 9-H), 2.68 (2H, br t, J=5.3 Hz, 7-H), 3.04 (2H, br t, J=5.3 Hz, 10-H), 3.82 (3H, s, CH_3), 7.0—7.6 (7H, m, 1- and 3-H and C_6H_5), 7.91 (1H, d, J=8.4 Hz, 4-H).

7,8,9,10-Tetrahydro-3-chloro-6-phenylphenenthridine (VIf): Obtained from Vf. Yield as its perchlorate, 78%. Prisms (petr. ether), mp 86—87°. *Anal.* Calcd. for $C_{19}H_{16}NCl$: C, 77.68; H, 5.49; N, 4.77. Found: C, 77.61; H, 5.46; N, 4.62. IR (KBr) cm^{-1}: 904, 875, 761, 715, 700. UV λ_{max}^{EtOH} mμ (ε): 233 (40900), 245 sh (18500), 317 (3120), 328 (3810). NMR δ (in $CDCl_3$): 1.5—2.2 (4H, m, 8- and 9-H), 2.71 (2H, br t, J=5.3 Hz, 7-H), 3.13 (2H, br t, J=5.3 Hz, 10-H), 7.25—7.8 (6H, m, 2-H and C_6H_5), 7.88 (1H, d, J=9.0 Hz,

1–H), 8.15 (1H, d, J=2.1 Hz, 4–H). Perchlorate: Prisms (EtOH), mp 245—246° (decomp.). *Anal.* Calcd. for $C_{19}H_{17}O_4NCl_2$: C, 57.85; H, 4.36; N, 3.55. Found: C, 57.95; H, 4.34; N, 3.66.

7,8,9,10-Tetrahydro-6-phenylbenzo[*c*]phenanthridine (VII): Obtained from Vg. Yield, 90%. Prisms (ether), mp 114—114.5°. *Anal.* Calcd. for $C_{23}H_{19}N$: C, 89.28; H, 6.19; N, 4.53. Found: C, 89.52; H, 6.19; N, 4.56. IR (KBr) cm^{-1}: 808, 798, 775, 758, 748, 735, 700. UV λ_{max}^{EtOH} mμ (ε): 243.5 (48900), 247 sh (48200), 274.5 (28000), 304 (10800), 335 (4610), 351.5 (4990). NMR δ (in $CDCl_3$): 1.5—2.15 (4H, m, 8– and 9–H), 2.82 (2H, br t, J=5.3 Hz, 7–H), 3.15 (2H, br t, J=5.3 Hz, 10–H), 7.3—8.0 (10H, m, ar H), 9.20—9.40 (1H, m, 4–H).

1,2,3,4-Tetrahydro-5-phenylbenzo[*b*]phenanthridine (VIII): Obtained from Ve. Yield as its perchlorate, 80%. Yellow needles (petr. ether–ether), mp 96—97°. *Anal.* Calcd. for $C_{23}H_{19}N$: C, 89.28; H, 6.19; N, 4.53. Found: C, 89.17; H, 6.19; N, 4.57. IR (KBr) cm^{-1}: 866, 744, 701. UV λ_{max}^{EtOH} mμ (ε): 233 (31400), 261 (73300), 336 sh (3800), 352 sh (5730), 364 (6450), 389 (3300). NMR δ (in $CDCl_3$): 1.5—2.3 (4H, m, 2– and 3–H), 2.73 (2H, br t, J=5.3 Hz, 4–H), 3.25 (2H, br t, J=5.3 Hz, 1–H), 7.35—7.8 (7H, m, 9– and 10–H and C_6H_5), 7.8—8.2 (2H, m, 8– and 11–H), 8.42 (1H, s, 12–H), 8.65 (1H, s, 7–H). Perchlorate: Red prisms (acetonitrile), mp 247—248° (decomp.). *Anal.* Calcd. for $C_{23}H_{20}O_4NCl$; C, 67.40; H, 4.92; N, 3.42. Found: C, 67.60; H, 4.95; N, 3.43. IR (KBr) cm^{-1}: 1120—1040 (ClO_4), 885, 755, 701. UV λ_{max}^{EtOH} mμ (ε): 231.5 (24300), 266.5 (58900), 339 sh (3710), 354 sh (6500), 367 sh (10400), 389 sh (3030), 417 sh (2090). NMR δ (in CF_3CO_2H): 1.8—2.6 (4H, m, 2– and 3–H), 3.00 (2H, br t, J=5.3 Hz, 4–H), 3.75 (2H, br t, J=5.3 Hz, 1–H), 7.65—8.0 (7H, m, 9– and 10–H and C_6H_5), 8.0—8.4 (2H, m, 8– and 11–H), 8.74 (1H, s, 12–H), 8.96 (1H, s, 7–H).

1,2,3,4-Tetrahydro-5-phenylbenzo[*a*]phenanthridine (IX): Obtained from Ve as a minor product in addition to VIII. Yield as its perchlorate, 9%. Needles (isopropyl ether), mp 112—113° (lit. [6] mp 117°). *Anal.* Calcd. for $C_{23}H_{19}N$: C, 89.28; H, 6.19; N, 4.53. Found: C, 88.79; H, 6.49; N, 4.62. IR (KBr) cm^{-1}: 833, 755, 730, 700. UV λ_{max}^{EtOH} mμ (ε): 216.5 (24300), 256 (47400), 272 sh (33000), 323 (1830), 338 (3700), 354 (4120). NMR δ (in $CDCl_3$): 1.6—2.2 (4H, m, 2– and 3–H), 2.7—3.1 (2H, m, 4–H), 3.45—3.85 (2H, m, 1–H), 7.3—8.2 (10H, m, ar H), 8.67—9.0 (1H, m, 12–H). Perchlorate: Prisms (EtOH), mp 225—226°. *Anal.* Calcd. for $C_{25}H_{26}O_5NCl$ ($C_{23}H_{20}O_4NCl \cdot C_2H_5OH$): C, 65.86; H, 5.75; N, 3.07. Found: C, 65.87; H, 5.59; N, 2.95. IR (KBr) cm^{-1}: 3410 (OH), 1140—1040 (ClO_4), 822, 755, 705. UV λ_{max}^{EtOH} mμ (ε): 217 (25700), 242.5 (32400), 279.5 (30300), 328 (4520), 354 (7550), 371 (7480).

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